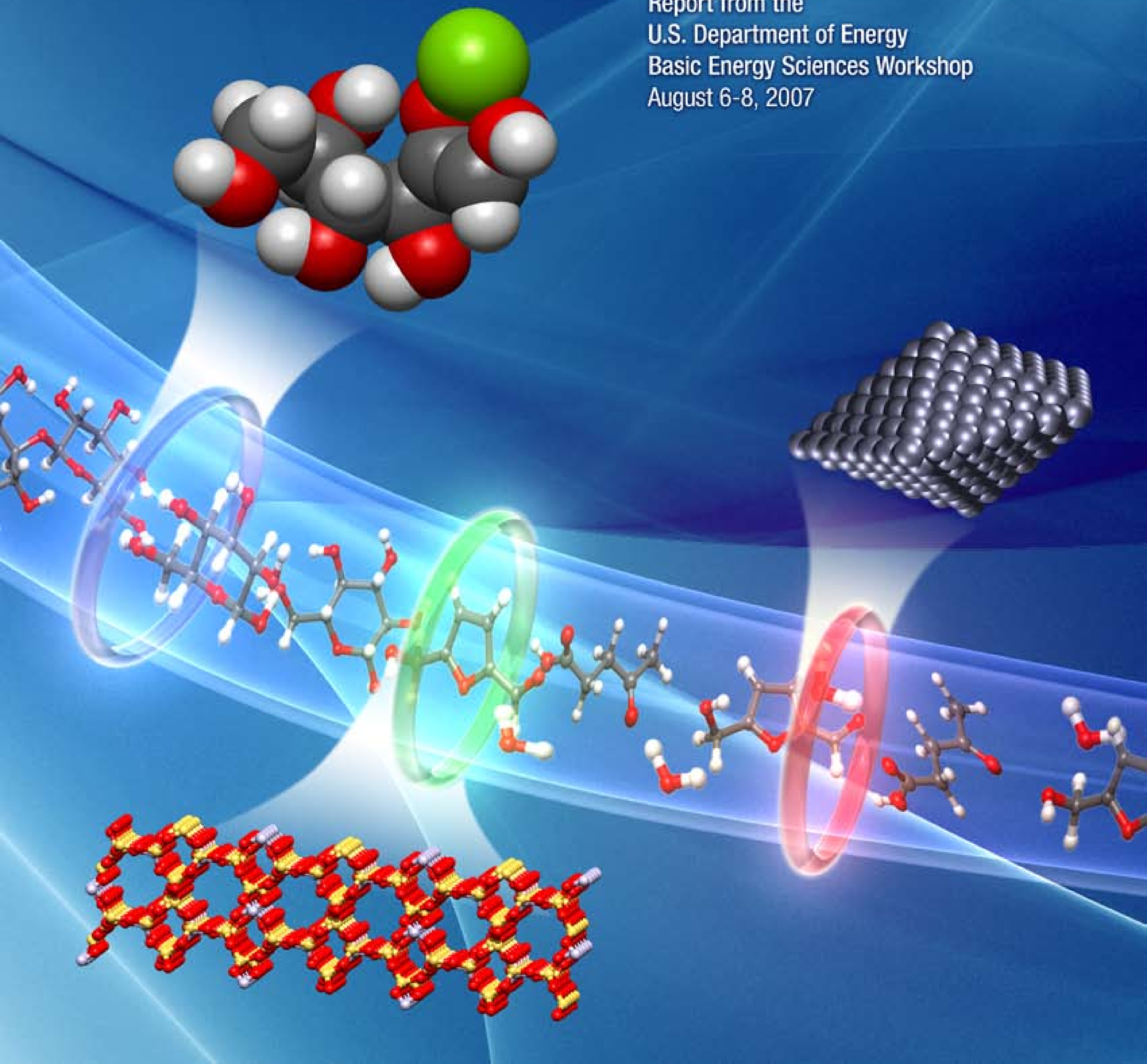
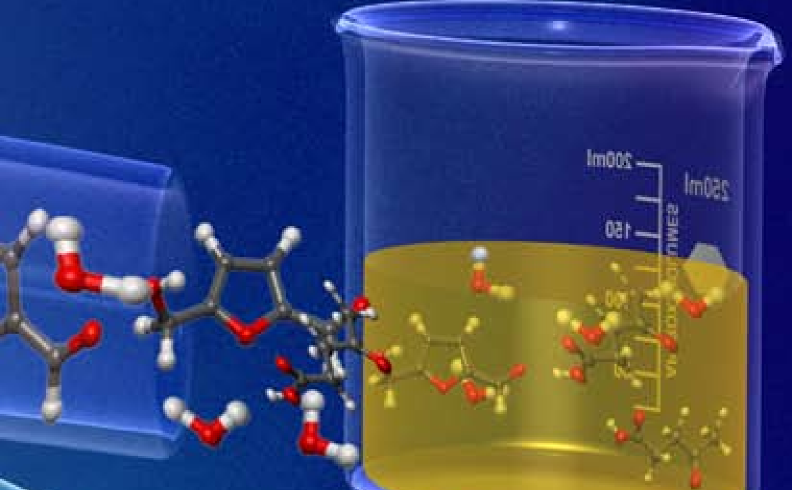
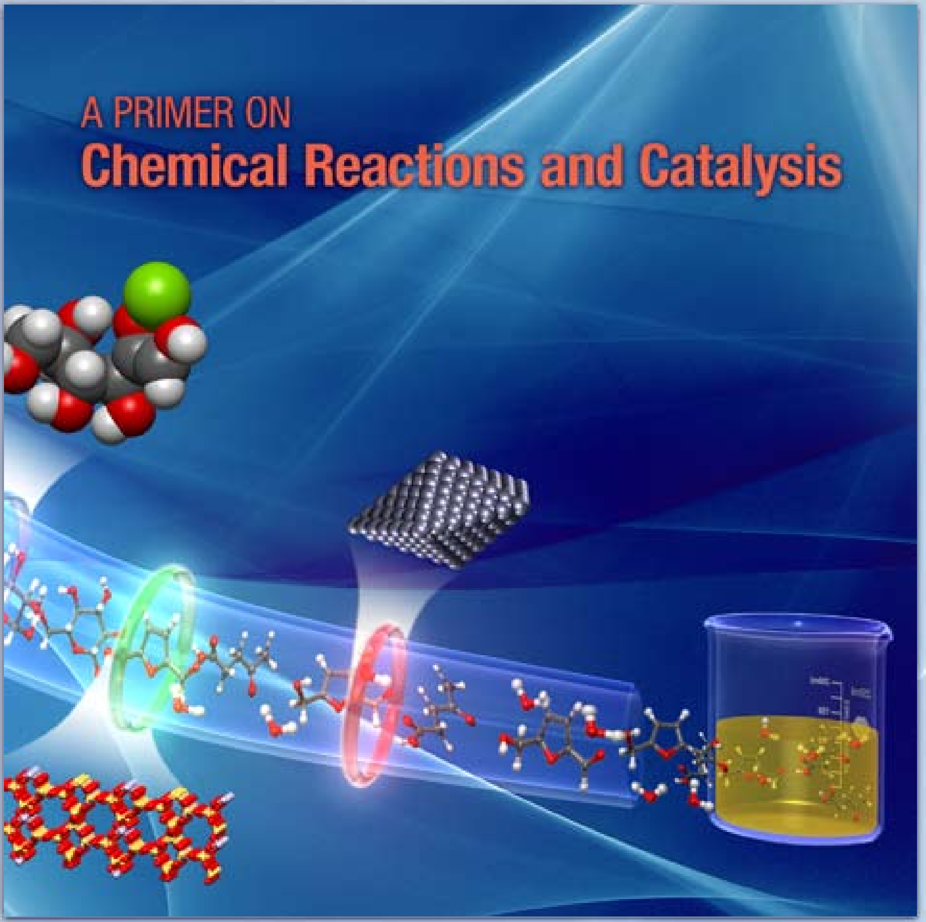
BASIC RESEARCH NEEDS:
CATALYSIS FOR ENERGY

Report from the
U.S. Department of Energy
Basic Energy Sciences Workshop
August 6-8, 2007





On the cover is an artist's rendering of the catalytic conversion of biomass-derived molecules to fuels and chemicals. Catalytic components include an enzyme, a transition metal complex, a mesoporous oxide, and a metal nanoparticle.



A PRIMER ON

Chemical Reactions and Catalysis

Chemical transformations are essential to all living organisms—and also to the manufacture of many products including fuels, plastics, and pharmaceuticals. Without catalysts and catalytic technologies, the ease of transportation and the ready access to all of the materials needed for our daily lives would not be possible.

The purpose of this primer is to show why catalysts are required for biological processes as well as those used in technology for the production of most fuels, chemicals, polymers, and pharmaceuticals. As we shall see, catalysts are the ultimate enablers of chemical transformation.

Catalysts Facilitate Molecular Transformations

The extent to which a chemical reaction could possibly transform one kind of molecule into another kind of molecule is governed by the principles of thermodynamics—some reactions are in principle possible, whereas others can, at most, occur to only an immeasurably small extent. But, the reactions that are thermodynamically possible may take place at such low rates as to be essentially stymied—we say that these reactions are limited by kinetics. **When the reaction is thermodynamically possible but too slow to be useful, then a catalyst is needed.** A catalyst increases the rate by intervening in the chemical change to open up a new, quicker pathway for change.

Thermodynamics and Chemical Reactions

Chemical reactions involve the transformation of reactant molecules to product molecules. A simple example is the combustion of hydrocarbons such as gasoline molecules to make carbon dioxide and water, a process that occurs at high temperature in the cylinder of an automobile engine. The Gibbs free energy change for this reaction, assuming hexane as a typical fuel, is downhill by ~ 68 MJ/L , and the energy released does the work to drive a typical automobile 12.5 miles.

The fact that the free energy change is downhill tells us that the reaction is favorable and that once it occurs, the products have a lower potential for doing work than the reactants do. Processes that are characterized by such downhill changes in the Gibbs free energy can, in principle, occur spontaneously. The larger the magnitude of the change in the Gibbs free energy, the larger the ultimate fraction of the reactants that can be converted to products.

Though the change in Gibbs free energy for hexane combustion is large, the reaction does not occur spontaneously. Thus, one can place liquid hexane in a glass and observe that it does not burst into flame when exposed to air at room temperature. The reason for the lack of combustion of hexane is that the molecules of hexane and oxygen are content to stay as they are for a very long time. To react, chemical bonds in both kinds of molecules must first break before new ones can form. To get these bonds to break, the temperature of the hexane-oxygen mixture is raised (as occurs in the automobile cylinder).

The need for the high temperature is associated with a barrier along the pathway from reactant to product molecules, known as the activation barrier. **When the reactant molecules are hot, they have the energy to cross the activation barrier, as the bonds between atoms in the reactant molecule are broken**

and the transformation of reactants to products ensues. The higher the barrier, the slower the reaction.

Kinetic Energy and Chemical Reactions

We emphasize that the reason reactions proceed more rapidly at higher temperatures is associated with the higher energy of the reactant molecules—we call this “kinetic energy.”

A collection of molecules has a distribution of kinetic energies, some high, some low, but the average value of kinetic energy is determined by the temperature. If a reaction is to occur, some fraction of the molecules in the collection must have enough kinetic energy to overcome the barrier.

If we think of reactant molecules as skateboarders at the bottom of a trough, then to surmount the walls of the trough and move over to a new trough, some fraction of the skateboarders will need to be moving fast enough (i.e., have sufficient kinetic energy) to surmount the barrier. Thus, the higher the temperature, the greater the fraction of the reactant molecules able to overcome the activation barrier and move over to the product side of the landscape.

If the activation barrier is very high, the temperature required to achieve a useful rate of product formation will have to be so high that the vessel walls used to contain the reaction may fail—or the reaction could be so fast that it gets out of control (an explosion could occur!).

Alternatively, the cost of the energy required to increase the temperature sufficiently for reaction to occur could become prohibitive. Furthermore, at high temperatures, some reactants may be fragile enough that they will decompose to useless products.

Thus, raising the temperature needed to achieve a useful reaction rate can lead to various problems, and a better way is needed to get the reactants over the barrier to form products.

Why Catalysts Matter

Catalysts provide the better way. They alter the pathway for the reaction, so that the barrier becomes smaller. **The catalyst works by interacting with the reactant molecules (forming chemical bonds with them) to alter the energy landscape for the reaction, leading to a lower activation barrier and, hence, a higher rate of reaction.**

Because nature has to do most of its biological chemistry at near- ambient conditions, it has evolved an enormous set of catalysts, mostly enzymes, which are exquisitely tuned so that each one facilitates a single chemical reaction for a single reactant. When a series of reactions is to be carried out as, for example, in the metabolism of food, nature uses a different enzyme for each step in the series, and all the enzymes work in the same medium at the same temperature.

Catalysts are also used to accelerate the chemical reactions used in the fuels and chemicals industry, but these catalysts are more primitive than nature's catalysts. Thus, for example, if we wanted to reduce the temperature of hexane combustion, we could expose a hexane-oxygen mixture to a catalyst containing very small particles—nanoparticles—of the precious metal platinum. This same catalyst converts unburned gasoline in automobile exhaust converters, minimizing the pollution it would otherwise cause, and it simultaneously converts toxic carbon monoxide and nitrogen oxides in the exhaust to the non-toxic products carbon dioxide and nitrogen.

Catalysts are also used to enhance the rate of a reaction to a preferred product relative to an undesired product. For example, silver catalyzes the oxidation of

ethylene to ethylene oxide, the precursor to ethylene glycol, which is used as antifreeze in automobiles or as one of the monomers for making polyethylene terephthalate, the polymer used for making soft drink bottles.

The beauty of a properly tuned silver catalyst is that it promotes the oxidation of ethylene to ethylene oxide rather than the combustion of ethylene to carbon dioxide and water. Thus, even though the thermodynamically preferred products are carbon dioxide and water, silver alters the reaction pathway so that more than 90 percent of the ethylene goes to ethylene oxide. The net effect is that ethylene is used efficiently to make the valuable product ethylene oxide and the undesired products, carbon dioxide and water, are minimized.

Driving Chemical Reactions that are Thermodynamically Uphill

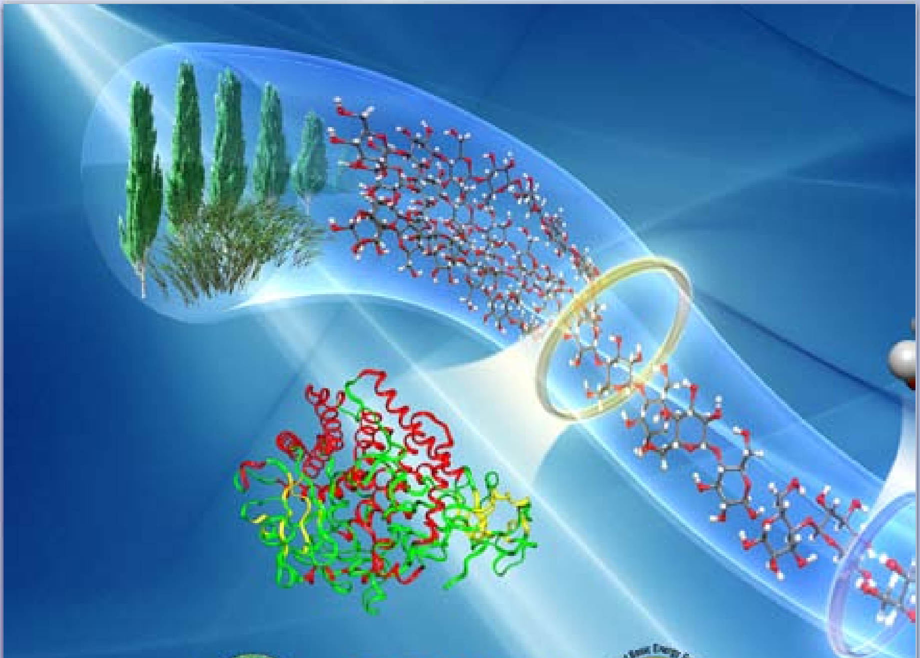
Some reactions are characterized by a change in the Gibbs free energy of reaction that is uphill. For such reactions, thermodynamics teaches us that the reaction cannot occur to a significant extent, unless energy is supplied in the form of photons (e.g., sunlight) or electrons (e.g., from a hydroelectric generator). For example, plants are able to drive an uphill reaction converting carbon dioxide and water to the sugar glucose and oxygen by using sunlight via the process of photosynthesis. Alternatively, the same reactants can be converted electrochemically into carbon monoxide and hydrogen, a mixture that can be used with well-developed catalytic technology to manufacture diesel fuel.

The kinetics of reactions that are uphill thermodynamically are often slow, even in the presence of light or electrons. But, the intervention of a catalyst opens a pathway for such reactions to occur at a higher rate with lower energy requirements for the photons or electrons. Catalysts of this type are referred to as photo- or electrocatalysts. Thus, for example, nature uses a series of enzymes to catalyze the photosynthesis of sugars from carbon dioxide and water, and platinum electrodes catalyze the conversion of the same reactants to carbon monoxide and hydrogen.

In Summary

Catalysts are required to facilitate chemical reactions so that they occur at useful rates and with preference to the desired product. If the rate of a reaction is too low, the size of the vessel in which the reaction takes place will be excessively large and expensive. If the product selectivity is low, the reactants are not used efficiently, and energy will be needed to separate the desired products from the undesired products. **Thus, the availability of catalysts that make the reaction go fast (active catalysts); make the reaction go to the desired products (selective catalysts); and last a long time or regenerate themselves (stable or regenerable catalysts) allows us to carry out chemical reactions in the most efficient, economical, and environmentally responsible manner.** Moreover, using catalysts to reduce the temperature at which reactions occur while achieving high conversions of reactants and high yields of desired products allows us to carry out the transformation with a maximum savings of the energy consumed.

Virtually all of the products used by modern societies for fuels, chemicals, polymers, and pharmaceuticals, as well as for abatement of air and water pollution, depend on catalysts. It is notable that the catalysts discovered and developed by humankind are quite primitive relative to those that nature has evolved. However, advances made in the understanding of how catalysts work, together with advances in strategies for making them and the lessons learned from nature, are opening the way towards the design, preparation, and implementation of catalysts that will rival nature's own and spare our precious energy and raw materials.



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ACRONYM, INITIALISM, AND ABBREVIATIONS LIST

AFM	atomic force microscopy
BTU	British thermal unit
COS	carbonyl sulfide
DDS	direct desulfurization
DFT	density functional theory
DOE	U.S. Department of Energy
EIA	(DOE's) Energy Information Administration
EXAFS	extended x-ray absorption fine structure
FCC	fluidized catalytic cracking
GC	gas chromatography
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HMF	hydroxymethylfurfural
HRTEM	high-resolution transmission electron microscopy
MIT	Massachusetts Institute of Technology
NMR	nuclear magnetic resonance
NOS	nitrogen, oxygen, sulfur (atoms)
NRC	National Research Council
NSLS	National Synchrotron Light Source
ONIOM	Our Own N-layered Integrated Molecular Orbital and Molecular Mechanics
PBC	periodic boundary condition
POX	partial oxidation
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
XAFS	x-ray absorption fine structure
XANES	x-ray absorption near edge spectroscopy
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
XRT	x-ray tomography

EXECUTIVE SUMMARY

The United States continues to rely on petroleum and natural gas as its primary sources of fuels. As the domestic reserves of these feedstocks decline, the volumes of imported fuels grow, and the environmental impacts resulting from fossil fuel combustion become severe, we as a nation must earnestly reassess our energy future.

Catalysis—the essential technology for accelerating and directing chemical transformation—is the key to realizing environmentally friendly, economical processes for the conversion of fossil energy feedstocks. Catalysis also is the key to developing new technologies for converting alternative feedstocks, such as biomass, carbon dioxide, and water.

With the declining availability of light petroleum feedstocks that are high in hydrogen and low in sulfur and nitrogen, energy producers are turning to ever-heavier fossil feedstocks, including heavy oils, tar sands, shale oil, and coal. Unfortunately, the heavy feedstocks yield less fuel than light petroleum and contain more sulfur and nitrogen. To meet the demands for fuels, a deep understanding of the chemistry of complex fossil-energy feedstocks will be required together with such understanding of how to design catalysts for processing these feedstocks.

The United States has the capacity to grow and convert enough biomass to replace nearly a third of the nation’s current gasoline use. Building on catalysis for petroleum conversion, researchers have identified potential catalytic routes for biomass. However, biomass differs so much in composition and reactivity from fossil fuels that this starting point is inadequate. The technology for economically converting biomass into widely usable fuels does not exist, and the science underpinning its development is only now starting to emerge.

The challenge is to understand the chemistry by which cellulose- and lignin-derived molecules are converted to fuels and to use this knowledge as a basis for identifying the needed catalysts. To obtain energy densities similar to those of currently used fuels, the products of biomass conversion must have oxygen contents lower than that of biomass. Oxygen must be removed by using hydrogen derived from biomass or other sources in a manner that minimizes the yield of carbon dioxide as a byproduct.

Catalytic conversion of carbon dioxide into liquid fuels using solar and electrical energy would enable the carbon in carbon dioxide to be recycled into fuels, thereby reducing its contribution to atmospheric warming. Likewise, the catalytic generation of hydrogen from water could provide a carbon-free source of hydrogen for fuel and for processing of fossil and biomass feedstocks. The underlying science is far from sufficient for design of efficient catalysts and economical processes.

This report is an account of the deliberations and conclusions of the Workshop on Basic Research Needs in Catalysis for Energy Applications, held August 6-8, 2007. It summarizes the research needs and opportunities for catalysis to meet the nation’s energy needs, provides an assessment of where the science and technology now stand, and recommends the directions for fundamental research that should be pursued to meet the goals described.

Grand Challenges

To realize the full potential of catalysis for energy applications, scientists must develop a profound understanding of catalytic transformations so that they can design and build effective catalysts with atom-by-atom precision and convert reactants to products with molecular precision. Moreover, they must build tools to make real-time, spatially resolved measurements of operating catalysts. Ultimately, scientists must use these tools to achieve a fundamental understanding of catalytic processes occurring in multiscale, multiphase environments.

The first grand challenge identified in this report centers on ***understanding mechanisms and dynamics of catalyzed reactions***. Catalysis involves chemical transformations that must be understood at the atomic scale because catalytic reactions present an intricate dance of chemical bond-breaking and bond-forming steps. Structures of solid catalyst surfaces, where the reactions occur on only a few isolated sites and in the presence of highly complex mixtures of molecules interacting with the surface in myriad ways, are extremely difficult to describe.

To discover new knowledge about mechanisms and dynamics of catalyzed reactions, scientists need to image surfaces at the atomic scale and probe the structures and energetics of the reacting molecules on varying time and length scales. They also need to apply theory to validate the results.

The difficulties of developing a clear understanding of the mechanisms and dynamics of catalyzed reactions are magnified by the high temperatures and pressures at which the reactions occur and the influence of the molecules undergoing transformation on the catalyst. The catalyst structure changes as the reacting molecules become part of it en route to forming products. Although the scientific challenge of understanding catalyst structure and function is great, recent advances in characterization science and facilities provide the means for meeting it in the long term.

The second grand challenge in the report centers on ***design and controlled synthesis of catalyst structures***. Fundamental investigations of catalyst structures and the mechanisms of catalytic reactions provide the necessary foundation for the synthesis of improved catalysts. Theory can serve as a predictive design tool, guiding synthetic approaches for construction of materials with precisely designed catalytic surface structures at the nano and atomic scales.

Success in the design and controlled synthesis of catalytic structures requires an interplay between (1) characterization of catalysts as they function, including evaluation of their performance under technologically realistic conditions, and (2) synthesis of catalyst structures to achieve high activity and product selectivity.

Priority Research Directions

The workshop process identified three priority research directions for advancing catalysis science for energy applications:

Advanced catalysts for the conversion of heavy fossil energy feedstocks

The depletion of light, sweet crude oil has caused increasing use of heavy oils and other heavy feedstocks. The complicated nature of the molecules in these feedstocks, as well as their high heteroatom contents, requires catalysts and processing routes entirely different from those used in today's petroleum refineries.

To advance catalytic technologies for converting heavy feedstocks, scientists must (1) identify and quantify the heavy molecules (now possible with methods such as high-resolution mass spectrometry) and (2) determine data to represent the reactivities of the molecules in the presence of the countless other kinds of molecules interacting with the catalysts.

Methods for determining reactivities of individual compounds within complex feedstocks reacting under industrial conditions soon will be available. Reactivity data, when combined with fundamental understanding of how the reactants interact with the catalysts, will facilitate the selection of new catalysts for heavy feedstocks and the prediction of properties of the fuels produced.

Understanding the chemistry of lignocellulosic biomass deconstruction and conversion to fuels

The United States potentially could harvest 1.3 billion tons of biomass annually. Converting this resource to ethanol would produce more than 60 billion gallons/year, enough to replace 30 percent of the nation's current gasoline use.

Scientists must develop fundamental understanding of biomass deconstruction, either through high-temperature pyrolysis or low-temperature catalytic conversion, before engineers can create commercial biomass conversion technologies. Pyrolysis generates gases and liquids for processing into fuels or blending with existing petroleum refinery streams. Low-temperature deconstruction produces sugars and lignin for conversion into molecules with higher energy densities than the parent biomass.

Scientists also must discover and develop new catalysts for targeted transformations of these biomass-derived molecules into fuels. Developing a molecular-scale understanding of deconstruction and conversion of biomass products to fuels would contribute to the development of optimal processes for particular biomass sources. Knowledge of how catalyst structure and composition affect the kinetics of individual processes could lead to new catalysts with properties adjusted for maximum activity and selectivity for high- and low-temperature processing of biomass.

Photo- and electro-driven conversions of carbon dioxide and water

Catalytic conversion of carbon dioxide to liquid fuels facilitated by the input of solar or electrical energy presents an immense opportunity for new sources of energy. Furthermore, the catalytic generation of hydrogen from water could provide a carbon-free source of hydrogen for fuel and for processing of fossil and biomass feedstocks. Although these electrolytic processes are possible, they are not now economical, because they depend on expensive and rare materials, such as platinum, and require significantly more energy than the minimum dictated by thermodynamics.

Scientists have explored the use of photons to drive thermodynamically uphill reactions, but the efficiencies of the best-known processes are very low. To dramatically increase efficiencies, we need to understand the elementary processes by which photocatalysts and electrocatalysts operate and the phenomena that limit their effectiveness. This knowledge would guide the search for more efficient catalysts.

To address the challenge of increased efficiency, scientists must develop fundamental understanding on the basis of novel spectroscopic methods to probe the surfaces of photocatalysts and electrocatalysts in the presence of liquid electrolytes. New catalysts will have to involve multiple-site structures and be able to drive the multiple-electron and hydrogen transfer reactions required to produce fuels from carbon dioxide and water. Theoretical investigations also are needed to understand the manifold processes occurring on photocatalysts and electrocatalysts, many of which are unique to the conditions of their use. Basic research to address these challenges will result in fundamental knowledge and expertise crucial for developing efficient, durable, and scalable catalysts.

Crosscutting Research Issues

Two broad issues cut across the grand challenges and the priority research directions for development of efficient, economical, and environmentally friendly catalytic processes for energy applications:

Experimental characterization of catalysts as they function is a theme common to all the processes mentioned here—ranging from heavy feedstock refining to carbon dioxide conversion to fuels. The scientific community needs a fundamental understanding of catalyst structures and catalytic reaction mechanisms to design and prepare improved catalysts and processes for energy conversion. Attainment of this understanding requires development of new techniques and facilities for investigating catalysts as they function in the presence of complex, real feedstocks at high temperatures and pressures.

The community also needs improved methods for characterizing the feedstocks and products—to the point of identifying individual compounds in these complex mixtures. The dearth of information characterizing biomass-derived feedstocks and the growing complexity of the available heavy fossil feedstocks, as well as the intrinsic complexity of catalyst surfaces, magnify the difficulty of this challenge.

Implied in the need for better characterization is the need for advanced methods and instrument hardware and software far beyond today's capabilities. Improved spectroscopic and microscopic capabilities, specifically including synchrotron-based equipment and methods, will provide significantly enhanced temporal, spatial, and energy resolution of catalysts and new opportunities for elucidating their performance under realistic reaction conditions.

Achieving these crosscutting goals for better catalyst characterization will require breakthrough developments in techniques and much improved methodologies for combining multiple complementary techniques.

Advances in ***theory and computation*** are also required to significantly advance catalysis for energy applications. A major challenge is to understand the mechanisms and dynamics of catalyzed transformations, enabling rational design of catalysts. Molecular-level understanding is essential to "tune" a catalyst to produce the right products with minimal energy consumption and environmental impact. Applications of computational chemistry and methods derived from advanced chemical theory are crucial to the development of fundamental understanding of catalytic processes and ultimately to first-principles catalyst design. Development of this understanding requires breakthroughs in theoretical and computational methods to allow treatment of the complexity of the molecular reactants and condensed-phase and interfacial catalysts needed to convert new energy feedstocks to useful products.

Computation, when combined with advanced experimental techniques, is already leading to broad new insights into catalyst behavior and the design of new materials. The development of new theories and computational tools that accurately predict thermodynamic properties, dynamical behavior, and coupled kinetics of complex condensed-phase and interfacial processes is a crosscutting priority research direction to address the grand challenges of catalysis science, especially in the area of advanced energy technologies.

Scientific and Technological Impact

The urgent need for fuels in an era of declining resources and pressing environmental concerns demands a resurgence in catalysis science, requiring a massive commitment of programmatic leadership and improved experimental and theoretical methods. These elements will make it possible to follow, in real time, catalytic reactions on an atomic scale on surfaces that are nonuniform and laden with large molecules undergoing complex competing processes. The understanding that will emerge promises to engender technology for economical catalytic processing of ever more challenging fossil feedstocks and for breakthroughs needed to create an industry for energy production from biomass. These new technologies are needed for a sustainable supply of energy from domestic sources and mitigation of the problem of greenhouse gas emissions.

INTRODUCTION

Background

The availability of inexpensive supplies of carbon-based fuels enabled the United States to develop a dynamic and vibrant national economy through most of the twentieth century. Today, even though U.S. sources of high-quality fossil fuel feedstocks are mostly exhausted, 85 percent of U.S. energy comes from fossil fuels. To meet the demand for these fuels, the United States imports more and more fuel. Today, 61 percent of our petroleum and 17 percent of our natural gas are imported.

The use of carbon-based fuels by the United States and other developed nations coupled with the growing demand by developing nations has adversely affected the environment. In 2007, the Intergovernmental Panel on Climate Change declared with 90 percent certainty that most atmospheric warming since 1950 has been driven by the buildup of carbon dioxide and other greenhouse gases from energy use.

Rapid economic growth in developing nations, starting at the end of the preceding century and continuing to the present, has sharply increased the demand for petroleum and natural gas, causing a steep rise in the inflation-adjusted cost of feedstocks. This rising demand has caused the price of fuels used for transportation, electrical power generation, and industrial manufacture to increase, and has contributed to a rise in the cost of all goods and services produced in the United States. A further consequence is that the U.S.-based chemical industry, long a positive contributor the nation's balance of trade, plans to build most of its new chemical plants where they can access low-cost resources and power—outside U.S. borders.

The current trend to high prices of petroleum and natural gas is not likely to change, as reserves are limited and demand is increasing. Known reserves of petroleum and natural gas are projected to last no more than 25 years and 45 years, respectively, if consumed at the rate projected for a growing global economy (Table 1). Recoverable reserves of coal, although significantly larger than those of petroleum and gas, are projected to last 100 years.

Table 1: Fossil fuel reserves.

Feedstock	Recoverable Reserves (Gigaton Carbon)[a]	Reserve Life at Current Consumption Rate (Years)[b]	Reserve Life at Projected GDP Growth (Years)[c]
Oil	120	35	25
Natural gas	75	60	45
Coal	925	400	100

a) Source: Energy Information Administration (EIA). 2007a. "Energy Information Administration: Official Energy Statistics for the U.S. Government Website," Washington, D.C. Available at: http://www.eia.doe.gov.
b) Estimated reserves divided by current consumption rate.
c) Source: Jeffrey Siirola.

Gerhard Ertl's Role in Surface Science Recognized with Nobel Prize

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The Nobel Prize in Chemistry for 2007 was awarded to Dr. Gerhard Ertl for groundbreaking studies in surface chemistry that have led to understanding of processes ranging from why iron rusts to how catalysts in cars work. Today, chemical reactions on catalytic surfaces play a vital role in many industrial operations. Surface chemistry can even explain the destruction of the ozone layer, as vital steps in the reaction actually take place on the surfaces of small crystals of ice in the stratosphere.

Ertl was one of the first to see the potential of the new science of surface chemistry that grew with the burgeoning semiconductor industry in the 1960s. Step by step, he created a methodology for the science of surface chemistry by demonstrating how various complementary experimental procedures can be used to provide a complete picture of a surface reaction.

Ertl founded an experimental school of thought by showing how reliable results can be attained by using advanced high-vacuum experimental equipment to observe the behavior of individual layers of atoms and molecules on extremely pure surfaces. Using these approaches, he developed a molecular-level understanding of the Haber-Bosch process, in which nitrogen is converted into ammonia, which is used to make synthetic fertilizers. This reaction, which is catalyzed by iron surfaces, has enormous economic significance because the availability of nitrogen for growing plants is often restricted. Ertl has also studied the oxidation of carbon monoxide on platinum, a reaction that takes place on automotive catalysts to clean exhaust emissions.

The insights provided by Ertl have provided the scientific basis for modern surface chemistry, and his methodology is used in both academic research and the industrial development of chemical processes.

Rising worldwide demand for petroleum and natural gas together with the finite availability is driving all nations to consider producing gaseous and liquid fuels from alternative feedstocks, such as tar sands, oil shale, and coal. However, these feedstocks will result in higher carbon dioxide emissions per unit of energy produced. For example, methane combustion produces 115 lb of carbon dioxide per million BTU, whereas coal combustion produces 205-227 lb per million BTU (EIA 2007b). Although carbon dioxide sequestration offers a means for offsetting the environmental effects of using heavier fossil fuels, technology implementation may not be sufficiently rapid to impact the rise in atmospheric carbon dioxide.

The recognition that carbon dioxide released to the atmosphere during fossil fuel combustion contributes significantly to global warming has awakened interest in using biomass as a major future source of fuels. Developing biomass-to-fuels technologies is also motivated by the assessment that up to 30 percent of the nation's transportation fuels could be provided by domestically grown biomass (Perlack et al. 2005). Clearly, the nation could benefit from developing this domestic resource, which could contribute to a reduction in the concentration of atmospheric carbon dioxide.

Catalytic Technologies

Catalytic technologies have played a critical role in the processing of petroleum and natural gas to produce fuels for transportation and heating (see “A Primer on Chemical Reactions and Catalysis”). Steady advances in catalytic science have enabled refiners to convert more petroleum in each barrel into finished products. Likewise, advances in catalytic hydroprocessing have enabled refiners to process progressively heavier crude oils and remove a continuingly larger fraction of the sulfur and nitrogen contained in them, lowering emissions. Furthermore, catalytic technologies have been essential in providing chemicals, polymers, and pharmaceuticals.

Advances in catalytic technologies have drawn heavily on advances in catalytic science (NRC 1992). The discovery and development of efficient methods for producing microporous zeolites, for example, have resulted in higher yields of gasoline per barrel of petroleum. Knowledge of how to disperse nanoscale particles of platinum and other precious metals onto high-surface-area supports has resulted in increasingly less expensive catalysts and continually improved octane numbers of the product gasoline (Antos and Aitani 2006). Atomic-scale characterization of catalysts has shed new light on the structures of catalysts used to remove sulfur from petroleum.

Catalyst formulation has also benefited from insights gained from combining experimental and theoretical studies. The finding that a rate-limiting reaction in synthesizing diesel fuel can be facilitated by alloying iron with nickel has led to the discovery of a catalyst that is more active than the traditional catalyst used for this synthesis (Greeley et al. 2002). An understanding of the elementary processes involved in this synthesis process and the role of reincorporating olefins, a family of hydrocarbons, in shaping the distribution of products has been used to identify the ideal distribution of nanoparticles of another metal inside porous alumina supports. The resulting catalysts maximize the production of diesel fuel and minimize the production of less valuable light alkanes (Iglesia 1997).

Future Challenges

The progressive shift to poorer quality fossil feedstocks, together with the prospect of using biomass and coal, creates a set of challenges for catalysis. The need will be twofold: first, for catalysts that can deconstruct and transform complex polyaromatic molecules with low ratios of hydrogen to carbon and second, for catalysts that can remove heteroatoms via hydroprocessing or other means. Novel classes of catalysts will also be required to deconstruct lignocellulosic biomass and convert the resulting products to fuel components, such as ethanol, butanol, and dimethylfuran (Huber et al. 2006).

The processing of heavy fossil resources will increase the demand for hydrogen needed to increase the average H:C ratio to approximately 2 and remove most of the sulfur, nitrogen, and metal contaminants. In the case of biomass, hydrogen is needed to remove oxygen to raise the volumetric energy density of the fuel.

The increased demand for hydrogen could be met by direct use of hydrogen-rich molecules, such as methane and ethane, and by electrochemical splitting of water to produce hydrogen with the required electrical power derived from the sun.

The discovery and development of new catalysts through the currently utilized process of repetitive formulation and evaluation are labor and capital intensive. Although today's tools make this work efficient, these efforts fall short because they are not guided by the scientific understanding needed for true breakthroughs. Thus, fundamental investigations demonstrating how catalyst composition and structure affect performance are essential to bolster rapid-throughput catalyst testing methods.

Major advances in understanding are needed to guide the preparation of catalysts with high activities, selectivities, and stabilities required to meet the need for a sustainable supply of fuels produced with minimal release of carbon dioxide. To meet this goal, the dynamics of elementary processes at catalytically active sites must be understood and the processes limiting catalyst activity and selectivity must be identified through the application of experimental and theoretical methods.

This report outlines the scientific challenges that must be met to enable development of novel catalytic technologies for processing the fuel feedstocks of the future.

Workshop Structure and Report Preparation

The U.S. Department of Energy (DOE) Office of Basic Energy Sciences held a workshop on basic research needs for catalysis for energy, August 6-8, 2007, in Bethesda, Maryland. The workshop was attended by 130 participants, coming from U.S. and foreign academic institutions, national laboratories, and government agencies, as well as U.S. and foreign industry. This group represented a broad mix of expertise in chemistry, chemical engineering, and biotechnology. At the workshop, participants identified the scientific challenges facing the field of catalysis and outlined the research directions of highest priority that should be pursued to meet these challenges. They identified the tools and capabilities required to enable researchers to meet the goals of the overall effort.

All attendees were provided with a factual document (Appendix I) that summarized the state of technology for processing fossil resources and biomass, and for the use of photon and electrical energy in combination with catalysts to enable the production of hydrogen from water and reduction of carbon dioxide. Attendees were informed about the need for developing catalysts to process new energy resources through a series of presentations made by speakers from industry, academe, and offices of the DOE. The workshop agenda and the names of the plenary speakers are presented in Appendix II. The participants are listed in Appendix III.

Four panels of workshop attendees devoted to their efforts the following themes:

- Grand Challenges in Catalysis as a Multidisciplinary Science and Technology
- Advanced Catalysts for the Conversion of Fossil Energy Feedstocks
- Advanced Catalysts for the Conversion of Biologically Derived Feedstocks
- Advanced Catalysts for the Photo- and Electro-Driven Conversion of Carbon Dioxide and Water.

A fifth group of attendees circulated among the panels to identify crosscutting themes.

The panels were charged with defining the gaps in current knowledge of the science relating to catalysis and identifying the major scientific challenges to be overcome to facilitate both the discovery and the development of catalysts for future catalytic technologies. At the end of the workshop, each panel presented priority research directions that should be pursued to address the identified opportunities and challenges.

This report was prepared by a core writing team from the four panels and the crosscutting team. The four panel reports and that of the crosscutting team summarize the current state of knowledge, the scientific challenges and the research directions to be pursued to meet the challenges, the potential scientific impact of the proposed research, and the potential technological impacts of the proposed research. The recommendations of the panels are summarized in the body of this report.

Taken together, these recommendations outline a program of catalysis research that will be critical for developing new energy resources in this century.

References

Antos, G. J., and A. M. Aitani, eds. 2006. *Catalytic Naphtha Reforming,* 2nd Ed., Chemical Industries, Vol. 100, CRC Press: New York, NY.

Energy Information Administration (EIA). 2007a. "Energy Information Administration: Official Energy Statistics for the U.S. Government," U.S. Department of Energy, Energy Information Administration, Washington, D.C. Available at: http://www.eia.doe.gov

Energy Information Administration (EIA). 2007b. "Voluntary Reporting of Greenhouse Gases Program," U.S. Department of Energy, Energy Information Administration, Washington, D.C. Available at: http://www.eia.doe.gov/oiaf/1605/coefficients.html

Greeley, J., J. K. Nørskov, and M. Mavrikakis. 2002. "Electronic Structures and Catalysis on Metal Surfaces," *Annual Review Physical Chemistry* **53**, 319-348.

Huber, G. W., S. Iborra, and A. Corma. 2006. "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews* **106**(9):4044-4098.

Iglesia, E. 1997. "Design, Synthesis, and Use of Cobalt-based Fischer-Tropsch Synthesis Catalysts," *Applied Catalysis: A-General* **161**, 59-78.

National Research Council (NRC). 1992. *Catalysis Looks to the Future.* National Academy Press, Washington, D.C. Available at: http://books.nap.edu/openbook.php?record_id=1903&page=R1

Perlack, R. D., L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, and D. C. Erbach. 2005. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply.* Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at: http://www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf

PANEL REPORTS

GRAND CHALLENGES IN CATALYSIS AS A MULTIDISCIPLINARY SCIENCE AND TECHNOLOGY

ADVANCED CATALYSTS FOR THE CONVERSION OF HEAVY FOSSIL ENERGY FEEDSTOCKS

ADVANCED CATALYSTS FOR CONVERSION OF BIOLOGICALLY DERIVED FEEDSTOCKS

ADVANCED CATALYSTS FOR THE PHOTO- AND ELECTRO-DRIVEN CONVERSION OF CARBON DIOXIDE AND WATER

GRAND CHALLENGES IN CATALYSIS AS A MULTIDISCIPLINARY SCIENCE AND TECHNOLOGY

Summary

Catalysis is a critical enabling science for our energy future. Improvements in the catalytic processes across the chemical and petroleum industries will increase resource and energy utilization efficiencies and reduce waste and overall environmental footprints. In the future, cost-effective, environmentally sound utilization of energy resources such as coal and biomass will require new catalysts and processes. Efficient photocatalysts for water splitting and electrocatalysts for fuel cells are needed if these technologies are to become practical on a large scale. Even hydrogen storage and carbon dioxide capture and sequestration could benefit from new abilities to catalyze solid-state reactions.

To meet these challenges, we must advance the field from *catalyst discovery* to *catalyst design*. This advance will require not only a new level of understanding of reaction mechanisms and dynamics to specify the structure and properties of the catalyst, but synthetic tools to construct catalysts at the atomic level and spectroscopic and computational tools to probe catalysts in working environments. We seek no less than the ability to design catalytic systems to accomplish any desirable transformation of chemical and energy resources and to minimize undesirable impacts of their utilization.

We have identified two grand challenges that are integral to achievement of this goal:

1. *Understanding mechanisms and dynamics of catalyzed transformations* – Connect catalytic and photocatalytic reaction rates and selectivities to the kinetics, energetics, and dynamics of individual elementary steps and relate these to the structure and dynamics of the catalytic sites involved.
2. *Design and controlled synthesis of catalytic structures* – Use theory as a predictive design tool, develop systematic approaches to construct and to characterize at the atomic level the molecules and materials designed, and develop the necessary understanding to control or direct chemical reactions in complex media.

The time to embark on these grand challenges is now. The need for new, sustainable energy resources and technologies grows daily with the population of the planet, as do the scientific opportunities. Tools that have come into widespread use over the past two decades, such as scanning probe microscopies and spectroscopies and density functional theory (DFT), have provided us with previously undreamt-of abilities to image surfaces and surface reactions, and to integrate theory with experiment in unraveling reaction mechanisms. These and other tools are rapidly being pushed to higher spatial, temporal, and energy resolution. New probes with in-situ capability, both synchrotron- and laboratory-based, have added to our understanding of catalysts under realistic process conditions. New materials and synthetic tools continue to emerge from efforts to design, construct, and characterize functional nanostructures. Single-site homogeneous catalysts have revolutionized olefin polymerization. Archetypal examples of solid catalysts from first principles have begun to appear. In short, although "catalyst design" has long seemed an empty promise, we are poised over the next decade and beyond to deliver on it for processes of increasing complexity and greater importance in securing a sustainable energy and environmental future. By meeting the grand challenges articulated here, we can revolutionize the energy and chemical industries of the twenty-first century.

Single-site Polymerization Catalysts

Single-site catalysts are structurally well-defined metal-organic molecules consisting of an active catalytic metal center attached to stabilizing organic groups known as ligands. Such catalysts are frequently highly electron-deficient (positively charged) and are paired with charge-balancing negatively charged anions/co-catalysts, which interact weakly with the catalytic center. By varying the nature of the metal, the surrounding ligands, and the counteranion, key catalyst properties such as the rate of the catalytic reaction, discrimination between incoming reactants, and suppression of undesired competing side reactions can be "tuned." Such catalysts can be anchored to solid surfaces (which are then ligands) to modify their properties and to confer the engineering advantages of ease of separation from products and minimization of corrosion.

Soluble and anchored single-site catalysts for the polymerization of olefins to produce polyolefin plastics on a huge industrial scale represent a triumph in rationally designed catalysts.

A representative catalyst structure is shown in Figure 1. Here, olefin monomer molecules such as ethylene or propylene undergo insertion into the linkage between the metal center and growing polymer chain to increase the polymer chain length. Such processes take place at rates of hundreds of thousands of insertions per minute. A single catalyst site can produce thousands of polymer chains. Subtle variations in the catalyst structure and reaction conditions can be used to engineer the polymer properties at will.

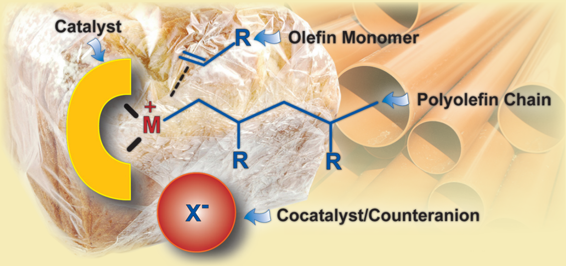

Figure 1: Single-site metal-organic ligand catalyst for the polymerization of olefin to produce polyolefin plastic materials. These materials are stronger, lighter weight, "cleaner" plastics than conventional materials. M is the metal atom in the catalytic site. Molecular image courtesy of Tobin Marks (Northwestern University).

Introduction

The world's energy needs will increase throughout this century, driven by population and economic growth. Meeting these needs will require both the development of new energy resources, especially carbon-free ones, and the efficient and environmentally responsible utilization of familiar ones such as fossil fuels. The design of new and improved catalytic processes is an essential part of solving our energy challenges, and we therefore begin by identifying grand challenges in catalysis science. Multidisciplinary advances in chemistry, materials science, engineering, and physics are converging to provide an unprecedented level of synthetic control, structural resolution, and mechanistic understanding at the atomic and molecular level. We have formulated the grand challenges for catalysis in terms of the *mechanism and dynamics* of catalyzed transformations and the elementary processes that comprise them, and the *design and creation of catalytic sites* that carry out these transformations, including the control and manipulation of the environment (both catalyst structure and the reaction media) in which these sites function. However, it is essential to recognize that these divisions are artificial. Indeed, what is ultimately needed is a systems approach to catalytic processes.

Molecular-level understanding of catalytic reactions requires that a key participant—the catalyst—be defined at a comparable level. No catalytic site operates independent of its surroundings; the environment influences the delivery of reactants and removal of products, and it may produce chemical and physical changes in the catalyst under reaction conditions. The environment therefore also provides an opportunity for control of catalyst performance.

Thus, the grand challenges articulated here point toward one overarching goal: the ability to design, and to implement new catalytic processes by design, at all relevant scales of length, time, and composition. Moreover, in considering catalysis for energy, chemicals, and fuels, a universal design criterion is *selectivity.* Higher selectivity means greater atom economy, better resource utilization, and higher energy efficiency in virtually every process.

Advances in active site design span length scales ranging from those of the molecule to the nanocluster to the surface of an extended solid. A broad array of new methods, including the use of molecular precursors, atom manipulation using new tips, and the soft cluster landing method, herald a new dawn in the synthesis of solids with precisely constructed surface sites. Design of such active sites is guided by a deep understanding of the chemical bond and orbital energetics, which is increasing rapidly with advances in computational science. The design and synthesis of active sites has benefited from modular ligand designs appropriate for rapid throughput techniques, new templating and encapsulation methods, better understanding of the role of capping agents, and control of the sizes and shapes of nanoclusters.

A catalyst is not defined solely by the active site, whether that be a molecule, nanocluster, or surface atom ensemble. The chemical composition, shape, motion, and energy flow of the environment help define the catalyst performance. Indeed, the working catalyst is the marriage of the active site and its environment. As we see in enzymes, the environment can deliver additional functionality to the active site and stabilize it, as observed in thermophiles or in core-shell nanoparticles. The environment below (i.e., subsurface) and external to the surface has enormous impact on catalytic activity. For example, the environment provided by the electrolyte is essential to the catalysis occurring at an electrode surface. In any of these constructs, the energy flow between the active site and its environment must be controlled if optimum catalytic efficiency is to be achieved. Understanding of the mechanisms of the processes is critical in guiding catalyst design, and atomic-level understanding of reaction mechanisms is coming to the fore in surface catalysis. Tip-enhanced ultrafast spectroscopy, environmental scanning transmission electron microscopy, synchrotron-based techniques with high spatial and temporal resolution, and adaptive Monte Carlo simulations are some of the tools that will provide deep insight into how catalysts function under realistic processing conditions.

The confluence of the knowledge that we acquire in this century about the active site, its relationship to its surrounding environment, and newfound mechanistic understanding of chemical transformations enabled by powerful experimental and theoretical tools sets the stage for the grand challenges presented in this panel report. Successful progress in addressing these challenges will be critical in meeting the energy needs of the twenty-first century. We will learn how to design efficient and highly selective catalysts for the myriad conversions of energy resources and fuels that will be needed by our society.

Grand Challenge 1: Understanding Mechanisms and Dynamics of Catalyzed Transformations

Summary

Our first grand challenge is to develop an understanding of reaction mechanisms and dynamics at catalytic reaction centers that is sufficiently complete to enable the creation of new catalytic processes for desirable chemical transformations while avoiding waste. For example, mechanistic understanding of olefin polymerization led to new catalysts with a multi-billion-dollar annual impact (Marks 2006). Our challenge is to gain a similar degree of mechanistic understanding of the catalytic transformations that will be critical to this nation's energy and environmental future. This understanding requires the connection of catalytic reaction rates and selectivities to the kinetics, energetics, and dynamics of individual elementary steps, and an understanding of how these factors are related to the structure and dynamics of the catalytic sites. To achieve this understanding, we must examine catalysts and catalytic reactions over a wide range of spatial, temporal, and energy scales. The geometries, energies, and electronic features of key intermediates and transition states must be determined, and the kinetic parameters of key steps examined. Conventional spectroscopic and mechanistic investigations must be augmented by computations, simulations, and new spectroscopic and imaging methodologies with high spatial and temporal resolution. Advances will be necessary in both experimental and theoretical techniques to describe quantitatively the structure and chemistry of the catalyst and the neighboring environment under reaction conditions. This knowledge will lead to a toolbox of catalytic sites and elementary steps for the on-demand breaking and making of specific bonds, novel catalytic transformations, and new paradigms for catalyst discovery. To achieve similar advances in photocatalysis and electrocatalysis to harvest solar and electrical energy as fuel, we must develop a similar understanding of reaction dynamics and concomitant electron transfer and energy flow rates, ranging from the very short timescales of electron and atomic motion to those reflective of elementary reaction processes.

Introduction

Knowledge of the reaction mechanism (i.e., the sequence of elementary steps by which reactants are converted to products) is central to understanding catalyzed reactions. The geometric structure (atomic positions), energies, and electronic structure of the initial state (reactant), final state (product), and transition state (activated complex) must be characterized for each elementary step. Further, the dynamics characterizing their interconversion must be addressed. More important for the design of improved catalysts and photocatalysts is an understanding of how these energies and the dynamics for each such step depend on the details of the dynamic structure of the active site and its surroundings, including the effects of reaction media. Achieving this depth of understanding will require temporal measurements on timescales ranging from 10^{-18} to 10^{4} s and beyond if we are to describe the following:

1. changes in electronic and atomic structure within single molecules or surface species involved in individual elementary chemical steps
2. the macroscopic rates of reactant to product conversions, which describe catalyst activity and selectivity
3. catalyst deactivation rates.

The Birth of a Carbon Dioxide Molecule: Scanning Tunneling Microscopy

Technologies such as scanning tunneling microscopy provide images of catalyst surfaces and reacting molecules at atomic resolution (Figure 2). These images provide important details of the sequence of events of a catalytic transformation and help researchers develop new catalysts. For example, researchers have been able to observe carbon dioxide formation during the reaction of carbon monoxide with atoms of oxygen catalyzed on a metal surface. Although this reaction is quite simple, the observations made in these studies may aid in the development of improved catalysts for vehicle emission control.

Four of the panels (A-C, E) illustrate some of the details of this reaction. Panel A depicts an isolated carbon monoxide molecule adsorbed on a silver surface. Panel B shows a pair of oxygen atoms on the silver. Panel C shows an absorbed carbon monoxide molecule and two separated oxygen atoms absorbed on the silver. When these chemical species are appropriately positioned to react with one another on the catalyst surface, they form an intermediate O–CO–O complex, as depicted in Panel E. This intermediate complex had not been observed previously. Subsequently, the O–CO–O complex decomposes and yields a carbon dioxide molecule and an oxygen atom. Panels D and F illustrate the atomistic arrangement of oxygen and carbon monoxide in Panels C and E, respectively.

A second experiment (Figure 3) illustrates the progression of this reaction through an alternative mode; in this case, the carbon monoxide molecule is introduced to the reactive metal surface, which contains absorbed oxygen atoms. In Panel A, a carbon monoxide molecule is indicated on the scanning tunneling microscope tip, and the figure illustrates that two oxygen atoms line up on the surface below the tip. Panel B shows the measurement of the microscope's tunneling current as a voltage is applied to make the carbon monoxide molecule migrate from the tip to the surface where it reacts with the adsorbed oxygen to form a carbon dioxide molecule. Figure C shows an image of the area after the reaction. Figures D, E, and F are schematic diagrams for A, B, and C, respectively (Hahn and Ho 2001).

Adding complexity, the ability to image the geometric and electronic structure of the catalyst with high spatial and temporal resolution, while actually operating under catalytic reaction conditions, is required. Furthermore, it will require measuring the energies of the catalytic intermediates.

These accurate measurements for selected model systems will also provide useful benchmarks for the development of theoretical methods that provide accurate energies and geometries of intermediates and that can accurately simulate chemical transformations occurring on catalysts over highly varied time and length scales, both near to and far from equilibrium. Such investments will then enable the development of multiscale, adaptive theoretical models that have predictive capabilities. With the continuing development of fast and relatively inexpensive computational methods, critical tools will become increasingly capable of contributing to the achievement of this grand challenge. The application of theory will then allow us to optimize catalyst structures and operating conditions to achieve transformations vital to the nation's energy and environmental future.

Fundamental investigations of thermally stimulated, photon-stimulated, and electron-stimulated reactions will allow us to understand how electrons and energy flow within molecular or surface species, plus the coupling of electron transfer and atom motion dynamics. Ultimately, we must

The Birth of a Carbon Dioxide Molecule (contd.)

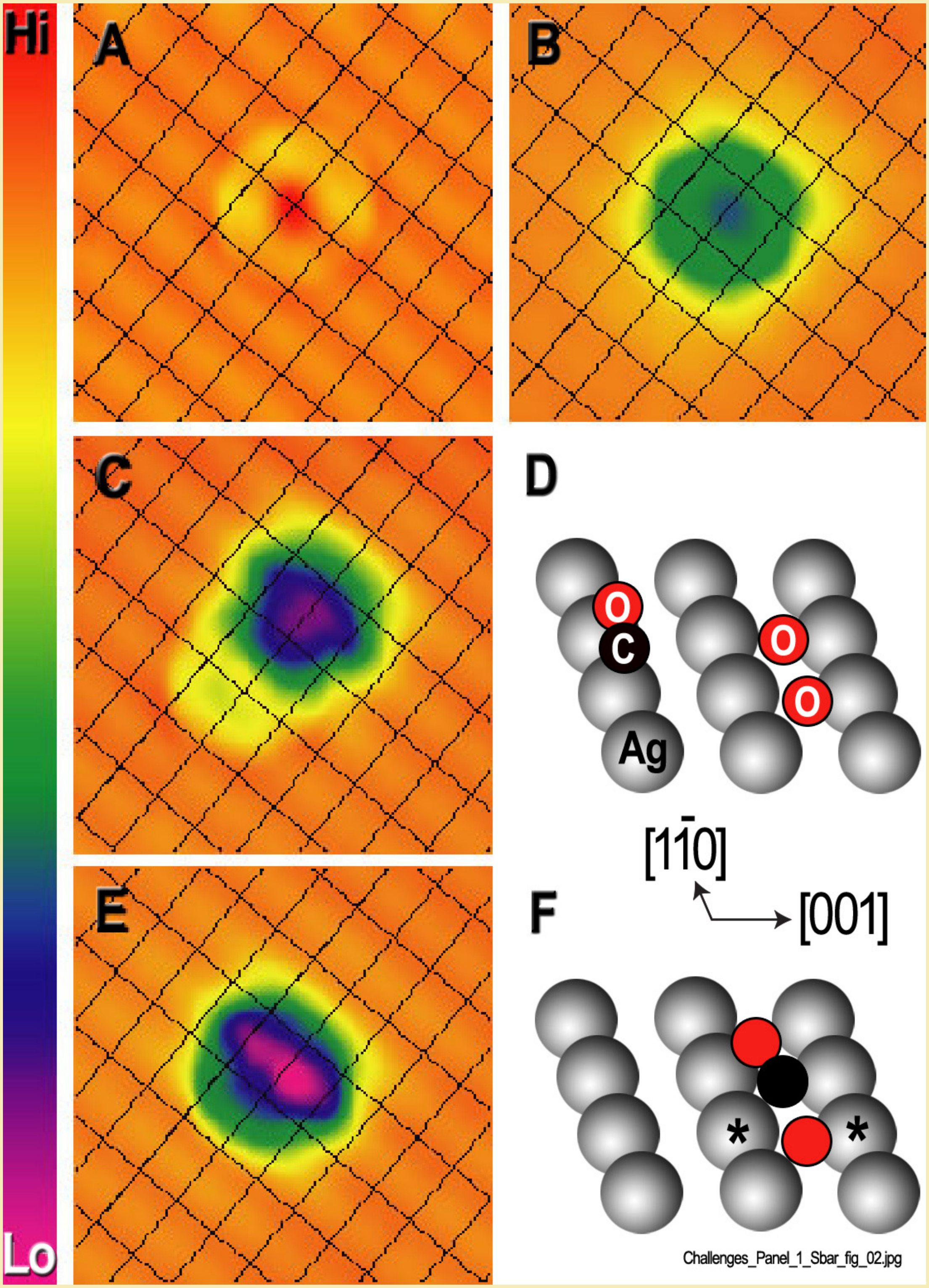

Figure 2: Atomic-scale view of carbon dioxide formation. Reprinted with permission from Hahn and Ho (2001). Copyright 2001 by the American Physical Society.

The Birth of a Carbon Dioxide Molecule (contd.)

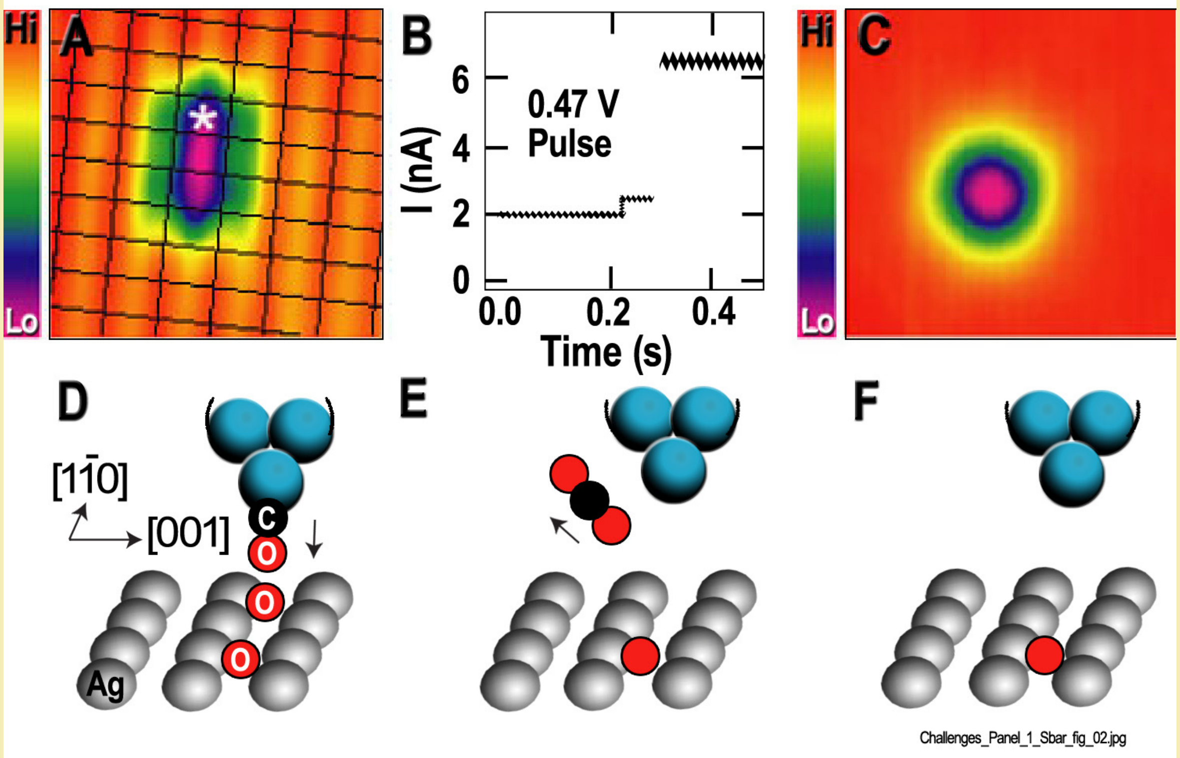

Figure 3: Reaction of a carbon monoxide molecule released from a scanning tunneling microscope tip with an oxygen atom on the surface. Reprinted with permission from Hahn and Ho (2001). Copyright 2001 by the American Physical Society.

strive to measure and predict structures and energies describing the full potential energy surfaces and how reactive fragments move on these static and fluctuating potential energy surfaces, and understand the coupled dynamics of atomic and electron motion over multiple length, time, and energy scales. These challenges will require a greater dependence on computation, and a deeper understanding of the elementary processes involved in electron-molecule and photon-molecule reactions. Simulation of atomic motion on non-adiabatic potential energy surfaces is particularly difficult. These challenges are formidable, but meeting them will allow us to design photocatalysts that can be used to produce liquid fuels or other energy forms, and electrocatalysts for fuel cells and other energy applications.

Scientific challenges

The scientific challenges for understanding the mechanisms and dynamics of difficult catalytic transformations include the following:

- determination of reaction mechanisms and kinetics of catalyzed processes
- imaging of catalyst structures at high spatial and temporal resolution under realistic catalytic reaction conditions
- theoretical representation of catalytic reaction dynamics over multiple length, time, and energy scales.

Recent advances make achieving these far-reaching challenges finally appear as realistic goals. The most recent advances in theory and experiments, coupled with those expected in the next decade, promise much more impressive strides towards definitive mechanistic research, understanding of structure-function relationships, and predictive catalysis. We envisage being able to extend these advances even into the domains of dynamics, electron transfer, and photochemistry.

1. *Determination of reaction mechanisms and kinetics of catalytic processes.* Efficient and effective catalysis consists of a closed cycle of elementary reaction steps in which particular bonds are broken and others are formed selectively. Key to effective design of new catalysts and improving existing catalysts is detailed understanding of the mechanisms and kinetics of these individual reaction steps. We need to know exactly how the catalyst participates in the cleavage and formation of the various bonds through the cycle. Essentially, we need to visualize the reaction path proceeding from reactants, through all intermediates, to products, including the effects of nearby adsorbates and their concentrations on the mechanism and kinetics. Information about the structure and energetics of intermediates and transition states must then be related quantitatively to the kinetics of the individual steps that transform one intermediate to the next. Gathering of this information will require the synergistic applications of a variety of experimental techniques and computational methods, many of which must still be developed. Such efforts will also reveal how reaction pathways and their associated energetics are linked to the local structure and composition of catalytically active sites. Combining knowledge of the mechanism and the kinetics of individual elementary steps into an overall description of reaction rates will lead to a deeper understanding of catalyst activity and selectivity.

   Currently available methods for investigating the mechanisms and kinetics of elementary processes occurring on a catalyst surface or at a catalytically active site are based almost exclusively on techniques that provide an average over all active sites, but do not describe what occurs at individual active sites. Although such information has proven invaluable and has led to a deep understanding of reaction mechanisms and kinetics, it does not provide an understanding of the diversity of activities at individual sites and how that relates to the local composition and structure of the site. As a result, a pressing need exists for the development of techniques that can enable observation of catalysis at single sites.

   Recent experimental and theoretical advances make achieving these very challenging goals appear realistic. These advances include the development of new spectroscopic techniques to measure excited-state dynamics and electron transport, which simultaneously achieve both high spatial and high temporal resolution (e.g., tip-enhanced, ultrafast spectroscopic and electron-transfer measurements) (Ogawa et al. 2007; Wu et al. 2006). They also include evolution of new theoretical methods for excited-state and non-adiabatic dynamics of many-atom and periodic-boundary-condition systems (Craig et al. 2005; Li and Tully 2007; Li et al. 2005; Stier and Prezhdo 2002).

   There is also a need to understand the motion and energy flows involved in single-event processes, such as those occurring in photo- and electrochemical systems. For example, it is now feasible to measure the detailed conformational dynamics of a single biomolecule. Furthermore, it is possible to achieve femtosecond temporal resolution and nanosecond spatial resolution of charge-transfer events. These are two areas of opportunity for incisive collaborative work between theorists and experimentalists, and because the three subareas of catalysis—biological, homogeneous, and heterogeneous—share common dynamical issues, there is a splendid opportunity to develop common ground in the area of dynamics. For example, the motions and rearrangements of the catalyst atoms are widely appreciated in homogeneous and biocatalysis, but are less well developed in heterogeneous catalysis, where the catalyst is generally less flexible. Laser-based techniques are now pushing temporal resolution of elementary processes to the attosecond (10^{-18} s) time scale (Bucksbaum 2007).

Another challenge is the development of methods to measure the movement of reactive fragments on multi-dimensional ground and electronic excited state surfaces, and the associated electron transfer dynamics and local energy exchange among modes of motion. Such measurements should be coupled with efforts to predict these effects computationally, because a full understanding of these processes would allow us to realize more efficient energy management in thermal catalysis, as well as energy, excited-state atom, and electron management in photocatalysis and electrocatalysis.

2. *High spatial and temporal resolution imaging of catalyst site geometry and structure under realistic reaction conditions.* The electronic and geometric structures of catalytic materials under reaction conditions determine their efficiency, selectivity, and lifetime. Experimental tools must be developed that can interrogate the geometric and electronic structures of catalytic materials and their associated reaction intermediates under reaction conditions. Of particular value will the observation of the temporal evolution of catalyst structure at temperatures, pressures, and reactant concentrations reflective of those used in industrial practice.

   Preliminary measurements of this type clearly illustrate that catalyst structure and morphology typically change under reaction conditions and over time. Even extended solid surfaces, traditionally thought to be static, may undergo thermal rearrangement and fluctuations, in addition to undergoing substantial changes in morphology during reaction because catalyst atoms are rearranged via bonding to atoms and molecules of reactants and products. Such fluxional behavior is even more important in the function and longevity of nanoscopic and molecular catalysts. Because the geometric and electronic structures of catalysts are inextricably linked, both are central to controlling catalytic efficiency and selectivity.

   The key to meeting the challenges of in-situ characterization of catalyst structure is advanced instrumentation and theoretical methods for the analysis of the data obtained from such instruments. Techniques such as scanning tunneling microscopy, atomic force microscopy, and aberration-corrected and environmental scanning transmission electron microscopies all provide information about catalyst structure with atomic spatial resolution—and they can be used for in-situ observations. Moreover, the application of powerful new computational methods for structural refinement can provide information about the local structure of complex catalysts with heretofore unprecedented detail. Examples of new computational methods include optimization of structures determined experimentally by diffraction/scattering based on quantum chemical computations of lowest-energy local structures; simulations of scanning tunneling microscopy images for computed low-energy surface structures for comparison with experimental images. Changes in the local environment of an element in the catalyst can also be followed in situ by using synchrotron-based techniques such as x-ray absorption near edge fine structure (XANES) and extended x-ray

Watching Catalysts as They Work: In-Situ Transmission Electron Microscopy

The quest to understand and to visualize the mechanisms of chemical reactions has often been described as the desire to watch “the dance of the molecules.” As with molecular catalysts such as soluble transition metal complexes and enzymes, bulk spectroscopic techniques such as nuclear magnetic resonance can provide information about the structure and dynamics of the catalyst as well as reactants, intermediates, and products. Solid catalysts provide a “dance floor” on which one might watch the transformation of reactants into products by microscopy techniques, but this is not as simple as it sounds. The “dance” takes place at the interface between solid and fluid phases, and to follow it, one needs techniques that provide spectroscopic information or imaging specifically at the interface, not in the bulk solid or fluid. As illustrated in the previous sidebar, scanning probe microscopies can provide images at atomic resolution of surfaces and reacting species on them, but the catalysts that one can examine are generally planar model systems rather than practical, high-surface-area catalysts.

Remarkable advances in the resolution of transmission electron microscopes and the design of reaction cells for these are literally changing the picture. Although access to state-of-the-art instruments is not widespread outside of industrial and national laboratories, exciting results are already beginning to emerge. One such example comes from the Haldor Topsøe research laboratories in Denmark. Workers there have utilized in-situ transmission electron microscopy to generate atom-resolved images of copper nanocrystals on various oxide supports, including working Cu/ZnO catalysts used for methanol synthesis and reforming for fuel cells (Hansen et al. 2002).

Figure 4 (Hansen et al. 2002) demonstrates how the shapes of copper nanocrystals on zinc oxide change in the presence of the reactants for methanol synthesis.

These images show the dynamic changes that occur in response to changes in the gas environment. These are particularly significant when both the

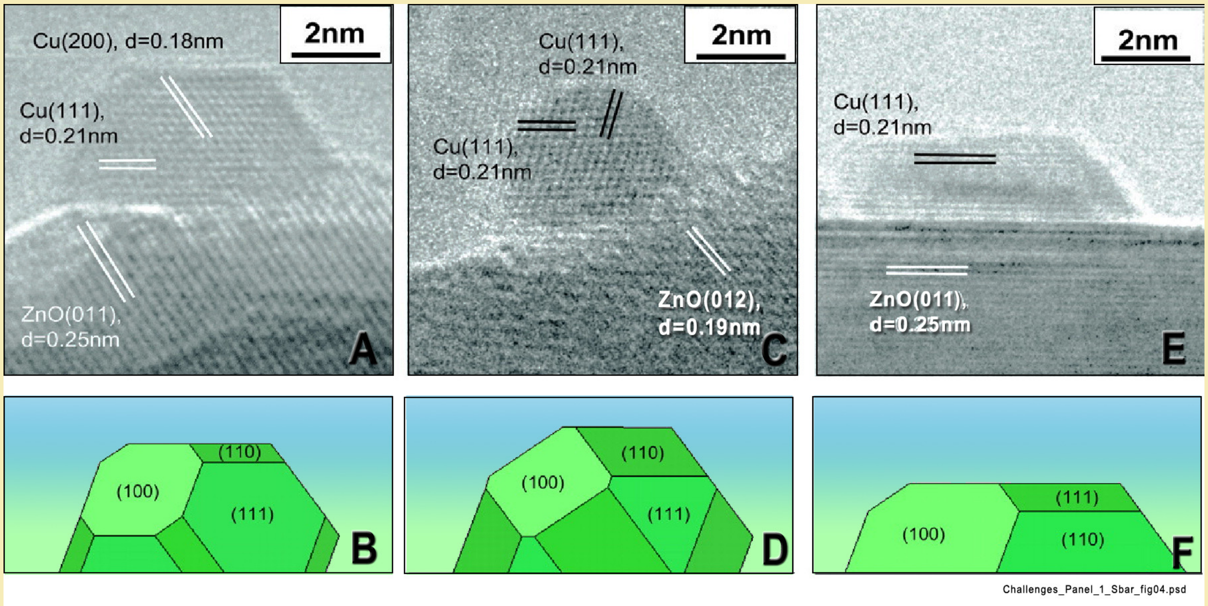

Figure 4: In-situ transmission electron microscope images (**A**, **C**, and **E**) of a Cu/ZnO catalyst in various gas environments with the corresponding Wulff constructions of the copper nanocrystals (**B**, **D**, and **F**). (A) The image was recorded at a pressure of 1.5 mbar of hydrogen at 220 °C. The electron beam is parallel to the [011] zone axis of copper. (C) Obtained in a gas mixture of hydrogen and water, H_2:H_2O = 3:1 at a total pressure of 1.5 mbar at 220 °C. (E) Obtained in a gas mixture of hydrogen (95 percent) and carbon monoxide (5 percent) at a total pressure of 5 mbar at 220 °C. From Hansen et al. (2002). Reprinted with permission from AAAS.

Watching Catalysts as They Work (contd.)

reactants (carbon monoxide and hydrogen) needed to make methanol are present in the gas phase; on zinc oxide, the copper nanoparticles flatten into disc-like structures due to increased wetting of the zinc oxide support. This flattening does not occur on other supports such as silica (Hansen et al. 2002). The nanocrystals are terminated primarily by densely packed (111) and (100) surfaces, with fewer high-energy edge and corner sites. As a result of this morphological transformation, the active surface area of the copper nanocrystals is increased (Topsøe 2003). Microkinetic models that take into account the actual distribution of surface crystallographic structures under reaction conditions are better able to account for catalyst performance than those based on a static initial surface structure (Johannessen et al. 2001).

Although this example perhaps illustrates the “dance of the surface” better than the “dance of the molecules,” the two are intimately connected. By coupling the results of model investigations, both theoretical and experimental, of the adsorption and reaction processes on surfaces of well-defined structure with in-situ observations of the atomic structure of the catalyst under reaction conditions, one can develop quantitative understanding and prediction of catalyst performance.

absorption fine structure (EXAFS) spectroscopies, which provide information about the oxidation states of elements and their local coordination and geometry. Such measurements are made even more useful when coupled with multiple scattering calculations of XANES and EXAFS spectra. Similar analyses can be used to interpret the results of neutron diffraction measurements. Further details on this subject are addressed in the chapter on crosscutting issues.

3. *Theoretical representation of catalytic reaction dynamics over multiple length, time, and energy scales.* Theory has come to play an increasingly important role in advancing understanding of the effects of local composition and structure on the properties of catalytically active sites. For example, it is now possible to predict the effects of ligand composition on the ability of a transition metal complex to coordinate and activate a reactant and to predict the overall reaction pathway, energetics, and even kinetics of reactions of small molecules occurring on the surfaces of metals and metal oxides. Electronic structure theory has also played an important role in the interpretation of EXAFS and Raman spectra. The challenge for the future is to develop quantum chemical approaches that provide accurate (within 5 kJ/mol) predictions of ground- and transition-state energies routinely for molecules and catalysts involving tens to hundreds of atoms. The achievement of this goal will require improvements in DFT approaches and novel, highly efficient strategies for finding transition states, as well as methods for finding free energies of activation for elementary processes that are not based on the harmonic approximation. Recent progress towards achieving these goals is promising and is described in more detail in the chapter on crosscutting issues.

Broader scientific impact

Successfully addressing the above challenges will have a broad scientific impact on chemistry broadly, extending well beyond catalysis. This impact will emerge from the development of new instrumentation for imaging catalysts, allowing determination not only of their structures at the atomic level, but also allowing determination of elemental compositions with atomic spatial resolution. Such capabilities will be of use in areas of integrated electronics, optoelectronics, sensors, etc. Likewise, it is expected that photon-based methods developed to probe the dynamics of elementary processes occurring at catalytically active sites will find application to investigations of surface phenomena in many other areas of application. The development and implementation of advanced theoretical methods will lead to a better and more complete interpretation of myriad processes involving chemical transformations and to the interpretation of data obtained from many experimental techniques.

Pursuit of the challenges described in the preceding section will enable researchers dealing with the development of new catalytic technologies to carry out their mission bolstered by a set of tools and principles that will have evolved from investigations of catalysis at its most elementary level. In the area of energy conversion, there are numerous types of metals, ligands, and surfaces, but only a few basic types of bonds that we need to understand how to break (via bond formation with catalytic centers) and make to effect desirable catalytic transformations. This group includes C–H, C–C, C–O, O–O, and O–H bonds. For example, the transformations of alkanes to alcohols, splitting of water, and transformation of biomass all include the cleavage and formation of such bonds. Through the examination of mechanisms and energetics of reactions in which these key bonds are cleaved or formed, we gain an understanding of the catalyst requirements for cleavage of each type of bond. Through investigation of a wide variety of catalytic and model systems, homogeneous and heterogeneous, commonalities and limitations with respect to these individual bond-cleavage and -formation reactions will emerge. When the barriers are understood, strategies to circumvent or surmount them can be formulated. The result will be a toolbox of catalytic sites and elementary steps that facilitate specific bond breaking/making and their effective coupling. Armed with a deep understanding of the kinetics, mechanisms, thermodynamics, intermediates, structures, and selectivities of each of the elementary reactions involved in energy conversion processes, and how they depend on the properties of the catalytic sites, scientists will be able to achieve the rational design of catalysts for new transformations in energy applications.

Potential impacts on catalysis for energy applications

Exploitation of microkinetics for improving reaction conditions and discovering new processes. The knowledge gained from investigations of the mechanisms, energetics, and kinetics of elementary reactions would greatly facilitate improvements in current catalysts and the rational discovery of new catalysts. The assembly of information about rate parameters for elementary reaction processes into a complete microkinetic model would open the way for predicting overall catalyst activity and selectivity. By combining the capabilities with the ability to relate rate parameters to catalyst composition and structure, it will become possible to explore the effects of changes in catalyst formulation on catalyst performance. Such advances could lead to the discovery of new catalytic transformations that will allow the exploitation of a wide variety of feedstocks for energy applications. For example, such an approach could be applied to develop catalysts for the activation and transformation of methane to transportable fuels such as methanol or higher alkanes. The splitting of water into oxygen and hydrogen and the reactions involved in processing of biomass all involve the cleavage and formation of specific bonds. With the knowledge provided from the investigations described previously, the rational development of such catalytic processes will ultimately become possible.

Photocatalytic routes to harvest and store solar energy. By meeting the scientific challenges described previously, we also will learn how to manage electron and energy flow in reactive systems, by proper nanoscale control of catalyst composition and structure. This knowledge could be used to great benefit in designing new photocatalysts for harvesting solar energy to effect chemical transformations such as fuels production and pollution abatement. Key to this advance is a much deeper understanding of reaction dynamics and especially how reactive fragments move on non-adiabatic potential energy surfaces defined by the photocatalysts.

As we have indicated, our central goal is to design efficient and selective catalysts for any desired transformation of energy resources, fuels, and chemicals. Understanding the mechanisms of these transformations is essential to accomplishing this mission.

Selective bond activation for conversion of emerging energy resources to liquid fuels and chemicals. Fossil-based feedstocks contain a variety of different functional groups and bonds that must be activated selectively by manipulation of C–C vs. C–H bond-breaking reactions. Furthermore, the selective breaking of carbon–heteroatom bonds is critical for the removal of nitrogen, sulfur, and oxygen from heavy feedstocks such as tar sands, shale oil, etc. Biomass feedstocks differ fundamentally from fossil resources in that they contain much larger numbers of C–O and O–H bonds. Furthermore, these feedstocks are most often processed in the liquid phase. New catalysts will need to be developed that can selectively cleave C–O vs. C–C vs. O–H bonds in biomass feedstocks in the liquid phase to generate valuable fuels and chemicals. The ability to create new bonds, in particular C–C bonds, from oxygenated reactants in condensed media, is important in developing our ability to construct molecules with suitable properties for energy and chemicals applications.

Grand Challenge 2: Design and Controlled Synthesis of Catalytic Structures

Summary

This challenge follows directly from Grand Challenge 1: to translate new mechanistic understanding into the design and realization of effective catalysts. Meeting this challenge will require the use of theory as a predictive design tool, the development of synthetic approaches to construct, at the atomic scale, the materials designed, whether highly uniform or deliberately multifunctional, and the advancement of characterization tools that can provide feedback on catalyst structure both during synthesis and during operation. Key targets include both catalysts designed for specific applications and those designed to test concepts such as structure-function relationships, thereby advancing the paradigm of rational catalyst design and the tools for its development.

Introduction

From the perspective of chemical transformations and processes, there are important opportunities for improved energy efficiency and energy independence in many areas, from traditional applications such as improved utilization of fossil fuels, to completely novel processes, such as catalysis of the conversion of solar energy and the production of fuels from biomass. The rational design of catalysts will play a crucial role in meeting each of these challenges. In some cases, the catalyst may be an improved, controlled-structure version of existing materials, with the design based on a new understanding of reaction mechanisms and taking advantage of recently developed capabilities for controlled synthesis of materials. In other cases, design of catalysts will lead to entirely new classes of materials for processes that do not yet exist.

Scientific challenges

The scientific challenges that relate to the design and realization of catalysts for specific transformations include the following:

- control of catalyst structures at the atomic and nanometer length scale
- understanding how catalyst structure evolves in a reactive environment
- integration of multiple catalytic functions
- synthesis of three-dimensional nanostructured catalysts
- utilization of principles employed by enzymes (biomimetic catalysts)
- development of non-precious-metal catalysts with superior performance
- combinatorial and high-throughput strategies for catalyst synthesis and evaluation.

One crucial goal in essentially all areas of catalyst development is that of improving catalyst *selectivity*. Whether or not the process of interest is in the energy/fuel chain, selectivity of *all* chemical processes has important consequences for energy efficiency. The higher the selectivity for desired products, the higher the efficiency of feedstock utilization and energy use, and the lower the production of waste with its attendant disposal and environmental costs. Realizing higher selectivity not only makes better use of feedstocks, but also translates into minimization and even avoidance of downstream separations; both reduce costs. Because these downstream processes often dominate the capital, operating, and energy costs of catalytic processes, selectivity improvement has an amplifying effect on energy efficiency well beyond efficiency of reactant utilization.

1. *Control of catalyst structures at the atomic and nanometer length scale.* The attainment of high selectivity is linked intrinsically to catalyst uniformity. Sites that are not optimal for the desired reaction may catalyze undesired side reactions instead. Thus, the challenge is to synthesize catalysts with uniform sites at the atomic or molecular scale. This strategy has been especially successful for olefin polymerization, whereby molecular catalysts allow precise control of product polymer microstructure. Achieving this kind of specificity in heterogeneous catalysis would have enormous potential for transforming the chemical industry.

   Progress is being made in the area of controlling materials synthesis on the atomic and nanometer length scales, making the goal of materials with uniform sites achievable. One example of a method that has become available for producing materials with controlled surface structures involves self assembly of nanoparticles of different materials into superlattices (Shevchenko et al. 2006). These self-assembly methods have been shown to provide a general and inexpensive path for producing a wide variety of materials with precisely controlled chemical compositions and tight placement of the components. Another technique that has become available for producing uniform materials is atomic layer deposition, which allows atomic layer control of films as fine as 0.1 nm in thickness inside deep trenches, porous media, and around particles.

   Rational catalyst design will have to go hand-in-hand with development of the process, especially for some new processes, such as the production of chemicals and liquid fuels from biomass. This combination is required because the success of the process will ultimately depend on the success of developing a catalyst. Because biomass feedstocks differ qualitatively, particularly in oxygen content, from crude oil and natural gas, it is likely that many of these applications will require entirely new catalysts, with materials tailored to the catalytic environment in which they will operate. For example, materials for processing biomass will almost certainly need to catalyze reactions in highly corrosive aqueous environments. Our ability to synthesize catalysts with the proper composition and structure will be critical. Similarly, the processing of more complex fossil fuels, such as tar sands and coal, into more usable liquid forms will require catalysts tailored to these feedstocks.

   An additional benefit to synthesizing specific structures in which atoms are arranged in a predetermined way is that these materials should lead to rapid assessments of theories on structure-property relationships, and to efficient assembly of the best “candidate structures” for carrying out a given reaction. At present, catalyst properties are known to be sensitive to structural features that span the atomic to the nanometer length scales. At the atomic level, the spatial arrangement of atoms at the active site plays a crucial role in the activation of

Using the Response to Environment to Stabilize Solid Catalysts

Many solid catalysts are composed of a metal or metal oxide dispersed as nanoparticles on a relatively inert support. Reaction rates are typically proportional to the surface area of the active component, and one role of the support is to maintain high surface areas of the expensive catalyst consisting of relatively small amounts of the material. Often, catalysts must operate at high temperatures, in harsh environments. As a result, deactivation is a serious problem because of loss of surface area or changes in structure of the active component. An important example involves automotive emissions-control catalysts, which are prepared from precious metals (platinum, rhodium, and palladium) on oxide supports. Relatively large amounts of the precious metals are required to maintain the necessary performance after the catalyst has been severely treated.

An opportunity has recently been demonstrated for using the response of the catalyst to changes in the gas-phase environment to maintain the catalyst in its highly dispersed, active form, using much less precious metal. Precious metal ions can be incorporated in their ionic state into a perovskite (ABO_3) host where they remain isolated under oxidizing conditions (Nishihata et al. 2002). When exposed to reducing conditions (as they are periodically in the cyclic redox environment of a catalytic converter), the precious metal ions are released by the host in the form of catalytically active nanoparticles. This environmental response appears to be a general phenomenon and has been characterized extensively for $BaCe_{1-\chi}Pd_{\chi}O_{3-\delta}$, as illustrated in Figure 5, by electron microscopy and calculations based on DFT. Under environmental conditions when metal particles would be expected to sinter and lose surface area (i.e., at high temperatures in excess oxygen), they can instead be re-absorbed into the perovskite lattice. The metal nanoparticles are recovered, however, upon exposure to a reducing atmosphere.

This example is important in demonstrating the principle that interactions between a catalyst and its support can be used to achieve high activity and stability. Fundamental understanding of the solid-solid interfaces in these materials is crucial for understanding how the catalyst will respond to its environment and for taking full advantage of catalyst-support interactions.

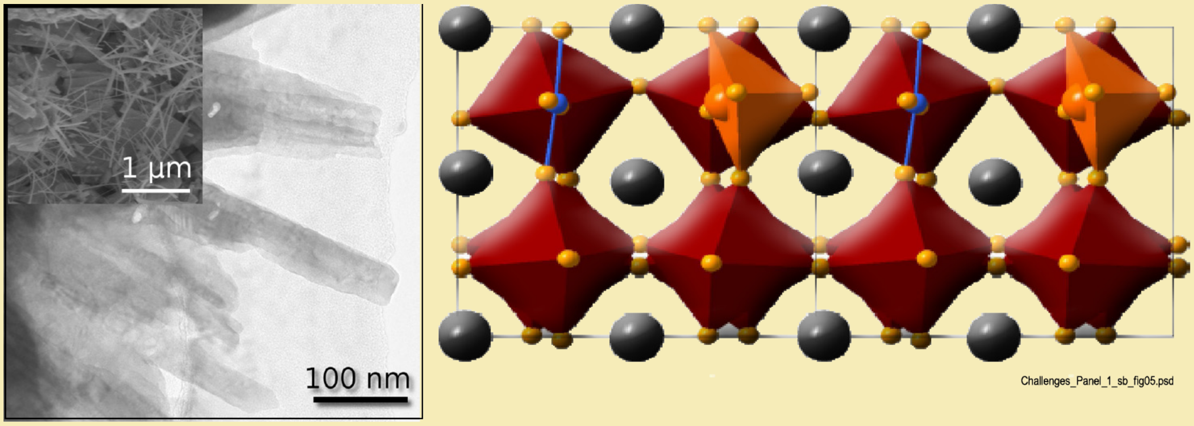

Figure 5: Transmission electron microscope image of perovskite nanowires that are formed when $BaCe_{1-\chi}Pd_{\chi}O_{3-\delta}$ is reduced and *fcc*-palladium is extruded. The inset is a scanning electron microscope image showing larger regions with such wires emerging. On the right is the DFT--generalized gradient approach calculated structure of $Ba_8Ce_7PdO_{23}$, showing square-planar palladium(II) in blue. Reprinted with permission from Li et al. (2007). Copyright (2007) American Chemical Society.

reactants. If the active sites involve more than one kind of metal atom (e.g., in bimetallic catalysts and in mixed metal oxides), the controlled synthesis of particular heteroatomic linkages is of great importance. Many important catalytic properties are also derived from nanoscaled structural features, such as particle size for metal catalysts, catalyst-support interfaces, and framework mesoporosity; gaining control of these features with the precision typical of atom-by-atom molecular chemistry is a worthy challenge.

2. *Understanding how catalyst structure evolves in a reactive environment.* Because most solid catalysts consist of more than one phase (e.g., a metal catalyst on a porous support), a fundamental understanding of how the solid phases interact, both during preparation and under reaction conditions, is essential for developing and stabilizing high-performance materials. Most catalysts deactivate over time, often because of sintering or changes in physical structure of the active component. These changes are the result of materials “moving” towards their equilibrium state characteristic of the actual reaction environment. However, if materials could be designed so that the equilibrium state is the active state, these materials could have intrinsic stability. An excellent example illustrating this principle is that of a palladium catalyst supported on $LaFe_{0.6}Co_{0.4}O_3$ perovskite (Nishihata et al. 2002),

Cooperativity between Chemical Functions in Imprinted Silicas Controls Catalyst Selectivity

The synthesis of microporous and mesoporous catalysts is frequently carried out with “templates” to control pore structure. Similar strategies may be employed to imprint amorphous materials such as silica or polymers with cavities that contain specific arrangements of chemical functions. If these are located in proximity to each other, they can act cooperatively (much as in enzyme catalysts) to produce new chemistry.

For example, by imprinting silicas with carbamates, one can produce cavities, each containing a single amine group tethered to the silica by an alkyl chain. Depending on the details of the synthesis, the material can be prepared such that these amine groups can have neighboring silanol (SiOH) groups, or these silanol groups can be capped with nitrile-containing functions. These groups can work cooperatively to catalyze new reactions, as illustrated in Figure 6.

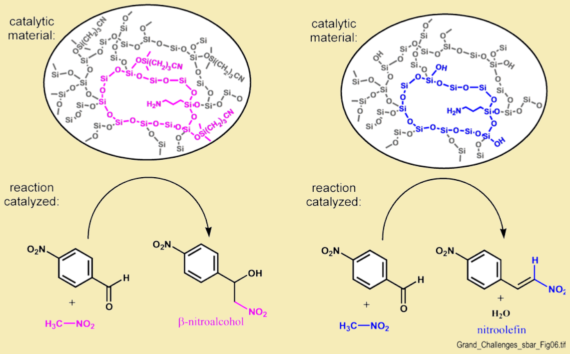

Figure 6: Effect of environment surrounding aminocatalyst active site on nitroaldol catalysis. Reprinted with permission from Bass et al. (2006). Copyright (2007) American Chemical Society.

Acid-base cooperativity between silanol and amine groups leads to a nitro olefin product in the reaction of nitrobenzaldehyde with nitromethane, as shown on the right side of Figure 6. In contrast, the primary amine site within the nitrile-rich environment on the left directs the reaction through an aldolate intermediate to form the nitroalcohol product with greater than 99 percent selectivity. This reaction is the first example of primary amine catalysis to form an alcohol in this reaction, illustrating the potential for designing and synthesizing multifunctional catalyst sites (Bass et al. 2006).

in which palladium was shown to remain highly dispersed, even after exposure to very harsh conditions, due to palladium movement in and out of a perovskite lattice during cyclic oxidation and reduction cycles. This concept is already being used in commercial catalysts to maintain palladium dispersion.

To design stability into most catalysts requires a fundamental understanding of solid-solid interfaces, which includes the vital role of the chemical environment. Traditionally, the practice of materials design and selection assumes a static role for the solid; the suitability of a material for a particular chemical application is determined in large part by its ability to *withstand* the widest possible range of temperature and environmental conditions that the solid is likely to encounter. In contrast, recognition that materials respond to their chemical environments should allow the development of materials in which the environment is crucial to its function. In some cases, the new materials may arise from a starting proto-material that evolves in response to stimuli from its chemical environment. In other cases, materials may exhibit *flexible (and desirable) responses* to environmental changes/stimuli, such as multiple functional states and structures.

Catalytic reactions that occur in multiphase systems are influenced by the physical and chemical characteristics of species in the interphase region, including the catalytically active site, other active phases or adjacent structural components of the catalyst, reactive intermediates, and solvents. To achieve the desired performance characteristics, including the production rates, selectivities, and durabilities, new tools and strategies must be developed to control the phase morphology, structure, and composition at length scales ranging from atomic to macroscopic.

3. *Integration of multiple catalytic functions.* Beyond the optimization and design of catalysts for individual chemical transformations, a further challenge is to *combine* functions to achieve highly selective multifunctional catalysts. At the molecular scale, meeting this goal involves the combination of multiple reactive groups within an active site, as in enzymes. At the microscopic scale, this strategy can be represented by examples such as the combination of metal and acid functions on a common support, or the introduction of additional chemical functionality via dense or structured fluid phases. The ability to carry out a sequence of desirable reactions in a chemical process, without intermediate separations of the products and reactants, can also lead to significantly improved energy efficiency and improved processes. In some cases, the ability to carry out multiple reactions in the same reaction vessel can be the difference between whether or not a product can even be made. For example, liquid alkanes can be produced from carbohydrates through a sequential aldol condensation with acetone, followed by the hydrogenation of the products in the same batch reactor. Because of high costs of product separation, this process can be practical only with a bifunctional catalyst that is able to carry out both chemical transformations in the same reactor (Barrett et al. 2006).

4. *Three-dimensional nanostructured catalysts.* Many state-of-the-art solid catalysts take advantage of three-dimensional porous structures for achieving a high level of selectivity. For example, on nanometer length scales, size and shape discrimination effects in zeolites have long been established. Given the great utility of these properties to improve catalytic selectivity, it is of interest to access a wider array of porous structures of this type. The catalysts may include structures that feature non-covalent interactions, such as hydrogen bonding, hydrophobic solvation, and electrostatic complexation. New three-dimensional

nanostructures may be based on oxide frameworks or inorganic-organic hybrid systems that incorporate multiple functionalities. The architectures of these catalysts should incorporate elements that lead to high degrees of stability and allow for tailoring (e.g., to provide highly specific reactant-catalyst-binding modes or sites that stabilize the transition state for a given reaction). Furthermore, incorporation of multiple catalytic centers may be the basis for design of tandem (cascade) reaction schemes. This goal may also be achieved with small particles of the three-dimensional nanostructure and by manipulation of particle morphology to promote cooperative, sequential reaction steps at different catalytic domains of a nanostructure. The importance of cooperative operation between components is shown by the example of ceria-supported metals for the water-gas shift reaction (Fu et al. 2003). The reaction, which is critical for hydrogen fuel cells, occurs at rates that are orders of magnitude higher on ceria-supported metal catalysts than on the metals or ceria separately.

5. *Utilization of principles employed by enzymes: biomimetic catalysts.* Biological catalysts often utilize dynamic, time-varying steric and electronic properties of the local machinery—the catalytic center itself and the surrounding sophisticated and complex “traffic control” environment—to achieve high levels of reactant specificity, turnover frequencies, and stability. These catalysts also offer multifunctional behavior caused by the proximity of Lewis acid and base sites, protons, and electrons. They also exhibit the highly tuned ability to control the timing by which reactants are delivered to the catalytic center, as well as strict spatial control that influences reactant positioning and the transport of reactants and products. Moreover, such catalysts may incorporate signaling functions that turn the enzymatic activity on and off. The development of biomimetic catalysts must therefore be based on understanding rules for cooperative catalysis that occur in biological systems, wherein multiple functional groups participate within an active site and may function in a concerted fashion to accelerate catalysis. Bio-inspired catalysts may be generated by incorporating structural motifs that are stimuli-responsive for regulation of mass transport. Furthermore, this class of catalyst often has the ability to adapt to a variety of environments, via structural rearrangements or “self-repair” mechanisms. It would be highly desirable to incorporate these properties into the design and synthesis of catalysts. This goal may be achieved via use of non-covalent interactions, as provided, for example, by second-coordination-sphere interactions, which allow a conformational and structural reorganization of the catalyst and/or the catalyst support system under different conditions.

6. *Development of non-precious-metal catalysts with superior performance.* Many of the most useful soluble and solid catalysts incorporate precious metals such as rhodium, palladium, platinum, and ruthenium. These metals are expensive. Furthermore, their supply is limited. In very large-scale applications, such as might be required for synthesis of fuels from solar energy or widespread use of fuel cells for power generation, there would likely not be enough of these metals to meet the need. Precious metals must be used more effectively, or non-precious-metal catalysts must be developed as replacements. One example of progress in using precious metals more effectively is in the use of carbon nanotubes as support materials. The unique environment offered by the nanotubes—the absence of micropores or surface oxygen—can be used to stabilize small metal particles in the acidic environments found in proton-exchange membrane fuel-cell applications (Joo et al. 2001).

Design and Synthesis of Extra-large-pore Zeolites

The discovery of the aluminophosphate VPI-5 with a unidimensional arrangement of pores formed by 18-membered rings demonstrated the possibility of achieving extra-large-pored crystalline molecular sieves. Since that discovery, aluminophosphates with up to 24-membered-ring pores have been prepared. However, in the case of zeolites, which are aluminosilicates, it has been difficult to obtain extra-large pores, and only recently have zeolites with 14-membered rings been prepared, but these still have low micropore volumes (UTD-1, CIT-5, SSZ-53, and SSZ-59) (Burton et al. 2003; Elomari and Zones 2001; Freyhardt et al. 1996; Wagner et al. 1997).

The syntheses of these zeolites emerged from the application of large organic structures as directing agents, illustrated in Figure 7.

Avelino Corma in Valencia, Spain, deduced that there may be a reason why so few extra-large-pored zeolites have been discovered, taking account of the work of Brunner and Meier (1989), who reported a correlation between the minimum framework density and the size of the smallest ring in the structure. Thus, Corma inferred that extra-large-pored zeolites or, even better, zeolites with very large micropore volumes, would have structures with a large number of 3- and 4-membered-ring sub-units. Indeed, very few of the known zeolites contain a large number of 3- and 4-membered rings in their structures.

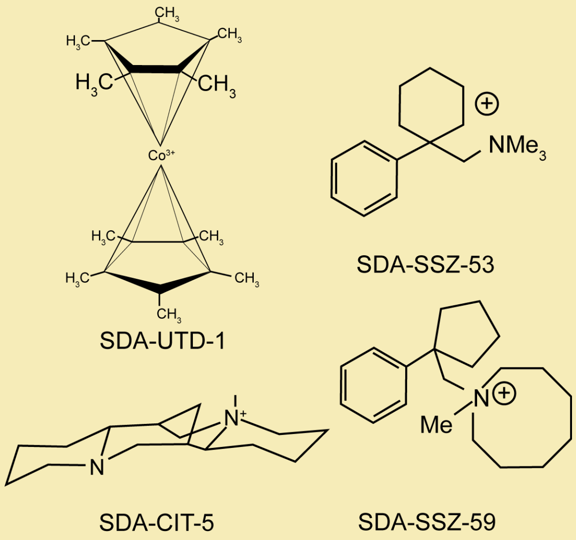

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Figure 7: Structure-directing agents for the synthesis of extra-large-pored zeolites. Reprinted with permission from Bass et al. (2006). Copyright (2007) American Chemical Society.

Thus, the Valencia group reasoned that one should use not only organic structure-directing agents, but also inorganic agents that can direct the formation of 3- and 4-membered rings by stabilizing secondary building units that contain these structures. The group led by Mark Davis at the California Institute of Technology was using zinc compounds to direct the formation of 3-membered rings; however, the presence of zinc also introduces two close negative charges into the framework, and this was suggested to hinder the synthesis of extra-large-pored zeolites.

7. *Combinatorial and high-throughput strategies for catalyst synthesis and evaluation.* It is often difficult to fine tune the structure of a catalyst to optimize efficiency. Thus, variations in reaction pathways may accompany slight changes in bond angles and distances near the active site and the positioning of functional groups within a catalytic center. In such cases, more rapid progress may be made by high-throughput synthetic methods, by which such structural parameters might be varied in a systematic way. For example, a catalytic center may make use of a basic site that aids in binding a reactant near an activating site. In optimizing catalytic efficiency, computational methods may be of limited use, because calculated activation energies may vary only slightly with repositioning of the base. Rapid, simultaneous testing of similar structures may allow discovery of the optimum catalytic site. In this way, structure-reactivity relationships may be mapped out in an effective manner, to more quickly provide quantitative information about the keys to selectivity and activity in a given system.

Design and Synthesis of Extra-large-pore Zeolites (contd.)

Corma hypothesized that F^- and, especially, germanium can stabilize double 4-ring zeolites and should direct the formation of such zeolites. The hypothesis was checked by results showing that indeed germanium directed the formation of structures with double 4 rings and moreover that germanium was preferentially sited in these rings (Blasco et al. 2002; Corma et al. 2001, 2002).

Building on those results, they succeeded in preparing several extra-large-pored zeolites; these have the largest pores and largest micropore volumes yet reported for zeolites. Examples are ITQ-15 (which has a three-dimensional pore structure) (Corma et al. 2004a); ITQ-33 (Figure 8, Corma et al. 2006); and ITQ-37 (Moliner et al. 2007).

Beyond this, the guiding principles of the synthesis led the researchers to synthesize the pure silica A (pure silica LTA) zeolite (Corma et al. 2004b). This material, with its very high pore volume, has shown good results for olefin separations as well as prospects as a low dielectric-constant material for electronics. The ITQ-33 structure (Figure 8) with 18- and 10-membered ring pores shows unique behavior as a cracking catalyst, breaking the paradigm that it is not possible to obtain high yields of diesel fuel and propylene and lower yields of gasoline with just one zeolite—this product distribution corresponds to today's market demands in Europe. These new zeolite materials also offer advantages as catalysts for hydrocracking, aromatic alkylation, and other fuel conversions, as well as fine chemicals production.

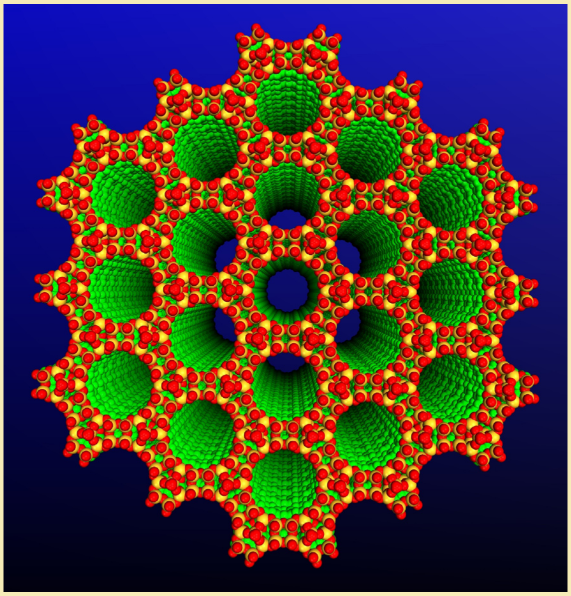


Figure 8: The ITQ-33 structure with 18- and 10-membered ring pores shows unique behavior as a cracking catalyst.

Broader scientific impacts

The discovery and development of synthetic strategies for producing catalysts with highly uniform properties will have broad scientific impacts. Foremost will be the evolution of the principles underlying the synthesis and assembly of materials possessing uniform composition and structure at the scale of 0.1 to 10 nm, which may also involve a hierarchy of levels of composition and structure. The discovery of how to build catalytic motifs emulating those found in nature would be immensely valuable and would lead to completely new classes of catalysts with previously unknown activities and selectivities.

The success of many critical advances in catalytic processing will depend on our ability to prepare specific, potentially complex (but well-defined) structures that facilitate the desired chemical conversions. For example, zeolite cracking catalysts, which are crystalline materials with well-defined and controlled structures, have had a major impact on catalyst technology and energy savings. Solid catalysts represent particularly difficult synthetic targets, because our ability to prepare detailed and variably controlled, tailored structures of complex solids is still at a rather primitive stage of development, especially for situations where large quantities of the material are required. Furthermore, solid catalysts usually operate in harsh reaction environments, and it is necessary that the active state be maintained, or perhaps even formed, in this environment.

Although significant progress has been made in the synthesis and understanding of molecular, homogeneous catalysts, important challenges still remain in both homogeneous and heterogeneous catalysis, both for preparing specific structures and for establishing key structure-activity relationships that would allow prediction of which structures are desired. Notwithstanding many recent breakthroughs in methodologies for solid-state synthesis, there are few general principles that can be used in the preparation of such structures (especially metastable ones) that will perform specific functions as catalysts. Thus, the development of generally useful synthetic principles remains a central theme in catalysis research.

Examples of some of the important approaches and classes of materials targeted as part of a grand challenge in the design and controlled synthesis of catalysts are as follows:

Homogeneous catalysts. One of the scientific challenges is to replace homogeneous catalysts that are presently incorporate precious metals. Therefore, the development of alternative catalysts that incorporate cheaper, more readily available metals such as iron, manganese, and nickel is essential. Attainment of this goal will also enable the use of catalytic processes on a very large scale, as might be required, for example, by certain schemes for solar energy conversion. Moreover, a high-impact research opportunity lies in developing not only generalizable ligand design principles for ensuring activity/selectivity with cheaper transition metals, but also catalyst thermal and oxidative stability. Success in this endeavor will require better integration of theoretical guidance into synthetic designs, quantitative measurements of metal-ligand bonding energetics, and thorough mechanistic investigations of catalyst decomposition/deactivation pathways. Building on the availability of these design principles, researchers should focus on understanding and differentiating steric and electronic factors that not only govern catalyst activity and selectivity, but also catalyst longevity. A combined focus could yield major intellectual and technological payoffs.

Surface-bound single-site catalysts. The surface of a solid represents a potentially useful support for the immobilization and tuning of reactive, single-site catalytic centers that display unique properties that are typically associated with homogenous catalysts. The surface may provide for site isolation and stabilization of reactive species and offer a platform for the creation of tailored, multifunctional catalysts. It is therefore important to establish reliable synthetic methods with a high degree of control for the generation of such catalysts, which may incorporate one or perhaps several metal centers at the active site. Such well-defined structures would be accessed via molecular design and prepared by a molecular precursor approach. Advances in this area of catalyst synthesis must be accompanied by breakthroughs in characterization methods that allow identification of detailed structures of isolated surface species of this kind. In general, it is important to develop an understanding of how various surfaces (e.g., zeolites, oxides, metals) act as ligands that can influence steric and electronic properties of an active metal center. Future generations of catalysts may well take advantage of the development of new solid supports with tunable surface properties. This tunability should facilitate chemical modifications of the surface that produce efficient multifunctional catalysts.

Nanoparticle catalysts. Although many of the most important industrial catalysts are composed of nanoparticles dispersed on a support material, our understanding of the role that size and shape play in catalytic activity is still very limited; with new tools, these properties can be measured directly and, thereby, provide new knowledge of great fundamental significance. For example, the importance of nanoparticle size and shape is evident from a scanning tunneling microscopy investigation of molybdenum disulfide nanoparticles. This investigation demonstrated that the edge sites of the nanoparticles have a very high electron density and are nearly as active as platinum for the electrochemical reduction of water (Jaramillo et al. 2007). The type of analysis used in the investigation of molybdenum disulfide particles cannot be immediately applied to all other types of materials, but the results underscore the importance for catalysis of probing the details of various sites on nanoparticles. An important goal of catalysis research involves precise control of the size and shape of nanoparticles, along with characterization of the unique catalytic properties that these materials provide.

Potential impacts on catalysis for energy applications

The ability to target desired catalyst compositions and then synthesize these materials at the atomic level and at longer length scales will have an enormous impact on catalytic science, chemical processing, and our utilization of energy. Some of these impacts are as follows:

Improvements in selectivity. Improved catalysts will provide better yields, better efficiency, and less waste in existing processes for the production of fuels and chemicals. If the products are based on petroleum, less petroleum will be required for producing the same amount of product. Better selectivity will usually generate less carbon dioxide.

New processes for production of fuels and chemicals. In many cases, the development of new catalytic processes, such as production of fuels and chemicals from biomass or the harvesting of solar energy to produce chemicals, will be viable only as we gain the ability to prepare materials that provide high activity for the desired reactions. Because many of these new processes will require that the catalysts tolerate harsh conditions, including corrosive environments and radiation, it is especially important to predict and then synthesize optimal catalyst compositions and structures. The ability to design and prepare catalytic materials will enable new commercial technologies.

Catalysts from available raw materials. The design and synthesis of effective catalysts from available raw materials will make some important technologies viable. For example, the cost of precious metals in the electrocatalysts used in low-temperature fuel cells is presently a major impediment to their large-scale use. The discovery and synthesis of catalysts that replace the precious metals, or at least use less precious metals, are critical.

More stable catalysts. Stability is an important issue in essentially all catalytic transformations. The ability to design and synthesize catalyst structures that are inherently stable will therefore impact many present and potential processes for the production of fuels and chemicals.

Interfaces and interphases in electrochemical systems. Catalysis at interfaces in ion- and electron-conducting media is at the heart of conversion of chemicals into electrical energy in fuel cells, as well as processes for conversion of electrical into chemical energy (e.g., water electrolysis, electrochemical syntheses). For example, ion transfer reactions taking place at water/metal or oxide/metal interfaces are critical for the performance of low-temperature proton-exchange membrane fuel cells and high-temperature solid oxide fuel cells, respectively. In addition to substantial structural complexities, a further complication in electrochemical systems is the significant potential drop across the interface under active electrochemical conditions. Thus, one must account for electric fields and concentration gradients that extend into separate phases in contact with each other. Photoelectrochemical systems are even more complex. The development of experimental and theoretical approaches aimed at the understanding and control of the elementary chemical steps at the interfaces is crucial for the formulation of efficient electrochemical systems that would perform with minimal over-potential losses. Moreover, synthesis strategies aimed at the control of the interface structure are needed to manipulate the active surface area involved in the transfer of charge species across the interface. Potential consequences of the previously mentioned advances would be the following:

1. identification of cheaper alternatives to platinum electrocatalysts (for fuel cells or water electrolysis)
2. discovery of solid-state electrolytes that can transport O^{2-} anions at low temperatures
3. identification of carbon-tolerant electrocatalysts (e.g., anodes for solid oxide fuel cells)
4. identification of electrocatalysts for carbon dioxide reduction.

Catalysis of solid-state reactions for energy storage and carbon capture. Although we tend to think of catalysis for energy applications primarily in terms of the processing of energy resources or the production and utilization of liquid fuels, there are critical problems to be solved in energy storage and carbon capture and sequestration. One of the significant barriers to the hydrogen economy is the lack of materials that can achieve reversible hydrogen storage to meet the U.S. Department of Energy's benchmarks. Understanding of how to catalyze solid-state reactions of metal hydrides and chemical hydrides would be a valuable breakthrough, but the development of the underlying principles is in its infancy. Likewise, it has been stated that "CO_2 capture and sequestration is the critical enabling technology that would reduce CO_2 emissions significantly while also allowing coal to meet the world's pressing energy needs" (MIT 2007). Reactions of carbon dioxide with solids, whether reversible (for capture purposes) or irreversible (for mineralization) could help to meet this critical challenge. Catalysis is needed to increase the rates and efficiencies of such processes in order to make them practical—but to meet the goal, we need to create a new discipline beyond traditional homogeneous and heterogeneous catalysis—the catalysis of solid-state reactions.

Control of catalytic processes: influence of the environment. Understanding of catalytic transformations requires knowledge of the structure of the catalyst and the catalytic sites. These structures are dynamic and depend on the environment in which the catalyst works; they are coupled to the environments. The scale of this coupling ranges from the atomic scale of catalytic sites to the macroscopic scale of the whole catalytic reactor.

There is a need—and a largely unmet set of opportunities—to effect *deliberate* control of catalyst performance via the environment. Many of the natural resources, including biomass and coal, that will be used to satisfy our nation's energy needs are complex in composition and structure and require multiphase catalytic processes for their conversion to fuels and chemicals. The introduction of additional phases and phase boundaries can create structure as well as functionality in proximity to the catalytic site. The challenge is to achieve a depth of understanding to allow control and design of catalysts working in environments that are complex, dense, inhomogeneous, and/or multiphase. Even incremental progress in this direction will advance our progress towards meeting scientific challenges that will impact a wide spectrum of timely energy conversion processes.

For example, conversion of bio-derived feedstocks in aqueous media provides opportunities for “one-pot” processes involving combinations of solid catalysts with soluble catalysts to carry out reactions in a desired sequence. Structures that exist within the fluid phases (e.g., dendrimers and micelles) might be used to introduce catalytic functions that are more complex than the simple soluble acids and bases that have been investigated so far. Other dense media, such as supercritical fluids, might be used to intervene in surface reactions directly. A possible advantage of carrying out reactions in such media would be a reduction in catalyst deactivation resulting from coke formation on the catalyst surface—because the supercritical fluid could solubilize and remove coke and coke precursors from the active sites. Furthermore, removal of reaction products from the catalytic site into a phase separate from that holding the reactants (e.g., by a second fluid phase or a membrane) could result in conversions exceeding the thermodynamic limits imposed if all of the reactants and products were present in the same phase. Selectivities of catalytic reactions can in prospect be manipulated by such strategies as well.

To achieve an understanding of catalysts and their manipulation in complex multiphase environments, new tools are required, both theoretical and experimental. Computational chemistry methods that can address catalytic reactions at the individual site level must be extended to include molecularly dense surrounding media. Such tools, which may involve various levels of structural definition of the catalytic sites and their environments, are under development, but they fall far short of being robust and general, failing to provide sufficient accuracy for quantitative guidance in catalyst design. Advances in the theoretical methods will facilitate the design of complex reacting systems in the presence of liquid media, as well as the selection of catalysts and conditions optimized for desired catalytic transformations.

New techniques and adaptations are needed, as discussed in the crosscutting sections of this report. For example, nuclear magnetic resonance spectroscopy can be applied in various modes to probe both solid- and liquid-phase species, as well as the dynamics of transport and reaction processes. Other spectroscopic methods, such as attenuated total internal reflectance techniques and sum frequency generation, may be needed to allow characterization of the catalytic sites and surface species in the absence of interference from liquid phases.

Advances in the characterization of solid catalysts in complex media will allow for unprecedented understanding of solid-fluid catalytic reactions in multiphase media. These in-situ techniques will be applicable beyond catalysis—to a variety of areas of scientific investigation when the ability to probe the solid-condensed fluid interface is important to understanding underlying chemical or physical phenomena.

Conclusions

The twenty-first century presents our nation, and indeed all of human society, with daunting energy and environmental challenges. Meeting these challenges in ways that do not compromise the planet for future generations will require new energy resources and efficient ways to utilize all resources with minimal environmental impact. Catalysis is central to this endeavor. It has enabled the development of the petroleum and petrochemical industries of the twentieth century and at the same time significantly reduced the pollution tied to the use of energy resources and fuels. Catalysis must enable the development and deployment of significant alternative energy resources and technologies in the twenty-first century, and do so in ways that further reduce environmental impact, especially of carbon dioxide release to the atmosphere.

The ultimate need is for new catalytic technologies, and these demand new catalysis science. We have at hand today an unprecedented set of experimental and theoretical tools to understand catalytic phenomena at the molecular level, and more are on the horizon. Our mandate is not only to create a new level of understanding of catalytic phenomena with predictive utility, but also to translate this knowledge into new catalysts and new technologies to meet the global energy challenge and the related environmental challenge.

We have articulated two grand challenges for catalysis. These are:

- understanding mechanisms and dynamics of catalyzed transformations
- design and controlled synthesis of catalytic structures.

These challenges are critical parts of an integrated whole: the ability to rationally design catalytic systems—the catalyst and the catalytic process—to accomplish any desirable transformation of energy and chemical resources. To do so, we must understand reaction mechanisms and the dynamic behavior of catalysts sufficiently to specify the nature of the catalytic site—its structure and its chemical and electronic properties. We must be able to synthesize catalysts according to our designs, and we must be able to integrate them into complex reaction environments that interact with the catalysts, reactants, and products in myriad ways. New and improved experimental and theoretical tools for spectroscopy, for imaging, for modeling and prediction, and for synthesis will be needed, not only to investigate model systems but especially to probe working catalysts.

Two critical adjectives describe the catalytic processes on which our energy future will depend. The first is *selective*. Achieving higher selectivities of catalytic transformations translates directly into reduced resource utilization, increased atom economy, increased energy efficiency, reduced capital and operating costs, and reduced waste! The ultimate goal is the design and realization of practical catalysts for 100 percent selectivity.

The second adjective is *complex*. The production of fuels and chemicals by selective catalytic conversion of heterogeneous feedstocks is by its nature complex. One challenge going forward is not only the efficient conversion of chemically complex feedstocks such as coal and biomass, but also achievement of the same level of selectivity, efficiency, and flexibility for the "bio-refinery" or the "Fischer-Tropsch refinery" that characterize the century-plus development of the petroleum refinery. We do not have a century to develop these alternative resources, but we do have an unprecedented and growing science base underpinning the field of catalysis. Our grand challenge is to expand and to marshal that base to meet the energy and environmental needs of humanity for this and future generations.

References

Barrett, C. J., J. N. Chheda, G. W. Huber, and J. A. Dumesic. 2006. "Single-reactor Process for Sequential Aldol-condensation and Hydrogenation of Biomass-derived Compounds in Water," *Applied Catalysis, B: Environmental* **66**(1-2):111-118.

Bass, J. D., A. Solovyov, A. J. Pascall, and A. Katz. 2006. "Acid-base Bifunctional and Dielectric Outer-sphere Effects in Heterogeneous Catalysis: A Comparative Investigation of Model Primary Amine Catalysts," *Journal of the American Chemical Society* **128**(11):3737-3747.

Blasco, T., A. Corma, J. Diaz-Cabanas, F. Rey, J. A. Vidal-Moya, and C. M. Zicovich-Wilson. 2002. "Preferential Location of Ge in the Double Four-Membered Ring Units of ITQ-7 Zeolite," *Journal of Physical Chemistry B* **106**:2634-2642.

Brunner, G. O., and W. M. Meier. 1989. "Framework Density Distribution of Zeolite-type Tetrahedral Nets," *Nature* **337**:146-147.

Bucksbaum, P. H. 2007. "The Future of Attosecond Spectroscopy," *Science* **317**(5839):766-769.

Burton, A., S. Elomari, C. Chen, R. C. Medrud, I. Y. Chan, L. M. Bull, C. Kibby, T. V. Harris, S. I. Zones, and E. Vittoratos. 2003. "SSZ-53 and SSZ-59: Two Novel Extra-large Pore Zeolites," *Chemistry - A European Journal* **9**(23):5737-5748.

Corma, A., M. T. Navarro, F. Rey, J. Ruis, and S. Valencia. 2001. "Pure Polymorph C of Zeolite Beta Synthesized by Using Framework Isomorphous Substitution as a Structure-directing Mechanism," *Angewandte Chemie International Edition* **40**:2277-2280.

Corma, A., M. Díaz-Cabañas, J. Martinez-Triguero, F. Rey, and J. Ruis. 2002. "A Large-cavity Zeolite with Wide Pore Windows and Potential as an Oil Refining Catalyst," *Nature* **418**:514517.

Corma, A., M. J. Díaz-Cabañas, F. Rey, S. Nicolopoulus, and K. Boulahya. 2004a. "ITQ-15: The First Ultralarge Pore Zeolite with a Bi-directional Pore System Formed by Intersecting 14- and 12-ring Channels, and its Catalytic Implications," *Chemical Communications* **12**:1356-1357.

Corma, A., F. Rey, J. Rius, M. J. Sabater, and S. Valencia. 2004b. "Supramolecular Self-assembled Molecules as Organic Directing Agent for Synthesis of Zeolites," *Nature* **431**:287-290.

Corma, A., M. J. Díaz-Cabañas, J. L. Jordá, C. Martínez, and M. Moliner. 2006. "High-throughput Synthesis and Catalytic Properties of a Molecular Sieve with 18- and 10-member Rings," *Nature* **443**:842-845.

Craig, C. F., W. R. Duncan, and O. V. Prezhdo. 2005. "Trajectory Surface Hopping in the Time-dependent Kohn-Sham Approach for Electron-nuclear Dynamics," *Physical Review Letters* **95**(16): Art. No. 163001.

Elomari, S., and S. I. Zones. 2001. "Zeolites and Mesoporous Materials at the Dawn of the 21st Century," *Proceedings of the 13th International Zeolite Conference,* Montpellier, France, 8-13 July 2001, eds. A. Galarneau, F. Di Renzo, and F. Fajula, Elsevier: New York. In *Studies of Surface Sciences Catalysis* **135**:479.

Freyhardt, C. C., M. Tsapatsis, R. F. Lobo, K. J. Balkus Jr., and M. E. Davis. 1996. "A High-silica Zeolite with a 14-tetrahedral-atom Pore Opening," *Nature* **381**:295-298.

Fu, Q., H. Saltsburg, and M. Flytzani-Stephanopoulos. 2003. "Active Nonmetallic Au and Pt Species on Ceria-based Water-gas Shift Catalysts," *Science* **301**(5635):935-938.

Hahn, J. R., and W. Ho. 2001. "Oxidation of a Single Carbon Monoxide Molecule Manipulated and Induced with a Scanning Tunneling Microscope," *Physical Review Letters* **87**(16): Art. No. 16610.

Hansen, P. J., J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, and H. Topsøe. 2002. "Atom-resolved Imaging of Dynamic Shape Changes in Supported Copper Nanocrystals," *Science* **295**(5562):2053-2055.

Jaramillo, T. F., K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch, and I. Chorkendorff. 2007. “Identification of Active Edge Sites for Electrochemical H_2 Evolution from MoS_2 Nanocatalysts,” *Science* **317**(5834):100-102.

Johannessen, T., J. H. Larsen, I. Chorkendorff, H. Livberg, and H. Topsøe. 2001. “Catalyst Dynamics: Consequences for Classical Kinetic Descriptions of Reactors,” *Chemical Engineering Journal* **82**(1-3):219-230.

Joo, S. H., S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, and R. Ryoo. 2001. “Ordered Nanoporous Arrays of Carbon Supporting High Dispersions of Platinum Nanoparticles,” *Nature* **412**(6843):169-172.

Li, J., U. G. Singh, J. W. Bennett, K. Page, J. Weaver, J. P. Zhang, T. Proffen, A. M. Rappe, S. L. Scott, and R. Seshadri. 2007. “$BaCe_{1-\chi}Pd_{\chi}O_{3-\delta}$ $(0 < x<0.1)$: Redox Controlled Ingress and Egress of Palladium in a Perovskite,” *Chemistry of Materials* **19**(6):1418-1426.

Li, X., and J. C. Tully. 2007. “Ab Initio Time Resolved Density Functional Theory for Lifetimes of Excited Adsorbate States at Metal Surfaces,” *Chemical Physics Letters* **439**(1-3):199-203.

Li, X., J. C. Tully, H. B. Schlegel, and M. J. Frisch. 2005. “Ab Initio Ehrenfest Dynamics,” *Journal of Chemical Physics* **123**(8): Art. No. 084106.

Marks, T. J., ed. 2006. “Introduction: Polymerization,” *Proceedings of the National Academy of Sciences of the United States of America* **103**(42):15288.

Massachusetts Institute of Technology (MIT). 2007. *The Future of Coal*, Massachusetts Institute of Technology: Cambridge, Massachusetts. Accessed October 29, 2007, at http://web.mit.edu/coal/The_Future_of_Coal.pdf.

Moliner, M. M., M. J. Diaz-Cabanas, A. C. Sanz, and A. C. Canos. 2007. “A Microporous Crystalline Material, Zeolite ITQ-37, Preparation Method and Use,” World Patente WO2007099190(A1).

Nishihata, Y., J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, and N. Hamada. 2002. “Self-regeneration of a Pd-perovskite Catalyst for Automotive Emissions Control,” *Nature* **418**(6894):164-167.

Ogawa, N., G. Mikaelian, and W. Ho. 2007. “Spatial Variations in Submolecular Vibronic Spectroscopy on a Thin Insulating Film,” *Physical Review Letters* **98**(16): Art. No. 166103.

Shevchenko, E. V., D. V. Talapin, N. A. Kotov, S. O’Brien, and C. B. Murray. 2006. “Structural Diversity in Binary Nanoparticle Superlattices,” *Nature* **439**(7072):55-59.

Stier, W., and O. V. Prezhdo. 2002. “Nonadiabatic Molecular Dynamics Simulation of Light-induced, Electron Transfer from an Anchored Molecular Electron Donor to a Semiconductor Acceptor,” *Journal of Physical Chemistry B* **106**(33):8047-8054.

Topsøe, H. 2003. “Developments in Operando Studies and In Situ Characterization of Heterogeneous Catalysts,” *Journal of Catalysis* **216**(1-2):155-164.

Wagner, P., M. Yoshikawa, K. Tsuji, M. E. Davis, M. Lovallo, and M. Taspatsis. 1997. "CIT-5: A High-silica Zeolite with 14-ring Pores," *Chemical Communications* (22):2179-2180.

Wu, S. W., N. Ogawa, and W. Ho. 2006. "Atomic-Scale Coupling of Photons to Single-molecule Junctions," *Science* **312**(5778):1362-1365.

ADVANCED CATALYSTS FOR THE CONVERSION OF HEAVY FOSSIL ENERGY FEEDSTOCKS

Current Status

Fossil fuels will be the backbone of the world's energy supply for the foreseeable future. Alternative energy resources, such as nuclear, solar, wind, and biomass, are not presently available in quantities approaching the current world energy demand—and the demand is increasing with the rapid economic growth in formerly developing countries such as China and India. In particular, transportation fuels, which currently account for approximately 40 percent of energy usage in the world, will continue to require liquid fuels that can be easily transported, stored, and used in widely distributed vehicles. Light, sweet crude oil reserves are being depleted rapidly. Consequently, much of the demand for transportation fuels is almost certain to be met by heavy fossil resources, including heavy oil, tar sands, shale oil, and coal. These resources are characterized by high concentrations of heteroatoms (i.e., sulfur, nitrogen, and metals) that must be removed to meet environmental standards or to protect downstream catalysts. As discussed in the sidebar, hydroprocessing is critical to removing heteroatoms. With this processing, coal and the high-molecular weight hydrocarbons in heavy oil, tar sands, and shale offer a carbon capacity that can, in principle, serve the energy needs of the United States and world for roughly 100 years.

Economic conversion of these heavy feedstocks into useful products presents massive technological challenges, and the scientific basis for creating the needed technology is weakly developed. The research needs are the focus of the following section of this report.

To meet the scientific challenges, we need a step-change improvement in the fundamental understanding of the following:

- compositions of the feedstocks
- the reactivities of the various components of the feedstocks in the presence of prototype catalysts
- a foundation of data to allow prediction of the reactivities of any feedstocks and mixtures of feedstocks (including added biomass-derived components), to allow prediction of process performance and product properties.

Such a knowledge base will make possible the transformation of current petroleum refining technology into technology for future fossil feedstocks and bridge it into technology for biomass conversion.

A foundation of understanding that will help guide future research on heavy fossil feedstock conversion is provided by the well-known chemistry of current petroleum conversion processes. Although most feedstocks today are simpler, lower-boiling mixtures than those that will become dominant, they contain many of the reactant types of future feedstocks and undergo processes that include the reaction classes needed in the future. Thus, the scientific challenge is largely to adapt to larger and more complex molecules as reactants and to higher contents of heteroatoms and structures that are not simple molecules—such as the semi-solids in petroleum that are classified as asphaltenes. Important strides in understanding the conversion of petroleum vacuum residua have already been made, and they provide valuable guidance for future research.

Model Hydrodesulfurization Catalysts Consisting of Molybdenum Disulfide Nanoclusters

Catalytic hydroprocessing, which includes reactions of fossil fuels with hydrogen to remove contaminant sulfur, is the largest-scale industrial application of catalysts. Researchers have worked for decades to understand and improve hydroprocessing catalysts, which are now understood to consist of nanostructures incorporating molybdenum, sulfur, and promoter cobalt or nickel, supported on aluminum oxide. Work in the 1970s led to the first primitive models of the catalytically active species based on sketchy spectroscopic results and inferences based on the solid-state chemistry of metal oxides and metal sulfides. Understanding the role of the promoters in the catalyst structures later emerged from investigations of model molybdenum sulfide structures supported on carbon and characterized at synchrotrons by x-ray absorption spectroscopy. High-resolution images determined by transmission electron microscopy further clarified the nature of the catalysts, showing the presence of supported layers of molybdenum disulfide only a few atoms thick (Figure 9).

Model catalysts consisting of molybdenum disulfide nanoclusters on gold surfaces and their imaging by scanning tunneling microscopy and modeling with density functional theory (DFT) led to fundamental understanding of the catalytic sites, present on the edges of the nanoclusters. The images show individual atoms and illustrate the size and morphology of the nanoclusters; the nanocluster morphology depends sensitively on the environment of the catalyst and is not the same as that of bulk molybdenum disulfide.

DFT calculations, consistent with earlier spectroscopic data, show details of the chemistry and give insights into the operation of the catalyst at the molecular level. Testing of industrial catalysts with various pure compounds selected from among those present in petroleum fractions (including heavy [residuum] fractions), showed which compounds react most slowly, exemplified by 4-methyldibenzothiophene.

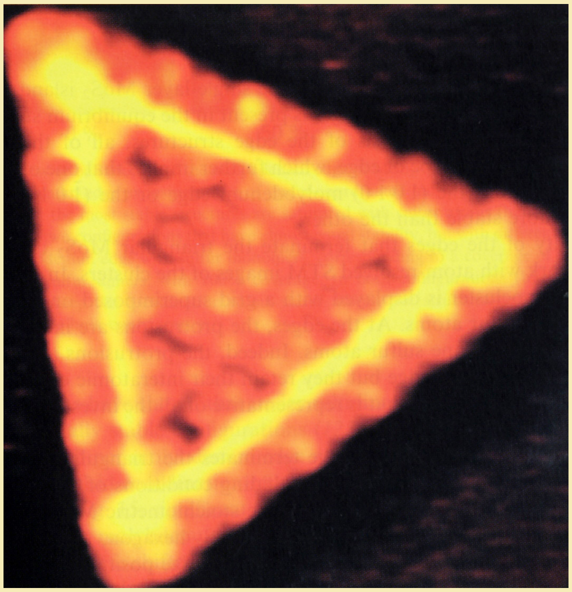


Figure 9: High-resolution transmission electron microscopy images show supported layers of molybdenum disulfide that are only a few atoms thick. Reprinted with permission from Helveg et al. (2000). Copyright 2000 by the American Physical Society.

Because the difficult-to-convert compounds have to be largely removed to meet current goals for sulfur removal to minimize pollution by sulfur oxides in fuel combustion, the processing goal could then be simplified to essentially the removal of these few compounds, as the others are converted so fast by comparison as to be considered infinitely reactive.

Continuing fundamental research including adsorption experiments and theory led to understanding of how the sulfur compounds bond to the catalytic sites, determining whether the hydrogen reacts to remove sulfur or instead reacts to saturate the molecules without removing the sulfur. There are now models of the reaction mechanism based on density functional theory.

This example illustrating how decades of fundamental research have identified both the essential characteristics of very complicated feedstocks and the key structures of the catalysts—the catalytic sites—and how they function for selective removal of sulfur to manufacture clean-burning fuel. Catalyst manufacturers have built on this fundamental understanding to make continually improved industrial catalysts for fuel hydroprocessing.

Basic Science Challenges, Opportunities, and Research Needs

Elucidation and prediction of heavy, complex fossil feedstock conversion

Heavy oils are complex in terms of the number and variety of the molecules in them as well as the interactions between the molecules—some of the molecules are so heavy and the structures so complex that solid-like components are present (asphaltenes). Recent advances in analytical methods present a major opportunity to understand these mixtures in depth as a basis for predicting their reactivities. High-resolution mass spectrometry has already been used effectively in the characterization of petroleum, identifying essentially all of the soluble compounds. This methodology needs to be extended to the characterization of the available heavy oils, liquids formed from tar sands, shale oil, coal liquefaction products, and biomass-derived products. When bolstered by complementary methods of analytical chemistry, such as fractionation of the feedstock by preparative liquid chromatography prior to analysis by mass spectrometry, and application of complementary spectroscopic methods including ^{13}C nuclear magnetic resonance (NMR) spectroscopy, analysis of these feedstocks will provide a strong foundation of understanding of their components, as a basis for elucidating and predicting their reactivities with various catalysts under wide ranges of reaction conditions. Regrettably, however, the existing capability for conducting this analytical chemistry is weak, and only little research in this direction is now being pursued.

Characterization of feedstock reactivities

To account for the reactions of mixtures of countless numbers of compounds, such as those comprising the heavy fossil feedstocks of the future, researchers have developed methods of accounting for reactions of the compound classes shown to be dominant. This approach is referred to as lumping, whereby many similar compounds are represented by—lumped as—a single prototypical compound. Lumping approximations have been applied to feedstocks ranging from the light hydrocarbon mixtures that are converted in naphtha reforming to petroleum vacuum residua (Jaffe et al. 2006).

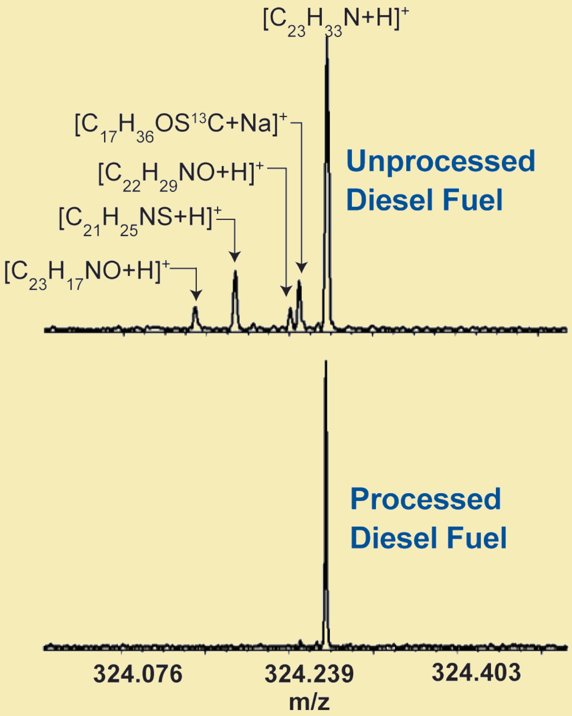
This approach forms part of a basis for understanding heavy feedstocks and their reactivities. Recent literature (Jaffe et al. 2006) describes the approach and provides testimony to its great economic value; however, it lacks the crucial quantitative information that would be of immediate value in applications and provides no information about the catalysts with which the data were obtained. Thus, this literature helps to provide a roadmap for setting a foundation of fundamental understanding needed to guide future technology of heavy fossil fuel conversion. In the following, we suggest how to proceed on the basis of this roadmap.

Identification of prototype compounds and determination of their reactivities. We already have a good idea of the classes of reactions that are needed for upgrading heavy fossil feedstocks. These include hydrogenation, removal of heteroatoms by reactions with hydrogen (hydrodesulfurization, hydrodenitrogenation, and hydrodemetallization) (Gates and Topsøe 1997; Prins et al. 2006; Rang et al. 2006; Song 2003); cracking, isomerization, hydrogenolysis, and dehydrocyclization.

Molecular Characterization of Catalyzed Hydrotreatment of Raw Diesel Fuel

The petroleum industry will soon be required to remove 95 percent of the sulfur from raw diesel feedstocks. Fortunately, ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry can now resolve and assign more than 10,000 elemental compositions for the organic components of petroleum and its distillates. Thus, determining the efficiency of removing all of the heteroatom-containing (nitrogen, oxygen, sulfur [NOS]) molecules in diesel fuel before and after catalytic processing is now possible. Those “NOS” species produce harmful emissions during the burning of fossil fuels and can also deactivate the catalysts designed to remove them.

Figure 10 shows a very small segment (approximately 1 atomic mass unit, or Dalton) of the mass spectrum of diesel fuel before and after processing. It is clear that all but one of the NOS-containing components of mass (approximately 324 Dalton) have been removed. Similar profiles are obtained simultaneously for several hundred other 1-Dalton segments of the same mass spectrum. Thus, the oil industry has a new tool with unprecedented ability to read the “chemical fine print” of the extraordinarily complex mixtures that compose petroleum, and thus evaluate (as the first step in improving) the performance of hydrotreatment catalysts (Marshall and Rodgers 2004).

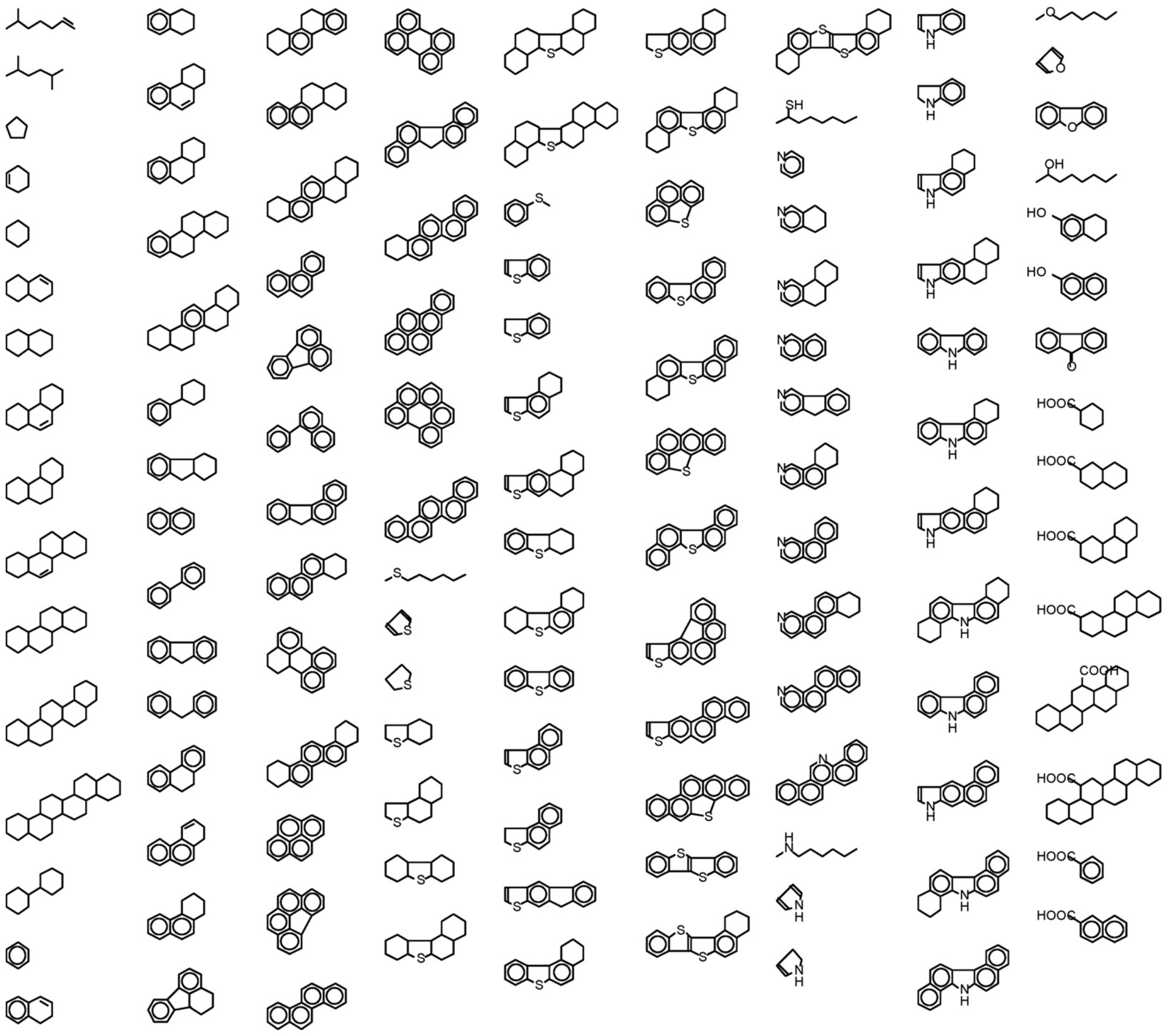


Panel_report_2_Feedstocks_sbar2_fig02.ai

Figure 10: Mass spectrum of diesel fuel before and after processing. Reprinted with permission from Hughey et al. (2001). Copyright 2001 American Chemical Society.

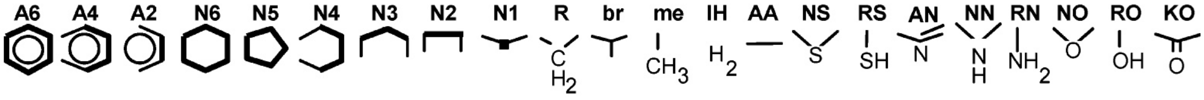
These are all known to occur in the conversion of current feedstocks. Realizing what these reactions are and having an in-depth understanding of what compounds are present in some petroleum vacuum residua, Jaffe and coworkers (2006) identified a set of groups characterizing the core structures in petroleum (Figure 11).

On the basis of the analytical chemistry and investigations of the reactions, they identified key reactive moieties (Figure 12).



Panel_Adv_Cat_Heavy_Fossil_Core_Structures_Fig03.psd

Figure 11: Core structures identified in petroleum. Reprinted with permission from Jaffe et al. (2006). Copyright 2006 American Chemical Society.



Panel_Adv_Cat_Heavy_Fossil_Depiction_Structural_Fig02.psd

Figure 12: Depiction of the extended structural increments (Jaffe et al. 2006). Reprinted with permission from Jaffe et al. (2006). Copyright 2006 American Chemical Society.

These represent the essential reactive groups in the list of compounds shown just above—hence in heavy petroleum fractions.

This set of compounds and reactive groups provides a starting point to be used with analytical data characterizing various feedstocks for identifying their components and key reactive groups. Investigations of the reactions of the feedstocks would lead to iterative improvement in the identification of which groups are important in the sense of the kinetics of the reactions (compounds that are essentially inert would be omitted, as would those with essentially infinite reactivities).

What is missing from this picture is quantitative data characterizing the reactivities of each class of compound and information about how various catalysts affect the reactivities. Therefore, research is needed, respectively, with (1) individual compounds found in all the heavy fossil feedstocks mentioned in this section, (2) groups of several such compounds, (3) groups of many such compounds, and (4) the full feedstocks themselves.

Investigations of reactivities carried out with individual compounds containing the key reactive groups are needed at the outset. The group labeled NS in Figure 12, for example, could be investigated with dibenzothiophene and methyl-substituted dibenzothiophenes. There is a need for systematic investigations of reactions of such compounds with catalysts that represent the fundamental constituents of the current petroleum refining catalysts. A preliminary list of prototypical catalysts (the list should be improved as research proceeds) includes acids (represented by silica-alumina, for example), metals (represented by supported platinum), and metal sulfides (represented by cobalt-promoted supported molybdenum disulfide). Some data characterizing such reactions on such catalysts under a range of processing conditions already exist.

Specific goals should include the following:

- perform analytical chemistry to understand the components in representative feedstocks of the future
- understand what are the core components
- select the set of reactants to include compounds representative of these feedstocks (e.g., more heteroatom-containing compounds and higher-molecular-weight compounds)
- gather a matrix of data for such compounds with each of the catalyst classes and expand the class of catalysts as progress is made
- use mixtures of compounds to understand competitive reaction and inhibition effects and how they depend on the catalyst.

The research should identify the most important compounds (e.g., those that react slowly and those that are strongly adsorbed and are reaction inhibitors), and increased attention should be focused on them.

The data representing these most important compounds should be expanded to allow elucidation of the reaction networks and quantitative kinetics, including competitive reaction and inhibition effects. This work would benefit from the application of isotopically labeled compounds for elucidation of the reaction networks of individual compounds in mixtures and the determination of kinetics. The work should focus on the catalysts that best represent the fundamental constituents of the catalysts that are judged most representative of those to be used in practice. As the research proceeds and the technology develops to include processing of feedstocks beyond current petroleum feedstocks, the feedstock compositions and catalyst compositions will change, and thus the catalysts to be investigated in fundamental research will change as well—but this change is expected to be gradual. Feedstocks containing more oxygen-containing compounds, for example, may necessitate the application of catalysts that have barely been investigated so far.

Because catalysts used in conversion of heavy feedstocks undergo massive changes during operation (for example, accumulating deposits of coke and of metal sulfides formed from the organometallic constituents in the feedstocks), their properties may change drastically. Thus, it will be necessary to include deactivated catalysts in the investigations and to elucidate how the compositions and structures present in the deactivated catalysts perform as catalysts.

We anticipate the benefits of developing high-throughput catalyst testing methodology to facilitate the measurement of fundamentally interpretable data (e.g., kinetics and quantitative reaction networks). It is a substantial challenge for reactions occurring at high temperatures and pressures and in the presence of heavy and complex feed mixtures to drive the high-throughput methods into the realm of fundamental research tools rather than just qualitative or semi-quantitative screening tools. Such an accomplishment would revolutionize the collection of catalyst performance data to maximize understanding and advancement of the processes of catalyst selection.

Fundamental investigations of reactant-catalyst interactions and reaction mechanisms. The basis of quantitative reaction networks, kinetics, and inhibition data described above will provide a starting point into fundamental investigations of fundamental reactivity patterns, including relationships between catalyst structure and activity, selectivity, and stability. The goals will be to determine catalyst structures in the presence of reactants and products, to determine the nature of the catalyst–adsorbate interactions and how the reaction environment changes the structures of the catalytic sites, and to determine mechanisms of the reactions. Much of the methodology for such investigations has been established (and is written about in the Grand Challenges section of this report). A major challenge is to extend the methods and develop new ones to accommodate the high molecular weights of the most representative reactant and inhibitor molecules, some of which are much larger than those that have been used in most of the fundamental catalysis research thus far. Another major challenge is to develop methods for investigating catalysts in reactive atmospheres and in the functioning state.

Conversion of complex feedstocks including determination of reactivities of individual compounds. Recently developed methods for determination of high-resolution mass spectra of heavy petroleum residua open the way to quantitative determination of reactivities of individual compounds in whole feedstocks under industrial reaction conditions, as well as of kinetics of the reactions. Such data will determine how these reactivities depend on the feedstock composition and catalyst as well as how well the data accord with those determined with simple mixtures of compounds and how reactivities change with catalyst aging. The data will help identify the key individual compounds, the ones that are most important and prototypical in the sense described above. Thus, the depth of fundamental understanding of catalytic reaction chemistry that is now attainable with light feeds such as petroleum naphtha will be attainable with the heavy feedstocks of the future.

Development of methods to carry out this ambitious research plan will require the extensive involvement of analytical chemists for quantitative analysis of the reactants and products, as well as extensive research to allow fundamental laboratory-scale reactor experiments with complex feedstocks that are often present in more than one phase in a reactor.

The research will benefit from experiments with feeds spiked with isotopically labeled compounds, allowing determination of quantitative reaction networks and kinetics from conversion of the labeled compounds combined with analysis of all the products of conversion of those compounds. In real feedstocks, the labeled compounds may be present in minute concentrations, and the analytical chemistry will be challenging.

When the analytical capabilities for the feeds and products are developed, then the quantitative reaction data can be determined for a range of catalyst types. Ultimately, rapid-throughput methods will allow determination of such quantitative information in experiments with complex feedstocks under conditions that mimic industrial-scale reactors.

In prospect, the recording of such data for blends of feedstocks (even including those derived from mixtures of fossil sources and from biomass) will lead to analysis of the conversion data to determine the effects of competitive reaction and inhibition and prediction of the performance of various catalysts under various conditions for any combination of feedstocks.

Ultimately, when these methods of quantitative fundamental investigation of whole feedstocks are established, the research described above with individual reactant compounds will become less needed. However, for years to come it will remain of importance until it becomes possible to do fundamental (e.g., spectroscopic) characterizations of the interactions between reactant molecules and catalyst surfaces in the presence of whole feedstocks.

Prediction of product properties. The work of Jaffe et al. (2006) with petroleum residua sketches the methods by which their lumping data guide the prediction of product properties. They have used their data to predict the following product properties:

- boiling-point distribution
- specific gravity vs. boiling point
- sulfur content vs. boiling point
- basic nitrogen content vs. boiling point
- nonbasic nitrogen content vs. boiling point
- nickel content vs. boiling point
- vanadium content vs. boiling point
- total acid number vs. boiling point
- asphaltene content vs. boiling point
- microcarbon residue vs. boiling point
- carbon content in aromatic rings vs. boiling point.

Development of these methods and their application to the broad range of future feedstocks and feedstock mixtures will provide an enormous benefit in terms of optimizing feedstock usage.

Conversions conducted at low temperatures and long times

The hydrocarbon resources that we categorize as crude oil are the result of chemical and biological conversions occurring underground over geological time frames, as biomass has been converted (via kerogen) to oil. There is an opportunity to modify and accelerate the chemical reactions involved in these slow natural processes. One method is to raise the temperature of the subsurface deposits at the geological source; oil shale (sedimentary rocks containing solid bituminous material) has been the subject of field research involving underground conversion processes. The temperature of the shale is gradually raised by electric heaters inserted into the field to turn the kerogen trapped inside the rock into light hydrocarbon liquids and gases, with virtually no residue. The light product is collected above ground, and the rock remains, with minimal environmental disruption. Much remains to be learned about the chemical reactions occurring underground, how they depend on the shale composition and temperature, and how to control them.

A complementary method is steam injection to reduce viscosity, which has already been practiced for some time in heavy oil recovery; in this case, the changes caused by the thermal treatments are more physical than chemical.

An alternative to underground thermal conversion is catalytic conversion. The underground application of catalysis is an essentially unexplored opportunity. There is an important basic research need here, as the combination of long reaction times and temperatures much lower than those used in refinery treatment takes us into uncharted territory. Initial work would be required to test various catalysts in terms of how well they could be brought in contact with the reactants underground; how fast they work; what reactions they catalyze; and how they could be used without detriments to the environment, such as underground water supplies.

Conversion of solid and solid-like components in fossil feedstocks

The molecules in the heavy, complex mixtures represented by heavy oil, tar sands, etc. present a set of issues that go far beyond the complexity of each individual molecule. The interactions between the molecules, for example, sometimes prevent reliable measurements of properties as fundamental as average molecular weight when current methods are applied. The mixtures are often covalent and physically crosslinked polymeric solids or highly viscous liquid mixtures. We need to understand the nature of the interactions between the molecules and the collective properties that emerge from these interactions and how they change as a result of catalytic processing. There is a need for measuring the fundamental thermodynamic properties of these complex materials and for understanding of the processes by which they are unzipped during thermal and catalytic conversions. Specifically, it is important to perform the following steps:

- identify the reaction pathways such as ring side-chain scrambling, ring expansion/contraction/opening, and other skeletal isomerizations in such complex mixtures
- delineate the extent to which each step in the conversion is thermal or catalytic, and which catalytic functions are involved
- develop the analytical methods for overall mass balances and carbon and other element mass balances
- develop methods for both spatial- and time-resolved identification of the reacting and transformed species.

Notwithstanding much prior work aimed at the defining the complex structures of coal, our level of understanding of these structures is minimal. There is also a daunting challenge in understanding the properties of heavy liquids derived from these solids by processes such as liquefaction, because the liquids are complex and because they are subject to "retrograde" reactions resulting, for example, from the presence of radicals formed during catalytic and/or thermal liquefaction processes; these reactions are poorly understood.

Multi-scale computational modeling and the attendant needs for characterization of structures and reactivities of the feedstocks. Accurate simulation of practical industrial processes for the heavy feedstocks considered here will require multiscale modeling over a much larger range of scales than is currently possible. New algorithms and computers will be needed. Specific research needs are as follows:

1. representing the structures of complex feeds and catalysts with appropriately simplified approximations
2. developing algorithms to represent reactions and reaction networks based on incomplete experimental results
3. using atomic-scale simulation and experimental structure-reactivity correlations to obtain kinetics and thermodynamic data for prediction of reaction rates
4. determining theoretically guided correlations to predict commercially relevant product yields and properties
5. representing catalysts in sufficient detail to account for changes in their compositions and structures during processing.

Details of some of these points follow: Graph theory provides a useful framework for the representation of molecular structure on the computer. The nodes and edges of a graph are the atoms and bonds of a molecule, respectively. Such representations are a target to account for the feeds and a starting point for the representation of reaction networks. The required algorithms will be for the identification of the number and uniqueness of the molecular structures.

The essence of item 1 in the list above is to convert analytical chemistry information into a representation of the molecular components of a feed. The challenge increases as the feedstock becomes heavier and more complex. With a feed as simple as naphtha, for example, this exercise is practically exact; for gas oils, it is a well-specified modeling problem; but for residua and even heavier feedstocks, it is an underspecified modeling problem that awaits each advancement in high-resolution mass spectrometry and complementary spectroscopic techniques.

It is emphasized that most techniques are iterative and involve the minimization of an objective function that compares the properties of the computer representation with a measured set of properties. Thus, the experimentation to guide establishment of structure-property correlations for heavy feeds, as mentioned early in this section, is a priority and prerequisite for progress in modeling and the application of computer methods.

Item 2 in the list above is the transformation of the reactant graphs into product graphs. This transformation leads to a list of reactions by use of a set of reaction matrix operations that convert reactants into products. The resulting list of reactions can be read by a parser algorithm to produce solvable code.

The rate and equilibrium constants in molecule-based models for heavy feeds are too numerous to be measured one at a time. Thus, atomistic simulation and structure-reactivity correlations will be needed to provide reactivity information. When the molecular structure of each species is explicit, the simulation or correlation can be easily probed to provide an estimate of the desired model parameter.

An important complication in the conversion of heavy fossil feedstocks is related to the strong interactions between the molecules. In contrast, in modeling of jet fuel combustion, for example, essentially all of the molecules are in the gas phase and their physical interactions are simply represented. However, for heavy carbon resources, the non-bonding molecule-molecule interactions can be as strong as chemical bonds, and these imply huge complications, for example, with regard to how reactive functional groups come into contact with a catalyst surface. Although some of the intermolecular attractions and stackings in asphaltenes have been characterized, it is not known how strongly these affect the transport and reactivities of the components. New analytical characterization techniques are needed to quantify how the functional groups interact and the strengths of the interactions. Functionalities such as OH groups in phenolic compounds, for example, may interact strongly with pyridines, thiophenes, etc. Understanding of these phenomena is critical for understanding of the catalytic upgrading processes.

At present, solvation models are not sufficiently accurate, and most atomistic simulations are restricted to relatively small numbers of atoms. Much more precise solvation models are needed to resolve the local variations in polarity, and open grand-canonical simulation technology will be needed.

Initially, research will focus on homogeneous mixtures with relatively few components and reaction types that are well understood for smaller molecules. However, the central carbon resource conversion challenge of the future involves strong couplings between reactions and mass transport, because the reacting structures are large. Furthermore, new chemical reactions unique to these large, aggregated structures will be discovered in the course of the research.

The detailed models that are needed to represent the feedstocks and their reactions must be simplified, both for routine use and to provide clear conceptual pictures of the catalytic and noncatalytic reactions, and new methods are needed for reducing the supercomputer models.

Analytical techniques. The structures of coals, heavy petroleum residua, and related hydrogen-deficient fuel feedstocks present daunting, long-standing analytical challenges. Given the refractory nature of some of these feedstocks and their tendency to repolymerize following initial unzipping and hydrotreatment, it is productive to look toward improved structural understanding to guide the development of more robust conversion chemistries. Modern methods of high-resolution mass spectrometry, NMR spectroscopy, and separation science, applied diligently, will provide answers to many of the key structural questions and form the basis for more rational treatment strategies that minimize hydrogen consumption.

Essentially, all these hydrogen-deficient feedstocks largely comprise polycyclic aromatic hydrocarbons and their O-, N-, and S- functionalized derivatives. The low volatilities of these heavy compounds and the multiple reaction sites for C–H bond activation, C–C bond cleavage, and hydrogenation provide challenging problems in the analytical chemistry and determination of reaction mechanisms. In basic research with traditional petroleum feedstocks, bench-top plug-flow catalytic reactors with on-line gas chromatography (GC)-mass spectrometry for product analysis remain the standard research tools. Analogous tools must be developed for fundamental work on the heavier hydrogen-deficient feedstocks and compounds in them. Because in many cases the conversions will require prolonged reaction times, stirred batch reactors (e.g., high-pressure, high-temperature autoclaves) will be used. Continuous sampling will be feasible with heated transfer lines followed, in favorable cases, by high-temperature GC separations optimized for polycyclic aromatics combined with mass spectrometers with high mass ranges. Other analysis strategies might include fiber optic, internal reflectance, or similar optical couples to permit infrared or ultraviolet-visible characterization of the organic reactants, products, and catalysts during the conversions. The experiments will require the development and optimization of in situ analytical methods for contacting of the catalysts with the reacting feedstocks, such as, for example, coatings on optical fibers.

The reactivities of even individual polycyclic aromatic hydrocarbons and their mixtures at elevated temperatures in the presence of hydrogen are poorly understood. For example, little is known about the rates of ring expansion/contraction reactions, side-chain-ring carbon scrambling, ring-opening processes, hydrogen-deuterium exchange reactions, and other fundamental processes occurring under reaction conditions. Moreover, this information needs to be related to prototypical catalyst, such as acids, metals, and metal sulfides. It would also be desirable to obtain data for molecules representative of those found in hydrogen-deficient feedstocks, such as the isomers of methylphenanthrenes in order to develop a fundamental understanding of how catalyst composition and structure, as well as substrate molecular structure, affect the basic reaction pathways involved in the processing of heavy fossil fuel feedstocks.

Environmental protection requires removal of heteroatoms, especially sulfur, from fossil fuels. It is expensive and difficult to reduce the concentrations of these heteroatoms to the stringent levels now mandated by law. Further, molecules from heavy carbon sources contain hard-to-access heteroatoms, such as the sulfur center in the refractory compounds 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (Gates and Topsøe 1997; Prins et al. 2006). Such centers present their own challenges to the design of energetically efficient and selective catalysts. Technologies available today that were developed to deal with the compounds present in petroleum are not necessarily appropriate for the higher-molecular-weight and heavily functionalized compounds present in coal, tar, and shale. The traditional method for removing heteroatoms such as sulfur and nitrogen is via catalytic hydroprocessing, a technology that requires large amounts of hydrogen, high pressures, and expensive, thick-walled reactors. Thus, there is a pressing need for improved catalytic methods for removal of heteroatoms from heavy feedstocks, especially for catalysts that facilitate selective reactions and minimize hydrogenation of alkene and aromatic functionalities; non-hydrogenation routes are also worthy of investigation. It is important to recognize that efficient heteroatom removal will not occur in isolation of other upgrading and conversion reactions, and, consequently, it is necessary to think about the chemistry of heteroatom removal in the context of upgrading heavy fossil fuel feedstocks.

The growing need for reaction efficiency to conserve feedstocks and the hydrogen needed in their upgrading demands unprecedented levels of catalytic selectivity in the formation of fuel molecules. Related to the need to manage hydrogen efficiently is a compelling opportunity to use—instead of hydrogen in reactions with the complex feedstocks—simple hydrogen-rich building blocks such as natural gas. Success in this direction will require new catalysts for the controlled breaking of the first C–H bond in light alkanes (e.g., methane), including the bonding of alkyl groups to nucleophiles. Furthermore, it may require the direct electrophilic substitution of the hydrogen in light alkanes.

The activation of refractory bonds in small molecules such as methane is only one part of what is needed. Equally important is the ability to control precisely the number of repetitive reactions from a pool of activated small molecules such as carbon monoxide, carbon dioxide, and methanol. Developing new chemistry for conversion of these small carbon resources into fuels and chemicals offers the prospect of new processing routes to exploit some of the most refractory carbon resources. We are at a very early stage in such research, and theory may be essential in providing starting points for further investigation.

In summary, all of the forgoing characteristics complicate the design of optimal catalysts, upgrading strategies, and environmental protection strategies for the use of heavy oil, tar sands, shale, coal, and lingo-cellulosic materials as alternative energy sources. Now is the time for research into these feedstocks, as the time has arrived when they dominate the needs for innovation in the industry. Advances in the analytical chemistry of the feedstocks and in experimental catalyst characterization require parallel advances in theory and computational methods to allow atomic and molecular-scale understanding of the catalytic processes and design of new catalysts and improved technologies.

Synthesis of gasoline and gasoline blending compounds via carbon monoxide hydrogenation

In contrast to petroleum reserves, the coal reserves in the United States are ample for decades to come. As the cost of petroleum and the fraction of imported petroleum continue to rise, there will be a strong incentive to convert coal into transportation fuels. The most attractive approach for doing so is to gasify the coal into synthesis gas and then raise the H_2/CO ratio so a level of roughly 2. For environmental reasons, the carbon dioxide generated by this means will need to be sequestered.

The use of synthesis gas for the production of diesel fuel via Fischer-Tropsch synthesis has been developed to a viable technology over the past 25 years by industrial researchers; the technology is now being implemented in an increasing number of countries around the world. However, because the demand for gasoline relative to diesel fuel in the United States remains high, there will be an increasing need to develop approaches for producing high-octane-number products, such as branched hydrocarbons, linear alcohols, and other oxygenated compounds that can be blended into gasoline produced from petroleum.

A homologous series of linear alcohols can be produced by carbon monoxide hydrogenation catalyzed by iron, cobalt, or copper oxide catalysts. Such catalysts facilitate termination of growing alkyl chains by carbon monoxide migratory insertion and subsequent reduction of the acyl, rather than by β-elimination to form olefins or reductive elimination to form alkanes.

Because very-long-chain alcohols are not useful as fuels, the challenge will be to develop catalysts that produce C_3–C_4 alcohols selectively.

Oxygenated compounds such as dialkoxy alkyls (e.g., dimethoxy methane) and dialkyl carbonates (e.g., diethyl carbonate) can be produced by alcohol oxidation or oxidative carbonylation. The challenge is to define the catalyst site requirements needed to achieve high activity and selectivity.

Linear alcohols can also be used to produce branched alkanes by aldol condensation, usually with a basic catalyst. Control of the product distribution and the relationships of product composition to catalyst structure and composition are not well defined. Hence, an important challenge is to define the mechanism and kinetics of forming branched hydrocarbons from linear alcohols.

Theoretical methods are expected to play an important role in addressing the issues raised in this section. Recent examples have shown that computational chemistry can give insights into the oxidation of alcohols, as well as their oxidative carbonylation.

Conclusions

The carbon sources that will soon dominate the energy landscape will be heavier and more complex than the most desirable light and sweet oils, which are being depleted rapidly. The predominant energy feedstocks of the future will be primarily heavy oils, tar sands, shale oil, and coal. The heavy molecules in these feedstocks and their molecular complexity produce strong intermolecular interactions that hamper the disentanglement of the solid state and the catalytic manipulation of the molecules. New catalytic chemistry is needed for the selective deconstruction of the heavy molecules in these feedstocks, for highly efficient removal of heteroatoms, and for inter- and intra-molecular hydrogen redistribution, as well as new chemistry to take advantage of the high H:C ratios of light feedstocks exemplified by natural gas as a source of hydrogen.

The necessary scientific advances require a new level of atomic- and molecular-level understanding of the structure and reactivity of the source molecules. This understanding will be the basis for designing and synthesizing new catalytic materials to selectively manipulate C–C, C–H, C–S, and other bonds with unprecedented temporal and spatial resolution to transform those complex molecules selectively into useable fuels.

The leap forward in fundamental understanding and control of catalytic selectivity that underlies all of these advances is daunting, but tractable in the long run if the commitment is sufficient. The high-resolution quantitative analysis of structures and reactivities needed for characterization of the complex molecular solids is beyond current capabilities, but progress can be built on recent advances in solid-state NMR spectroscopy, environmental transmission electron microscopy, scanning probe and spectroscopic and mass spectrometric methods. Extensions of quantum theory to larger systems, modeling of nonbonding interactions, and development of new methods for determination and analysis of chemical kinetics and in situ catalyst characterization in multiphase reaction environments are needed to understand and predict the dynamic behavior of the complex reacting systems over all the relevant length scales. Atomic and meso-scale theory, informatics approaches to analysis, and new approaches to managing complexity will guide insights into new structure-catalytic activity relationships for rational design of catalysts needed for the reactions mentioned here. Design of such catalytic materials will be demanding and will surely draw on continuing advances in the fabrication of nanomaterials.

From all that has been summarized here, it is clear that the resources required to meet the challenges far exceed what has been provided recently—and the support must continue with some reliability to assure success. The catalytic challenges before us are defined by the nature of the available and sure-to-be-used heavy fossil energy resources; the challenges are great, but energy needs demand that we succeed in meeting them.

References

Gates, B. C., and H. Topsøe. 1997. “Reactivities in Deep Catalytic Hydrodesulfurization: Challenges, Opportunities, and the Importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene,” *Polyhedron* **16**, 3213-3217.

Helveg, S., J. V. Lauritsen, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe, and F. Besenbacher. 2000. “Atomic-scale Structure of Single-layer MoS_2 Nanoclusters,” *Physical Review Letters* **84**, 951.

Hughey, C. A., C. L. Hendrickson, R. P. Rodgers, and A. G. Marshall. 2001. “Elemental Composition Analysis of Processed and Unprocessed Diesel Fuel by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry,” *Energy & Fuels* **15**, 1186.

Jaffe, S. B., H. Freund, and W. N. Olmstead. 2006. “Extension of Structure-oriented Lumping to Vacuum Residua,” *Industrial & Engineering Chemistry Research* **44**, 9840-9852.

Marshall, A. G., and R. P. Rodgers. 2004. “Petroleomics: The Next Grand Challenge for Chemical Analysis,” *Accounts of Chemical Research* **37**, 53-59.

Prins, R., M. Egorova, A. Rothlisberger, Y. Zhao, N. Sivasankar, and P. Kukula. 2006. “Mechanisms of Hydrodesulphurization and Hydrodenitrogenation,” *Catalysis Today* **111**, 84-93.

Rang, H., J. Kann, and V. Oja. 2006. “Advances in Desulfurization Research of Liquid Fuel,” *Oil Shale* **23**, 164-176.

Song, C. 2003. “An Overview of New Approaches to Deep Desulfurization for Ultra-clean Gasoline, Diesel Fuel and Jet Fuel,” *Catalysis Today* **86**, 211-263.

ADVANCED CATALYSTS FOR CONVERSION OF BIOLOGICALLY DERIVED FEEDSTOCKS

Current Status

Currently, biofuels, such as ethanol, are produced largely from grains, but a large, untapped resource (estimated at more than a billion tons per year) of plant biomass exists in the form of lignocellulosic material that could be utilized as a renewable, domestic source of liquid fuels. Although age-old processes are available for converting the starch content of grain into sugars, which can then be fermented to ethanol, the conversion of lignocellulose to sugars is much more difficult. The recalcitrance of lignocellulose lies in its structure, which has evolved to provide resistance to pests and pathogens. Thus, the development of processes for converting lignocellulosic biomass to fuels is hampered by the lack of energy-efficient and cost-effective processes for the deconstruction and conversion of this feedstock (Lynd et al. 1999).

Many pathways have been explored for converting biomass to biofuels, as illustrated in Figure 13 (Huber et al. 2006a). These can be divided into processes using only enzymatic catalysts and those using non-enzymatic catalysts. The principal example of biological processing is the fermentation of sugars to ethanol and butanol, with the sugars being obtained either by extraction from sugarcane or enzymatic hydrolysis of cornstarch. Enzymatic hydrolysis of cellulose and hemicellulose and the subsequent fermentation of the sugars derived from these sources have also been investigated.

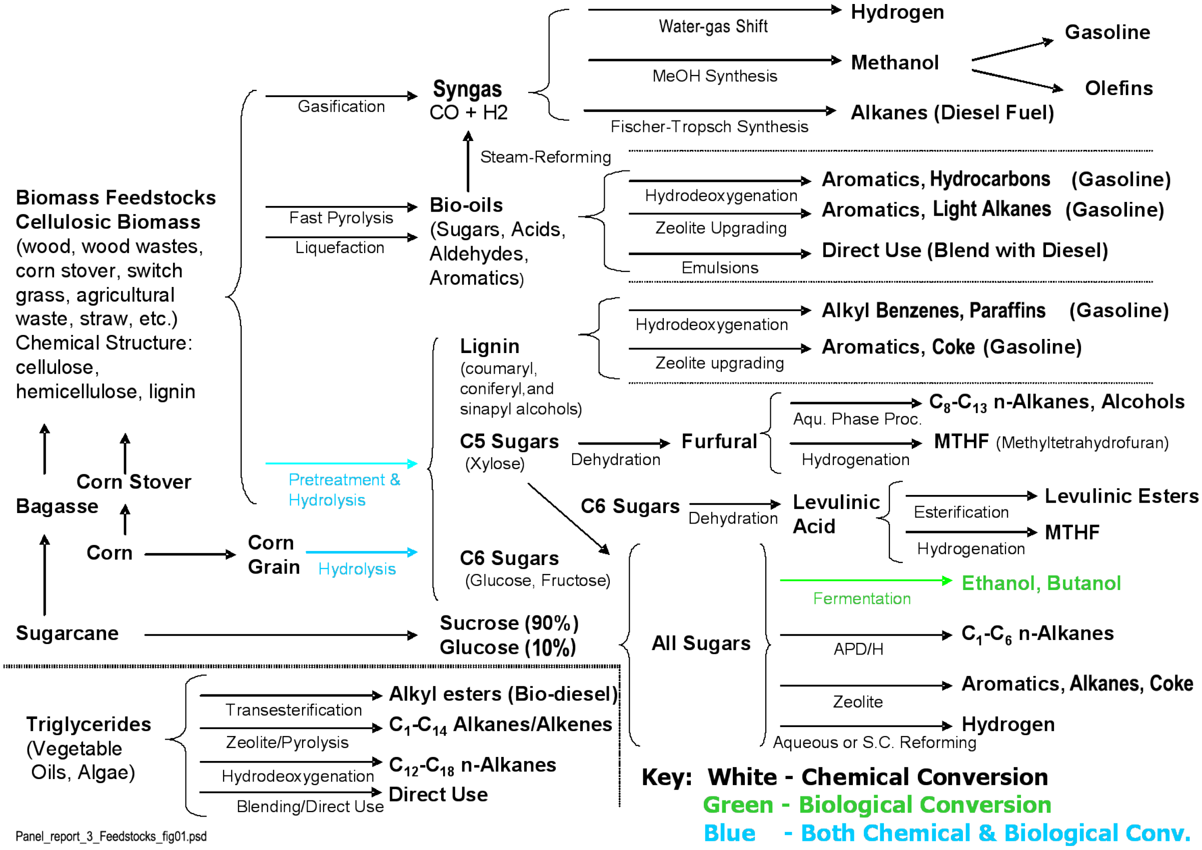


Figure 13: Routes to make a biofuel. Reprinted with permission from Huber et al. (2006a). Copyright 2006 American Chemical Society.

The non-biological processing of lignocellulosic biomass can be subdivided into high- and low-temperature processes. High-temperature processes include the processes of pyrolysis and gasification. Pyrolysis is generally not catalyzed, but solid catalysts are used to upgrade the pyrolysis oil into components that can be blended into gasoline or diesel fuel. Gasification involves the steam reforming of biomass to produce synthesis gas (a mixture of hydrogen and carbon monoxide), which can, in turn, be used to produce methanol or diesel fuel. Solid catalysts can convert the tars produced during biomass gasification into additional synthesis gas. Further, synthesis gas conversion with other solid catalysts can be used to promote the synthesis of

What Are Our Biofuel Options?

A biofuel is a liquid transportation fuel made from feedstocks, such as corn or corn stover, animal or vegetable oils, trees, grasses, waste paper, etc. Unlike fuels derived from fossil sources such as crude oil, biofuels are renewable and emit less carbon during consumption. A wide variety of biofuels are possible, including single-molecule fuels or additives as well as traditional complex mixtures of chemicals:

Single-molecule fuels or additives

Ethanol or ethyl alcohol can be made from cellulosic biomass via fermentation routes. Polysaccharides are depolymerized to yield monomeric sugars, which are then enzymatically fermented into ethanol. Moreover, new technologies are emerging for the synthesis of ethanol and other alcohols from biomass-derived synthesis gas via non-biological catalysis (e.g., Hu et al. 2006).

Butanol or butyl alcohol is a four-carbon alcohol. This biofuel can be made from cellulosic biomass via fermentation routes or synthesized from synthesis gas.

Hydroxymethylfurfural (HMF) and *furfural* are sugars derived from biomass and do not have to be biocatalytically processed via fermentation to make fuels. Sugars can also be dehydrated via chemical catalysis to yield HMF (from 6-carbon sugars such as glucose) and furfural (from 5-carbon sugars such as xylose). These molecules are building blocks for transformation into potentially viable transportation fuels such as ethyl levulinate, dimethylfuran, and γ-valerolactone.

Routes to prepare *dimethyfuran*, a six-carbon cyclic ether, from sugars in high yields have recently been reported (Román-Leshkov et al. 2007). Dimethylfuran has many appealing properties for potential use as a transportation fuel, such as a gasoline additive or replacement.

Similar to dimethylfuran, γ-*valerolactone* can be synthesized from decomposition products of sugars. Processes exist for the production of levulinic acid in high yield from monomeric sugars, as well as for the catalytic transformation of levulinic acid into γ-*valerolactone* (Manzer 2003). Because of its high energy content and low vapor pressure, γ-*valerolactone* may be suitable for use as a transportation fuel (Horvath 2006).

Ethyl levulinate is derived from levulinic acid, which is made by the reaction of ethanol and levulinic acid to make an ester. This molecule has been suggested as a fuel additive (Manzer et al. 2005a, b).

Mixture of compounds – classical fuels

Green gasoline or diesel can be synthesized from lignocellulosic biomass by catalytic deoxygenation. Technologies such as biomass reforming can be used to provide hydrogen for reduction of components of cellulosic biomass, such as sugars, as well as lignin fractions of biomass, into gasoline or diesel-range hydrocarbons. In some cases, the small biomass fragments need to be coupled to allow for proper molecular weights (Davda et al. 2005). Green diesel can also be prepared via the catalytic deoxygenation of fatty acids derived from virgin or waste vegetable or animal oils. These same oils can be transformed into biodiesel by a transesterification reaction with methanol.

methanol or a homologous series of alkanes via Fischer-Tropsch synthesis. The aim of low-temperature biomass conversion is to produce fuels by hydrolysis of cellulose and hemicellulose to their component sugars and subsequent deoxygenation and transformation of products that can be derived from the sugars. In this case, both soluble and solid catalysts have proven useful.

Understanding the elementary processes involved in non-biological conversion of lignocellulosic biomass to fuels and the types of catalysts that are best suited for such processes is still rudimentary in comparison with what is known about the processing of fossil fuels. This situation is largely a consequence of the relatively recent attention paid to the catalytic conversion of biomass feedstocks. Thus, enormous opportunities exist for establishing reaction pathways involved in processing biomass and identifying catalysts for the formation of targeted fuels. Specific research challenges and opportunities are identified and discussed in the next section.

Basic Science Challenges, Opportunities, and Research Needs

Characterization of lignocellulosic biomass

The efficient conversion of biomass to fuels requires an understanding of the chemical composition and structure of biomass. Most of the available scientific models presented to date depict the components found within biomass as a polymeric liquid crystal with the cellulose microfibril networks embedded in hemicellulose, lignin, and pectin matrices. The bulk cellulose found in microfibrils has a significant degree of crystallinity, and the exact dimensions of the microfibrils depend on the species of biomass from which they are derived, the time at which the biomass was harvested, and how it was stored.

Only very limited knowledge of the structural and chemical transformations that occur during the processing of lignocellulosic biomass to produce fuels exists. How the initial structure of the biomass affects these transformations is not well understood either. Therefore, a major challenge is to image the changes that occur during biomass conversion at the same time that analyses are conducted on the molecular and supra-molecular products that are released. The application of various types of scanning electron microscopy and transmission electron microscopy would be invaluable, particularly those utilizing recently developed techniques for characterizing biological and polymeric materials. On a more macroscopic level, x-ray diffraction could be used to detect the loss of crystallinity, and nuclear magnetic resonance, infrared, and Raman spectroscopy could be used to determine changes in the overall distribution of functional groups. Analysis of the liquid and gaseous products produced during the processing of biomass by liquid and gas chromatography in combination with mass spectrometry would provide information that can be linked to structural transformations. The ultimate goal is a molecular-scale resolution of the biomass-derived products in much the same manner that is now becoming possible for products present in and derived from fossil energy sources (see “Advanced Catalysts for the Conversion of Heavy Fossil Energy Feedstocks,” earlier in this report).

The Potential of Lignocellulosic Biomass as a Feedstock

Biomass is the most abundant renewable carbon source and has the potential to be a new source of liquid fuels by conversion of its three constituent polymers: cellulose, hemicellulose, and lignin. The composition of biomass varies with its source. Sugarcane and beetroots store large amounts of simple sugars; corn grain and wheat kernels store carbon as starch; and cellulose and hemicellulose are found in the leaves of all agricultural crops as well as in the leaves and wood of trees. Most ethanol for fuel use today is produced from corn grain, and the technology for breaking down starch into simple sugars is well developed. Cellulosic biomass, such as wood, forest product residues, grasses, agricultural residues, and specialty energy crops, can provide much larger amounts of biomass for production of transportation fuels. However, cellulosic biomass is resistant to breakdown; plants have evolved complex means to employ cellulose and hemicellulose as structural materials that are very resistant to microbial attack. Lignin serves to strengthen the cellulosic material to form the plant cell wall, which provides resistance to pests and pathogens. The crystalline cellulose core of cell walls (Figure 14) is highly resistant to chemical and biological breakdown, and the complex structures of the cell wall also contribute to its recalcitrance. The cell walls of plants, which typically comprise 40 to 50 percent cellulose (a polymer of glucose), 20 to 35 percent hemicellulose (predominately a polymer containing xylose or arabinose), with lignin (a complex polyphenolpropanoid) as the third major component, provides the feedstock material for biofuels.

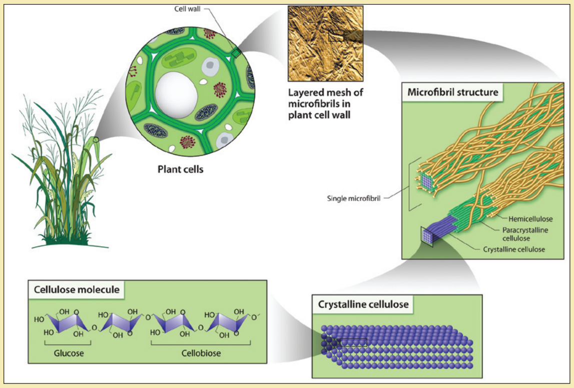


Figure 14: Cellulose in the cell walls of plants. Genome Management Information System, Oak Ridge National Laboratory http://genomics.energy.gov/gallery/gtl/detail.np/detail-36.html (DOE 2005).

Plant biomass availability varies with region in the United States (Figure 15). Currently, approximately 190 million tons of biomass are converted to energy. Ninety percent is combusted, and only 10 percent is converted to ethanol. The U.S. Department of Energy and U.S. Department of Agriculture estimated potential lignocellulosic biomass production for fuels in the United States at more than 1.3 billion tons annually, sufficient to replace more than 30 percent of current transportation fuel use (Perlack et al. 2005).

Figure 15: Plant biomass availability in the United States. Adapted from Oak Ridge National Laboratory Biomass Program http://genomicsgtl.energy.gov/biofuels/ (DOE 2006).

Understanding the chemistry of biomass processing at high temperature

Three high-temperature (or thermochemical) routes are available for the conversion of lignocellulosic biomass into lower-molecular-weight products and liquid fuels: gasification to produce synthesis gas, pyrolysis to produce bio-oils, and liquefaction to produce bio-oils.

Biomass gasification to synthesis gas followed by conversion of this product to diesel fuel by Fischer-Tropsch synthesis is the most technologically advanced route to biofuels. During gasification of biomass, a considerable amount of char is produced which, if not eliminated, can foul catalysts used for the further processing of the synthesis gas. A challenge is to develop poison-resistant catalysts for the conversion of these chars. These catalysts would require minimal regeneration. A further challenge with high-temperature treatments is improving the selectivity to desired products. Work by Schmidt and co-workers (Salge et al. 2006) has shown how rhodium-containing catalysts can be used to make clean synthesis gas from solid biomass. Tomishige et al. (2004) have shown that addition of $Rh/CeO_2/SiO_2$ catalysts to a gasification reactor can reduce the coke yield from 40 percent to less than 1 percent based on a carbon yield.

In pyrolysis, biomass is heated in the absence of air to produce a mixture of solid, liquid, and gaseous products depending on the pyrolysis temperature and residence time. Figure 16 shows the primary, secondary, and tertiary pathways involved in the thermochemical conversion of biomass. However, these pathways are understood only on a superficial level, and, hence, the challenge is to develop a clear understanding of the elementary processes occurring at each step. The use of catalysts to accelerate pyrolysis is relatively unexplored and represents another area of opportunity. New catalysts developed for this purpose could increase the yield of desired liquid products.

The products produced by biomass pyrolysis are thermally unstable and degrade with time. Thermal decomposition reactions can be minimized by converting these products to more thermally stable compounds. Zeolites can be used for this purpose, taking advantage of the shape-selectivity of these materials (Chen et al. 1986). One of the challenges of this chemistry is to avoid high levels of coke (Corma et al. 2007). Because zeolites have been designed for petroleum-based feeds, future shape-selective catalysts will likely be designed specifically for biomass-derived feeds.

Biomass compounds, including vegetable oils, pyrolysis oils, and liquefaction oils, can also be converted to liquid fuels by hydrotreating and/or hydrocracking. Vegetable oils can be hydrotreated together with petroleum feedstocks (Huber et al. 2007), with standard sulfided hydrotreating catalysts (Elliott 2007). However, such catalysts tend to deactivate in the presence of biomass-derived species. Catalysts are also needed to hydrogenate targeted biomass linkages selectively to avoid excessive hydrogen consumption (Elliott 2007). The ultimate goal is the design of stable catalysts that hydrogenate biomass species selectively to liquid products with low hydrogen consumption.

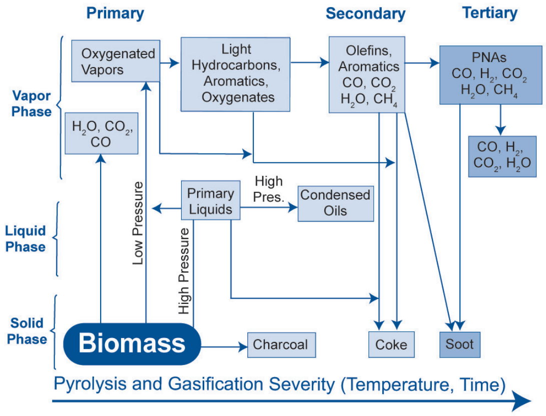


Figure 16: Gasification and pyrolysis reaction pathways. Reprinted with permission from Huber et al. (2006a). Copyright 2006 American Chemical Society.

The products of biomass pyrolysis bear some resemblance to those present in petroleum. For this reason, the techniques and strategies proposed for investigating the mechanism and kinetics of upgrading heavy fossil energy feedstocks could be applied equally well to the upgrading of biomass-derived pyrolysis products. Further details of these strategies are described in the panel report entitled "Advanced Catalysts for the Conversion of Heavy Fossil Energy Feedstocks."

Understanding the chemistry of biomass processing at low temperature

Biomass processing at low temperatures occurs in the liquid phase and involves three more or less distinct phases: deconstruction of the original biomass structure to release cellulose and hemicellulose, hydrolysis of cellulosic components to produce sugars, and conversion of the sugars to fuel products. Each of these steps is usually conducted with the reactants in the liquid phase, using solvents that may include water, dimethyl sulfoxide, and ionic liquids.

Low-temperature deconstruction of lignocellulosic biomass. Low-temperature deconstruction and pretreatment methods, mostly derived from the pulp and paper industry, have been investigated for integration with biological catalysts. Such pretreatments include processing with dilute acids (hydrochloric and sulfuric acids), explosive decompression (steam explosion), hydrothermolysis, or treatments with organic solvents (organosolv) (Wyman 1999; Wyman et al. 2005a, b). Glucose and xylose degradation products that result from some of these pretreatment methods, especially those involving acids at elevated temperatures, typically include hydroxymethylfurfural (HMF) and furfural, which subsequently produce levulinic and formic acids. These products are undesired for microbial fermentation of glucose and xylose to ethanol; however, these products are desirable intermediates for certain routes to biofuels that use solid catalysts. This example illustrates the importance of developing a pretreatment process that (1) converts the initial lignocellulosic material into an easily processed output stream and (2) does not produce inhibitor components that negatively affect any element of the downstream processing of that biomass into fuels.

The scientific challenge is to understand the elementary processes occurring during the pretreatment of biomass and the dependence of the rate and extent of pretreatment on the structure and chemical composition of the biomass feed. The use of ionic liquids as solvents holds a great deal of promise, because recent work has shown that a cellulose solubility of up to 30 wt% can be achieved in such solvents (Heinze et al. 2005). Ionic liquids in combination with acidic catalysts could also be used to promote the hydrolytic deconstruction of cellulose and hemicellulose to five- and six-membered sugars (Zhao et al. 2007).

Liquid-phase processing of sugars to fuels. The high functionality and low volatility of biomass make it particularly amenable to liquid-phase processing (Cortright et al. 2002; Davda et al. 2005; Huber and Corma 2007; Huber and Dumesic 2006; Huber et al. 2006b; Shabaker et al. 2003). Thus, liquid-phase catalytic processing is advantageous because thermally unstable compounds can be converted selectively to liquid fuels. A wide variety of products can be formed by liquid-phase processes, including liquid alkanes (diesel fuel replacement), light alkanes (gasoline range alkanes), gaseous alkanes (natural gas), and hydrogen (Cortright et al. 2002; Davda et al. 2005; Huber and Corma 2007; Huber and Dumesic 2006; Huber et al. 2006b; Shabaker et al. 2003). The sidebar illustrates how aqueous-phase processing can be used to produce liquid alkanes, which can be used as a diesel fuel replacement. The goal of liquid-phase catalytic processing of biomass-derived compounds (e.g., sugars) is to produce next-generation liquid fuels that (1) can be used with the existing infrastructure, (2) do not involve energetically

Applications of Heterogeneous Catalysis to Liquid-Phase Processing of Biomass to Fuels

Ethanol production is a liquid-phase process that has been practiced for thousands of years (e.g., by the brewing industry) and does produce a transportation fuel. However, the current process has several disadvantages including high energy costs associated with the distillation of ethanol, low rates of production per unit volume of reaction vessel, and high capital costs. Solid catalysts, which are used in the fuels and chemical industry, can overcome the limitations of current biological catalysts (yeast). Compared to the production of bioethanol by fermentation, the production of next-generation liquid fuels by liquid-phase catalytic processing can be carried out at higher rates. The time-scale of a fermentation process is measured in days; the time-scales of a liquid-phase catalytic reaction is measured in minutes. A key advantage of liquid-phase catalytic processing is that thermally unstable reactant molecules, such as sugars, can be processed at low temperatures, at which undesirable thermal degradation reactions are slow, leading potentially to high selectivities for targeted products.

Figure 17 illustrates how aqueous-phase processing can be used to produce selectively targeted alkanes from glucose. This is a multi-step process that requires acid catalysts for dehydration reactions, base catalysts for aldol condensation, metal catalysts for hydrogenation reactions, and bifunctional metal/acid catalysts for dehydration/hydrogenation reactions. Furthermore, the final step requires a four-phase reactor: (1) a gas phase containing hydrogen, (2) a solid phase composed of a bifunctional catalyst containing metal and acid sites, (3) an aqueous phase containing the sugar reactant, and (4) a liquid alkane phase used to remove hydrophobic species from the catalyst surface before they react further to form carbonaceous deposits that deactivate the solid catalyst.

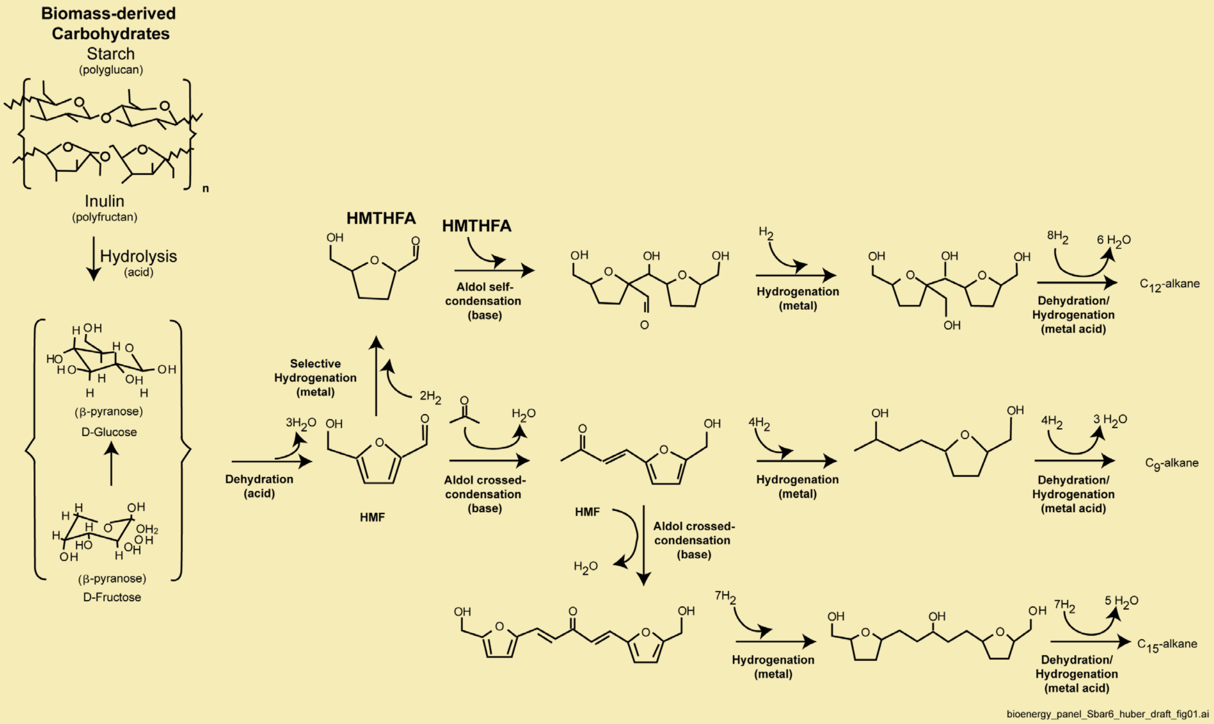


Figure 17: Reaction pathways for conversion of polysaccharides into liquid alkanes by aqueous-phase processing. Analogous chemistry can be depicted for conversion of C_5 polysaccharides to C_{10}, C_8, and C_{13} alkanes, respectively, via furfural as a reaction intermediate. From Chheda et al. (2007), copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

intense distillation and separation steps, and (3) have high rates of production per unit of reactor volume. Future-generation liquid fuels produced by liquid-phase processing should have higher energy densities per volume (30-40 MJ/L) and properties that are closer to those of gasoline and diesel fuel than ethanol (19 MJ/L).

High yields of well-defined liquid fuels can be produced by liquid-phase catalytic processing at temperatures less than 200 °C in contrast to what can be achieved by pyrolysis. However, whereas these latter processes can operate with complex biomass feedstocks (e.g., containing cellulose, hemicellulose, and lignin components), liquid-phase catalytic processing typically requires specific products of cellulose deconstruction, such as sugars or polyols. Thus, an advantage of liquid-phase catalytic processing is that high selectivities and yields of targeted fuel compounds can be achieved. A disadvantage of such processing is that biomass feedstocks must be pretreated to prepare a feed solution that is appropriate for subsequent liquid-phase catalytic processing.

Four challenges for scientific research can be defined for the low-temperature liquid-phase processing of sugars. These are as follows:

- design of catalytic systems for the liquid phase
- evolution of catalyst structure and activity under reaction conditions
- elucidation of reaction mechanisms in liquid media
- description of reaction kinetics and product distribution during liquid-phase processing.

Each of these challenges is discussed in the following text.

Design of catalytic systems for the liquid phase. Thus far, most of the catalysts used for liquid-phase processing of biomass have not been developed specifically for this application. These catalysts include solid acids and supported metals. Therefore, opportunities exist for using novel types of catalysts designed specifically for the conversion of sugars to fuels (e.g., metal cations, metal complexes, and bio-inspired catalysts). The use of metal cations in ionic liquids, for example, has recently been shown to be highly selective for the synthesis of HMF (Zhao et al. 2007). Bi-phasic systems can also be used to good advantage. Román-Leshkov et al. (2006) have shown that HMF and furfural can be produced selectively from aqueous sugar solutions using a bi-phasic reactor system, in which HMF or furfural is extracted from the aqueous solution before undesired homogeneous reactions occur (Chheda and Dumesic 2007).

As discussed in the chapter on grand challenges, the development of catalysts that capture some of the features of enzymes offers particularly interesting challenges and opportunities. In enzymes, the active center, usually a metal cation or set of cations, is contained in a hydrophobic pocket. This pocket has a shape that is complementary to that of a particular reactant or the transition state to a particular product. The design of materials that emulate the sophisticated compositions and structures of enzymes is a large challenge; however, some modest steps in meeting this challenge have already appeared. Thus, Mbaraka and Shanks (2005, 2006) have shown that the use of organosulfonic acid incorporated onto the walls of a hydrophobic, mesoporous solid enhances the rates at which fatty acids are etherified to biodiesel and inhibits deactivation of the catalyst (Mbaraka and Shanks 2005, 2006). Likewise, ideas for bio-inspired catalysts, with controlled hydrophobicity–hydrophilicity, have been developed for esterification reactions to produce fine chemicals (Diaz et al. 2000) and could be adapted for the synthesis of biofuels with such reactions. Bio-inspired catalysts that combine several functionalities into one catalyst might also prove highly advantageous for promoting the conversion of sugars to targeted products. The challenge is to identify which catalytic functions are needed and to then build them into a carrier. Success in this area could open up exciting opportunities for efficient production of a very narrow range of products.

Given the wide variety of materials that may prove useful for the liquid-phase conversion of biomass, it is likely that techniques for the rapid screening of catalysts may prove effective. Such methods would enable investigators to examine broad classes of potential catalysts with the aim of establishing which ones or combinations are most attractive. The required technology would require a large number of mini-reactors that can be loaded with reactants and catalysts using robotic methods and then brought to prescribed reaction conditions and analyzed at the end of the defined period of reaction. The best candidate materials selected on the basis of such rapid-screening investigations would then be examined more carefully to define reaction pathways, including elucidation of the factors controlling product selectivity.

Evolution of catalyst structure and activity under reaction conditions. The structure of solid catalysts and the conformation of enzyme catalysts are affected by solution pH, ionic strength, surfactants, impurities, temperature, etc. A supported bimetallic catalyst, for example, may experience segregation of the metals, dissolution of the support, disruption of the metal-support interface, and migration of metal particles, depending on the nature of the aqueous environment at the interface. Moreover, trace impurities present in biomass feedstocks may selectively poison catalyst surfaces or denature enzyme catalysts, thus deactivating the system. For example, polyphenolic structures of lignin and tannin may inhibit catalytic activity by binding to the inorganic or biological catalysts. In-situ spectroscopic, scattering, and imaging tools need to be developed that allow real-time monitoring of catalyst structure at the nanometer level. High-energy x-ray methods are particularly suitable for investigating the structure of catalysts in water (Ketchie et al. 2007a, b; Maris et al. 2006).

Elucidation of reaction mechanisms in liquid media. Catalytic conversion of biomass-derived molecules to fuel products is likely to involve a series of elementary processes, some of which are facilitated by solid catalysts and others, by soluble enzymatic catalysts. However, information is lacking on the reactive intermediates involved in these transformations. Moreover, because water is frequently the solvent, acquiring data in situ is difficult. For example, infrared spectroscopy can suffer from excessive absorption of the radiation by water. Therefore, surface-sensitive in-situ spectroscopic tools that are capable of identifying reactive species on catalyst surfaces in aqueous solution need to be developed. Techniques such as surface-enhanced Raman spectroscopy and, in particular, attenuated-total-reflectance infrared spectroscopy may find broad application in this arena (Ferri et al. 2002; McQuillan 2001; Ortiz-Hernandez and Williams 2003). Moreover, development of transient methods to interrogate reaction dynamics at the solid-solution interface is necessary to relate catalyst structure to reactivity. Electro-analytical methods combined with surface spectroscopy would enable simultaneous identification of reactive intermediates and measurement of kinetic phenomena (Shao and Adzic 2005). Many of the same methods recommended for application in the investigation of reaction pathways involving molecules derived from heavy fossil energy feedstocks could be used for the investigation of molecules derived from biomass feedstocks.

Description of reaction kinetics and product distribution during liquid-phase processing. The evolution of products during the liquid-phase processing of sugars is understood only at a rudimentary level, and consequently, the effects of changes in catalyst composition and reaction conditions cannot be related to the distribution of products formed. Such information is essential to guide the formation of targeted products. The challenge, therefore, is to measure systematically the kinetics of product formation for a variety of compositionally and structurally related catalysts, so that the relationships between catalyst properties and the rate coefficients for particular reactions can be defined. This knowledge will help to establish which steps are critical to defining product selectivity and which catalyst properties are essential for achieving high activity and product selectivity. Theoretical investigations of the most critical steps could shed additional light on the effects of catalyst structure and composition, as well as solvent composition, on rates of these steps. Advances towards this goal will require improved methods for carrying out electronic structure calculations for complex systems containing many degrees of freedom (see crosscutting challenges). Ultimately, it would be desirable to develop predictive methods for mapping out the manifold of reactions occurring during the liquid-phase processing of sugars given the composition and structure of the catalyst and solvent. The methods suggested for the investigation of reaction pathways for biomass-derived molecules are similar, if not identical, to those recommended previously in this section for the investigation of molecules derived from heavy fossil fuel feedstocks. Although the reaction conditions required for the processing of the two types of feedstocks differ significantly, the theoretical methods and approaches proposed to develop a fundamental perspective of the underlying catalytic chemistry are identical.

Conclusions

The large supplies of lignocellulosic biomass in the United States offer opportunities for producing a significant fraction of the nation’s transportation fuels. However, none of the recently conceived processes for converting biomass to fuels is fully developed and ready for commercialization, and all are in need of a more fundamental understanding of the physical and chemical transformations that occur during the various stages of processing.

Opportunities exist for discovering and developing catalysts for the high-temperature pyrolysis of biomass to fuels, which could maximize the yield of liquid products and simultaneously minimize the yield of char. The mechanism and kinetics of pyrolysis are poorly understood, as are the structural transformations by which solid biomass is converted to gaseous and liquid products. Thus, a major challenge is to define the elementary processes involved in biomass pyrolysis and the rate coefficients associated with these processes. Such investigations will require the use of advanced microscopic techniques in combination with analytical methods that can identify the complex spectrum of liquid and gaseous products produced during pyrolysis.

Low-temperature processing of biomass offers the opportunity to produce a range of products suitable as transportation fuels. The major challenge is to understand the elementary processes—physical and chemical—involved in the deconstruction and hydrolysis of biomass to produce low-molecular-weight products, mainly sugars. Another challenge is to understand the chemical processes by which sugars can be converted to targeted fuel components. Knowledge is required to define which types of catalysts will be most effective for the deconstruction and hydrolysis of biomass and what types of catalysts can be used to promote the conversion of sugars to fuels. The mechanism and kinetics of these processes are very poorly understood at present, and, hence, the challenge is to develop a qualitative and quantitative understanding of these elements of biomass conversion. A notable challenge is the design and synthesis of bio-inspired catalysts that could be used to achieve high product selectivity by virtue of the composition and shape of a "pocket" surrounding the active center. The combination of several such bio-inspired centers onto one support represents a further challenge, which if met, would allow the sequential conversion of reactants to products, with minimal production of byproducts.

Many of the approaches identified in the "Grand Challenges in Catalysis as a Multidisciplinary Science and Technology" and "Advanced Catalysts for the Conversion of Heavy Fossil Fuel Feedstocks" will be useful as well for studies of biomass conversion to fuels.

References

Chen, N. Y., J. T. F. Degnan, and L. R. Koenig. 1986. "Liquid Fuel from Carbohydrates," *Chemtech* **16**, 506-511.

Chheda, J. N., and J. A. Dumesic. 2007. "An Overview of Dehydration, Aldol Condensation, and Hydrogenation Processes for Production of Liquid Alkanes from Biomass-derived Carbohydrates," *Catalysis Today* **123**(1-4):59-70.

Chheda, J. N., G. W. Huber, and J. A. Dumesic. 2007. "Liquid-phase Catalytic Processing of Biomass-derived Oxygenated Hydrocarbons to Fuels and Chemicals," *Angewandte Chemie International Edition* **46**(38):7164-7183.

Corma, A., G. W. Huber, L. Sauvanaud, and P. O'Connor. 2007. "Processing Biomass-derived Oxygenates in the Oil Refinery: Catalytic Cracking (FCC) Reaction Pathways and Role of Catalyst," *Journal of Catalysis* **247**, 307-327.

Cortright, R. D., R. R. Davda, and J. A. Dumesic. 2002. "Hydrogen from Catalytic Reforming of Biomass-derived Hydrocarbons in Liquid Water," *Nature* **418**(6901):964-967.

Davda, R. R., J. W. Shabaker, G. W. Huber, R. D. Cortright, and J. A. Dumesic. 2005. "A Review of Catalytic Issues and Process Conditions for Renewable Hydrogen and Alkanes by Aqueous-phase Reforming of Oxygenated Hydrocarbons over Supported Metal Catalysts," *Applied Catalysis B, Environmental* **56**, 171-176.

Diaz, I., C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, and E. Sastre. 2000. "Combined Alkyl and Sulfonic Acid Functionalization of MCM-41-Type Silica - Part 2. Esterification of Glycerol with Fatty Acids," *Journal of Catalysis* **193**(2):295-302.

Elliott, D. C. 2007. "Historical Developments in Hydroprocessing Bio-Oils," *Energy and Fuels* **21**, 1792-1815.

Ferri, D., T. Burgi, and A. Baiker. 2002. "Probing Boundary Sites on a Pt/Al_2O_3 Model Catalyst by CO_2 Hydrogenation and In Situ ATR-IR Spectroscopy of Catalytic Solid-Liquid Interfaces," *Physical Chemistry Chemical Physics* **4**, 2667-2672.

Heinze, T., K. Schwikal, and S. Bathel. 2005. "Ionic Liquids as Reaction Medium in Cellulose Functionalization," *Macromolecular Bioscience* **5**(6):520-525.

Horvath, I. T. 2006. "Gamma-Valerolactone: A Sustainable Liquid for Energy and Carbon Based Chemicals," Presented at the 10th Annual Green Chemistry and Engineering Conference, Washington, D.C.

Hu, J., Y. Wang, C. Cao, D. C. Elliott, D. J. Stevens, and J. F. White. 2006. "Conversion of Biomass-derived Syngas to Alcohols and C_2 Oxygenates Using Supported Rh Catalysts in a Microchannel Reactor," *Catalysis Today* **120**(1):90-95.

Huber, G. W., and J. A. Dumesic. 2006. "An Overview of Aqueous-phase Catalytic Processes for Production of Hydrogen and Alkanes in a Biorefinery," *Catalysis Today* **111**(1-2):119-132.

Huber, G. W., S. Iborra, and A. Corma. 2006a. "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews* **106**(9):4044-4098.

Huber, G. W., J. W. Shabaker, S. T. Evans, and J. A. Dumesic. 2006b. "Aqueous-phase Reforming of Ethylene Glycol over Supported Pt and Pd Bimetallic Catalysts" *Applied Catalysis B* **62**, 226-235.

Huber, G. W., and A. Corma. 2007. "Synergies Between Bio- and Oil Refineries for the Production of Fuels from Biomass," *Angewandte Chemie International Edition* **46**(38):7184-7201.

Huber, G. W., P. O'Connor, and A. Corma. 2007. "Processing Biomass in Conventional Oil Refineries: Production of High Quality Diesel by Hydrotreating Vegetable Oils in Heavy Vacuum Oil Mixtures," *Applied Catalysis A* **329**, 120-129.

Ketchie, W. C., E. P. Maris, and R. J. Davis. 2007a. "In-Situ X-Ray Absorption Spectroscopy of Supported Ru Catalysts in the Aqueous Phase," *Chemistry of Materials* **19**(14):3406-3411.

Ketchie, W. C., M. Murayama, and R. J. Davis. 2007b. "Selective Oxidation of Glycerol over Carbon-Supported AuPd Catalysts," *Journal of Catalysis* **250**(2):264-273.

Lynd, L. R., C. E. Wyman, and T. U. Gerngross. 1999. "Biocommodity Engineering," *Biotechnology Progress* **5**(15):777-793.

Manzer, L. E. 2003. "Production of 5-Methylbutyrolactone from Levulinic Acid." U.S. Patent 6,617,464.

Manzer, L. E. 2005a. "Preparation of Levulinic Acid Esters from Alpha-Angelica Lactone and Alcohols Assigned to DuPont." U.S. Patent Application 20050210738.

Manzer, L. E. 2005b. "Preparation of Levulinic Acid Esters from Alpha-Angelica Lactone and Olefins: Use of Ester Compositions as Fuel Additives Assigned to DuPont." U.S. Patent Application 20050171374.

Maris, E. P., W. C. Ketchie, V. Oleshko, and R. J. Davis. 2006. "Metal Particle Growth during Glucose Hydrogenation over Ru/SiO_2 Evaluated by X-ray Absorption Spectroscopy and Electron Microscopy," *Journal of Physical Chemistry B* **110**(5):7869-7876.

Mbaraka, I. K., and B. H. Shanks. 2005. "Design of Multifunctionalized Mesoporous Silicas for Esterification of Fatty Acid," *Journal of Catalysis* **229**(2):365-373.

Mbaraka, I. K., and B. H. Shanks. 2006. "Acid Strength Variation due to Spatial Location of Organosulfonic Acid Groups on Mesoporous Silica," *Journal of Catalysis* **244**(1):78-85.

McQuillan, A. J. 2001. "Probing Solid-Solution Interfacial Chemistry with ATR-IR Spectroscopy of Particle Films," *Advanced Materials* **13**(12-13):1034-1038.

Milne, T. A., R. J. Evans, and N. Abatzoglou, 1998. *Biomass Gasifier Tars: Their Nature, Formation and Conversion.* NREL/TP-570-25357, National Renewable Energy Laboratory: Golden, Colorado. Available at: http://www.nrel.gov/docs/fy99osti/25357.pdf.

Ortiz-Hernandez, I., and C. T. Williams. 2003. "In Situ Investigation of Solid-liquid Catalytic Interfaces by Attenuated Total Reflection Infrared Spectroscopy," *Langmuir* **19**, 2956-2962.

Perlack, R. D., L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, and D. C. Erbach. 2005. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply.* Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at: http://www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf.

Román-Leshkov, Y., J. N. Chheda, and J. A. Dumesic. 2006. "Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose," *Science* **312**(5782):1933-1937.

Román-Leshkov, Y., C. J. Barrett, Z. Y. Liu, and J. A. Dumesic. 2007. "Production of Dimethylfuran for Liquid Fuels from Biomass-derived Carbohydrates," *Nature* **447**, 982-986.

Salge, J. R., B. J. Dreyer, P. J. Dauenhauer, and L. D. Schmidt. 2006. "Renewable Hydrogen from Nonvolatile Fuels by Reactive Flash Volatilization," *Science* **314**, 801-804.

Shabaker, J. S., G. W. Huber, R. R. Davda, R. D. Cortright, and J. A. Dumesic. 2003. "Aqueous-phase Reforming of Ethylene Glycol over Supported Platinum Catalysis," *Catalysis Letters* **88**(2):1-8.

Shao, M. H., and R. R. Adzic. 2005. "Spectroscopic Identification of the Reaction Intermediates in Oxygen Reduction on Gold in Alkaline Solutions," *Journal of Physical Chemistry B* **109**(35):16563-16566.

Tomishige, K., M. Asadullah, and K. Kunimori. 2004. "Syngas Production by Biomass Gasification Using Rh/CeO_2/SiO_2 Catalysts and Fluidized Bed Reactor," *Catalysis Today* **89**(4):389-403.

U.S. Department of Energy Office of Science. August 2005. *Genomics:GTL Roadmap,* DOE/SC-0090, U.S. Department of Energy: Washington, D.C. Available at: http://genomicsgtl.energy.gov/roadmap/.

U.S. Department of Energy Office of Science. 2006. *Breaking the Biological Barriers to Cellulosic Ethanol: A Joint Research Agenda,* DOE/SC/EE-0095, U.S. Department of Energy: Washington, D.C. Available at: http://genomicsgtl.energy.gov/biofuels/.

Wyman, C. E. 1999. "Biomass Ethanol: Technical Progress, Opportunities, and Commercial Challenges," *Annual Review of Energy and the Environment* **24**, 189-226.

Wyman, C. E., B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, and Y. Y. Lee. 2005a. "Coordinated Development of Leading Biomass Pretreatment Technologies," *Bioresource Technology* **96**(18):1959-1966.

Wyman, C. E., B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, and Y. Y. Lee. 2005b. "Comparative Sugar Recovery Data from Laboratory Scale Application of Leading Pretreatment Technologies to Corn Stover," *Bioresource Technology* **96**, 2026-2032.

Zhao, H., J. E. Holladay, H. Brown, and Z. C. Zhang. 2007. "Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural Haibo," *Science* **316**(5831):1597-1600. DOI: 10.1126/science.1141199.

ADVANCED CATALYSTS FOR THE PHOTO- AND ELECTRO-DRIVEN CONVERSION OF CARBON DIOXIDE AND WATER

Current Status

Increasing levels of atmospheric carbon dioxide have been recognized as the principal cause of current trends in global warming, according to the 2007 Intergovernmental Report on Climate Change (Denman et al. 2007). Awareness of the global problem of rising atmospheric carbon dioxide concentrations, largely from combustion of fossil fuels, has not abated demands for inexpensive energy sources. Prospects of higher global rates of carbon dioxide emission must also be faced as the quality of fossil fuel feedstocks declines and coal and other heavy fossil feedstocks are increasingly substituted for petroleum. Even substitution of conventional energy sources with biomass-derived feedstocks, which have the appearance of no net increase in atmospheric carbon dioxide through photosynthesis, results in net increases in atmospheric carbon because of production and conversion processes. To avoid increasing atmospheric carbon dioxide concentrations, efforts must be increased to capture and sequester carbon dioxide and to recycle carbon dioxide as a fuel feedstock.

Currently, no commercially available processes exist for the conversion of carbon dioxide to fuels and chemicals, although various recycling schemes have been explored (Olah 2005; Olah and Prakash 1999). The major obstacle preventing efficient conversion of carbon dioxide into energy-bearing products is the *lack of catalysts* that can readily couple an abundant energy source (e.g., electricity from solar, wind, or nuclear sources or direct solar radiation) with inexpensive reducing agents (e.g., hydrogen derived from water or methane) to achieve rapid and selective cleavage of C–O bonds in carbon dioxide and formation of C–H bonds in the product. All known electrocatalysts or photocatalysts showing activity for carbon dioxide conversion to simple energy-storage products, such as carbon monoxide or formic acid, are inefficient and/or require use of sacrificial reducing agents.

Only intermittent research has been conducted into the electrochemical reduction of carbon dioxide over the last 20 years, despite the fact that electrochemical generation of chemical products is a mature technology and already practiced on enormous scales in the production of chlorine and aluminum and in water electrolysis. Several reviews exist on the electrochemical reduction of carbon dioxide (DuBois 2006; Gattrell et al. 2006; Hori 2003; Sánchez-Sánchez et al. 2001). Efforts are generally still at the laboratory or bench scale and involve noble metal electrodes. Electron conversion efficiencies of greater than 50 percent can be obtained, but at the expense of very high overpotentials (~1.5 V). In only a few studies has methane or methanol been the primary product of the reduction (Figure 18); however, the overall yields are low in the absence of high overpotentials and the electrode surface is susceptible to poisoning. Synthesis gas, a mixture of hydrogen and carbon monoxide, is perhaps the easiest product to obtain (Yamamato et al. 2002). Opportunities exist for discovering and developing such catalysts with the goal of achieving higher selectivity and efficiency. At present, only

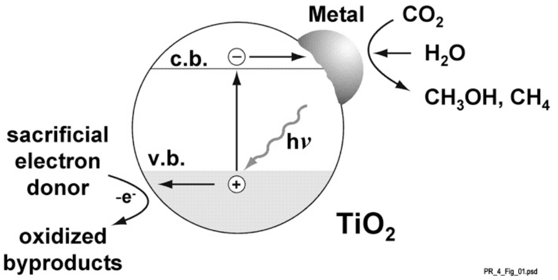


Figure 18: Electron transfer processes involved in the conversion of carbon dioxide to C_1 molecules.

Electron Donors: A Key Issue for Photo- and Electro-driven Chemical Fuel Production

Producing useful fuels (hydrogen, methanol, etc.) from carbon dioxide, water, and sunlight involves the careful coupling of two processes. Reducing (adding electrons to) readily available compounds such as carbon dioxide and water produces fuels. But, where do the compounds come from? The answer is that as solar fuels are produced by reducing some compounds, others must be oxidized (electrons removed). These other compounds are called "electron donors." If very large amounts of solar fuels are going to be produced in the future, the electron donors consumed in these processes must be abundant and inexpensive. Furthermore, the products generated by oxidizing them must be environmentally benign. One such electron donor that is utilized by natural photosynthetic systems is water, which is used as the electron donor for conversion of carbon dioxide into cellulose. This same chemistry, in concept, can be used when carbon dioxide is photo- or electro-chemically reduced to fuels such as methanol or methane. However, because of the overall energy input required in these processes, other electron donors are frequently used. Examples of common electron donors include organic compounds such as alcohols and amines, and easily oxidized inorganic species such as sulfite ion. These species cannot be used for practical, large-scale production of fuels using sunlight, and thus are referred to as "sacrificial electron donors." By decreasing the energetic requirements for the overall process, these sacrificial reagents allow scientists to focus on the fuel-forming reductive process from the coupled oxidation process. However, use of sacrificial reagents significantly complicates the meaning of solar energy conversion efficiencies.

laboratory-scale proof-of-concept systems produce carbon monoxide and formic acid with reasonable electron conversion efficiencies, but still at high overpotentials (greater than 0.6V) (Halmann and Steinberg 1999).

Molecular catalysts have also shown promise for photochemical reduction of carbon dioxide. These catalysts may employ a metal center acting as both a light absorber and a catalytic site. Photocatalytic conversion of carbon dioxide to carbon monoxide and formate (in some cases together with hydrogen) has been carried out with various metal complexes in solution (Arakawa et al. 2001; Fujita 1999). The quantum efficiency for the formation of carbon monoxide has been reported to reach to 38 percent with a rhenium(I) complex; however, sacrificial electron donors are required in all of the systems reported (Fujita 1999; Sato et al. 2007). Although metallocarboxylates and metallocarboxylic acids have been proposed as intermediates for carbon monoxide production, such species have been observed only in a few photocatalytic systems (Hayashi et al. 2003; Ogata et al. 1995) for which the mechanisms and kinetics of carbon monoxide formation have been investigated.

Numerous investigators have examined the heterogeneous photoreduction of carbon dioxide on high-surface-area oxide semiconductor materials, with and without the presence of a noble metal co-catalyst. These photocatalysts rely on the generation of electron-hole pairs through light absorption in the semiconductor, followed by charge separation and surface redox chemistry. For example, titania-based photocatalysts have been well investigated, particularly for organic photooxidation reactions. Carbon dioxide reduction to important fuel precursors has been observed on these and other solid photocatalysts, but rates and yields are generally very low and the photoexcitation source is usually restricted to ultraviolet light (Guan et al. 2003; Pathak et al. 2004; Tseng et al. 2002; Wu et al. 2005).

Photons to Fuels: Design of an Electrochemical Cell Producing Syngas by Carbon Dioxide and Water Reduction at Room Temperature

A new electrolysis cell design for simultaneous electrochemical reduction of carbon dioxide and water to make syngas at room temperature (25 ºC) was developed (Figure 19). This design was based on a technology very close to that of proton-exchange-membrane fuel cells (i.e., based on the use of gas-diffusion electrodes so as to achieve high current densities). The modified configuration is based on the insertion of a pH-buffer layer (aqueous potassium bicarbonate) between the cathode catalyst layer and the Nafion® membrane in the cell. This design allows for a great enhancement of the cathode selectivity for carbon dioxide reduction to carbon monoxide.

Investigations were performed with both silver and gold catalysts at the cathode. Each catalyst was shown to be very selective for carbon dioxide reduction to carbon monoxide. The results are quite similar: 75 ± 3 percent and 83 ± 3 percent current efficiency for carbon dioxide reduction to carbon monoxide at an overall current density of 20 mA/cm^2, for silver and gold, respectively, with the balance corresponding to hydrogen.

The main difference between the two catalysts is a lower cathode overpotential on the gold-based electrode, ca. 200 mV lower than for silver. As the overall current density increases, a decrease of carbon monoxide current efficiency is observed, likely related to carbon dioxide mass-transport limitations. Maxima of partial current densities for carbon monoxide evolution are approximately 30 to 35 mA/cm^2 for both silver and gold with the present cell design. Energy efficiency for the overall cell (with an alloy of platinum-iridium as the anode catalyst) is ca. 47 percent at 20 mA/cm^2 and decreases to ca. 32 percent at 100 mA/cm^2, for both catalysts, which is mostly due to Joule heating losses.

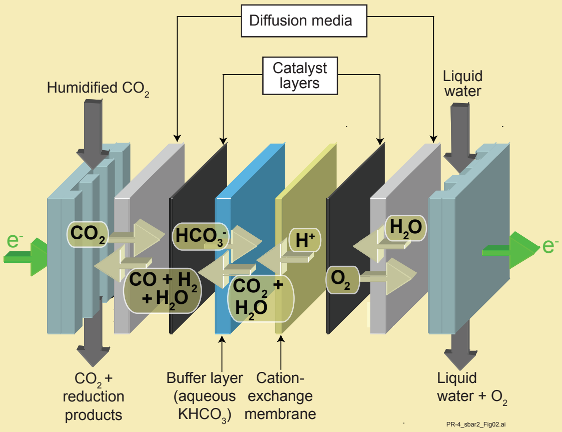


Figure 19: Schematic representation of an electrochemical cell for producing synthesis gas (a mixture of carbon monoxide and hydrogen) by reduction of carbon dioxide and water.

Recent investigations with a partially optimized supported gold catalyst as cathode have shown that carbon monoxide partial current densities as high as 135 mA/cm^2 can be obtained for short electrolysis periods. This result illustrates the importance of the design of the gas-diffusion cathode. Unfortunately, a decrease of the catalyst selectivity for carbon monoxide evolution with time has been identified. This result is more pronounced for the cells with the supported gold catalyst.

Mathematical modeling was carried out and underlines the complexity of the phenomena occurring in the pH-buffer layer, where a two-phase (gas + liquid) flow takes place, with carbon dioxide gas being generated near the buffer-membrane interface and flowing to the cathode catalyst.

Some of the scientific issues related to photo- and electro-chemical water oxidation have been discussed in an earlier basic research needs report (DOE 2005). However, the ability to oxidize water in multi-electron steps remains a critical scientific challenge that requires a fundamental understanding of the elementary processes involved as well as a basis for discovering new catalysts. Our present inability to oxidize water to oxygen with stable and abundant catalyst materials remains the Achilles' heel for virtually all photo- and electro-catalytic carbon dioxide conversion schemes. Two fundamental aspects of water oxidation in biology are the ability of these catalysts to channel energy between sequential catalytic sites to drive uphill reactions (McEvoy and Brudvig 2006) and to exploit long-range effects, such as protein conformational changes, to adjust and control the activity of the active site (Agarwal 2005; Barry et al. 2006; Bricker 2006; Haumann et al. 2005).

Basic Science Challenges, Opportunities, and Research Needs

Carbon dioxide reduction to fuels

The catalytic conversion of carbon dioxide to liquid fuels is a critical goal that, when met, can impact the carbon balance by recycling carbon dioxide as fuels. The challenges are immense, but the potential rewards are also immense. Carbon dioxide is an extremely stable molecule generally produced by fossil fuel combustion and respiration. Returning carbon dioxide to a useful chemical state on the same scale as its current production rates is well beyond our current scientific and technological ability. Managing carbon dioxide as an energy feedstock will require the following:

- deeper fundamental understanding of the chemistry of carbon dioxide activation
- development of new, multifunctional catalysts that efficiently convert an abundant energy source (e.g., solar, wind, or nuclear) into specific C–O bond-breaking and C–H (and even C–C) bond-forming reactions involving carbon dioxide.

These basic science challenges call for advances in catalyst design and understanding the elementary processes involved in the progress of reactions that are uphill thermodynamically.

Catalytic conversion of carbon dioxide. Conversion of carbon dioxide to liquid fuels and useful chemicals will require new methods for activating the carbon dioxide molecule. For example, the first logical step in a carbon dioxide reduction might be the hydrogenation of carbon dioxide to formic acid, HCOOH, as illustrated in Figure 20. Carbon dioxide is an "amphoteric" molecule (possessing both acidic and basic properties). The carbon atom is susceptible to attack by nucleophiles, and the oxygen atoms are susceptible to attack by electrophiles. In the hydrogenation of carbon dioxide, therefore, one can think of activation of carbon dioxide activation as occurring by simultaneous attack of a nucleophilic metal hydride (H^-) at the carbon dioxide carbon atom and a Bronsted acid (H^+) at the oxygen atom. In the limit of these interactions, one can consider the hydrogenation of carbon dioxide to result from a heterolytic process that adds H^- to the carbon and H^+ to the oxygen.

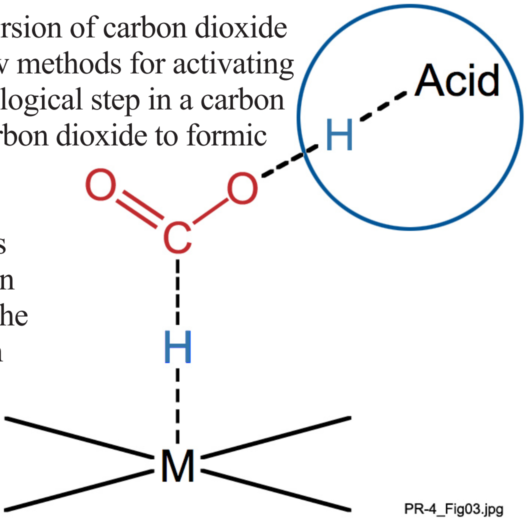


Figure 20: Schematic model for the concerted action of a metal hydride and proton-donor acid in activating carbon dioxide.

The next logical step in the reduction of carbon dioxide would then be the deoxygenation of formic acid to formaldehyde, H_2CO. In photosynthesis, for example, carbon dioxide is reduced to formaldehyde equivalents that are combined to form saccharides $(H_2CO)_6$. The reduction of formic acid to a formaldehyde equivalent can again be thought of as proceeding by H^- addition to the carbon atom and H^+ addition to the OH group. However, the details of this next reductive step (strength of hydride and proton equivalents, geometry of addition, etc.) can be expected to be quite different from those required for the production of formic acid.

Similarly, the third step—reduction of formaldehyde to methanol (CH_3OH)—may proceed by a completely different mechanism such as the direct addition of hydrogen across the C=O double bond of formaldehyde.

This discussion illustrates the need for detailed mechanistic and theoretical knowledge in the development of multifunctional catalysts (i.e., catalysts able to catalyze more than one particular type of chemical transformation) for the conversion of carbon dioxide to liquid fuels. Moreover, this discussion underscores the need for catalytic systems with well-managed hydrogen delivery capability. Many catalytic reactions require delivery of hydrogen to the catalytic center in a form that is seldom H_2. Effective hydrogen delivery requires fine-tuned structural and electronic parameters at both the hydrogen donor and catalytic sites. The donor can be any of several groups, such as O–H or N–H, but the most useful appear to involve metal–H bonds. The remarkable diversity of reactivity patterns exhibited by metal–H bonds, particularly in molecular complexes but also in heterogeneous settings, enables a tremendous versatility in the design of catalysts that can deliver hydrogen. As shown in generalized form in Figure 21 with respect to a homogeneous catalyst, cleavage of the metal–H bond can occur as a proton (H^+), a hydrogen atom (H•), or as a hydride (H^-) (Cheng et al. 1998; Eisenberg and Norton 1991; Kristjánsdóttir and Norton 1991). Not only are all three modes of cleavage observed in homogeneous metal catalysis, but in some cases, the *same* metal hydride complex can exhibit *all three* modes of cleavage, in reactions with different species (Bullock 1991). This result provides an extraordinary opportunity for control of hydrogen delivery in its various forms. Much less is known about how to control the delivery of hydrogen in heterogeneous and electrocatalytic settings. Incorporation of design concepts inherent to homogeneous catalysis into solid and electrochemical catalysis is needed to better control hydrogen delivery in these systems.

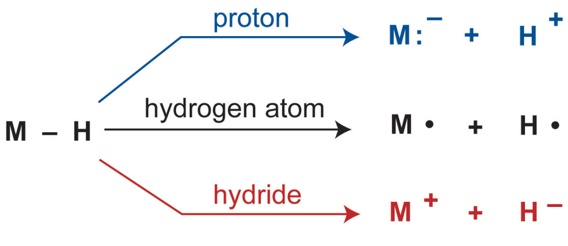


Figure 21: Elementary pathways for cleavage of a metal–hydride bond. In this generalized scheme, ligands on the metal complex are not shown, and the organic or inorganic acceptor of the hydrogen is not specified. From Bullock (2004), Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Design of catalysts that exploit metal-H reactivity patterns requires a detailed understanding of the kinetics and thermodynamics of the cleavage modes of metal–H bonds. Thermochemical information about the homolytic bond dissociation energies (typically 60-80 kcal/mol) (Ryan et al. 1990; Tilset and Parker 1989; Wang and Angelici 1996) enables evaluation of the feasibility of hydrogen atom transfer reactions. These reactions may proceed as single-step hydrogen atom transfers or as proton-coupled electron transfers, whereby the hydrogen atom and electron may not be delivered to the same site on the catalyst. Evaluation of proton transfer reactivity, whereby the metal–H bond serves as an acid, requires detailed thermodynamic and kinetics data. The thermodynamic acidity of metal–H bonds ranges over more than 20 orders of magnitude (Kristjánsdóttir and Norton 1991). Hydride transfer reactions can be similarly evaluated, often through thermochemical cycles determined from electrochemical data to evaluate thermodynamic hydricity. Thermodynamic hydricity of metal–H bonds ranges over more than 40 kcal/mol (Berning et al. 1999; Miedaner et al. 2004; Price et al. 2002). These elementary reactions constitute critical steps of many types of catalytic cycles, and evaluation of the kinetics and thermodynamics of each of these types of reactions will guide the design of catalysts for fuel formation.

The spectroscopic characterization of relevant transient catalytic intermediates that lead to carbon monoxide, formic acid, formaldehyde, and methanol will provide important knowledge of mechanistic pathways in carbon dioxide reduction. In general, under catalytic reaction conditions, very short lifetimes and very low concentrations are expected for these intermediates. Novel in-situ methods that utilize ultrafast spectroscopy or scattering methods involving pump-probe techniques will be required to resolve intermediates and establish their reaction paths. Fast laser pulses may induce the photo-driven chemistry and populate a high concentration of transient species that may be detected at various delay times, thus allowing for the resolution of various transient species and activation barriers, and for an understanding of how energy dissipates during the reaction sequence. The challenge is to develop ultrafast methods that are highly sensitive and selective in probing various intermediates and their dynamics in situ under reaction conditions. For example, surface science techniques that operate under ultrahigh vacuum conditions have significantly advanced understanding of structure-reactivity relationships in heterogeneous catalysis and electrocatalysis (Markovic and Ross 2002; Somorjai 1996; Stamenkovic et al. 2007). New approaches are needed that permit examination of the catalyst's active sites under realistic reaction conditions. Figure 22 illustrates the impact that scanning tunneling microscopy has had in characterizing active sites in electrocatalysis. This technique is capable of resolving features down to the atomic scale.

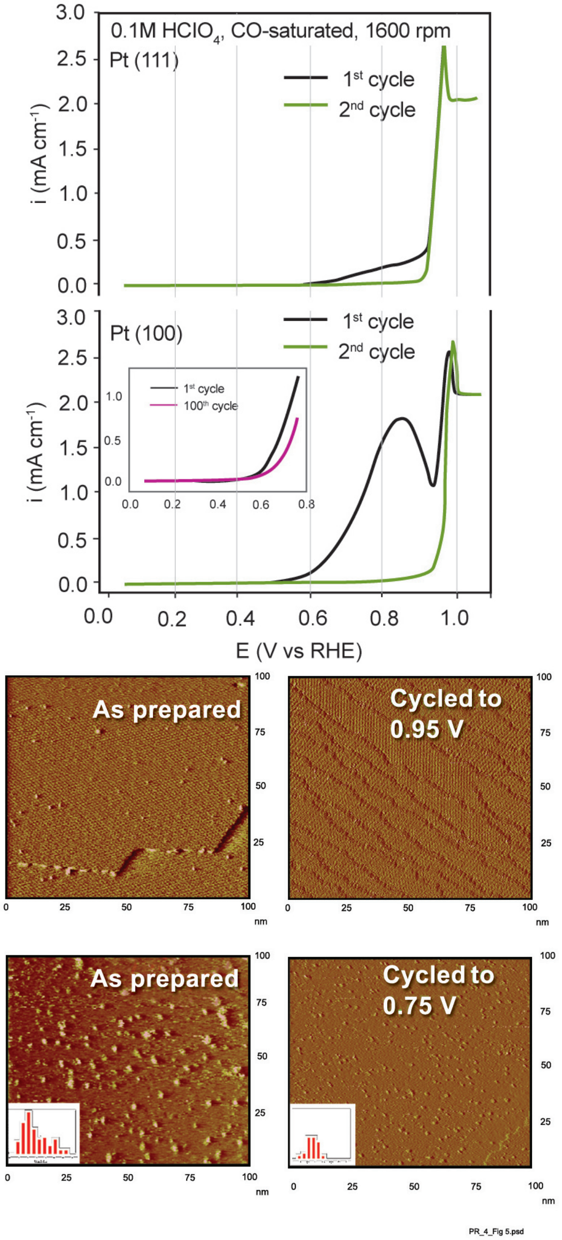


Figure 22: Appearance of metal nanoclusters is correlated with the promotion of carbon monoxide electrochemical oxidation at low overpotentials. The scanning transmission microscopy images were obtained ex situ after protection of the surfaces with a monolayer of carbon monoxide. Courtesy of N. M. Markovic (Argonne National Laboratory).

Applications of this form of microscopy to image surfaces of electrocatalytic materials have been limited, in part because of the tendency of the surfaces to be poisoned under the conditions of investigation. Currently, researchers often rely on ex-situ imaging of catalytic electrodes. In-situ capabilities will open new avenues of discovery and mechanistic understanding.

Achieving the ability to follow photo- and electro-chemically driven reactions at a level necessary to understand carbon dioxide catalytic reduction presents mechanistic challenges well beyond those in thermal catalysis. These challenges include understanding and optimizing the properties of the following:

- multi-step, multi-electron chemical transformations
- coupled electron and atom transfer reactions
- kinetics of strongly endothermic processes possessing metastable or unstable intermediates
- the interplay between various catalytic sites and the catalyst environment in a multifunctional catalyst.

Although ultrafast spectroscopic techniques and high-level multi-reference wave function methods exist to establish the nature of excited states and their transitions, the ability to map out the dynamics of such states does not currently exist. Detailed knowledge about the free energy landscape for thermal, photo- and electro-chemical conversions is obscured by the complexity of the reaction environment and by the fact that many of these bond-breaking and -forming processes involve simultaneous proton and electron transfer steps. Ab-initio methods can currently be used to calculate with some reliability the energetics of simple systems and overall thermodynamics of important reactions in homogeneous and heterogeneous catalysis. These results have been used to subsequently construct static overall potential energy surfaces. Because of the size of the systems modeled, most of the published research has been based on density functional theoretical (DFT) methods and has been focused on idealized model surfaces and organometallic complexes under very idealized conditions. DFT, which has been the workhorse in modeling catalytic systems, is a ground-state method unsuited to simulating excited states. Advances in theoretical development as well as the implementation of time-dependent DFT have occurred over the past few years which now make it possible to simulate small-molecule systems. The development of methods to treat complex organometallic and solid-state systems is still in its infancy. Notwithstanding this progress, a more comprehensive understanding of the influence of the complex reaction environment on the intrinsic elementary reaction processes under working reaction conditions is still a tremendous theoretical (and experimental) challenge. In homogeneous systems, the effects of electrolyte, ligand architecture, solvation, and deactivation processes all pose significant difficulties in determining the intrinsic kinetics. Heterogeneous catalytic systems pose even further complications as the result of the effects of particle size and morphology, support, nanoscale architectures, electrolyte, and deactivation and the ill-defined surface structures.

Following photo- and electro-chemical reaction systems presents challenges well beyond those found in thermally driven catalysis. For example, in semiconductor-based photocatalytic systems, chemistry resulting from separated electron-hole pairs, resulting from photon absorption, can be modeled with separate reduction and oxidation sites. In the presence of a solution, this approach becomes akin to modeling electrocatalytic systems. Recent developments have made it possible to examine the influence of applied potentials and electric fields. A more accurate treatment of electrocatalytic systems, however, would require the development of Grand Canonical methods that treat constant-potential systems. Currently, most ab-initio methods are constant-electron systems based on Canonical ensembles. As another example, the prediction of accurate electron transfer kinetics is challenging. Only little work has been done on modeling coupled proton electron transfer systems. The methods to accurately model the kinetics of electron transfer present a major challenge.

Efficient carbon dioxide reduction catalysts. At present, both homogeneous and heterogeneous catalytic systems have been demonstrated for relevant half reactions of carbon dioxide reduction, using redox equivalents in the oxidation half reaction from sacrificial or stoichiometric sources. This catalysis includes efficient electrochemical or visible light-driven reduction of carbon dioxide to carbon monoxide or formic acid. However, the direct and efficient coupling of both half reactions *without the need for artificial reagents* is still a major scientific obstacle. Achieving this goal will require new, multifunctional catalysts designed for optimal performance in both redox processes. To avoid unwanted or wasteful products and to obtain a good selectivity to desired products, precise control of electronic and geometric structures of catalysts and reaction conditions is needed. Simultaneously, the structural features of these catalysts must be understood sufficiently at the molecular level to permit examination and refinement with advanced theoretical methods. For example, conversion of carbon dioxide to methanol requires delivery of 6 electrons and 6 protons in a reaction mechanism involving multiple steps. Rational design of new catalysts will require experimental and computational investigations to develop a predictive understanding of what influences such reactivity patterns. Advances in computational treatment of long-range influences, such as those derived from a solvent, will contribute greatly to the realization of efficient carbon dioxide catalysts.

Energy-efficient reduction of carbon dioxide demands catalysts that operate near thermodynamic potentials with high rates. The multiple electron and proton/hydride transfers involved in the reduction of carbon dioxide to fuels will require complex catalysts and catalyst assemblies including hybrid catalysts, hierarchal nanostructured systems, and multiple site catalysts that work in concert to achieve the overall carbon dioxide reduction process. In photochemical systems, efficiency requires the vectorial arrangement of the oxidation and reduction units across a barrier or membrane to prevent destructive cross and back reaction of the reduced products with the evolving oxygen. Hierarchical organization of (photo)catalytic sites is equally important for efficiently converting the two-electron reduction intermediates to more complex products. Many of the elementary steps required for fuel formation are dark (thermal) reactions. The properties and interdependencies of these dark reactions with those involving photo- or electro-chemical events are poorly understood.

Catalyst stability is a central issue. Semiconductor materials in aqueous electrolytes are generally susceptible to corrosion. Holes capable of oxidizing water are powerful oxidizing agents, although electrons capable of reducing water or carbon dioxide are generally weak reducing agents. Single electron transfer events from semiconductor surfaces to outer-sphere redox couples are usually slow in comparison with capture by surface states and/or inner-sphere processes. This observation has implications for catalyst design and incorporation into photo-electrochemical conversion assemblies.

Catalyst systems that accomplish the demanding multi-electron reduction of carbon dioxide to C_1 intermediates are likely to be very different in nature from the bond-breaking and -forming catalysts needed for subsequent conversions to more complex products. Incorporation of both catalytic functions into one system is a significant challenge. Titanium- or zirconium-grafted

Photocatalytic Carbon Dioxide Reduction by Inorganic Complexes

Rhenium(I) diimine complexes act as photocatalysts and/or electrocatalysts for carbon dioxide reduction to carbon monoxide. Although the kinetics and efficiency of photocatalysis are far from what would be needed for practical solar photocatalysis, the mechanism has been worked out sufficiently well to provide understanding of the catalytic cycle. The mechanism illustrates the challenges of carbon dioxide reduction catalysis and the importance of understanding the mechanism to design improved catalysts and better catalysis cycles. The reaction has been conducted in nonaqueous solvents such as acetonitrile or tetrahydrofuran. The two-electron reduction is accomplished by the binding of two one-electron-reduced rhenium monomers to one carbon dioxide molecule to form a carbon dioxide bridged dimer (Figure 23), which reacts with a second carbon dioxide molecule to form carbon monoxide and CO_3^{2-}. The active one-electron reduced form of the catalyst is regenerated by light and a sacrificial electron donor to form a full catalytic cycle.

Ultimately, in a practical carbon dioxide reduction scheme, the electrons must be derived by coupling to water oxidation. Moreover, the rates of formation and reaction of the carbon dioxide bridged dimer are low. In particular, the binding of carbon dioxide competes with coordination by solvent to the metal center, which shifts electron density onto the ligands and decreases the reactivity of the metal center. The reaction of the one-electron reduced monomer has a rate (< 0.1 s^{-1} under 1 atm carbon dioxide) that is two to three orders of magnitude lower than needed for solar conversion. Assuming a catalyst coverage density of 1 nm^{-2} and a 100 percent conversion, the catalyst turnover number rate to produce carbon monoxide must be more than 50 s^{-1} to keep up with the solar generation of electrons. This result suggests that carbon dioxide reduction with this type of rhenium catalyst must be done in supercritical carbon dioxide or a non-coordinating hydrocarbon solvent with a high pressure of carbon dioxide. Extensive mechanistic investigations combined with computation of intermediates were important in establishing these pathways (Hayashi et al. 2003).

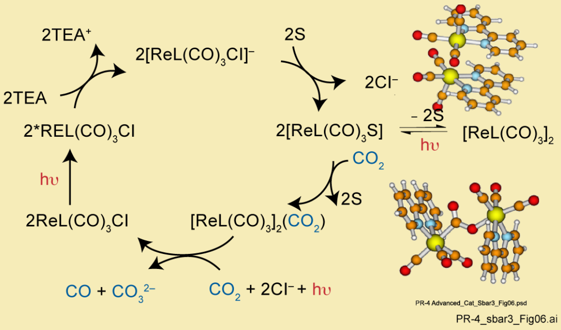


Figure 23: Reducing carbon dioxide to carbon monoxide with a rhenium(I) diimine complex. Courtesy of Etsuko Fujita (Brookhaven National Laboratory).

zeolites have been used to produce carbon monoxide together with a trace amount of methanol and methane under ultraviolet irradiation (Anpo et al. 1997, 1998; Lin et al. 2004; Matsuoka and Anpo 2003); however, products of homogeneous photo- and electro-chemical reduction of carbon dioxide have been limited to carbon monoxide and/or formic acid. In homogeneous electrochemical reduction of carbon dioxide, a few additional C_2 species have been reported as minor products. Coupling carbon dioxide reduction catalysts to catalysts that can accomplish formation of heavier fuels is a priority research need. To work efficiently in a concerted fashion, catalytic systems must be built to facilitate directional energy flow charge, and atom/ion transport between the catalytic sites (and their associated rates) precisely synchronized. Efficient and selective photo- or electro-catalytic conversion of carbon dioxide to a C_2 or higher product has not been achieved. The very rapid advances in nanostructured materials and methods to functionalize these offer opportunities for the hierarchical arrangement of catalytic units on the appropriate length scale for communication of energy, charge, and mass. The synthesis and organization of multi-site catalytic assemblies into solar or electrochemical conversion systems are major scientific challenges. A report on solar energy use (DOE 2005) identified revolutionary concepts for converting solar energy to electrical energy at acceptable low costs. Many of these third-generation solar conversion strategies require the fabrication of interdigitated nanostructured systems that contain advanced materials such as quantum dots, conducting polymers, fullerenes, carbon nanotubes, and multifunctional molecular systems. The same type of emphasis is needed in the development of catalyst systems that can channel solar or solar-derived electricity into *specific* bond-forming and -breaking reactions. New, stable, and abundant catalytic materials should be incorporated into these energy-harvesting and -relaying systems in ways that optimize efficient chemical conversion. Equally important is the emergence of wholly new synthetic methods to produce complex structures in quantities that are relevant to the scale of energy needs. Powerful, convenient, and rapid tools for characterizing the critical properties of composition and atom/electronic structure will be critical in enabling the evaluation, understanding, and design of these catalyst systems.

Development of new catalysts for the reduction of carbon dioxide to fuels will also benefit from lessons from biology. The production of carbohydrates from carbon dioxide in natural photosynthesis involves dark reactions, and many of the details of the catalysis of these processes are directly relevant to artificial systems. The biological carbon monoxide dehydrogenases are the only catalysts known that efficiently catalyze the reduction of carbon dioxide to carbon monoxide. Extremely challenging multi-electron/proton transfer processes take place in a multi-site catalytic system that contains a series of active sites with seemingly well-defined and concerted roles (most of which are still unknown). Moreover, the actual active sites are surrounded by a dynamic medium that is almost perfectly adapted to facilitate and enhance the overall rate of the catalytic process.

Water oxidation

Understanding of how to control water oxidation to oxygen is a prerequisite for achieving efficient photo- or electro-chemical reduction of carbon dioxide in the absence of sacrificial electron donors and constitutes in a grand challenge in science. The availability of water as an electron donor opens up a wide variety of reductive processes that can be driven with electricity or sunlight. Because the ultimate products of fossil fuel combustion are carbon dioxide and water, the conversion of these stable molecules back into fuel involves thermodynamically uphill reactions that remove oxygen atoms. Water oxidation to oxygen is an especially challenging problem because it requires two 2-electron/2-proton ($2e^-/2H^+$) transfer processes occurring simultaneously on two separate water molecules. In carbon dioxide reduction, one can consider a series of $2e^-/2H^+$ (hydrogenation) steps, because the standard potentials for the various half reactions are within a few hundred millivolts of each other. This relationship between steps is not true for water oxidation. The standard reduction potential for the H_2O_2/H_2O couple is 1.78 V, which is about 0.55 V positive of the O_2/H_2O couple. Therefore, if water is oxidized through hydrogen peroxide at the potential for oxidation of water to oxygen (1.23 V), the maximum concentration of hydrogen peroxide that can exist, as determined by the Nernst equation, is about 10 orders of magnitude lower than the surface concentration of water. Therefore, subsequent reactions that oxidize hydrogen peroxide to oxygen must have enormously high rate constants to succeed. This complexity in balancing the two redox steps requires a high level of understanding for catalyst design. To overcome this and other obstacles in achieving efficient water oxidation catalysis, basic research is needed in the following areas:

- computational and experimental methods to properly characterize complex catalytic systems including the effect of the environment
- mechanistic understanding and control of multi-electron transformations and charge management
- determination of the mechanisms of water oxidation
- development of efficient, robust, and inexpensive water oxidation catalysts.

The development of new catalytic systems for water oxidation (and hence conversion of carbon dioxide to fuels) will require a strong interplay between the synthesis of new artificial systems and the adaptation of the best concepts and models that emerge from our understanding of natural photosynthesis.

Catalytic Oxidation of Water

Water oxidation is performed by nature every day with extraordinary elegance (Eisenmesser et al. 2005; McEvoy and Brudvig 2006). However, little is known about the catalytic aspects of this complex reaction. A sequence of events initiated after charge separation induced by photosynthesis includes an oxidation chain that has several cations in various degrees of oxidation, proteins, and water as solvent, as the main protagonists. Various length scales and time scales are involved. Although many details of the reaction mechanism are debated, this sidebar illustrates some details of one of the proposed catalytic cycles (Figure 24). To advance the science and technology of designing advanced catalysts for this task, the workings of this admirable molecular machine must be elucidated.

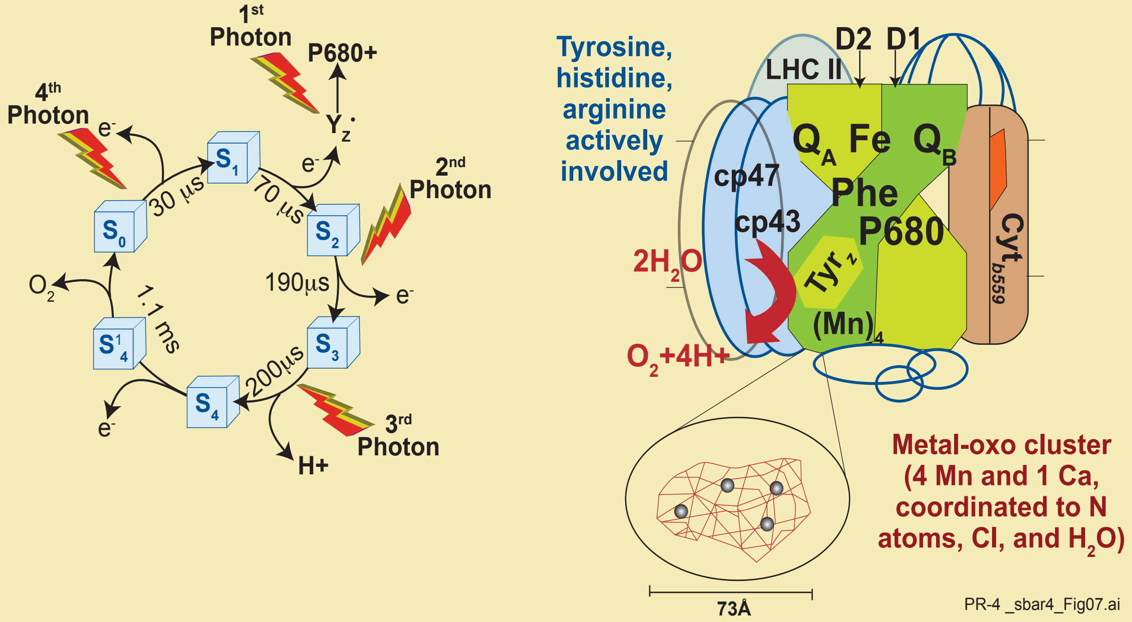


Figure 24: Proposed catalytic cycles for oxidation of water. From Sun et al. (2001). Reproduced by permission of The Royal Society of Chemistry. From Haumann et al. (2005). Reprinted with permission from AAAS.

References

Agarwal, P. K. 2005. “Role of Protein Dynamics in Reaction Rate Enhancement by Enzymes,” *Journal of the American Chemical Society* **127**:15248-15256.

Anpo, M., H. Yamashita, Y. Ichihashi, Y. Fujii, and M. Honda. 1997. “Photocatalytic Reduction of CO_2 with H_2O on Titanium Oxides Anchored within Micropores of Zeolites: Effects of the Structure of the Active Sites and the Addition of Pt,” *Journal of Physical Chemistry B* **01**:2632-2636.

Anpo, M., H. Yamashita, K. Ikeue, Y. Fujii, S. G. Zhang, Y. Ichihashi, D. R. Park, Y. Suzuki, K. Koyano, and T. Tatsumi. 1998. “Photocatalytic Reduction of CO_2 with H_2O on Ti-MCM-41 and Ti-MCM-48 Mesoporous Zeolite Catalysts,” *Catalysis Today* **44**(1-4):327-332.

Arakawa, H., M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, and W. Tumas. 2001. “Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities,” *Chemical Reviews* **101**(4):953-996.

Barry, B. A., I. B. Cooper, A. DeRiso, S. H. Brewer, D. M. Vu, and R. B. Dyer. 2006. “Time-resolved Vibrational Spectroscopy Detects Protein-based Intermediates in the Photosynthetic Oxygen-evolving Cycle,” *Proceedings of the National Academy of Sciences* **103**:7288-7291.

Berning, D. E., B. C. Noll, and D. L. DuBois. 1999. “Relative Hydride, Proton, and Hydrogen Atom Transfer Abilities of $[HM(diphosphine)_2]PF_6$ Complexes (M = Pt, Ni),” *Journal of the American Chemical Society* **121**:11432-11447.

Bricker, T. M. 2006. “A Time-resolved Vibrational Spectroscopy Glimpse into the Oxygen-evolving Complex of Photosynthesis,” *Proceedings of the National Academy of Sciences* **103**:7205-7206.

Bullock, R. M. 1991. “Metal-hydrogen Bond Cleavage Reactions of Transition Metal Hydrides: Hydrogen Atom, Hydride, and Proton Transfer Reactions,” *Comments Inorganic Chemistry* **12**:1-33.

Bullock, R. M. 2004. “Catalytic Ionic Hydrogenations,” *Chemistry: A European Journal* **10**, 2366-2374.

Cheng, T. Y., B. S. Brunschwig, and R. M. Bullock. 1998. “Hydride Transfer Reactions of Transition Metal Hydrides: Kinetic Hydricity of Metal Carbonyl Hydrides,” *Journal of the American Chemistry Society* **120**:13121-13137.

Denman, K. L., G. Brasseur, A. Chidthaisong, P. Ciais, P. M. Cox, R. E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S. Ramachandran, P. L. da Silva Dias, S. C. Wofsy and X. Zhang. 2007. “Couplings Between Changes in the Climate System and Biogeochemistry.” In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change,* eds. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller. Cambridge University Press: Cambridge, United Kingdom.

DuBois, D. L. 2006. “Carbon. Electrochemical Reactions of Carbon Dioxide.” In *Encyclopedia of Electrochemistry* **7a**:202-225.

Eisenberg, D. C., and J. R. Norton. 1991. “Hydrogen-atom Transfer Reactions of Transition-metal Hydrides,” *Israel Journal of Chemistry* **31**:55-66.

Eisenmesser, E. Z., O. Millet, W. Labeikovsky, D. M. Korzhnev, M. Wolf-Watz, D. Bosco, J. J. Skalicky, L. E. Kay, and D. Kern. 2005. “Intrinsic Dynamics of an Enzyme Underlies Catalysis,” *Nature* **438**:117-121.

Fujita, E. 1999. “Photochemical Carbon Dioxide Reduction with Metal Complexes,” *Coordination Chemical Reviews* **185-186**:373-384.

Gattrell, M., N. Gupta, and A. Co. 2006. “A Review of the Aqueous Electrochemical Reduction of CO_2 to Hydrocarbons at Copper,” *Journal of Electroanalytical Chemistry* **594**:1-19.

Guan, G., T. Kida, T. Harada, M. Isayama, and A. Yoshida. 2003. “Photoreduction of Carbon Dioxide with Water Over $K_2Ti_6O_{13}$ Photocatalyst Combined with Cu/ZnO Catalyst Under Concentrated Sunlight,” *Applied Catalysis A, General* **249**(1):11-18.

Halmann, M. M., and M. Steinberg. 1999. “Greenhouse Gas Carbon Dioxide Mitigation,” In *Science and Technology.* Lewis Publisher: Boca Raton, Florida.

Haumann, M., P. Liebisch, C. Muller, M. Barra, M. Grabolle, and H. Dau. 2005. “Photosynthetic O_2 Formation Tracked by Time-resolved X-ray Experiments,” *Science* **310**:1019-1021.

Hayashi, Y., S. Kita, S. B. Brunschwig, and E. Fujita. 2003. “Involvement of a Binuclear Species with the Re-C(O)O-Re Moiety in CO_2 Reduction Catalyzed by Tricarbonyl Rhenium(I) Complexes with Diimine Ligands: Strikingly Slow Formation of the Re-Re and Re-C(O)O-Re Species from $Re(dmb)(CO)_3S$ (dmb = 4,4’-dimethyl-2,2’-bipyridine, S = Solvent),” *Journal of the American Chemical Society* **125**:11976-11987.

Hori, Y. 2003. “CO_2 Reduction Catalyzed by Metal Electrodes.” In *Handbook of Fuel Cells – Fundamentals, Technology and Applications* **2**:720-733.

Kristjánsdóttir, S. S., and J. R. Norton. 1991. “Acidity of Hydrido Transition Metal Complexes in Solution.” In *Transition Metal Hydrides*, Chapter 9, pp. 309-359, ed. A. Dedieu, VCH: New York, NY.

Lin, W. Y., H. X. Han, and H. Frei H. 2004. “CO_2 Splitting by H_2O to CO and O_2 under UV Light in TiMCM-41 Silicate Sieve,” *Journal of Physical Chemistry B* **108**(47):18269-18273.

Markovic, N. M., and P. N. Ross. 2002. “Surface Science Studies of Model Fuel Cell Electrocatalysts,” *Surface Science Reports* **45**:117-229.

Matsuoka, M., and M. Anpo. 2003. “Local Structures, Excited States, and Photocatalytic Reactivities of Highly Dispersed Catalysts Constructed within Zeolites,” *Photochemical & Photobiological Sciences* **3**:225-252.

McEvoy, J. P., and G. W. Brudvig. 2006. “Water-splitting Chemistry of Photosystem II,” *Chemical Reviews* **106**:4455-4483.

Miedaner, A., J. W. Raebiger, C. J. Curtis, S. M. Miller, and D. L. DuBois. 2004. “Thermodynamic Studies of $[HPt(EtXantphos)_2]^+$ and $[(H)_2Pt(EtXantphos)_2]^{2+}$,” *Organometallics* **23**:2670-2679.

Ogata, T., S. Yanagida, B. S. Brunschwig, and E. Fujita. 1995. “Mechanistic and Kinetic Studies of Cobalt Macrocycles in a Photochemical CO_2 Reduction System: Evidence of Co-CO_2 Adducts as Intermediates,” *Journal of the American Chemical Society* **117**:6708-6716.

Olah, G. A. 2005. “Beyond Oil and Gas: The Methanol Economy,” *Angewandte Chemie – International Edition* **44**:2636-2639.

Olah, G. A. and G. K. Prakash. 1999. “Recycling of Carbon Dioxide into Methyl Alcohol and Related Oxygenates for Hydrocarbons.” U.S. Patent 5,928,806. July.

Pathak, P., M. J. Meziani, Y. Li, L. T. Cureton, and Y. P. Sun. 2004. “Improving Photoreduction of CO_2 with Homogeneously Dispersed Nanoscale TiO_2 Catalysts,” *Chemical Communications* (Cambridge, United Kingdom) **10**:1234-1235.

Price, A. J., R. Ciancanelli, B. C. Noll, C. J. Curtis, D. L. DuBois, and M. R. DuBois. 2002. “$HRh(dppb)_2$, a Powerful Hydride Donor,” *Organometallics* **21**:4833-4839.

Ryan, O. B., M. Tilset, and V. D. Parker. 1990. “Chemical and Electrochemical Oxidation of Group-6 Cyclopentadienylmetal Hydrides – 1st Estimates of 17-electron Metal Hydride Cation Radical Thermodynamic Acidities and Their Decomposition to 17-electron Neutral Radicals,” J*ournal of the American Chemical Society* **112**(7):2618-2626.

Sánchez-Sánchez, C. M., V. Montiel, D. A. Tryk, A. Aldaz, and A. Fujishima. 2001. “Electrochemical Approaches to Alleviation of the Problem of Carbon Dioxide Accumulation,” *Pure and Applied Chemistry* **73**:1917-1927.

Sato, S., K. Koike, H. Inoue, and O. Ishitani. 2007. “Highly Efficient Supramolecular Photocatalysts for CO_2 Reduction using Visible Light,” *Photochemical & Photobiological Sciences* **6**:454-46.

Somorjai, G. A. 1996. “Modern Surface Science and Surface Technologies: An Introduction,” *Chemical Reviews* **96**:1223-1235.

Stamenkovic, V. R., B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, and N. M. Markovic. 2007. “Improved Oxygen Reduction Activity on $Pt_3Ni(111)$ via Increased Surface Site Availability,” *Science* **315**:493-497.

Sun, L., L. Hammarstrom, B. Akermark, and S. Styring. 2001. “Towards Artificial Photosynthesis: Ruthenium-manganese Chemistry for Energy Production,” *Chemical Society Reviews* **30**, 36-49.

Tilset, M., and V. D. Parker. 1989. “Solution Homolytic Bond Dissociation Energies of Organotransition-metal Hydrides,” *Journal of the American Chemical Society* **111**(17):6711-6717, as modified in *Journal of the American Chemical Society* 1990, **12**(7):2843.

Tseng, I. H., W. C. Chang, and J. C. S. Wu. 2002. “Photoreduction of CO_2 Using Sol-gel-derived Titania and Titania-supported Copper Catalysts,” *Applied Catalysis B, Environmental* **37**(1):37-48.

U.S. Department of Energy (DOE). 2005. *Basic Research Needs for Solar Energy Utilization, Report of the Basic Energy Science Workshop on Solar Energy Utilization,* April 18-21, 2005, Office of Science, U.S. Department of Energy: Washington, D.C.

Wang, D. and R. J. Angelici. 1996. "Metal-hydrogen Bond Dissociation Enthalpies in Series of Complexes of Eight Different Transition Metals," *Journal of the American Chemical Society* **118**:935-942.

Wu, J. C. S., H. M. Lin, and C. L. Lai. 2005. "Photoreduction of CO_2 to Methanol Using Optical-Fiber Photoreactor," *Applied Catalysis A, General* **296**(2):194-200.

Yamamoto, T., D. A. Tryk, A. Fujishima, and H. Ohata. 2002. "Production of Syngas Plus Oxygen from CO_2 in a Gas-Diffusion Electrode-Based Electrolytic Cell," *Electrochimica Acta* **47**:3327-3334.

CROSSCUTTING CHALLENGES

CHARACTERIZATION OF SOLID CATALYSTS WITH ENHANCED SPATIAL, TEMPORAL, AND ENERGY RESOLUTION

THEORY AND COMPUTATION FOR CATALYSIS

CHARACTERIZATION OF SOLID CATALYSTS WITH ENHANCED SPATIAL, TEMPORAL, AND ENERGY RESOLUTION

Summary

Fundamental understanding of catalysts and how they function is the foundation for design and preparation of new and improved catalysts and catalytic energy-conversion processes. Such understanding can be achieved only by breakthroughs in the development of new and improved techniques and facilities for investigation of catalysts in the presence of reacting feedstocks under realistic processing conditions. Breakthrough advances in catalysis for energy needs require incisive characterization of the feedstocks and products of fuel manufacture and complementary characterization of the catalysts needed for these processes. The challenge is magnified by the lack of available information characterizing biomass-derived feedstocks and by the increasing complexity of the available heavy fossil feedstocks (many containing uncountable kinds of molecules, and even solid and solid-like structures that are beyond elucidation by molecular characterization tools). The challenge is further magnified by the intrinsic complexity of catalyst surfaces and the mechanisms of catalytic transformations occurring on them, which take place at high temperatures and often high pressures.

Characterization of catalysts in the presence of reacting mixtures at the temperatures and pressures of practical operation is critical because catalyst structures and the mechanisms of catalytic reactions depend on the reaction environment, often sensitively. Because this statement pertains to all catalysts and feedstocks, the challenge is crosscutting. This challenge implies the need for advanced experimental and theoretical methods and instrument hardware and software far beyond current capabilities—to achieve deeper fundamental understanding, specifically for significantly enhanced temporal, spatial, and energy resolution of catalysts in the presence of complex reacting mixtures under realistic reaction conditions.

Scientific Challenges and Research Approaches

Characterization of catalysts

This section is a summary of the typical instrument resolutions and capabilities that will be required to achieve fundamental, atomic-scale characterization of catalytic materials and reaction mechanisms for energy applications:

1. Temporal resolution: To understand the mechanisms of fast electron transfer in electrochemical and photoelectrochemical conversions, as in carbon dioxide reduction or water oxidation, the temporal resolution must be in the range of picoseconds or better. To determine bond-scission/bond-formation sequences on catalyst surfaces, and for dynamic investigations of catalysts and the species on their surfaces, the resolution needs to be in the range of vibrational motions, typically between picoseconds and nanoseconds. To determine catalytic reaction rates, typically between 1 and 1000 reaction events (turnovers) per surface site per second, the resolution must be in the range of milliseconds to seconds.

2. Spatial resolution: Fundamental understanding of the mechanisms of catalysis requires not only characterization of catalyst surface structures and mechanisms of catalytic reactions, but also direct imaging of the key structures. The structures include nanostructured catalytic species, the sites on their surfaces, the species adsorbed on these sites, and the supports on which the catalyst structures are mounted. Thus, the scale of investigation extends from the macroscopic down to the atomic level.
3. Energy resolution: Characterization of transitions such as electronic or vibrational transitions is essential for molecular-scale understanding of catalysis. An energy resolution of 0.1 eV is often sufficient for measurement of electronic transitions, for example. An energy resolution of 1 meV or better is often required for measurement of vibrational transitions.
4. Measurements in reaction environments: Measurements under catalytic reaction conditions are challenging because the temperatures and pressures are often high; catalyst structures are complex; and multiple phases containing the catalysts, reactants, and products are usually present. Reactants and products exist in gas and/or liquid and/or solid phases as well as at surfaces—and so the key structural information characterizing the catalyst and its surface species must be extracted from the maze of information in such complex mixtures.

The primary physical characterization techniques that have provided essential fundamental information that underlies the technology of catalysis include the following:

- x-ray absorption fine structure (XAFS) spectroscopy to provide information about the atomic oxidation states (near-edge region) and short-range structural information, such as atom-atom coordination numbers of catalytic species
- x-ray diffraction (XRD) crystallography to identify the long-range bulk structures of catalysts and catalyst supports
- x-ray photoelectron spectroscopy (XPS) to determine electronic and compositional properties of catalysts
- inelastic neutron scattering spectroscopy to characterize dynamics, most prominently including transformations of hydrogen-containing species in and on catalysts
- solid-state nuclear magnetic resonance (NMR) spectroscopy and NMR imaging to evaluate compositions and structures of catalysts, supports, and adsorbates
- electron microscopy techniques—scanning electron microscopy, high-resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscopy, all coupled with energy dispersive x-ray fluorescence, to determine catalyst structures, particle sizes, and elemental compositions, and atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to determine catalyst and adsorbate structures on relatively flat surfaces
- ultraviolet/visible/near infrared spectroscopies to determine electronic properties of catalysts
- vibrational spectroscopies, laser Raman and infrared, to identify the structures of oxide catalysts and adsorbates.

Currently, none of these techniques alone comes close to meeting the requirements of temporal, spatial, and energy resolution ranges stated previously. For some relatively simple catalysts and reactions, the goals can be met in part by the concerted application of combinations of these methods. However, the needed advances require breakthrough developments in techniques and instruments and new capabilities for using them in combination.

Breakthrough improvements in catalyst characterization require advances on three fronts:

1. significant enhancements in temporal, spatial, and energy resolution that can be achieved by instrument development
2. a marked increase in the capabilities for applying multiple techniques in concert—with the sample environment being strictly controlled—either simultaneously or sequentially
3. improvement in the design of reactors that are also cells to provide environments mimicking the realistic reaction conditions of temperature, pressure, and reaction media (solid, liquid, and/or gas phase) during the measurements.

Promising techniques and the major associated challenges, as well as examples of the concerted application of multiple techniques, are described in the following pages.

Synchrotron x-ray techniques

XAFS is a workhorse technique in catalyst characterization because of the wealth of local structural information it provides, combined with the photon-in/photon-out nature of the spectroscopy that makes it directly applicable to characterization of functioning catalysts. This method, for example, has been used to investigate the surroundings of promoter ions in supported nanoparticles of molybdenum sulfide used for hydroprocessing reactions to remove sulfur from fossil fuels. This method helps provide understanding of the structure and function of catalytic sites and ultimately the manufacture of improved catalysts.

Excellent opportunities present themselves to make the XAFS technique far more powerful and widely applicable than it is today (see sidebar). The advances demand future developments in synchrotron facilities and the attendant equipment needed for characterization of catalysts in the working state. Indications of what lies ahead are provided by promising early results obtained by using high-energy-resolution fluorescence detection, which enabled measurement of the first selective x-ray absorption spectra of catalysts—such measurements can be site-selective, oxidation state-selective, edge-selective, and spin-selective. The concept is simple—position the detector at an x-ray emission line for a specific state, and only that state is tracked over time. To date, this technique has been used to separate spin states, metal oxidation states, and L_2 from L_3 edge data—these properties of the elements (usually metals) in catalysts are important in determining fine-grained details of how the catalysts function. So far, only a few feasibility experiments have been performed (e.g., differentiating ferrous from ferric ions), none of them characterizing a working catalyst.

The anticipated capabilities in XAFS spectroscopy promise to revolutionize the technique, if significant resources are dedicated to the task: specialized detectors; high-brightness beamlines (as planned at the National Synchrotron Light Source [NSLS]-II); and cells that also serve as catalytic reactors at high pressures and temperatures.

High-energy-resolution fluorescence detection has already been coupled with advanced theoretical calculations to characterize the adsorption sites accommodating simple molecules on supported metal nanoclusters. There is a compelling opportunity to extend the technique to many other catalysts and reactions with the goal of increasing the temporal resolution and measuring the spectra of working catalysts. Today, the time required to measure a typical XAFS spectrum of a catalyst at a U.S. synchrotron ranges from several minutes to about an hour. Researchers at a synchrotron in Japan (the Photon Factory) are now routinely making measurements in seconds and even milliseconds by using energy-dispersive XAFS spectroscopy (see sidebar).

Real-time Characterization of Fuel Cell Cathode Catalysts under Reaction Conditions

To make proton-exchange-membrane fuel cells for automobiles a reality, the activity and lifetime of the Pt/C cathode catalyst must be improved. Towards this goal, a novel time-gating quick XAFS technique with 1-s time resolution and an energy-dispersive XAFS system with 4-ms time resolution was used (Figure 25) to observe in real time the following:

- evidence of the electrochemical reaction mechanism and dynamic surface events involving dissolution of platinum at the Pt/C cathode
- reaction kinetics of the electron transfer processes
- redox structural changes
- a significant time lag among those events under fuel-cell operating conditions.

The results led to the inference of eight elementary steps on the platinum cathode catalysts as well as the population of the bound OH species, which are crucial for the performance of the Pt/C fuel cell catalyst (Tada et al. 2007).

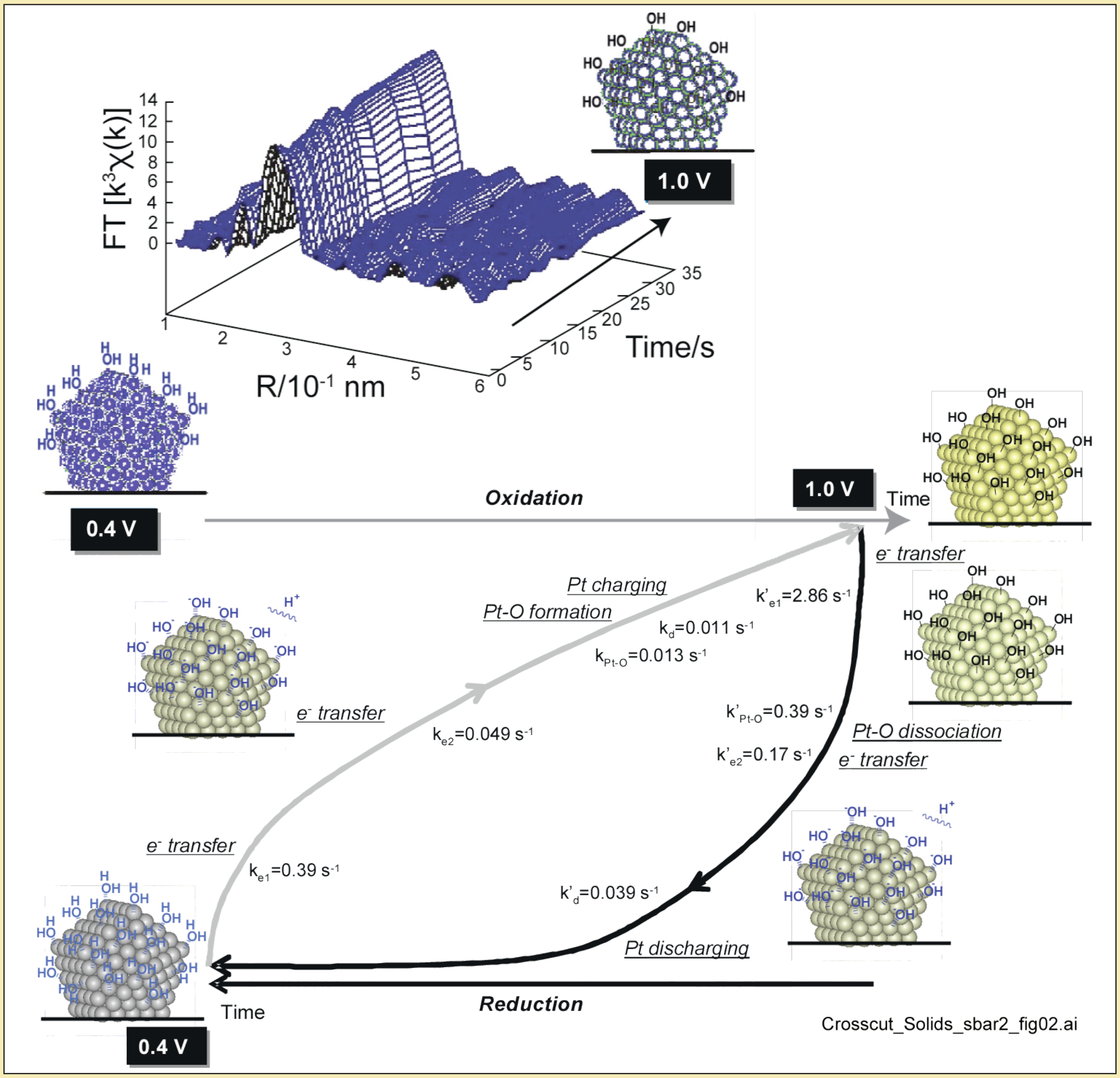


Figure 25: X-ray absorption fine structure measurements of changes at proton-exchange-membrane fuel cell cathode during reaction. From Tada et al. (2007), vol. 46, 4310. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

XAFS spectroscopy has been used for the most part as a spatially averaged technique. With advances in the development of beamlines with capabilities for micro- and nano-focusing, this method could be turned into a microscopic technique. This new capability could be developed by using micro-focused x-ray beams or by using full-field illumination of the sample and a spatially resolving detector. Early results have been reported by use of full-field illumination with a charge-coupled device camera as the detector, allowing mapping of the oxidation-state distribution of the active metal in a working catalyst bed at a resolution of a few microns. The challenge is to improve the spatial resolution to the scale of tens of nanometers—and combine it with increased time resolution.

Many opportunities exist to make much-needed advances in the technique, for example, by coupling XAFS spectroscopy with other techniques (e.g., x-ray diffraction and infrared spectroscopy) at current synchrotrons to bolster the information content of the experiments. The combined use of synchrotron XAFS spectroscopy and XRD is being pursued at the NSLS at Brookhaven National Laboratory. One of the main advantages of these two techniques used in concert is the demonstrated capability to conduct measurements under reaction conditions, in the presence of both gas and liquid phases, with sufficient energy resolution to differentiate materials with contrasting physical and chemical properties. The two techniques provide complementary information about the structures of catalytic materials: XRD is effective for crystalline materials, whereas XAFS spectroscopy provides short-range order structural features in less-ordered (amorphous) catalysts. Moreover, XAFS spectroscopy in the near-edge region (XANES) also gives information about the electronic properties of catalysts. These two methods have been developed and advanced independently of each other at synchrotron sources in the United States and abroad. The combination of the two techniques, with the catalyst sample in a single reaction cell, will allow simultaneous measurements of changes in the physical structures, electronic properties, and catalytic activities of solid catalysts (including electrocatalysts). Similar efforts are at various stages of advancement in European synchrotrons, HASYLAB/DESY (Hamburg) and SRS (Daresbury).

At present, XAFS and XRD measurements can be performed at NSLS-I, but only at separate beamlines, with acquisition times of $10\text{-}10^3$ s for XAFS and $10\text{-}10^2$ s for XRD. A recent example of time-resolve XRD was the determination of the oxygen occupancy in ceria lattice under catalytic water gas shift reaction conditions through Rietveld refinement of XRD data. With improved hardware and software, it will be possible to enhance the temporal resolution of both quick-XRD (3 ms) and quick-XAFS (1 s) during surface-catalyzed (and electrochemical) reactions with simultaneous measurements of catalytic or electrocatalytic rates.

The same experimental combination can also be used to investigate the nucleation and growth of nanostructured catalysts from precursors as a function of time at various temperatures and pressures. Both types of measurements will provide critical information about the synthesis and structure of novel catalytic materials—one of the central themes of this report. Furthermore, by using selective XAFS spectroscopy with high-resolution fluorescence detection, it should be possible to obtain two-dimensional and three-dimensional images of electronic and chemical information representing the catalysts, based on oxidation state-selective, edge-selective, or spin-selective methods with 1 μm or better spatial resolution. With the significant increase in photon flux anticipated in the new NSLS-II facility, it should be possible to improve by a factor of 10 the temporal and spatial resolution. The increased radiation flux will allow investigation of structural changes of catalysts undergoing fast reactions. The additional brightness might even allow for investigation of diffraction from individual nanoparticles in supported catalysts. Furthermore, it is possible to add a vibrational spectroscopy tool (in particular, infrared spectroscopy) to the combined XRD/XAFS, which will further expand the combined XAFS/XRD capabilities and provide insights into the surface chemistry—by allowing researchers to follow the identities and bonding configurations of adsorbates on the catalysts.

A complementary technique is x-ray tomography (XRT), an imaging method of soft x-ray microscopy that allows retrieval of three-dimensional structural information representing the sample in the focal region of the x-ray beam. This technique is used extensively in environmental and biological sciences and is attractive for characterization of working catalysts. Projected capabilities of x-ray nano-tomography will feature 50-nm spatial resolution and allow collection of tomographic data in less than 5 min (the method is limited presently by computational complexity). Such specifications are relevant for many catalysis applications and are especially promising when coupled with XAFS/XRD capabilities for characterization of functioning catalysts. X-ray tomography will allow tracking of the three-dimensional structure and composition of reaction components as a function of time, temperature, or potentiostatic control. For example, by coupling of nanotomography and x-ray fluorescence in the nanoprobe experiments that will potentially be possible at NSLS-II, both the microstructure and element specificity can be investigated in real time. Advanced applications, including holo-tomography, are promising for investigations of three-dimensional distributions of electron density, critical information that may reveal the nature of chemical bonding between catalysts and adsorbates.

Conventional XPS is a well-established technique for the characterization of electronic and compositional properties of catalysts under high vacuum (pressures $<10^{-7}$ Torr). The concept of differential pumping for moderate-pressure XPS was first applied by Siegbahn and colleagues in 1969 for investigation of gases at pressures of up to a few tenths of a Torr. In recent years, the instrumental development of differentially pumped electron-energy analyzers equipped with fast multichannel detectors and with access to a third generation of synchrotron sources has opened exciting new possibilities, such as investigation of chemical transformations on surfaces by using photoemission under conditions that are much closer to realistic reaction environments. With the existing synchrotron facilities, one can typically obtain an x-ray photoelectron spectrum in 10^2-10^3 s. Moderate-pressure (>10 Torr) XPS instruments with submonolayer sensitivity are currently installed at synchrotron facilities in Europe (BESSY, ELETTRA) and the United States (Advanced Light Source). At present, XPS can be used to follow the kinetics of surface reactions, as demonstrated by recent investigations of the active sites and mechanism for methanol synthesis on copper catalysts. With the anticipated increases in the photon flux from future light sources such as NSLS-II, it will be possible to perform XPS with sub-second temporal resolution and high-energy resolution (0.1-0.2 eV), at pressures >10 Torr. This operability will allow measurements under conditions more closely approaching those of practical catalysis. Because of the vacuum requirement for the detection of photoelectrons, however, it will be difficult to increase the pressures to those of almost all practical catalytic reactions.

Although the temporal and spatial resolutions of many of the aforementioned techniques will fall short of those most desirable for catalysis research, they will nonetheless be sufficient for characterization of many catalysts and reactions that do not demand these ultrahigh temporal and spatial resolutions. To best meet the requirements, the challenges in advancement of the synchrotron-based techniques will be to improve the temporal resolution to the picosecond regime and the spatial resolution to the nanometer range while maintaining the capability for measurements under reaction conditions. Achieving these goals will require breakthrough developments in the hardware, software, and theory for data analysis.

Probing samples with neutrons

Although XAFS and XRD are excellent techniques for probing the physical and chemical states of heavy elements, such as the metals in most catalysts, they are not nearly as effective for molecular dynamics or for probing the chemical state of hydrogen. Hydrogen is crucially important in most conversions of fossil fuels (and, potentially, biomass). Hydrogen may be present as hydrogen atoms, protons, and/or hydrides in the catalysts. Because neutrons easily penetrate steel reaction vessels or high-pressure gases or liquids, while still being effectively scattered by hydrogen atoms within, neutron spectroscopies and neutron diffraction uniquely provide information about hydrogen. Specifically, the data allow elucidation of molecular dynamics and weak interactions, even for catalysts working with very complex reaction mixtures at high pressures and temperatures. The techniques have to date barely been used to characterize working catalysts, but they offer compelling prospects because of the importance of hydrogen in so many of the energy conversion reactions mentioned in this report.

For example, all of the following can be probed with neutrons under high-pressure, high-temperature reaction conditions:

- the buildup of carbonaceous deposits during hydrocarbon processing (causing catalyst deactivation)
- molecular transformations on surfaces and in hydrogen-containing molecules, such as those being converted in hydrodesulfurization of sulfur-containing molecules.

A technique based on measurement of losses in inelastic neutron scattering can provide precise information about the energetics of adsorbed H_2 molecules and hydrogen atoms. Such information is critical to understanding how the energy in thermal-excitation or photo-excitation is stored in hydrogen and hydrogen-containing reactants during catalytic reactions. The ability to probe the state and transfer of hydrogen and water, as well as the molecular configurations and motions during electron transfer of water, are important for understanding the electrochemical and photoelectrochemical oxidation of water. Inelastic neutron scattering has also been used to probe the dynamics of methyl groups adsorbed on oxides and the transformation of methanol into dimethyl ether on alumina, which are important for the understanding needed to build larger molecules from methane and light alkanes. These issues are addressed more specifically in several Priority Research Directions in this report.

Neutron Spectroscopy To Study Dynamics of Hydrogen Storage Materials

Hydrogen-bonding interactions are ubiquitous in nature and play an important role in controlling the chemical and physical properties in complex molecules ranging from structures in biological molecules to the supramolecular assemble of molecular crystals. One unusual form of hydrogen bonding arises from the attractive interaction between protonic and hydridic hydrogen. The molecular crystal ammonia borane, NH_3BH_3, (19 mass% hydrogen) has recently drawn significant interest as a potential material for onboard hydrogen storage. This di-hydrogen bonding interaction has been proposed as an important feature in materials that release molecular hydrogen at moderate temperatures that are required for vehicles powered by fuel cells. However, little is understood about the details of these H–H interactions.

Given the large interactions between neutrons and hydrogen, neutron scattering techniques provide insight into some of the basic questions associated with structure and dynamics of hydrogen in condensed phase materials. Single crystal neutron diffraction studies of ammonia borane by Klooster and co-workers (1999) enabled the assignment of not only the positions of hydrogen but also the assignment of the positions of nitrogen and borane given their unique interactions with neutrons. This investigation resolved the ambiguity over the directionality of the hydridic and protic hydrogen-bonding interactions. A combination of experiment and theory provides insight into the structure and dynamics of hydrogen-rich materials. Allis and co-workers (2004) combined periodic DFT calculations with inelastic neutron scattering methods to assign crystal normal modes of ammonia borane at 15 K. The low frequency modes and lattice modes provide key insights into the di-hydrogen bonding interactions.

The spatial representations of the hydrogen derived from the Fourier transform of the experimental neutron scattering intensity mapped onto the refined crystal structure obtained from neutron powder diffraction experiments at a temperature above (a) and below (b) the phase transition are shown in Figure 26. The refined crystal structure includes information about the symmetry, atomic position, occupancy, and the complex structure factors for each atom. In this figure, boron is aqua and nitrogen is blue. For comparison, the hydrogen positions were calculated using only the experimental lattice parameters from neutron powder diffraction for the lowest energy structures using periodic electronic structure combined with dynamics [CP2K, full periodic DFT 2x2x2 unit cell] at the same temperatures above (c) and below (d) the phase transitions. Both experiment and theory show that the orthorhombic to tetragonal phase transition in ammonia borane catalyzes the motion of the hydrogen in the solid state. The hydrogen in the orthorhombic phase (180 K) is highly localized in contrast to the hydrogen in the tetragonal phase (275 K).

It is interesting that the hydrogen is hydrogen is highly delocalized. The neutron powder diffraction experiment cannot even define a position, and theory concurs that the hydrogen is highly mobile even though there is significant di-hydrogen bonding.

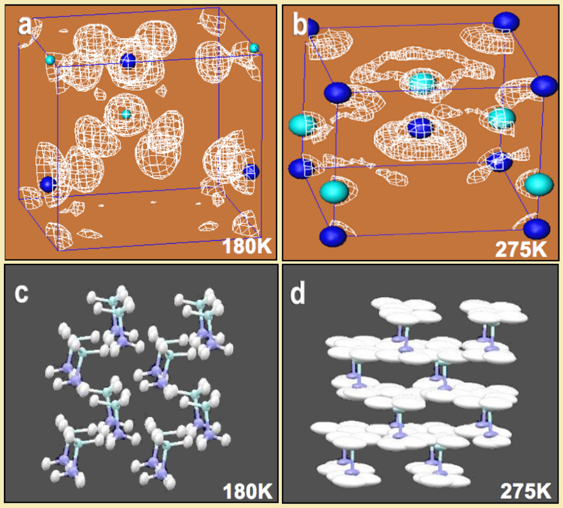


Figure 26: Spatial arrangement of hydrogen in ammonia borane.

Other neutron methods permit the probing of pore structures, nanoparticle size distributions, paramagnetic species, and long- and short-range ordering in catalysts. Neutron spin echo experiments can probe dynamic motions in complex molecules and, for example, have been used to probe long-chain movements in polymer melts.

With the recent completion of the Spallation Neutron Source at Oak Ridge National Laboratory, the United States now leads the world in the production of neutrons for research. This facility and its beamlines provide unique opportunities for catalysis research that are expected to develop strongly throughout the next decade. One of the main hurdles in using neutron techniques for catalysis research is the inefficiency in spatial resolution. This inefficiency can be overcome by combining neutron experiments with synchrotron techniques, provided that the catalysts and reactions are suitable for both types of characterization.

Solid-state NMR spectroscopy and imaging

Solid-state NMR spectroscopy is uniquely suited to the characterization of catalysts and adsorbed species, especially in crystallographically disordered samples typified by supported catalysts. Recent developments in methodology, theory, and instrumentation (especially magnets and probes) have resulted in remarkable new capabilities: It is now possible to identify sites, structures, and multidimensional intersite correlations with unprecedented sensitivity and resolution, and to probe a wide range of dynamic processes in liquid and solid phases. Similarly, an arsenal of sophisticated liquid-state and solid-state NMR methods has been developed in the preceding few years for extraction of structural information from biological samples, including proteins. These recent advances will make it possible to investigate various classes of catalysts, including those inspired by biology, and to characterize new types of feedstocks, such as fossil and biomass-derived materials, as described in Priority Research Directions. The structures of these complex systems can be further refined by combining the experimental NMR results (e.g., chemical shifts, internuclear correlations, bond lengths) with state-of-the-art theoretical computations. Although this emerging area of spectroscopy is often being referred to as “NMR crystallography,” it can be applied to describe three-dimensional structures involved in non-periodic catalytic structures. Many of the catalysts and reactions for energy applications will involve multiple phases with complex dynamics and interphase regions, as described in the Grand Challenges. NMR spectroscopy and imaging are well suited to probe liquid-solid and solid-gas interfaces at length scales ranging between 0.1 and tens of nanometers. Furthermore, NMR imaging can be applied to characterize the morphologies and reactivities of catalysts, as well as to understand the transport of reactants and products in catalyst pores. By closely coupling NMR analysis with synthetic efforts and reaction experiments, it will be possible to obtain fundamental correlations of catalytic performance with the influence of chemical compositions and structures of catalysts. The anticipated developments of new NMR methodologies and computational tools will offer means for more incisive and rapid characterization of catalysts. The main challenges of the NMR techniques will be the availability of magnets operating at very high fields (≥ 18.8T) and specialized probes capable of ultrafast magic angle spinning (at rates exceeding 3 million rpm), as well as the development of better NMR capabilities for characterizing functioning catalysts at high resolutions.

Imaging techniques

Several imaging techniques, including HRTEM, AFM, and STM, offer superior atomic-scale spatial resolution. HRTEM is one of the most widely used techniques for the structural characterization of supported catalysts. With recent advances, HRTEM measurements can routinely provide atomic-scale information. In particular, in many cases it is possible to obtain information about the structural, electronic, and compositional properties of individual catalyst nanoparticles. This goal can be achieved by measuring the diffraction to determine the lattice spacing, electron energy loss spectra (comparable to XAFS) to determine the electronic properties, and energy dispersive spectroscopy to determine elemental compositions of the individual particles. Significant progress has been made in designing reaction cells (the technique is termed environmental HRTEM) to image catalysts under conditions more nearly relevant to catalytic reactions. Because of the availability of state-of-the-art HRTEM facilities in many academic institutions and national laboratories, HRTEM will remain the most commonly used technique for characterization of the structural properties of supported catalysts. Recent experimental and theoretical work has indicated that catalyst particles commonly undergo dynamic changes under reaction conditions. *Therefore, the main challenges of the HRTEM technique for catalyst characterization will be to improve the temporal resolution and to design cells that can handle pressures and temperatures more relevant to realistic catalytic conditions.*

The AFM and STM techniques have provided revolutionary, atomic-scale images of well-defined surfaces and adsorbates on them. Both techniques can be used under reaction conditions, with AFM being more often used for liquid-solid interfaces and STM for gas-solid interfaces. STM investigations of surfaces in reacting environments have provided direct images of the dynamic changes of the surface structures. The AFM and STM techniques will continue to provide direct information regarding surface structures and dynamics on model surfaces. As for HRTEM, the main challenges of AFM and STM for catalyst characterization will be to improve the temporal resolution.

Raman spectroscopy

Raman spectroscopy is one of the most powerful techniques for characterization of solids and surfaces of technological importance. It is one of the few instrumental methods that in a single measurement can provide information about both solid catalysts and the molecules reacting on them. The energy (~1 cm^{-1}) and temporal (~1 ps) resolutions of Raman spectroscopy are limited only by laser technology. Its wide spectral range (50-5000 cm^{-1}) enables examination of the nature of molecular species, identification of crystalline solid phases, and determination of the structures of non-crystalline surface phases. Raman intensity can be increased dramatically when the wavelength of the exciting laser is in resonance with an electronic absorption of the sample; the process is referred to as resonance Raman spectroscopy. Enhancements in the cross section for Raman spectroscopy as large as 10^8-fold have been reported. Resonance Raman spectra typically exhibit patterns of peak intensities that vary with excitation wavelength and differ significantly from the patterns observed in normal Raman spectra. In a sample containing a mixture of compounds, individual species may be resonance enhanced at different wavelengths. In some cases, it may be possible to measure resonance Raman spectra of individual components in a mixture by selective excitation of specific absorption bands. Moreover, the assignment of resonance-enhanced vibrations provides detailed information about the local symmetry of the species. Resonance Raman spectroscopy has been used widely to characterize biological samples in which electronic transitions occur at visible excitation wavelengths, and commercial continuous wave lasers are readily available.

Resonance Raman spectroscopic characterization of solid catalysts and adsorbed species, however, has been limited. Many catalytic materials are white, but their electronic transitions often occur at ultraviolet wavelengths. Thus, the measurement of resonance Raman spectra of selected catalytic or molecular species becomes possible with ultraviolet excitation at several wavelengths. *A general challenge in the application of the Raman technique is to improve significantly the spatial resolution in characterization of supported catalysts.*

Characterization of Complex Feedstocks and Products of Their Conversion

The utilization of alternative feedstocks, such as fossil- (coal, shale, and tar sands) and biomass-derived materials, requires determination of new reaction pathways and new processes. In turn, these new pathways and processes require a quantitative understanding of the molecular types and structures of these feedstocks and their conversion products, as described in the Priority Research Directions. Fundamental understanding of structure-catalytic activity relationships, which is critical for the understanding and control of catalysis with alternative feedstocks, requires such knowledge.

The analytical techniques currently used to characterize petroleum, even the heaviest fractions (e.g., vacuum residua), especially high-resolution mass spectrometry and gas chromatography combined with mass spectrometry, are limited in availability and underused for characterization of complex fossil fuels. They need to be developed and made widely accessible and applied to establish a foundation of analytical results characterizing the complex mixtures in fossil- and biomass-derived feedstocks.

Several standard instrumental methods are currently used to characterize the structural properties of biomass-derived materials. These methods include infrared and Raman spectroscopy, coupled with multivariate analysis to monitor the nature of the chemical bonds; fluorescence spectroscopy to track lignin content; and XRD to measure cellulose crystallinity. Infrared and Raman vibrational spectroscopies with multivariate analysis can provide quantitative analysis of lignocellulosic biomass, including cellulose structure, lignin content, hemicellulose content, and polysaccharide identification without the use of tags or dyes. Carbohydrates and lignin give both infrared adsorption and Raman spectra. Infrared spectra provide information about the various types of polysaccharides present in complex mixtures. The spectra include main band maxima that are distinctive to the type of polysaccharide present, and they include features that depend on the axial and equatorial positions of the OH groups. However, care must be taken as infrared spectra are also sensitive to changes in the conformations of polysaccharides.

Polarized infrared spectra are sensitive to bond orientation and, therefore, can be used to distinguish hydrogen-bonding patterns in the various types of cellulose. Visible and near-infrared Raman spectroscopy can also be used to investigate changes in polysaccharides, if measures are taken to reduce fluorescence arising from lignin. Solid-state NMR spectroscopy, used in cross polarization-magic angle spinning mode, is sensitive to variations in polysaccharide conformations, but is not sensitive enough to detect the relatively rare covalent crosslinks believed to hold the cell wall together. NMR relaxation experiments can reveal the relative mobilities of various components in a complex mixture, as well as the relative mobilities of main chains and side-chain groups. Drying of samples, typically required for techniques such as electron microscopy and mercury porosimetry, may collapse biomass pores and/or cause aggregation of the microfibrils that may impart artificial variation in the observed microfibril sizes. To eliminate this effect, high-pressure cryo-TEM, AFM, and hyperspectral confocal imaging can be used to image biomass with minimal feature damage. Neutron and x-ray scattering and diffraction techniques may offer new insight into the static and dynamic structural components of biomass. In principle, similar combinations of multiple analytical techniques can be adopted and modified to characterize the molecular structures in fossil feedstocks and the corresponding reaction products. *A concerted effort is needed to provide a basis of information from these complementary techniques.*

Work is also needed to determine fundamental thermodynamic properties of biomass-derived compounds, based on appropriate experimental and theoretical methods. This point is not developed here as it goes beyond the intended scope of the report; however, it is emphasized that progress towards the new catalytic processes anticipated here cannot be made without knowledge of the thermodynamic properties of biomass-derived compounds.

Conclusions

Combining modern synthetic strategies with advanced characterization techniques and theory is essential for understanding the dynamics and reaction mechanisms of catalytic processes at the molecular level. The anticipated new types of catalysts and catalytic processes described in the current report will pose new challenges for the characterization of both catalysts and feedstocks. Ideally, the new characterization techniques should have the following characteristics: temporal resolution in the picosecond range or faster, spatial resolution in the nanometer regime or better, energy resolution of 1 meV or better, and opportunities for measurements under realistic catalytic reaction conditions. Achieving these goals will require breakthrough developments in new and existing techniques and much improved methodologies for combining multiple complementary techniques.

References

Allis, D. G., M. E. Kosmowski, and B. S. Hudson. 2004. "The Inelastic Neutron Scattering Spectrum of $H_3B{:}NH_3$ and the Reproduction of Its Solid-state Features by Periodic DFT," J*ournal of the American Chemical Society* **126**(25):7756-7757.

Klooster, T., T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson, and R. H. Crabtree. 1999. "Study of the N–H···H–B Dihydrogen Bond Including the Crystal Structure of BH_3NH_3 by Neutron Diffraction," *Journal of the American Chemical Society* **121**(27):6337-6343.

Tada, M., S. Murata, T. Asaoka, K. Hiroshima, K. Okumura, H. Tanida, T. Uruga, H. Nakanishi, S. Matsumoto, Y. Inada, M. Nomura, and Y. Iwasawa. 2007. "In Situ Time-Resolved Dynamic Surface Events on the Pt/C Cathode in a Fuel Cell under Operando Conditions," *Angewandte Chemie International Edition* **46**:4310-4315.

THEORY AND COMPUTATION FOR CATALYSIS

Summary

An ultimate goal of catalysis research is to control chemical reactions—the making and breaking of chemical bonds—so that we can synthesize any molecule or material. Catalysts control chemical change by enabling reactions to be guided quickly and efficiently along desirable pathways rather than those that are inefficient or lead to unwanted byproducts. As with many catalytic processes, it is still unclear just how the catalyst works, and understanding the mechanisms and dynamics of catalyzed transformations has been identified as a grand challenge for catalysis. Molecular-level understanding is essential to "tune" a catalyst to have the desired effect of producing the right product with minimal energy consumption and minimal environmental impact. Computational methods, derived from advanced theoretical models and implemented in efficient algorithms on advanced computer architectures, are crucial to the fundamental understanding of catalytic processes and ultimately to first-principles catalyst design. Ab-initio catalyst design will require quantitative information about the reaction pathways, especially the nature of transition states. This information includes kinetics parameters for critical reaction processes and an understanding of the influence of the reaction environment.

Theory and computation are essential to advancing the goals of all of the priority research directions stated in this report. As discussed in the panel reports, catalytic conversions of fossil energy and biologically derived feedstocks, and conversions of water and carbon dioxide by photo- or electro-catalysis provide an extremely rich set of high-level challenges for theory and computation. Both fossil feedstocks and biologically derived feedstocks include large, multifunctional molecules (which are often liquids and solids), such as polycyclic aromatics or carbohydrates. The size and conformational complexity of these molecules present challenges for electronic structure and dynamical calculations because of the size of the system and the large number of different conformers. Conversions of water and carbon dioxide take place via photo-chemical processes involving electronically excited states and electrochemical processes involving transport of electrons, holes, and protons. These processes also present a major challenge for theory and computation because of the need to treat electronically excited states and their dynamics in complex, interfacial, and molecular systems at the quantum level. Furthermore, catalysts work in complex environments with many possible sites and different phases, which can change over time and influence reactivity at multiple length and time scales. Modeling catalytic processes under operating conditions provides additional complexity that will have to be met in the future.

The goal of developing a fundamental understanding of how catalysts function as a basis for the design of improved catalysts can be met only by breakthroughs in the development of new and improved theoretical and computational methods. These methods would be capable of treating the complexity of the molecular reactants and condensed-phase and interfacial catalysts inherent in the conversion of new energy feedstocks to useful products. The combination of computation with advanced experimental techniques is leading to broad new insights into catalyst behavior and the design of new materials. However, it is extremely difficult to obtain all of the necessary details of reaction pathways from current experimental techniques, especially for transition state regions that are visited for extremely short times. New developments in high-intensity photon sources with femtosecond temporal resolution hold the promise of experimental investigations of the transition state region that in combination with computational investigations of reaction

surfaces promise to unravel details of the complex chemical processes that occur under catalytic conditions. The development of new theories and computational tools that accurately predict thermodynamic properties, dynamical behavior, and coupled kinetics of complex condensed-phase and interfacial processes is a crosscutting priority research direction needed to address the grand challenges of catalysis science, especially in the area of advanced energy technologies. Understanding of the fundamentals of reaction mechanisms and design and synthesis of new catalysts require computational approaches and tools that can do the following:

- Create simplified models of the operating catalyst that account for the essential elements of complex, multicomponent catalytic materials and feedstocks to accurately predict thermodynamic and kinetic properties.
- Enable calculations of accurate energetics for large, multifunctional reactant molecules interacting with complex catalysts.
- Identify the critical regions of the potential energy surfaces of working catalysts, which control the catalytic processes.
- Sample ensembles sufficiently to map out the free-energy landscapes that determine thermodynamic properties and kinetics (i.e., address the issues of complexity and entropy).
- Unravel the effects of the local reaction environment on intrinsic potential energy surfaces.
- Enable the treatment of electronically non-adiabatic processes in complex, multiphase systems.
- Couple temporal and spatial scales, ranging from those relevant at the molecular scale to those in macroscopic systems.

Scientific Challenges and Research Approaches

Advances in theoretical methods, computational software tools, and computer hardware have positioned theory and computation to be essential tools for understanding known catalytic processes and designing new ones. Although the advancement of theoretical and computational methods is rapid and impressive (Kohn 1999; Pople 1999), these methods are still insufficient for the challenges of designing new and more efficient catalysts to meet the needs of future advanced energy technologies. The complexity of the molecular reactants and condensed-phase and interfacial catalysts inherent in new feedstock conversion requires breakthrough developments of new and improved theoretical methods implemented in usable and highly efficient algorithms. What follows in this section is a brief summary of recent advances and future challenges for the application of theoretical and computational methods to catalysis research for energy applications.

Advances in the fundamental understanding of catalytic reaction mechanisms to allow design of new catalysts having unprecedented activities and selectivities require close coupling of theory and computation with experiment. This coupling benefits from recent advances in experimentation, such as methods for synthesis of nanoscale catalysts, probes of interfaces at the atomic scale, instrumentation that allows precise observation of ultrafast processes, and techniques to probe complex processes under catalyst operating conditions (Gai 1999). Furthermore, recent advances in experimentation present new challenges and opportunities for theory and computation. For example, the interpretation of infrared, nuclear magnetic resonance (NMR), and extended x-ray absorption fine structure spectra in studies of acetylene cyclotrimerization by a single-site zeolite-supported rhodium complex were substantially aided by calculations of the vibrational frequencies, structures, and NMR chemical shifts. The calculations were able to map out the energetics on the potential energy surface to identify the transition states and identify a possible mechanism (Kletnieks et al. 2007). Theoretical and computational tools are also essential for interpretation of experimental observations, guidance in the design of experiments, and selection of catalytic materials for experimental investigations. Experiments play an essential complementary role in providing tests of the computational predictions and new data to be explained and interpreted by new rounds of computations. The synergistic feedback loops lead inexorably to the development of new theoretical/computational methods, new experimental methods, new insights into complex processes and catalytic behavior, and ultimately to the design of more effective catalysts.

Defining molecular models of reactants and catalysts

Catalysts, particularly heterogeneous materials that are typically solids, have essential structural components that can be sufficiently large or so complex in terms of the number of sites that calculations are not currently possible for the full system of interest. Hence, smaller (simplified) models must be used in the calculations. Computational investigations of catalytic reaction energetics and kinetics begin with a definition of the part of the reacting system that must be treated explicitly (and its structure) to develop a simplified molecular model. For example, for the complex, multifunctional reactants in energy feedstocks, one might include only the part of the molecule where the reaction occurs, and substitute hydrogen atoms for fragments of the molecule and/or solid that are omitted. Moreover, one might simplify the treatment of a zeolite catalyst by using a suitably terminated nanoscale fragment of the zeolite as a model of the larger crystal, or represent the surface of a metal catalyst particle as a periodic metal surface, or $P(C_6H_5)_3$ group in a catalyst with a PH_3 group.

At present, insight into the structures of catalysts as they react typically comes from a combination of experimental observations, and calculations are instrumental in the interpretation of results. In a number of examples, calculations are used in refining these structures. For example, calculations can be used to determine orientations of ligands around metal centers and to predict properties such as cone angles and binding energies that can be used to interpret experimental results for complex reactions such as carbon-carbon coupling reactions (Moore et al. 2007). There is little information about structures of energy feedstocks in catalytic processes to guide the development of models for these systems. Significant effort is needed, both experimentally and computationally, to build up our knowledge base on the structures of complex energy feedstocks, particularly under reaction conditions.

A critical issue often not addressed because of size limitations is that the calculated properties of interest (e.g., barrier heights for reactions) need to be converged with respect to the size of the model, which includes the reactant molecule, catalyst, and any solvent present as well as to the computational method itself. It is essential that the model include the parts of the local environment that control access to the catalytic site and significantly influence reaction energetics. It is also important to predict the reaction rate and the role of access of reactant molecules to the active site and changes to the active site that occur under catalytic reaction conditions. At this time, we do not know how large multifunctional molecules, that are present in energy feedstocks, interact with active sites, what parts of the reactant molecule are converted, and what parts of the molecule are reoriented in the catalytic process.

With regard to reactions on surfaces, the environment should include the effects of the extended bulk solid, which affects interfacial interaction energies, and co-adsorbed molecules, which can interact with reactants and lead to surface coverage effects on reaction kinetics, including inhibition of catalysis. Periodic boundary conditions (PBCs) for an extended system can be used to imitate but not duplicate size effects in solids, particularly when many sites require the use of large unit cells or when the surface is highly irregular. Solvents do not have a long-range order and therefore require a much larger unit cell for applying PBCs. Solvent rearrangement is a dynamic process that is extremely important in the prediction of reaction rates, yet it is extremely difficult to model quantitatively. The creation of capabilities for modeling the liquid/solid interface will be important for heavy fossil fuel conversion and for biomass processing (which is often performed in aqueous solution). The ability to predict reactions in aqueous solution will have an impact on a range of catalytic processes that use water (in contrast to organic solvents) as a benign solvent.

The challenge of creating simplified models of operating catalysts that allow accurate prediction of reaction energetics and dynamics is becoming less daunting with the advent of larger computer systems that enable the representation of larger models. However, we are far short of meeting the challenges for the complex feedstocks of the future, and the proper choice of the model will always be important.

Accurate prediction of potential energy surfaces

Advances in ab-initio electronic structure methods have made them the standard tool used for obtaining the energetic information needed in calculations of stable structures and reaction pathways. Errors of the order of only 6 kJ/mol in a barrier height can lead to errors in the rate constant of a factor of 10 at 25 °C—hence, the need for highly accurate computational results. Currently, it is extremely difficult to calculate the energetics to the level of accuracy required for truly predictive catalyst design. Furthermore, reliable electronic structure calculations for the complex, multiphase reactant-catalyst combinations important in future energy applications present a major challenge.

Density functional theory (DFT) (Kohn and Sham 1965) is currently the most commonly used computational method for calculations of catalytic processes, but the available DFT methods are not sufficiently accurate for the reliable prediction of barrier heights in general, especially for radical reactions. The accurate prediction of reaction energetics requires high-level treatments of electron correlation, which today usually require wavefunction-based methods. However, for the most accurate methods, such as the "gold-standard"—coupled cluster with single and double excitation and perturbative treatment of triple excitations CCSD(T) (Bartlett and Musial 2007)—the computational costs scales as the system size to a power that is formally 7, thereby significantly limiting the model size that can be treated to only tens of atoms. Furthermore, a substantial amount of work has shown that modest size basis sets without diffuse functions are, in general, inadequate for the prediction of transition state energies. DFT scales formally (depending on the form of the exchange-correlation functional) as the system size to a power of 3 or 4 and, therefore, offers a compromise between accuracy and computational cost as the system increases in size—because it includes only approximate treatment of the exchange and correlation energies.

Historical Perspective on Electronic Structure Methods

From the beginning of the age of computational science (roughly, the 1960s), advances in hardware and software have occurred hand-in-hand. In the early days, it was impossible to do ab-initio electronic structure calculations, partly because the available computers were so primitive (memory was measured in kilobytes, disks in megabytes, a single processor in a computer filled a room) and partly because the algorithms were equally primitive. The computers drove innovation in software development, and novel new algorithms caused chemists, especially quantum chemists, to demand better hardware so they could study more complex chemical systems. Critical innovations included the switch from exponential to Gaussian basis sets, the development of systematic methods to generate Gaussian basis sets (Dunning 1989), the innovative design of robust many-body methods including most notably coupled cluster theory (Bartlett and Musial 2007), the introduction and adaptation of DFT (Kohn and Sham 1965), and the development of efficient approaches for computing multi-reference and Full CI (essentially exact) wavefunctions. Figure 27 shows how more and more accurate treatment of electron correlation and basis set size contribute to the convergence of electronic structure calculations.

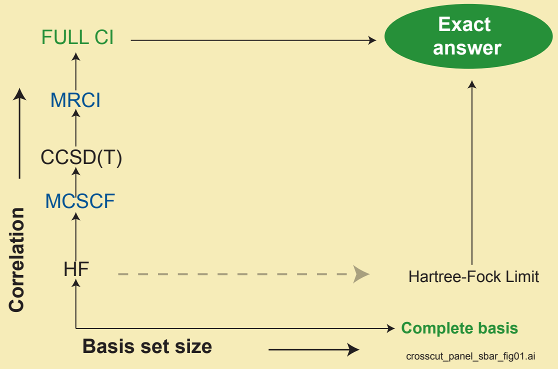


Figure 27: Schematic diagram, first popularized by J. A. Pople in 1964, depicting convergence of electronic structure calculations with respect to both basis set size and treatment of electron correlation.

Many of the methods mentioned are so demanding of computational resources (memory and disk, as well as time), that they have traditionally been limited to model systems that are merely "representative" of the actual chemical system of interest. This simplification has limited direct computational-experimental comparisons. Consequently, major new advances have occurred recently in the design of reduced scaling (from N^{5-7} to N^{2-3}) and highly scalable methods. Methods based on fragmenting large molecular systems (such as enzymes and polymers) into essentially independent fragments (Deev and Collins 2005; Hirata et al. 2005; Komeiji et al. 2003) have enabled high-level computations on molecules of importance to biology and materials science. It is now feasible to combine high-level electronic structure methods such as coupled cluster approaches in quantum mechanical electronic structure theory (QM) with empirical or molecular mechanics (MM) approaches with appropriate statistical sampling to obtain potentials of mean force with accurate energetics. These types of approaches are essential to investigations of catalytic reactions. It is now possible to use these combined approaches to study homogeneous catalysis and, along with extension to interfacial systems, they hold the promise of becoming routine tools for both homogeneous and heterogeneous catalysis. The fragment and QM approaches are essential to studies of the large molecular reactants important in future energy feedstocks and will allow high-level electronic structure calculations for the bond-breaking and -making processes in these complex systems.

Although DFT is currently the method of choice for many catalysis applications, it has a number of deficiencies that limit its reliability:

- There is no general prescriptive way for improving the form of the exchange-correlation functional as there is in molecular orbital theory for addressing the correlation energy problem.
- Although DFT is currently the most efficient way to include correlation effects in periodic calculations of solid surfaces and works quite well for metallic systems, it often does not work as well for metal oxides. Substantial improvements are needed, especially for treating properties such as the convergence of the bandgap from the cluster to the bulk. A critical issue is that functionals can behave differently for different transition metals, for example, in the technologically important metal oxides, and there is no current general method to treat all metals on an equal footing with DFT (Li and Dixon 2007).
- The treatment of weak interactions, such as hydrogen bonds and van der Waals interactions, is not formally correct with current DFT functionals.

The requirements of calculating energetics for both extended (periodic) solids and molecules (including reaction energetics and weak interactions) within the same calculation present a major challenge. The development of a computationally efficient electronic-structure approach that balances these two aspects is needed. One approach to be considered is quantum Monte Carlo, which has some potential computational advantages but currently has many limitations and requires substantial work (Hammond et al.1994).

Advances in multi-level methods, which (1) incorporate more than one level of electronic structure theory into a single computation, such as Our Own N-layered Integrated Molecular Orbital and Molecular Mechanics (ONIOM) method (Maseras and Morokuma 1995; Morokuma 2002; Svensson et al. 1996), or which (2) interface QM and MM potentials, provide an attractive approach to computing reaction energetics for complex systems (Bash et al. 1987; Gao 1996). The combined QM and MM (QM/MM) approach has been used extensively to investigate enzymatic reactions and can be put to use for the complex molecular systems in biomass and fossil feedstocks. For example, reactions occurring in a sugar unit of cellulose can be treated at a relatively high level of theory, with fragments of the cellulose adjacent to the reaction site treated at a lower level of theory, and the remainder of the cellulose molecule and the solvent treated with a MM potential. The ONIOM method has been used extensively in the prediction of homogeneous catalyst activity. A future challenge in this area is to interface layered and QM/MM approaches to similar treatments of interfacial catalysts and reactions.

Nanoscale catalysts have the complexity of intermediate size, containing from hundreds to millions of atoms. It is not clear whether multi-level methods will be appropriate for these types of systems, particularly for metal nanoparticles, for which the delocalized nature of the electrons will require a uniform treatment of the electronic structure. It is a challenge to understand the electronic structures of these catalysts in their working environments, including the effects of the support, the reactants, and other adsorbed species, as well as the effects of size and morphology of the nanostructures on the reaction energetics. Even the evolution of the electronic structure of these materials from small cluster to nanoscale particles to bulk material is not well understood, and available electronic structure methods (Frauenheim et al. 2000, 2002) do not offer the accuracy that may be needed for the treatment of larger nanoclusters.

Design of an Industrial Catalyst

Computational chemistry has aided in the design of an industrial catalyst for the liquid-phase synthesis of the refrigerant HFC-134a, CF_3CH_2F. HFC-134a is a replacement for the chlorofluorocarbons that were important in a wide range of applications involving refrigeration for the food supply and air conditioning but which raised serious environmental issues in terms of stratospheric ozone depletion. Computational chemistry based on molecular orbital theory methods, notably MP2, had already been used to provide critical thermodynamics and kinetics data for the successful design of a chemical plant for the high-temperature production of HFC-134a starting from chlorofluorocarbons, and involving gas-phase reactants. The complexity of the potential routes, all of which could involve a catalyst is shown in Figure 28. DuPont engineers also were interested in the development of a process with liquid-phase reactants for the production of HFC-134a as an alternative. Experimental measurements have shown the transfer of a fluoride anion from a transition metal fluoride to be a critical step. The fluoride anion was being transferred from transition metal fluorides which were acting as the catalytic species. At the time of the research, there was no generally available fluoride affinity scale to predict how to change the metals to better control the reaction. The fluoride affinity is defined as the negative of the enthalpy of the reaction $A + F^- \rightarrow AF^-$ and provides a measure of the Lewis acidity of the species. Molecular orbital theory at the level of MP2 was used in conjunction with effective core potentials and appropriate basis sets to calculate the fluoride affinities of a wide range of metal fluorides as well as other main group and organic compounds relative to a standard with a fluoride affinity that was available from experiment, backed up by calculations. The development of this scale required access to the most powerful supercomputers of the time, the Cray YMP and C90. For the transition metal complexes, monomers and dimers were used as models of the heterogeneous species thought to be important in the process. The calculations showed that the mixed transition metal Ta/Nb fluoride was in the right region of Lewis acidity and that the catalyst could be tuned by using a mixed metal cluster. Doping with other strong Lewis acid atoms such as antimony or bismuth led to proposed catalysts with Lewis acidities that were too strong. A mixed Ta/Nb fluoride catalyst was synthesized and led to the development of the only liquid-phase process for converting chlorofluorocarbons to HFC-134a. As this solid catalyst operates in the presence of liquid, there was a solubility issue that could not then be addressed computationally. The solubility issue highlights the need to understand all of the fundamental steps in a catalytic process and illustrates the need to continue the development of new theoretical and computational approaches to address the complex behavior of catalysts operating in real environments.

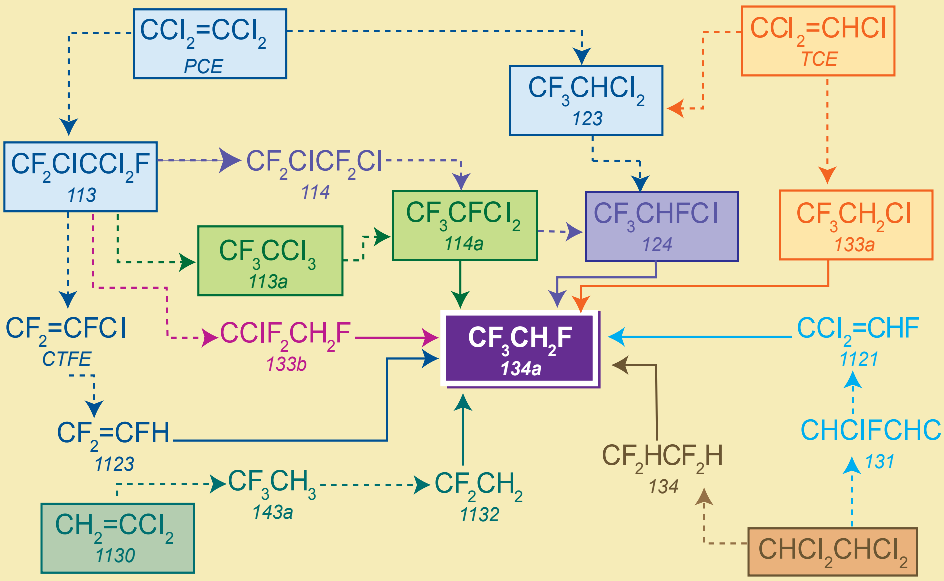


Figure 28: Potential routes to HFC-134a.

Characterizing potential energy surfaces—understanding the structures of working catalysts

The complexity of catalysts and reactants in fossil and biomass feedstocks presents daunting challenges for locating reactant and product structures, and even more so for saddle points, intermediates, and reaction pathways. There are still substantial needs for determining the transition states in complex reactions, an extremely difficult process, as well as finding global minima. The development of tools that can capture current knowledge from experiment, theory, and chemical knowledge and use them to constrain the transition state searching process, for example, will enable substantially improved search algorithms and minimize the time spent on searching inappropriate regions of phase space. The problem of identifying saddle points on reaction pathways is much more difficult when the product states are not identified. Rare-event discovery tools, such as accelerated dynamics methods (Uberuaga et al. 2005), could provide approaches to locating saddle points in these cases. They are computationally intensive and have been applied only to relatively simple problems, and have not been applied to catalytic processes in general, much less the complex molecules of interest here.

Nanostructured and/or multifunctional catalysts cannot be treated as static structures; they respond dynamically to their environments. Large bio- or fossil-fuel molecules introduce more challenges than small molecules, because of the many possible stable conformations, especially on surfaces of solid catalysts, complicating the exploration of potential energy surfaces. Furthermore, relatively weak hydrogen bonding and van der Waals interactions become increasingly important with the increasing size of reactant molecules. Multifunctional catalysis presents further computational challenges because coupling of the functional sites affects their mutual function.

Simulation has already demonstrated its ability to partner with experiment to establish the structures of supported catalysts under working conditions. For example, supported gold in nanoparticle form exhibits remarkable activity for catalytic oxidations, but the exact oxidation states of gold in these particles under reaction conditions has been difficult to pin down. A recent partnering of DFT simulations with scanning transmission microcopy experiments (Matthey et al. 2007) demonstrated that these particles exist in an oxidized form that involves oxygen shared between the gold particle and support (Figure 29). These results help to explain the large effect of the support on the activity of the gold.

Accurate prediction of entropies and free energies

Thermodynamics and kinetics of catalytic processes are determined by free energies, including free energies of reaction for equilibrium constants and activation free energies for rate constants. Although the electronic energy is an important component in these quantities, accurate calculations of entropies are also needed, which require adequate sampling of the accessible configuration space. Reactions on surfaces involve contributions from many possible configurations of active sites and intermediates that must be sampled in any model. Catalytic reactions for biomass and fossil feedstocks involve large molecules that have many stable conformations and present formidable challenges for simulation methods, especially if solvent effects have to be included. Although there have been many advances in statistical mechanical approaches for the calculation of equilibrium properties, such as free energies of stable structures—and free-energy landscapes, also known as potentials of mean force for reaction pathways—future applications of these approaches require new advances. For example, some potentially important catalytic conversions of biomass occur in liquids, such as aqueous solutions or ionic liquids, and require treatment of the liquid-phase environment in addition to the large molecular reactants. Aqueous processing of biomass with solid catalysts will require statistical sampling of even more complex environments.

Simulation already offers some notable successes in capturing the statistical mechanics of catalytic reactions at surfaces. One example is the reaction of carbon monoxide and oxygen to carbon dioxide on the surface of ruthenium dioxide. The coverage of this surface by reactant molecules is a function of the relative concentrations of reactant gases and their relative interactions with the surface. Electronic structure methods can predict the interactions of individual adsorbates with the surface, but statistical thermodynamics is the link to actual surface coverages and reactant arrangements (Reuter and Scheffler 2003). This static picture is translated into a dynamic one again by marrying electronic structure calculations of elementary step rates with a statistical, kinetic Monte Carlo method, with sampling over all possible surface arrangements (Reuter et al. 2004).

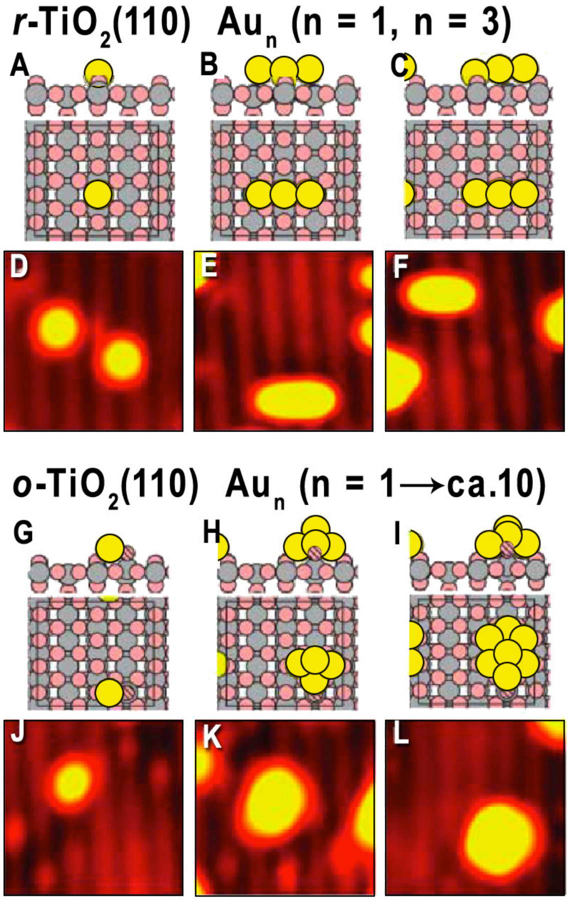


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Figure 29: Oxidation states of gold nanoparticles. (Top) Most favorable structures found in DFT calculations for Au_1 trapped in an O_{br} vacancy (A), Au_3 symmetrically attached on a bridging oxygen vacancy (B), and nonsymmetrically attached Au_3 (C) on a clean, reduced TiO_2(110) surface. (D to F) Zoom-in scanning transmission microscopy images (40 x 40 $Å^2$) showing Au_n clusters that are ascribed to the calculated Au_n cluster configurations. (Bottom) Most favorable structures found in DFT calculations for Au_1 (G), Au_4 (H), and Au_7 (I) on an oxidized TiO_2(110). (J to L) Zoom-in scanning transmission microscopy images (40 x 40 $Å^2$) of Au_n clusters attached in the vicinity of oxygen atoms that are tentatively assigned to the calculated Au_n cluster configurations. From Matthey et al. (2007). Reprinted with permission from AAAS.

This example involves a well-ordered surface and a simple reaction. More complex materials and reactants place greater demands on the representation and calculation of the configuration energies, because convergence of the ensemble averages that determine free energies typically requires at least millions of evaluations of the interaction potential. The demands of statistical averaging over environmental variables currently limit these types of calculations primarily to analytical potential functions, such as lattice models or empirical or MM potentials. However, neither is adequate for describing the bond breaking and making that is important in catalysis, and electronic structure methods are required. Combined QM/MM methods can decrease the computational expenses, but the simulations still require that an electronic structure calculation be performed at millions of configurations, which is not feasible at present except with semi-empirical methods. An alternative approach is to perform simulations with MM potentials to converge averages, then to evaluate corrections to the averages for the QM or QM/MM potential by an approach that requires the QM or QM/MM evaluation at a limited number of configurations “resampled” from the MM ensemble (Valiev et al. 2007; Wood et al. 1999).

Another challenge is determining the appropriate ensemble for predicting thermodynamic properties. Catalytic reactions always involve the exchange of matter, work, and thermal energy with the surroundings, physics that are captured formally in constant chemical potential, pressure, and/or temperature ensembles. Although important advances have been made in the use of novel thermodynamic ensembles for simulations at fixed chemical potential—which can be used to simulate electrochemical processes in which the number of electrons can fluctuate—approaches are still needed to go beyond the microcanonical, closed-system models of traditional electronic structure to describe systems at realistic chemical and electrical potentials. Clever approximations have been developed to simulate external electrochemical potentials by varying the number of electrons in a simulation, but these are neither rigorous nor general (Rossmeisl et al. 2006). We also need to be able to predict the effect of solution properties on reactions, including pH and ionic strength. Significant advances are needed on all these fronts to model condensed-phase catalysis, fuel cells, and photo- and electrochemical conversion of water and carbon dioxide.

Accurate prediction of reaction rate constants

Calculations of rate constants for reactions involving fossil and biomass feedstocks are a significant challenge because of the size and complexity of active sites and reactant molecules. Transition state theory-based methods are the most common approaches for use of electronic structure information directly in calculations of reaction rate constants (Fernandez-Ramos et al. 2007; Glasstone et al. 1941; Johnston 1966; Kreevoy and Truhlar 1986; Steinfeld et al. 1989; Truhlar et al. 1996; Truhlar and Garrett 2007). These approaches are used routinely in catalysis studies (Truhlar and Morokuma 1999). One advantage of these approaches is that they require limited information about the potential energy surface and in the simplest form require information only about reactant and transition state structures, frequencies, and energetics. The number of reaction pathways often increases with reactant size, and, for chemical reactions with many degrees of freedom, the simple concept of a single reaction path may not be meaningful, because there could be many transition states with similar energies leading to many competitive reaction paths that contribute significantly to observed rates. Even if transition states can be located, the accuracies of rate constants calculated using transition state theory approaches based on harmonic treatment of vibrational modes are limited because of anharmonic effects. These effects are typically large for these reactant-catalyst combinations, particularly in the region of the transition state, and they are computationally expensive to treat. The accurate treatment of anharmonic effects, which are important for calculating entropies of reaction, increases in difficulty as the size of the molecular system increases. Routine approaches to include these effects are not yet available.

Transition state theory-based approaches have been extended in recent years to liquid-phase, interfacial, and enzymatic reactions (Fernandez-Ramos et al. 2007). With regard to reactions in condensed phases, the effects of the environment can have a significant influence on rate constants, requiring appropriate and usually substantial sampling of the environmental variables to yield accurate free-energy landscapes for the reactions. A significant challenge for complex reactant-catalyst combinations is the identification of a reaction coordinate (i.e., the degrees of freedom that participate appreciably in the reaction progress). Although advances, such as transition path sampling (Bolhuis et al. 2002; Dellago et al. 1998) and the dimer method (Henkelman and Jonsson 1999), have provided a route to discovering the motions that promote reactions, applications to large molecular systems and interfaces remain a significant challenge that will not be addressed by the simple application of more computational power.

Advances in Computational Approaches for Electrocatalysis

A number of technologies targeted to play important roles in securing our energy future involve heterogeneous catalytic transformations in the presence of aqueous phases. Examples include the conversion of biorenewables into chemicals and fuels, polymer electrolyte membrane fuel cells, and the photoelectrocatalytic oxidation of water. Elucidating the elementary physicochemical steps that govern the catalytic transformations, however, has been obscured by the difficulty in resolving the surface reaction intermediates and their catalytic transformations under reaction conditions as their spectroscopic features are masked by the presence of the solution. Moreover, the application of theory and simulation to such systems has traditionally been limited by the complexity of the interface. Significant advances in computing, as well as algorithm development, however, have allowed for the simulation of increasingly larger system sizes, thus enabling more realistic models of complex aqueous-metal interfaces. Recent ab-initio DFT simulations have allowed examination of the influence of the metal as well as the solution phase on the surface chemistry. This modeling includes the structure and reactivity of water on various metals as well as the catalytic hydrogenation of model oxygenates (chosen to mimic platform chemicals derived from biorenewable resources at an aqueous-metal interface) (Desai and Neurock 2003).

The extension of theory and simulation to electrocatalysis and fuel cell systems is further complicated by the presence of an electrified aqueous/metal interface, which forms as a result of the potential at the interface. Ab-initio quantum mechanical methods, however, are typically carried out in a canonical form whereby the number of electrons is held constant. Simulations of electrochemical systems instead require that the potential be held constant. A recently developed constant-potential ab-initio approach (Filhol and Neurock 2006; Taylor et al. 2006), which is based on DFT that mimics a half-cell electrochemical system, has been used to simulate the electrooxidation and reduction of water at various transition metal surfaces. Furthermore, it can be used to predict the onset potentials for the activation of water and surface oxide formation and dissolution as well as surface Pourbaix diagrams (Taylor et al. 2007). The approach was subsequently extended and used to follow the elementary reaction pathways and the kinetics of the electrocatalytic oxidation of methanol, formic acid, and carbon monoxide on platinum as well as a number of other metal alloys (Janik and Neurock 2007). These simulations of pure platinum and PtRu alloys and overlayers as well as other binary alloys suggested the novel PtRuAu alloy presented in Figure 30 would lead to significantly improved methanol oxidation activity at the anode of the direct methanol polymer electrolyte membrane fuel cell. Although a number of idealized approximations were made in these calculations, it is clear that theory can begin to be used to simulate some of the critical features in complex aqueous-metal interfaces and the presence of applied potentials, and to provide suggestions for new materials for biorenewable processes and electrocatalytic systems.

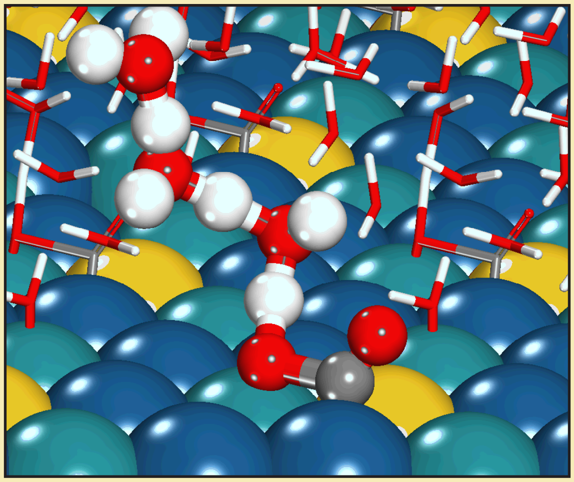

Figure 30: Ab-initio-based constant potential simulations of methanol oxidation on platinum-containing alloys. Predicted PtRuAuML/Ru(0001) ternary alloy, which leads to markedly low potentials necessary for the oxidation of carbon monoxide and methanol. Reprinted from Janik et al. (2007) with kind permission from Springer Science and Business Media.

Another computational challenge presented by bioinspired catalysis is to treat cooperative catalysis through concerted mechanisms by using multiple, organized functional groups. These catalysts can involve extended hydrogen-bonded assemblies, electron delocalization in molecular scaffolds, and the need to treat charge transfer (e.g., coupled electron/proton transfer or redox chemistry) to allow understanding of the fundamental structure-function relationships on a molecular scale.

Coupling the dynamics of electrons and nuclei

Understanding mechanisms of photo- and electro-catalyzed reactions such as for carbon dioxide reduction and water splitting present new challenges for theory and computation. Photocatalytic processes initially involve electronically excited states. The treatment of electronically excited states is much more challenging for theory than processes that occur on a single potential energy surface, both from the perspective of electronic structure theory and from the perspective of dynamics and kinetics. Although dramatic advances have been made in the treatment of excited states in condensed phases (Ben-Nun and Martinez 2002; Levine and Martinez 2007), the calculation of accurate excited states, nonadiabatic couplings between the different electronic states, and their nonadiabatic dynamics are significant challenges for complex catalysts.

Photoexcitations in a solid can lead to separated electrons and holes or to electron-hole pairs that form quasi-stable self-trapped excitons. The dynamics of the electrons, holes, and excitons in solids and their coupling to phonon modes are not well understood and require new theoretical developments. Progress has been made in recent years in the treatment of charge transport through models of crystals, but the treatments of transport and exciton dynamics in more complex media are beyond current capabilities. Moreover, the development of methods to treat charge transport through extended heterogeneous interfaces at fixed electrochemical potentials is urgently needed to facilitate understanding of electro- and photo-chemical proton/electron transfer; extant methods are not sufficient to treat these processes with chemical accuracy.

Many catalytic processes involve simultaneous electron transfer and proton transfer (e.g., proton-coupled electron transfer)—and consequently highly disparate time scales, as well as potential breakdown of the Born-Oppenheimer approximation. Substantial advances are required, as we cannot even predict the band gap today for many important materials. Furthermore, recent work has shown that many of the new photo- or electro-catalytic materials will involve doping at small percentages to substantially improve performance (e.g., doped titanium dioxide to change the band gap). The role of dopants at low concentrations presents problems for current methods as the size of the system to be modeled increases substantially, leading to computational difficulties; new methods are needed. The same kinds of issues will need to be addressed for understanding of the role of impurities in operating catalysts.

Spanning temporal and spatial scales—multiscale methods

Catalytic conversion of complex carbon resources such as coals, tars, shales, and biomass involves close coupling across multiple length scales and time scales, with a level of chemical complexity far beyond anything modeled successfully to date. As previously discussed, the critical reaction steps usually occur on sub-nanometer to 1 nm length scales and require highly detailed quantum chemical treatments. These reactions occur in local microenvironments determined by the interactions between the reactant, catalyst, and adjacent molecules, with a length scale of ≤10 nm. The transport of reactant molecules into pores of a catalyst or the transport of catalysts into the structures of the solvent-swollen coal or biomass occurs on the next-longer length scale.

Beyond these scales are all the practical micron-to-meter scales of macroscopic heat and mass transport that must be accounted for in reactor design. Changes at each of these scales strongly affect phenomena at both higher and lower scales, and they all affect the requirements for new catalysts and overall process efficiencies. New methodologies will be required for handling multiscaling in such complicated systems. Although some progress has been made in multiscale methods, they generally do not yet have the error control that leads to results of predictive quality. The ultimate goal is to couple seamlessly different computational approaches appropriate for difference scales, as depicted in Figure 31, to develop multiscale tools that go beyond ad hoc approaches to providing rigorous mathematical models that couple the appropriate equations for each scale.

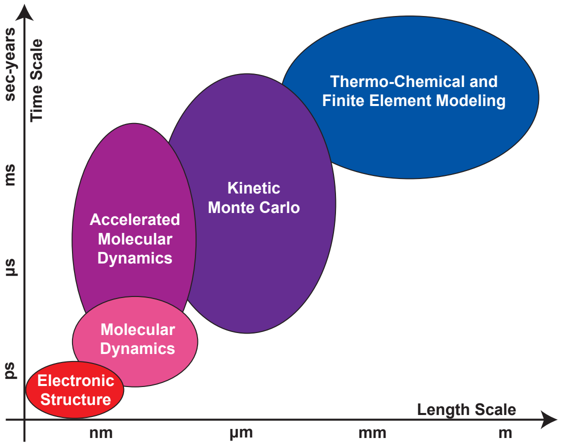

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Figure 31: Temporal and length scales spanned by various computational methods.

Current work on kinetic Monte Carlo methods, reaction networks, coupling of discrete and continuum methods, and coarse graining suggests that this goal is attainable. New and efficient algorithms implemented on current and future high-performance computers, such as those available at U.S. Department of Energy sites, will be needed for integrating these different types of simulations at different scales; also needed will be substantially improved data management systems. Validation of these extremely complex simulations is expected to be particularly challenging, and is expected to benefit from new methodologies now being developed in various complementary fields.

High-performance computing—harnessing the power of petascale and exascale computational resources for computational catalysis

A hierarchy of hardware resources is required to meet the needs of catalysis research (McCurdy 2005). The complexity of the structures and phenomena inherent in catalysis for energy applications demands that the computational tools be available in the near future on high-end computational resources operating at the petascale—and at the exascale—over the next decade. Significant advances need to be made in parallel applications of electronic structure methods that allow these codes to be implemented efficiently on current and proposed high-end computer platforms. In the future, the high-end computers will have tens of thousands of processors—but the scaling of current algorithms is generally not favorable for more than about 2000 processors. Thus, development is needed of new algorithms that can take advantage of 10,000 processors or more, and these algorithms need to be made available in accessible computational tools.

There is also a need to develop new computational technologies to deal with the complex knowledge base underlying catalysis science. A large knowledge base about catalysis is emerging from experiment and more recently from theory and simulation that is not well organized and often not broadly available to researchers in catalysis. There are issues regarding the types of data that are available, and often the data are qualitative in nature. Standard definitions of catalytic properties are often not well defined; for example, how is the turnover frequency defined? There are many different definitions of catalyst performance, and how a catalyst operates depends on the operating conditions. Yet, a practical catalyst may only require a small improvement to become commercially viable. The smallness of this increment makes it difficult to compare computation and experiment and to generate general theories of catalytic behavior that link homogeneous, heterogeneous, and biological catalysis. Organization of the knowledge about catalysts and their activities, selectivities, and lifetimes into databases and tools to manipulate the databases and mine them for new knowledge is expected to have a substantial impact on catalysis science.

Design and controlled synthesis of catalytic structures—a new challenge for theory and computation

Molecular-scale computations can play an important role in designing catalysts. The design of new catalysts will benefit from the development of models that build upon the fundamental information obtained from the tools described previously and from experiment to predict catalyst performance and properties and develop catalysis design guidelines to help focus experimental work. As a first step, computational approaches have been successfully applied for the activation of small gas molecules at metal surfaces. Several examples demonstrate the potential to select metal alloy catalysts optimal both for carrying out desired catalysis and for resistance to poisoning or deactivation. An example is shown in the sidebar on the use of "volcano" plots to enable the rapid identification of active and selective catalysts. In another example, such an approach was successfully implemented for the reaction $2H^+ + 2e^- \rightarrow H_2$, as shown in Figure 32 (Greeley et al. 2006). The stabilization free energy can be thought of as a free energy of formation for the surface alloys; the stability of the alloys with respect to various reconstructive/deactivating processes (including surface segregation, island formation, water splitting/oxygen adsorption, and metal dissolution) is evaluated for each alloy, and the most pessimistic such energy (that is, the energy that would give the maximum probability that the alloy would destabilize) is plotted. A similar approach has been applied to identify Cu/Pt "near surface alloys" for the water-gas shift reaction that retain the desired segregation of metal

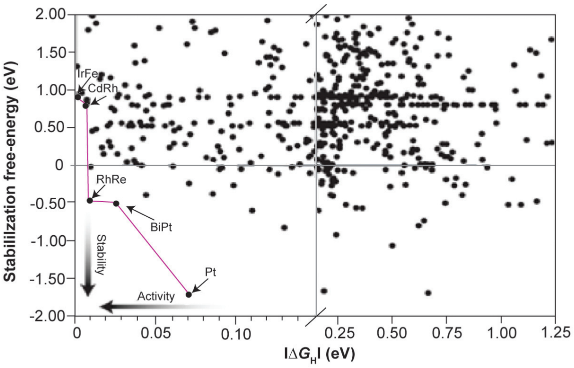

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Figure 32: Pareto-optimal plot of stability and activity of surface alloys for the hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2$). The pareto-optimal line indicates the best possible compromise between activity and stability, but given the simplicity of the model, other alloys could certainly be worth considering for use as hydrogen evolution reaction catalysts; the alloys in the lower left quadrant, in particular, are promising. With regard to the labeled points, a single element indicates a pure metal. As for the bimetallic alloys, the solute is listed first; the solute coverages are 1/3 monolayer (BiPt), 1 monolayer (RhRe), 1/3 monolayer (CdRh), and 2/3 monolayer (IrFe). Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials*, Greeley et al. (2006).

components under the intended reaction conditions (Knudsen et al. 2007). In another example, the Lewis acidity of transition metal fluoride clusters for converting chlorofluorocarbons was predicted and used to design a mixed metal catalyst. The catalyst worked but could not be used commercially because of solubility issues that computational methods cannot currently predict reliably. This example further illustrates some of the many issues that need to be addressed in catalyst design. The future challenges are to develop more general single-scale descriptors capable of treating complex reaction environments and to move from single-scale simulations of the binding energies of simple gases to a metal surface to multiscale simulations of the kinetics of condensed macromolecular mixtures. Other recent advances to be incorporated into catalyst design include molecule-based informatics and the results of descriptor-based combinatorial approaches.

Combinatorial screening of catalysts is a well-established experimental technique for catalyst discovery in the pharmaceutical and chemical industries. However, the development of methods required for computational catalyst screening and design is still in its infancy. Descriptor-based approaches, as described previously, represent a potential way forward in this respect. Catalysis for energy applications presents new challenges to this approach. Complex materials, reactive environments, and multifunctional catalysts require the development of new classes of descriptors that will enable the extension of computational catalyst design paradigms to the next generation of catalytic problems. More sophisticated models are needed to capture knowledge needed to develop catalysis design “rules.” The development of databases of experimental and computational results (e.g., structural and microkinetics data that can be efficiently mined so that new fundamental concepts and models can be developed) will enable improvements in catalyst design leading to further integration of theory and experiment. Molecule-based informatics approaches are being developed that draw on molecular-scale information from computations and experiment to develop the knowledge base and provide the model construct for predicting the performance and properties of catalysts. However, the ability of theory and computation to assist in discovering synthetic routes to make the catalysts identified by the design methods is greatly limited by the lack of theories that link precursors with nucleation, growth, and assembly of nanoscale materials. Computational approaches to guide synthesis of catalytically active sites consisting of functional group assemblies currently do not exist.

Conclusions and Summary

Computational catalysis research has emerged as a result of the confluence of computational methods driven by advances in highly correlated molecular orbital methods, DFT, solid-state theories, solvation theories, modeling of kinetics and transport processes, and efficient, usable software implemented on advanced high-performance computers such as the ones at U.S. Department of Energy-supported computer centers. Although significant progress has been made in advancing computational methods and tools, the scientific challenges identified in this report demand continued efforts to drive this field further. Critical research directions include the following:

- development of approaches that enable the creation of simplified models of the catalyst and the essential elements of complex feedstocks
- improvement in the quantitative reliability and efficiency of electronic structure algorithms (wavefunction-based theories, DFT, and hybrid methods)

First-principles Design of Ammonia Synthesis Catalysts

Ammonia is one of the most important industrial chemicals. The discovery enabled the Haber-Bosch process, which revolutionized the production of ammonia and enables its use to make fertilizer, nitric acid, and many other derivative products, including explosives, during World War I. In the Haber-Bosch process, nitrogen (N_2) and hydrogen (H_2) are combined at high pressures and temperatures in the presence of an iron catalyst to make ammonia. The process is highly energy intensive—the dissociation of nitrogen on the catalyst was shown experimentally to be the rate-limiting step in this process (Ertl et al. 1981)—motivating the search for improved catalysts and operating conditions.

Reports illustrate the potential of computational methods to contribute to catalysis science and application. The “volcano curve” is a well-known empirical relationship between ammonia synthesis catalyst composition and activity. Electronic structure simulations have been shown to be able to explain the underlying atomistic origins of this relationship and opened the way to prediction of new, highly active catalyst compositions (Jacobsen et al. 2001). The performance of an ammonia synthesis catalyst is a function not only of its composition: reaction conditions (temperature and pressure) also affect the performance of different catalyst materials very differently. The origins of this behavior again can be traced to reactivity properties determined at the atomic level; integrating these results into microkinetics models allows predicting of optimal reaction conditions as a function of catalyst properties (Jacobsen et al. 2002).

The ultimate test of atomistic models, however, is not just to suggest catalyst formulations and reaction conditions; it is to *predict* the performance of real catalysts under real reaction conditions. The challenges include bridging the “materials gap” between the necessarily idealized metal surfaces of an electronic structure simulation and the complexity of real metal particles dispersed on supports; the “pressure gap” between surface models of isolated reaction intermediates and the complicated, reactant-covered surfaces present under real reaction conditions; and even the “accuracy gap” between DFT-calculated and real reaction energies. Recently this test has been passed for one model system (Figure 33), a ruthenium catalyst on a spinel support (Hellman et al. 2006; Honkala et al. 2005). With only the number of active sites as input and careful attention to each of these gaps and the errors they introduce, the performance of this catalyst can be predicted from first principles with startling accuracy.

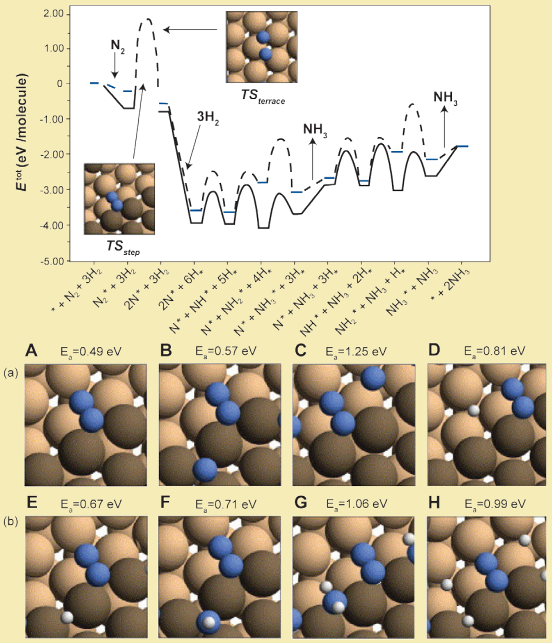


Figure 33: Ammonia synthesis catalysts (a) The reaction pathway for ammonia synthesis on the flat (dashed line) and stepped (solid line) ruthenium surfaces. The transition state configurations of nitrogen (N_2) dissociation on the terrace and step sites are shown in the insets. (b) The variation in transition state energy as a result of the presence of different intermediates. From A to D, a step site with (A) no adsorbates in the neighboring sites, (B) adsorbed nitrogen on the upper step, (C) adsorbed nitrogen on the lower step, and (D) adsorbed hydrogen on the lower step. From E to H, (E) adsorbed hydrogen, (F) adsorbed NH, (G) adsorbed amine on the upper step, and (H) adsorbed hydrogen both on the upper step and lower step. Nitrogen atoms are shown in blue, hydrogen in white, and ruthenium in light and dark brown. In part (A), * denotes a catalyst surface site. In part (B), E_a is the activation energy. Reprinted from Hellman et al. (2006) with permission from Elsevier.

Ammonia synthesis is in some ways the simplest of catalytic reactions: it involves only two diatomic gases combining along a well-understood reaction path. Clearly much more work is necessary to provide the theory, algorithms, and tools to simulate more complicated reactions, materials, and conditions. The theoretical and practical successes on this simple system clearly demonstrate the path and potential for simulation to progress as an increasingly important element of catalysis research.

- creation of efficient approaches to simulate catalytic processes by integrating electronic structure methods with statistical mechanical approaches
- development of approaches for including the influence of complex molecular environments, arising from large molecular systems, surfaces, and solvents, on the dynamics and kinetics of chemical reactions
- extension of electronic structure and dynamics approaches to treat electronically non-adiabatic processes in complex, multiphase systems
- development of theoretical methods to describe complex, multiphase systems that involve widely different length and time scales
- development of massively parallel codes for molecular and multiscale simulations that can utilize petascale computational capabilities and beyond
- creation of models (e.g., descriptor-based combinational approaches and molecule-based informatics) that capture molecular-level understanding to aid in catalysts design
- incorporation of these models and data using database technologies so that they can be effectively mined for new knowledge about catalytic behavior.

Understanding the mechanisms of complex catalytic reactions requires concerted advances in theoretical and computational approaches and close coupling to experiment. Advances in theory and computation will allow predictions with unprecedented reliability of reaction thermodynamics and kinetics, which are needed to assist in catalyst and process design. Recent advances in experimental approaches, such as methods to synthesize nanoscale materials for catalysis, probes of interfaces at the atomic scale, and instrumentation that allows observation of ultrafast processes and of complex processes with greater precision, present opportunities for evaluating theoretical and computational approaches. The availability of simulation tools to interpret observations from complex experimental probes will greatly facilitate the translation of experimental observables into molecular-scale knowledge. As computational tools become more sophisticated and capable of rapidly generating accurate information about the performance of catalysts, models will be available to translate this fundamental knowledge into guidelines for designing new catalysts. It is clear that theory and computations integrated with experiment are critical to advances in catalysis science. The development of new computational approaches and tools will enable theory and computations to be better used as tools for catalyst design and even for catalyst synthesis leading to energy-efficient processes with minimal environmental impact that will help to address the energy needs of the nation.

References

Bartlett, R. J., and M. Musial. 2007. “Coupled-cluster Theory in Quantum Chemistry,” *Reviews of Modern Physics* **79**(1):291-352.

Bash, P. A., M. J. Field, and M. Karplus. 1987. “Free-Energy Perturbation Method for Chemical-Reactions in the Condensed Phase – A Dynamical-approach Based on a Combined Quantum and Molecular Mechanics Potential,” *Journal of the American Chemical Society* **109**(26):8092-8094.

Ben-Nun, M., and T. J. Martinez. 2002. “Ab Initio Quantum Molecular Dynamics,” *Advances in Chemical Physics* **121**:439-512.

Bolhuis, P. G., D. Chandler, C. Dellago, and P. L. Geissler. 2002. “Transition Path Sampling: Throwing Ropes over Rough Mountain Passes, in the Dark,” *Annual Review of Physical Chemistry* **53**:291-318.

Deev, V., and M. A. Collins. 2005. “Approximate Ab Initio Energies by Systematic Molecular Fragmentation,” *Journal of Chemical Physics* **122**, Art. No. 154102.

Dellago, C., P. G. Bolhuis, F. S. Csajka, and D. Chandler. 1998. “Transition Path Sampling and the Calculation of Rate Constants,” *Journal of Chemical Physics* **108**(5): 1964-1977.

Desai, S. K., and M. Neurock. 2003. “First-principles Study of the Role of Solvent in the Dissociation of Water over a Pt-Ru Alloy,” *Physical Review B* **68**(7), Art. No. 075420.

Dunning, T. H. 1989. “Gaussian Basis Sets for Use in Correlated Molecular Calculations. 1. The Atoms Boron through Neon and Hydrogen,” *Journal of Chemical Physics* **90**(2): 1007-1023.

Ertl, G., M. Huber, S. B. Lee, Z. Paal, and M. Weiss. 1981. “Interactions of Nitrogen and Hydrogen on Iron Surfaces,” *Applied Surface Science* **8**, 373-386.

Fernandez-Ramos, A., B. A. Ellingson, B. C. Garrett, and D. G. Truhlar. 2007. “Variational Transition State Theory with Multidimensional Tunneling.” In Chapter 3 of *Reviews in Computational Chemistry*, Vol. 23, pp. 125-232, eds. K. B. Lipkowitz, T. R. Cundari, and D. B. Boyd, Wiley: Hoboken, New Jersey.

Filhol, J. S., and M. Neurock. 2006. “Elucidation of the Electrochemical Activation of Water over Pd by First Principles,” *Angewandte Chemie International Edition* **45**, 402-406.

Frauenheim, T., G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz. 2000. “A Self-consistent Charge Density-functional Based Tight-binding Method for Predictive Materials Simulations in Physics, Chemistry and Biology,” *Physica Status Solidi B-Basic Research* **217**(1):41-62.

Frauenheim, T., G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Amkreutz, M. Sternberg, Z. Hajnal, A. Di Carlo, and S. Suhai. 2002. “Atomistic Simulations of Complex Materials: Ground-state and Excited-state Properties,” *Journal of Physics-Condensed Matter* **14**(11):3015-3047.

Gai, P. L. 1999. “Environmental High Resolution Electron Microscopy of Gas-catalyst Reactions,” *Topics in Catalysis* **8**(1-2):97-113.

Gao, J. 1996. "Methods and Applications of Combined Quantum Mechanical and Molecular Mechanical Potentials." In Chapter 3 of *Reviews in Computational Chemistry*, Vol. 7, pp. 119-185, eds. K. B. Lipkowitz, D. B. Boyd, VCH: New York.

Glasstone, S., K. J. Laidler, and H. Eyring. 1941. *The Theory of Rate Processes.* McGraw-Hill: New York.

Greeley, J., T. F. Jaramillo, J. Bonde, I. B. Chorkendorff, and J. K. Nørskov. 2006. "Computational High-throughput Screening of Electrocatalytic Materials for Hydrogen Evolution," *Nature Materials* **5**(11):909-913.

Hammond, B. L., W. A. Lester, Jr., and P. J. Reynolds. 1994. *Monte Carlo Methods in Ab Initio Quantum Chemistry*. World Scientific: Singapore.

Hellman, A., K. Honkala, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen, and J. K. Nørskov. 2006. "Insights into Ammonia Synthesis from First Principles," *Surface Science* **600**(18):4264-4268.

Henkelman, G., and H. Jonsson. 1999. "A Dimer Method for Finding Saddle Points on High Dimensional Potential Surfaces Using Only First Derivatives," *Journal of Chemical Physics* **111**(15):7010-7022.

Hirata, S., M. Valiev, M. Dupuis, S. S. Xantheas, S. Sugiki, and H. Sekino. 2005. "Fast Electron Correlation Methods for Molecular Clusters in the Ground and Excited States," *Molecular Physics* **103**(13-15):2255-2265.

Honkala, K., A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen, and J. K. Nørskov. 2005. "Ammonia Synthesis from First-principles Calculations," *Science* **307**(5709):555-558.

Jacobsen, C. J. H., S. Dahl, B. S. Clausen, S. Bahn, A. Logadottir, and J. K. Nørskov. 2001. "Catalyst Design by Interpolation in the Periodic Table: Bimetallic Ammonia Synthesis Catalysts," *Journal of the American Chemical Society* **123**(34):8404-8405.

Janik, M. J., and M. Neurock. 2007. "A First Principles Analysis of the Electro-oxidation of CO over Pt(111)," *Electrochimica Acta* **52**(18):5517-5528.

Janik, M. J., C. D. Taylor, and M. Neurock. 2007. "First Principles Analysis of the Electrocatalytic Oxidation of Methanol and Carbon Monoxide." *Topics in Catalysis.* In Press. DOI 10.1007/s11244-007-9004-9.

Johnston, H. S. 1966. *Gas Phase Reaction Rate Theory.* Ronald Press: New York.

Kletnieks, P. W., A. J. Liang, R. Craciun, J. O. Ehresmann, D. M. Marcus, V. A. Bhirud, M. M. Klaric, M. J. Haymann, D. R. Guenther, O. P. Bagatchenko, D. A. Dixon, B. C. Gates, and J. F. Haw. 2007. "Molecular Heterogeneous Catalysis: A Single-site Zeolite-supported Rhodium Complex for Acetylene Cyclotrimerization," *Chemistry-A European Journal* **13**(26):7294-7304.

Knudsen, J., A. U. Nilekar, R. T. Vang, J. Schnadt, E. L. Kunkes, J. A. Dumesic, M. Mavrikakis, and F. Besenbacher. 2007. "A Cu/Pt Near-surface Alloy for Water-gas Shift Catalysis," *Journal of the American Chemical Society* **129**(20):6485-6490.

Kohn, W. 1999. “Nobel Lecture: Electronic Structure of Matter-wave Functions and Density Functionals,” *Reviews of Modern Physics* **71**(5):1253-1266.

Kohn, W., and L. J. Sham. 1965. “Self-consistent Equations Including Exchange and Correlation Effects,” *Physical Review B* **140**(4A):1133-1138.

Komeiji, Y., T. Nakano, K. Fukuzawa, Y. Ueno, Y. Inadomi, T. Nemoto, M. Uebaysai, D. G. Fedorov, and K. Kitaura. 2003. “Fragment Molecular Orbital Method: Application to Molecular Dynamics Simulation, ‘Ab Initio FMO-MD’,” *Chemical Physics Letters* **372**(3-4):342-347.

Kreevoy, M. M., and D. G. Truhlar. 1986. “Transition State Theory.” *In Investigations of Rates and Mechanisms of Reactions*, 4th ed., Vol. 6, p. 13, ed. C. F. Bernasconi, Wiley: New York.

Levine, B. G., and T. J. Martinez. 2007. “Isomerization through Conical Intersections,” *Annual Review of Physical Chemistry* **58**:613-634.

Li, S., and D. A. Dixon. 2007. “Benchmark Calculations on the Electron Detachment Energies of MO_3- and M_2O_6- (M = Cr, Mo, W),” J*ournal of Physical Chemistry A* **ASAP**, DOI:10.1021/jp074768i.

Maseras, F., and K. Morokuma. 1995. “IMOMM - A New Integrated Ab Initio Plus Molecular Mechanics Geometry Optimization Scheme of Equilibrium Structures and Transition States,” *Journal of Computational Chemistry* **16**:1170-1179.

Matthey, D., J. G. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Laegsgaard, B. Hammer, and F. Besenbacher. 2007. “Enhanced Bonding of Gold Nanoparticles on Oxidized TiO_2(110),” *Science* **315**:1692-1696.

McCurdy, C. W. 2005. *Opportunities for Discovery: Theory and Computation in Basic Energy Sciences,* U.S. Department of Energy Subcommittee on Theory and Computation of the Basic Energy Sciences Advisory Committee, Washington, D.C. Available online: http://www.science.doe.gov/production/bes/reports/files/OD_rpt.pdf.

Moore, L. R., E. C. Western, R. Craciun, J. M. Spruell, D. A. Dixon, R. Timkovich, K. P. O’Halloran, and K. H. Shaughnessy. 2007. “Sterically Demanding, Sulfonated, Triarylphosphines: Application to Palladium-catalyzed Cross-coupling, Steric and Electronic Properties, and Coordination Chemistry,” *Organometallics* (in press).

Pople, J. A. 1999. “Nobel Lecture: Quantum Chemical Models,” *Reviews of Modern Physics* **71**:1267-1274.

Reuter, K., D. Frenkel, and M. Scheffler. 2004. “The Steady State of Heterogeneous Catalysis, Studied by First-principles Statistical Mechanics,” *Physical Review Letters* **93**, Art. No. 116105.

Reuter, K., and M. Scheffler. 2003. “First-principles Atomistic Thermodynamics for Oxidation Catalysis: Surface Phase Diagrams and Catalytically Interesting Regions,” *Physical Review Letters* **90**, Art. No. 046103.

Rossmeisl, J., J. K. Nørskov, C. D. Taylor, M. J. Janik, and M. Neurock. 2006. “Calculated Phase Diagrams for the Electrochemical Oxidation and Reduction of Water over Pt(111),” *Journal of Physical Chemistry B* **110**:21833-21839.

Steinfeld, J. I., J. S. Francisco, and W. L. Hase. 1989. *Chemical Kinetics and Dynamics*. Prentice-Hall: Englewood Cliffs, New Jersey.

Svensson, M., S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, and K. Morokuma. 1996. "ONIOM: A Multilayered Integrated MO+MM Method for Geometry Optimizations and Single Point Energy Predictions. A Test for Diels-Alder Reactions and $Pt(P(T\text{-}Bu)_3)_2+H_2$ Oxidative Addition," *Journal of Physical Chemistry* **100**:19357-19363.

Taylor, C. D., S. A. Wasileski, J. S. Filhol, and M. Neurock. 2006. "First Principles Reaction Modeling of the Electrochemical Interface: Consideration and Calculation of a Tunable Surface Potential from Atomic and Electronic Structure," *Physical Review B* **73**, Art. No. 165402.

Taylor, C., R. G. Kelly, and M. Neurock. 2007. "Theoretical Analysis of the Nature of Hydrogen at the Electrochemical Interface between Water and a Ni(111) Single-crystal Electrode," *Journal of the Electrochemical Society* **154**:F55-F64.

Truhlar, D. G., and B. C. Garrett. 2007. "Variational Transition State Theory in the Treatment of Hydrogen Transfer Reactions." In *Hydrogen-Transfer Reactions*, Vol. 2, pp. 833-875, eds. H. H. Limbach, J. T. Hynes, J. Klinman, and R. L. Schowen. Wiley-VCH: New York.

Truhlar, D. G., B. C. Garrett, and S. J. Klippenstein. 1996. "Current Status of Transition State Theory," *Journal of Physical Chemistry* **100**:12771-12800.

Truhlar, D. G., and K. Morokuma, eds. 1999. *Transition State Modeling for Catalysis*, American Chemical Society: Washington, D.C.

Uberuaga, B. P., F. Montalenti, T. C. Germann, and A. F. Voter. 2005. "Accelerated Molecular Dynamics Methods." In *Handbook of Materials Modeling, Part A – Methods*, ed. S. Yip. Springer: Dordrecht, pp. 629-648.

Valiev, M., B. C. Garrett, M. K. Tsai, K. Kowalski, S. M. Kathmann, G. K. Schenter, and M. Dupuis. 2007. "Hybrid Approach for Free Energy Calculations with High-level Methods: Application to the $S(N)_2$ Reaction of $CHCl_3$ and OH- in Water," *Journal of Chemical Physics* **127**, Art. No. 051102.

Wood, R. H., E. M. Yezdimer, S. Sakane, J. A. Barriocanal, and D. J. Doren. 1999. "Free Energies of Solvation with Quantum Mechanical Interaction Energies from Classical Mechanical Simulations," *Journal of Chemical Physics* **110**:1329-1337.

PRIORITY RESEARCH DIRECTIONS

SELECTIVE CATALYTIC CONVERSION OF FOSSIL FEEDSTOCKS

UNDERSTANDING THE CHEMISTRY OF LIGNOCELLULOSIC BIOMASS: DECONSTRUCTION AND CATALYTIC CONVERSION TO FUELS

PHOTO- AND ELECTRO-DRIVEN CONVERSION OF CARBON DIOXIDE AND WATER

SELECTIVE CATALYTIC CONVERSION OF FOSSIL FEEDSTOCKS

Abstract

The efficient, economical conversion of fossil feedstocks requires improvements in the control of the individual reactions, better management of hydrogen, and more selective removal of heteroatoms. The challenges are increasing as feedstocks such as heavy oils, tar sands, shale, and coal become heavier. Progress requires the detailed understanding of the compositions of the feedstocks and the products of their reactions by application of modern methods of analytical chemistry. Existing catalytic approaches based on chemistry known from light petroleum conversion are insufficient because of the greatly increasing complexity of the feedstocks. Development of a next generation of catalysts and processes for heavy feedstocks requires molecular-scale understanding of the structures of the components, including the interactions between large complex molecules. Novel process approaches may involve the highly selective removal of heteroatoms from large complex structures and the use of light alkanes as selective reductants. The practical consequences of research breakthroughs in heavy feedstock conversion include better utilization of resources (e.g., hydrogen) and minimization of environmental effects of fuel production and burning.

Executive Summary

The emerging sources of fossil fuels (heavy oils, tar sands, shale oil, and coal) are substantially heavier than those used today, with lower H/C ratios and higher heteroatom contents. The molecules in these feedstocks are complex, and their reactions are not well understood. They are also characterized by strong intermolecular interactions, leading to the formation of aggregates and solid-like structures that are difficult to characterize. The challenge of understanding the reactions, including disentangling of the aggregated structures, and selective conversion of the molecules requires new insights into the conversions and new catalysts for the processes.

Researchers have so far investigated these complex feedstocks by representing them in global (or lumped) terms rather than molecular terms. Thus, the reactants and products have generally been described in terms of physical properties such as solubility or boiling point groups. This approach is limited, but recent advances in analytical chemistry, illustrated by high-resolution mass spectrometry, and computational power are now opening the way to investigation of these feedstocks in molecular terms. These advances point the way to future representations of reactivity on a compound-by-compound basis. There is a compelling need to advance the fundamental understanding of the reactions of heavy feedstocks by taking advantage of the opportunities offered by modern analytical chemistry of these feedstocks.

Key scientific challenges are as follows:

- analysis of feeds and products in molecular detail as a basis for understanding individual reactions and mechanisms
- fundamental understanding of the interactions of heavy molecules with model catalysts
- investigations of catalytic pathways and mechanisms for heteroatom removal, including new reactions that selectively oxidize organosulfur compounds to sulfur dioxide and olefins or oxygenates
- selective conversion of small molecules such as methane and carbon dioxide into fuels, and reactions of these compounds with fuels to produce better fuels, such as those with higher hydrogen contents and lower heteroatom contents.

Understanding the Reactions of Heavy Feedstocks

Summary of research directions

As fossil feedstocks are becoming increasingly heavy, new refining goals are emerging. The higher molecular weights, aromaticities, and molecular complexities and the accompanying lower hydrogen/carbon ratios demand a substantial increase in our understanding and control of catalytic selectivity. Current catalytic science is well matched to the demands for processing at least 70 percent of a barrel of crude oil. The combination of thermal and catalytic cracking can reduce the high-molecular-weight fraction to manageable-sized molecules, and subsequent catalysis by acids, metals, and bifunctional and shape-selective catalysts involves isomerization, aromatization, hydrogen redistribution, and ring opening for optimization of the products.

Our current understanding reaches its limit, however, when the size and structural complexity of the reactant molecules prevent their explicit identification and make the networks of their reactions intractably complicated. Many components of heavy feedstocks are so large and complex that only their surfaces can come in contact with catalyst surfaces. Work is needed to understand what the components of these feedstocks are, how they interact with catalysts, how partial conversions (such as hydrogenation) affect the structures of the species and these interactions, and how deconstruction of the aggregates takes place and affects the reactivities of the molecules contained in them.

Scientific challenges

Heavy oils, coal, shale, and other high-molecular-weight multi-component mixtures (including those derived from lignocellulosic biomass) are more difficult to process than traditional petroleum feeds, and understanding of the chemistry of their processing is largely lacking, for the following reasons:

1. These resources are complex mixtures, with thousands of individual molecules having been identified and countless more presumed present, and consequently they are not well characterized. Specifically, most of the molecules in these mixtures have molecular weights that prevent analysis by traditional methods of analytical chemistry. They are often found as solid or highly viscous liquid mixtures.

2. The molecules are multifunctional, containing many sites or structural moieties, the reactions of which are all potentially significant in the conversions.
3. The molecules in these mixtures generally interact with each other in complex ways, preventing reliable measurements of properties as fundamental as average molecular weight by current methods.

All of these characteristics complicate characterization of the reactions involved in upgrading and therefore the design of optimal catalysts, upgrading strategies, and environmental protection strategies. To make significant progress in the directions mentioned above, researchers will face the demanding scientific challenges of determining the following:

1. Better understanding of the molecular structures that comprise the various feedstocks, which requires advances in analytical chemistry, such as modern high-resolution mass spectrometry. Such understanding is a prerequisite to determining structure-reactivity patterns and mechanisms of the reactions, needed for discovery of improved catalysts and processes. At the same time, researchers will need to understand that mixtures of the complex molecules in heavy feedstocks bring their own conceptual challenges. In developing kinetics models, for example, it will not be appropriate to neglect the non-covalent intermolecular interactions among the feed molecules. New computational methods and simulation models are needed to account for this level of complexity.
2. Better understanding of how each of the important functional groups in the feedstocks interacts with and is converted on each of a set of prototypical catalysts—those containing acid sites, metals, metal sulfides, etc., and combinations of these. The identification of which catalysts should be considered prototypical will evolve as the research is conducted. Determination of the relationships between molecular structure of heavy molecules and reactivity in selective reactions such as hydrogenation, hydrogen transfer, ring contraction, ring opening, and heteroatom removal is needed. The dynamics of interactions of polynuclear aromatic compounds with solid catalysts is poorly understood, and the goal of predicting the reactivities of such compounds based on molecular-level understanding of reaction mechanisms is especially ambitious in the case of the heaviest molecules and aggregated structures. Researchers will need to select models that faithfully represent the chemistry of the complex species present in the heavy feedstocks interacting with well-characterized catalyst surfaces to generate intrinsic chemical information that will provide fundamental understanding of structure/reactivity relationships.
3. Data showing how the many other compounds present in the complex feedstocks affect the reactions of individual compounds. Further details of this approach are stated in the panel reports concerned with fossil fuels and (briefly) biomass.
4. A foundation emerging from this research of structure-reactivity data to guide the selection of more active, selective, and stable catalysts for fuel processing.

Scientific impacts

An important scientific goal is improved understanding of the mechanisms of conversion of the molecules in heavy fossil feedstocks, including deconstruction of aggregates, C–C and C–H bond activation, hydrogen transfer, and heteroatom removal. The anticipated results will shed light on how such processes are catalyzed by acids, metals, metal sulfides, etc., and the role of non-catalytic free-radical reactions.

Technology impacts

This understanding will result in a better control of the conversions and management of hydrogen and ultimately will lead to catalysts with higher selectivities that will work under milder conditions than is possible today. The results will be better technology for conversion of heavy oils, tar sands, shale, and coal and minimization of the environmental impact of the conversions.

Improved Utilization of Light Molecules in Hydrocarbon Fuel Production

Liquid hydrocarbons combine fungibility together with a high energy density required by transportation fuels. Although current liquid transportation fuels (gasoline, diesel, and jet fuels) consist largely of mixtures of hydrocarbon molecules, not every component in the mixture is optimal for energy conversion in its designated applications. Some molecules, for example, are preferred on the basis of their octane or cetane numbers. Thus, there is a motivation to produce mixtures of compounds selectively for specific applications.

One path forward is to improve catalyst selectivities for conversions of mixtures; another is to achieve direct conversions to desired products by combining small carbon-containing building blocks with each other and/or with fractions of fossil feedstocks. The building blocks include, in prospect, carbon monoxide, carbon dioxide, methanol, formaldehyde, and light olefins such as ethylene and propylene. Of particular potential value in this context is methane, which comprises a major portion of the available hydrocarbon resource pool, but which with current science and technology cannot be efficiently converted to valuable products such as functionalized C_1 and C_2 derivatives or desired higher hydrocarbon products relevant to transportation fuels (Labinger 2004; Lunsford 2000; Pyatnitskii 2003). As a result, methane (natural gas) in this context currently serves only as an indirect source of molecular hydrogen (e.g., via steam reforming).

The efficient catalytic conversion of methane to functionalized products remains a major unsolved scientific problem; nature's catalysts (enzymes) do it, but we cannot. Strategies that rely on initial C–H bond homolysis suffer from the susceptibility of more reactive product C–H bonds to further bond-breaking and, in the case of oxidation strategies, to complete conversion to carbon dioxide. Only partial and inefficient conversion to desired products has been demonstrated. The conversions are thermodynamically possible, but the catalysts needed to carry them out are lacking. Some examples of methane activation and functionalization by alternative heterolytic bond activation schemes have been reported (Cheng et al. 2006; Li and Yuan 2006; Periana et al. 1998; Otsuka and Wang 2000; Shilov 1984; Zerella and Bell 2006), but practical applications of these strategies seem far away. These examples, with guidance from theory and biology, offer hope for progress towards selective activation of methane, but the challenge remains daunting.

The conversion of small precursors into larger fuel molecules involves the formation of C–C bonds. Control and selectivity of the bond formation is crucial to energy and carbon utilization efficiency in the production of liquid fuels, because carbon loss implies byproduct formation and uneconomical reprocessing. There are two major processes of chain growth reactions now practiced, the major one being the Fischer-Tropsch process, which typically converts CO and H_2 into linear hydrocarbon chains, as long as C_{30+}, with low selectivities (the appended factual document provides details on this process).

C–C bond formation also occurs in several single-step processes, such as methanol carbonylation to acetic acid, olefin metathesis, aldol condensation, and alkylation. Although these reactions proceed with high specificity, only one C–C bond is formed, and multiple steps with intermediate purification are needed to further assemble molecules requiring multiple C–C bond formation.

Consequently, there is a need for new catalysts for economic conversion of small molecules into fuels. Some specific research targets include (1) selective partial oxidation and functionalization of methane, (2) oxidative coupling of small hydrocarbons, (3) integrated hydrogen transfer (hydrogen donation) from methane to hydrogen-poor hydrocarbons, and (4) selective alkylation and methane homologation strategies. Hydrocarbon "construction" strategies to form targeted molecules involving multiple C–C bond formations require catalytic sites with capabilities beyond the limits of known chemistry. Novel approaches might involve multiple catalytic sites, strategically positioned to enable efficient energy and material flow for the desired sequences of reactions that are of interest. Manipulation of dipolar and van der Waals interactions and charge stabilization may facilitate specific transformations by stabilizing transition states while rendering the undesirable pathways unfavorable.

Scientific challenges

The controlled synthesis of complex products from simple molecules and the discovery of new functionalization pathways for simple alkane C–H and C–C bonds remain a primary bottleneck in hydrocarbon and small molecule chemistry; the challenge is large and the way forward is not obvious. Advances require an increased understanding of primary bond-breaking and -making processes guided by theory and perhaps inspired by biology.

Potential scientific impact

Understanding the fundamental chemistry of these processes will guide hypotheses to be tested in specific conversions of a wide range of reactants that have so far been underutilized in fuel production; the working hypotheses will guide research leading to new catalysts and new chemistries of C–H and C–C bond-breaking and bond-forming.

Novel Routes to Heteroatom Removal

Summary of research directions

The heteroatoms (i.e., sulfur, nitrogen, and oxygen) in fossil feedstocks constitute a major part of the challenge of catalytic upgrading because sulfur and nitrogen are sources of air pollutants formed when the fuels are burned (SO_x and NO_x are principal precursors of acid rain and photochemical smog). Moreover, the compounds incorporating these elements act as poisons or attenuators to metal- and acid-function catalysts that are typically used in refinery processes, reducing catalyst life or necessitating harsher processing conditions. Thus, conversion of these compounds is essential for reducing undesirable emissions and improving their processability in downstream conversions.

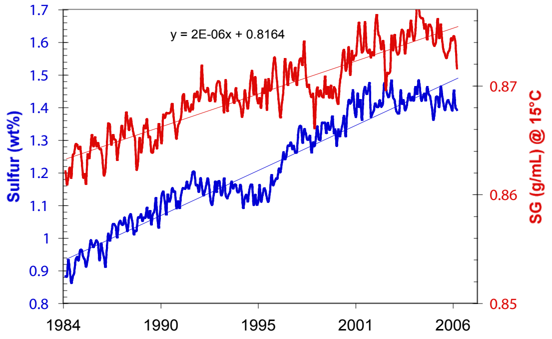


Figure 34: As the highest-quality crude oil is being consumed, that entering the United States is becoming heavier, containing increasing amounts of sulfur. SG here refers to specific gravity.

The molecules containing these heteroatoms, as well as metals and other impurities, are present in high concentrations in heavy feedstocks. Because the light, sweet crude oils are being depleted, the heavy feedstocks are being used more; the data in Figure 34 illustrate the trend. Heavy feedstocks in addition to petroleum (tar sands, shale, and coal) also have high contents of these heteroatoms.

The traditional means for removing heteroatoms is via catalytic hydroprocessing. The technology is practiced on an enormous scale in refineries today, but it presents some major challenges. It requires large amounts of hydrogen, which is expensive and in short supply. Furthermore, it is carried out at high pressures (typically, >70 bar), which requires the use of energy-intensive compressors and expensive, thick-walled reactors.

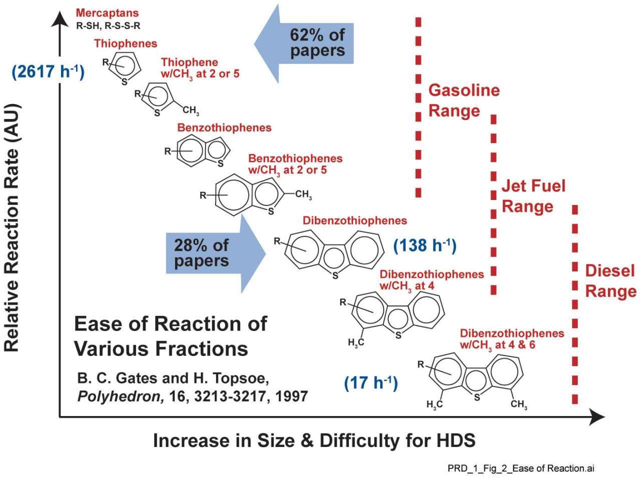
Many of the heteroatoms (especially in coals and biomass) reside in large molecules that are sterically hindered and do not come in contact with catalyst surfaces; hence, they react slowly and, in the case of compounds containing nitrogen, unselectively.

Therefore, there is a pressing need for improved processes for removal of heteroatoms from increasingly heavy fossil feedstocks. Improvements in the selectivity of hydroprocessing catalysts that allow for sulfur and nitrogen removal with only limited hydrogen consumption would by themselves represent a significant advance, and there is a strong incentive for discovery of new catalytic strategies for removal of heteroatoms without hydrogen consumption.

Scientific challenges

In heavy oils and other heavy feedstocks, the heteroatoms are concentrated in the heaviest and most complex fractions and difficult to analyze. Part of the difficulty is associated with the aggregated and solid-like structures, such as asphaltenes, the alkane-insoluble, aromatic-soluble component of the 1000+ °F boiling fraction of petroleum. Important heteroatoms in these asphaltenes are sulfur, nitrogen, vanadium, and nickel. The hydrocarbon structure is characterized by large fused-ring components that can contain as many as 6-8 rings. It is still unclear whether the fused-ring structures are linked as mini-polymers. Coal is an aggregate of molecules that also contain heteroatoms, as well as bulk mineral components.

The specific goal of selectively and efficiently removing heteroatoms is complicated by the heteroatom–carbon bond strengths, which generally are in the order C–O > C–N > C–S. It is expensive and difficult without massive inputs of hydrogen to react with these compounds and weaken the carbon–heteroatom bonds to reduce the concentrations of these heteroatoms to the stringent levels mandated by law to protect the environment. Furthermore, molecules from heavy carbon sources contain hindered heteroatoms, such as the sulfur centers in the refractory compounds 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (Figure 35). These inaccessible centers present their own challenges to the design of energetically efficient and selective catalysts, and whole new approaches to the catalyst design are needed.



B. C. Gates and H. Topsoe, *Polyhedron,* 16, 3213-3217, 1997

Figure 35: The challenging problem in hydrodesulfurization is in the heavy ends. The numbers in parentheses are relative values of pseudo-first-order rate constants. Reprinted from *Catalysis Today,* **86**, Song, C., "An Overview of New Approaches to Deep Desulfurization for Ultra-clean Gasoline, Diesel Fuel and Jet Fuel." p. 53, 2003, with permission from Elsevier.

Non-hydrotreating methods for heteroatom removal are appealing as alternatives, but at this stage, there are no clear leads; one should consider reactions with oxygen. Research, guided by theory, is needed to find methods for activation, cleavage, and healing of C–heteroatom bonds.

Specific research directions are as follows:

- Investigation of the interactions of heteroatom-containing molecules with model catalysts and those used in industry. This work may involve a homologous series of molecules on single-site catalysts to develop structure-property relationships for heteroatom removal.
- Investigation of catalytic oxydesulfurization pathways that selectively oxidize organosulfur compounds to form sulfur dioxide and olefins or oxygenates.
- Attempts to couple heteroatom hydrogenation with alkane dehydrogenation. Theory might provide guidance for the selection of candidate catalysts for such novel pathways towards optimal hydrogen utilization.
- Investigation of how hydroprocessing catalysts are deactivated, on the basis of fundamental understanding of how sulfur and nitrogen compounds interact with the catalyst surfaces. This work should involve characterization of the mechanisms of adsorption and structures of adsorbed species and the fate of the adsorbed species under catalytic reaction conditions.

Scientific impacts

Research in the recommended directions is expected to lead to improved fundamental understanding of the heavy feedstock compositions and the patterns of their catalytic reactions in the presence of various prototype catalysts. Such understanding will guide improvements in selection of catalysts and improved efficiencies of fuel production. New catalytic chemistry of C–C, C–H, and carbon–heteroatom bond activation is expected to point the way to new, selective catalytic routes for converting small molecules such as carbon dioxide and methane into fuels and removal of the heteroatoms from heavy feedstocks.

Technological impacts

Research in these directions is expected to lead to the following results:

- efficiency improvements in catalytic processes, including lower hydrogen consumptions and more economical processing of lower-value feedstocks
- a decreased need for hydrogen and reduced production of carbon dioxide in refining processes
- the development of poison-resistant catalysts
- new approaches to removal of heteroatoms that may lead to technological breakthroughs.

References

Cheng, J., Z. Li, M. Haught, and Y. Tang. 2006. “Direct Methane Conversion to Methanol by Ionic Liquid-dissolved Platinum Catalysts,” *Chemical Communications* 4617.

Gates, B. C., and H. Topsøe. 1997. “Reactivities in Deep Catalytic Hydrodesulfurization: Challenges, Opportunities, and the Importance+ of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene,” *Polyhedron* **16**:3213-3217.

Labinger, J. A. 2004. “Selective Alkane Oxidation: Hot and Cold Approaches to a Hot Problem,” *Journal of Molecular Catalysis A: Chemical* **220**:27.

Li, F., and G. Yuan. 2006. “Hydrated Dibromodioxomolybdenum(VI) Supported on Zn-MCM-48 for Facile Oxidation of Methane,” *Angewandte Chemie International Edition* **45**:6541.

Lunsford, J. H. 2000. “Catalytic Conversion of Methane to More Useful Chemicals and Fuels: A Challenge for the 21st Century,” *Catalysis Today* **63**:165.

Otsuka, K., and Y. Wang. 2000. “Direct Conversion of Methane to Oxygenates,” *Applied Catalysis A: General* **222**:145.

Periana, R. A., D. J. Taube, S. Gamble, H. Taube, T. Satoh, and H. Fujii. 1998. “Platinum Catalysts for the High-Yield Oxidation of Methane to Methanol Derivative,” *Science* **280**(5363):560-564.

Pyatnitskii, Y. I., 2003. “Contemporary Methods for the Direct Catalytic Conversion of Methane,” *Theoretical and Experimental Chemistry* **39**:201.

Shilov, A. E. 1984. *Activation of Saturated Hydrocarbons by Transition Metal Complexes.* Springer: Berlin.

Song, C. 2003. “An Overview of New Approaches to Deep Desulfurization for Ultra-clean Gasoline, Diesel Fuel and Jet Fuel,” *Catalysis Today* **86**:211–263.

Zerella, M., and A. T. Bell. 2006. “Pt-Catalyzed Oxidative Carbonylation of Methane to Acetic Acid in Sulfuric Acid,” *Journal of Molecular Catalysis A: Chemical* **259**:296.

UNDERSTANDING THE CHEMISTRY OF LIGNOCELLULOSIC BIOMASS: DECONSTRUCTION AND CATALYTIC CONVERSION TO FUELS

Abstract

Lignocellulose is the most abundant form of biomass on the planet and is a renewable resource that can serve as a feedstock for fuels and chemicals. A critical step in processing biomass is the deconstruction of this material into components that can be catalytically converted into fuels and chemicals. Deconstruction transforms lignocellulosic biomass to aqueous- and/or organic-soluble compounds and gas-phase compounds, all of which can be catalytically upgraded to fuels and chemicals. Current methods for deconstructing biomass do not produce high yields of these products. Catalytic processes for converting the products of biomass deconstruction to fuels currently suffer from poor efficiency and poor product selectivity. The conversion of lignocellulosic biomass to a liquid or gaseous fuel is a multi-phase process involving the solid biomass phase, a hydrophilic phase, and a hydrophobic phase. Computational tools that can model the multi-phase, multi-scale features of biomass deconstruction and catalysis in static and dynamic environments will provide rational approaches to the most efficient conversion technologies. The development of chemical and biological catalysis to improve biomass deconstruction and catalytic conversion may significantly improve economic routes to biofuel production. Opportunities exist to develop catalysts for the targeted synthesis of liquid fuels from biomass deconstruction products.

Executive Summary

Lignocellulose is a complex material containing polysaccharides built from the following: xylose monomers, glucose monomers, and lignin, a highly aromatic material. The efficient and complete deconstruction of lignocellulosic biomass and other biomass feedstocks into reactive intermediates, such as sugars, furfural, levulinic acid, bio-oil, triglyceride, glycerol, lignin-derived compounds, and syngas, is a critical step in processing biomass. To efficiently convert biomass into fuels, the chemical composition and structure of biomass must be better understood. Biomass recalcitrance to processing originates from the connectivity between the chemical linkages and the structures formed during plant cell wall synthesis. Less is known about the dynamic changes in structure and composition of biomass and biomass-derived chemicals in the chemical environments found in pretreatment chambers and catalytic reactors. A consistent, high-yield pretreatment method that can accommodate a wide range of feedstocks is one of the most critical steps in realizing an efficient and cost-effective biorefinery.

Processing the products of biomass deconstruction to produce fuels requires developing catalysts that can provide high yields of targeted products. Liquid-phase processing is a promising pathway for conversion of biomass-derived oxygenates because it allows the selective conversion of thermally unstable compounds. It is likely that heterogeneous catalysis will play important role in the use of biomass as a feedstock; however, catalysts must be designed to minimize coke formation. A critical challenge is developing a fundamental understanding of the reaction mechanisms and kinetics involved in these processes, and establishing the relationships of catalyst composition and structure to their activity and selectivity.

Summary of Research Directions

Atomistic to macroscopic understanding of biomass on the basis of advanced imaging and real-time diagnostics

The cellulosic component of biomass is typically depicted as a polymeric liquid crystal forming a microfibril network embedded in hemicellulose, lignin, and pectin matrices (Faulon et al. 1994) (Figure 36). The exact dimensions of the microfibrils depend on the plant species (Donaldson 2007). New insight into the static and dynamic interplay between the chemical linkages found in biomass, and the three-dimensional structures present, could be provided by existing and proposed high-resolution, real-time analytical techniques.

The morphology, size, and degree of cellulose crystallinity present before and after deconstruction, the kinetics of the deconstruction reactions, the chemical linkages present, and the degree of polymerization of all three major lignocellulose constituents are of interest. Determining these parameters will enable researchers to achieve unprecedented insight into lignocellulose. Moreover, knowledge of the parameters will guide tailored pretreatment techniques and conversion technologies with increased yield and decreased inhibitor formation. The data will also be used to develop a hierarchical modeling approach to describe the structural and chemical elements that are most susceptible to deconstruction.

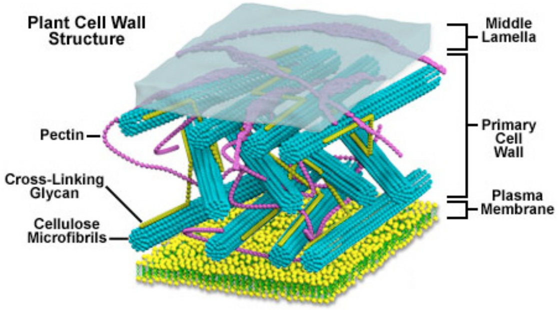


Figure 36: Schematic representation of the plant cell wall structure and composition. Used with permission from Michael W. Davidson, Florida State University (http://micro.magnet.fsu.edu/cells/plants/cellwall.html).

Identification, design, and development of advanced pretreatments and catalysts

Biomass pretreatment at a large scale involves one or more chemical reactions coupled with heat, mass, and momentum transfer that are essential to providing adequate thermal energy, chemical constituents, and mass flow, respectively, for the process reaction (Stuhler and Wyman 2003). Unless addressed, the limitations arising from heat, mass, and momentum transfer will adversely affect performance. Reaction chemistry sets the upper limit on performance, and, thus, determining reaction kinetics and reaction mechanisms is vital.

A clear need exists to develop deconstruction routes for use with synthetic or chemical catalysts. Biomass deconstruction methods have been developed primarily for use with fermentation (Wyman et al. 2005a). Species that poison biological catalysts do not necessarily poison chemical catalysts. Furfural, hydroxymethylfurfural (HMF), and levulinic acid, for example, are desirable reaction intermediates in the production of liquid alkanes by chemical catalytic processing (Huber et al. 2005, 2006).

Another challenge lies in discovering new biological or chemical catalysts that can efficiently convert the cellulose, hemicellulose, and lignin into intermediates and products. The development of optimized enzymatic and synthetic catalysts that can hydrolyze all of the glycosidic linkages present in biomass remains elusive. The development of enzymes that can tolerate high temperatures and extremes of pH would enable the potential consolidation of pretreatment and enzymatic hydrolysis unit operations. Identifying and testing new modes of enzyme immobilization and scaffolding may also yield operational advantages, with the organized cellulosome (Kosugi et al. 2006) found in anaerobic organisms serving as a bio-inspired design guide. Bi-phasic reaction systems provide a route for the selective production of monomers, such as HMF and furfural, with chemical catalysts (Chheda et al. 2007b; Roman-Leshkov et al. 2006). New solvents, such as ionic liquids that dissolve substantial amounts of cellulose, may permit catalytic hydrolysis of the polysaccharides to component monomers that can be further reacted to fuels (Zhao et al. 2007).

Biomass can also be converted into lower-molecular-weight products and liquid fuels by three thermochemical routes: gasification to syngas (Hashaikeh et al. 2006), pyrolysis or liquefaction to bio-oils (Bridgwater and Peacocke 2000; Elliott et al. 1991; Mohan et al. 2006; Yang et al. 2007), and hydrolysis to sugars and lignin (Wyman et al. 2005b). Catalytic pyrolysis is relatively unexplored, and new catalysts that increase process efficiency should be pursued.

Development of computational tools to describe the dynamics of biomass conversion

The development of computational tools capable of describing the deconstruction and subsequent conversion of biomass with chemical precision over multiple length scales in a dynamic fashion would be significant. Such tools would enable the predictive tailoring of pretreatments and catalysts to specific biomass types using multi-scale computational approaches. Most biomass pretreatment models have focused on the kinetics of lignocellulose depolymerization. These constitutive models are effective for process optimization, but they do not describe the relationship between lignocellulose structure and pretreatment efficiency. Data gathered in the characterization of biomass under static and dynamic conditions would establish the basis for multi-scale computational efforts. For example, a micromechanical model of fluid flow and solute transport through biomass would enable investigations into the effects of microstructure on the material response and transport parameters, such as the fluid permeability and solute mobilities. At the continuum scale, a mixture theory approach for modeling the coupled processes of mechanical deformation, transport and chemical conversion involved in lignocellulose degradation can be employed. The chemical process of material degradation could also be incorporated into mixture theory through mass source and sink terms, which would be modeled on the basis of measured reaction kinetics of the deconstruction process.

Development of molecular understanding of the conversion of biomass-derived products to targeted liquid fuels

A variety of compounds can be produced from biomass, including sugars, furfural, levulinic acid, bio-oils, lignin-derived compounds, triglycerides, glycerol, and syngas. The challenge for converting these biomass-derived oxygenates to a liquid fuel is efficient removal of oxygen from the biomass to produce a liquid product with good combustion and thermochemical properties (Huber and Corma 2007; Huber et al. 2006). Oxygen can be removed as carbon monoxide, carbon dioxide, and water. The general stoichiometry for biomass conversion to liquid fuels (with glucose as the feedstock) is shown in Equation 1, where $C_xH_yO_z$ represents the biofuel produced, which could include alkanes, aromatics, or oxygenated fuels. See the sidebar entitled "What are our biofuel options?" The overall reaction scheme shown in Equation 1 can occur in multiple steps (i.e., gasification of biomass to syngas, followed by water-gas shift and Fischer-Tropsch synthesis) or a single step (i.e., liquefaction). In Equation 1, all of the hydrogen in the final fuel product comes from the feedstock. If an inexpensive source of hydrogen is available, the optimal pathway will have all the oxygen rejected as water. In this case, the energy of the hydrogen is being stored in the biofuel product, and the biofuel can be viewed as a medium for storing hydrogen (Lynd et al. 1991).

$$C_6H_{12}O_6 \rightarrow a\ C_xH_yO_z + b\ CO_2 + c\ CO + d\ H_2O \qquad (1)$$

The conversion of biomass-derived oxygenates can occur in multiple phases, including a solid biomass phase, a catalytic phase (immersed in various phases), an aqueous phase, a condensed organic phase, and a gas phase. The phases in which the chemistry occurs can change during the conversion of biomass into a liquid fuel. In the conversion of sugars to liquid alkanes, for example, sugars are first hydrophilic species, and, as oxygen is removed, are converted into hydrophobic species (Huber et al. 2004, 2005). This phase transformation can be advantageous because catalytic processes can be designed that eliminate expensive separation steps, such as distillation. Bi-phasic processes can also be used whereby one phase absorbs biomass-derived species that would otherwise participate in undesired reactions (Chheda et al. 2007b; Roman-Leshkov 2006).

Design of improved catalytic materials

Traditional catalysts have been designed to convert petroleum-derived feedstocks. These catalysts can serve as starting materials for conversion of biomass-derived feedstocks. For example, supported sulfided cobalt-molybdenum and nickel-molybdenum catalysts, which are traditionally used in the petroleum industry for hydrotreating oil, are being used for hydrotreating biomass-derived feedstocks such as vegetable oils and bio-oils (Elliott and Oasmaa 1991; Elliott et al. 1991; Huber et al. 2007). These catalytic materials show the technical feasibility of producing biofuels with heterogeneous catalysis. However, new catalytic materials are needed that are specifically designed for biomass-derived feedstocks. These feedstocks have different functionalities (i.e., organic acids, aldehydes, ketones) and impurities (i.e., amino acids, sodium, potassium) that are not present in petroleum feedstocks. The synthesis of these new catalytic materials will require a fundamental understanding of the reaction chemistry combined with the ability to synthesize nanostructured catalyzed material at the molecular level.

Development of model biomass-derived oxygenated systems

Biomass-derived feedstocks can be very complex. Bio-oils generated by fast pyrolysis of biomass, for example, can contain up to four different phases and more than 300 compounds (Bridgwater 1994; Bridgwater and Peacocke 2000; Elliott et al. 1991; Huber et al. 2006; Laurent and Delmon 1994a, b; Milne et al. 1997; Mohan et al. 2006). Conversion of these complicated feedstocks can result in an increased number of compounds, making it very difficult to understand the chemistry of biomass conversion. Simplified representative model biomass feedstocks are needed for better understanding of the conversion chemistry. These model biomass feedstocks will result in fewer products and intermediates, allowing a more realistic understanding of the chemistry. Model biomass compounds can also be used for theoretical investigations. Such efforts will yield insight into transition states, reaction intermediates, and catalytic sites involved in the conversion of biomass-derived oxygenates.

Scientific Challenges

Understanding of the structure, composition, and chemistry of biomass

Elucidation of the interdependence between the chemical linkages and structures in biomass will involve the use and development of new advanced analytical instruments. A critical variable in the processing of biomass is the time- and species-dependent chemical composition and structure of the material. There is also a time-dependence on the biomass chemistry and composition during deconstruction that is directly linked to the stage of plant growth at time of harvest (Hamman et al. 2005), harvesting method, storage conditions, and initial size diminution technique. The current approach to dealing with this variability is to implement technologies that are focused on a particular feedstock with a limited number of fuel and chemical outputs. A fundamental understanding of the chemical and structural motifs present in biomass would permit biorefineries to process several feedstock types into multiple outputs.

Analytical techniques capable of these measurements include Raman and infrared (IR) spectroscopy coupled with multivariate analysis (Avgerinos et al. 2005), fluorescence spectroscopy to track lignin content (Esparza-Soto and Westerhoff 2001), porosimetry, thermal analysis, viscometry, and x-ray diffraction to measure cellulose crystallinity (Moharram and Mahmoud 2007). Raman and IR spectroscopies with multivariate analysis can provide quantitative analysis of lignocellulosic biomass including cellulose structure, lignin content, hemicellulose content, and polysaccharide identification, all without the use of tags or dyes. Polarized IR spectroscopy is sensitive to bond orientation and, therefore, can be used to distinguish hydrogen-bonding patterns in the various types of cellulose. Visible and near-IR Raman can also be used to investigate changes in polysaccharides if measures are taken to reduce interference from lignin. Solid-state nuclear magnetic resonance spectroscopy (Freitas et al. 2001), used in cross polarization-magic angle spinning mode, is sensitive to variations in polysaccharide conformations but is not sensitive enough to detect the relatively rare covalent crosslinks. Nuclear magnetic resonance relaxation experiments can reveal the relative mobilities of components in a complex mixture, as well as the relative mobilities of main chains and side-chain groups. Drying of samples for analysis may collapse biomass pores and/or cause aggregation of the microfibrils that may result in artificial variation in the observed

X-ray and Neutron Scattering and Diffraction in the Analysis of Biomass

For biomass to be efficiently converted into fuels and chemicals, a fundamental understanding of the structure and composition of the materials must be developed. This understanding will aid in the design of next-generation catalysts and processes that can efficiently convert biomass (Figure 37). X-ray and neutron scattering and diffraction can be used to provide detailed information about the structure and dynamics of biomass across time and length scales that range from pico- to nanosecond resolution and from 1-10,000 Angstroms spatial resolution, respectively. These techniques can complement established analytical techniques such as electron microscopy, optical microscopy, spectroscopy, and porosimetry. These approaches enable the precise determination of the structure and composition of complex or composite materials and allow individual components to be distinguished in situ according to their bulk hydrogen contents. For example, progress has been made in recent years using x-ray and neutron diffraction to determine detailed structures of the various forms of crystalline cellulose.

Neutron and x-ray diffraction can be used to determine the detailed crystal structure and hydrogen-bonding system in cellulose. X-ray diffraction can be used to determine the positions of the carbon and oxygen atoms present in biomass. Neutron and x-ray scattering and diffraction may also establish other characteristics of lignocellulosic materials, including crystalline structures, microfibril size, and extent of fibrillation. By the use of deuterated solvents, crystalline fibers can be prepared in which all the -OH groups in the crystalline unit cell are replaced by -OD. From neutron diffraction data from both samples, the positions of the hydrogen atoms can be determined.

Neutron scattering can be used to establish the extent of hydration of crystalline fibers, which may correlate with enzyme binding sites and thus hydrolysis rates. When enzymes can be obtained enriched in deuterium, the quantity of bound enzymes could be determined in the presence of other species by neutron scattering. Similarly, knowledge of when certain cellulose binding domains in cellulases bind to one of these phases more readily than the other would be helpful. Another potentially fruitful area of research is diffraction investigations performed at different stages of pretreatment and enzymatic hydrolysis.

In lignocellulosic materials, lignin will scatter neutrons differently from cellulose and hemicelluose, so the scattering signal and structure of each component can be distinguished and determined. Neutron scattering is thus a powerful tool for characterization and analysis of complex structure-function and interfacial relationships between mixed membrane, polymer, and other macromolecular components, providing insight and understanding from the atomic to cellular levels. This new information is expected to provide unprecedented insight into the conversion of biomass into biofuels.

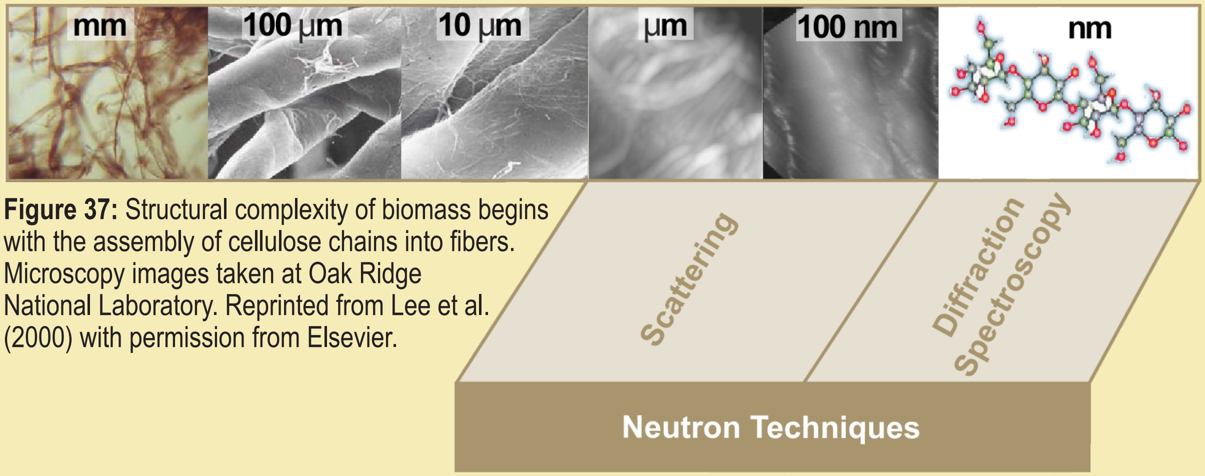


Figure 37: Structural complexity of biomass begins with the assembly of cellulose chains into fibers. Microscopy images taken at Oak Ridge National Laboratory. Reprinted from Lee et al. (2000) with permission from Elsevier.

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microfibril sizes. To eliminate this effect, high-pressure cryo-transmission electron microscopy (Serp et al. 2002), confocal-atomic force microscopy (Filip et al. 2006), in-situ atomic force microscopy (Zhang et al. 2007), and hyperspectral confocal imaging (Timlin et al. 2006) can be used to image biomass with minimal feature damage during sample preparation. Neutron and x-ray scattering and diffraction techniques may offer new insight into the static and dynamic structural components of biomass.

Complete and efficient deconstruction of targeted chemical linkages in biomass

Selective thermal deconstruction of biomass. In pyrolysis, biomass is heated in the absence of air to produce a mixture of solid, liquid, and gaseous products depending on the pyrolysis temperature and residence time. When biomass is heated at low temperatures and for long times (i.e., slow pyrolysis), charcoal is the dominant product. Gases are up to 80 wt% of the product when biomass is heated at temperatures above 700 °C. Liquid products are up to 75 wt% moisture-free organic liquids on a dry feed basis by fast or flash pyrolysis in which biomass is rapidly heated to temperatures ranging from 400-650 °C with residence times of typically less than 2 s (Chheda et al. 2007b; Huber et al. 2004; Roman-Leshkov et al. 2006). Although flash pyrolysis can produce bio-oils from various feedstocks, these oils are acidic, chemically unstable, and require upgrading.

Liquefaction of biomass produces a bio-oil that has a higher heating value and is more stable than bio-oils produced by flash pyrolysis. Liquefaction involves deconstruction of the biomass at temperatures ranging from 250-450 °C at high pressures (e.g., 50 atm), usually in the presence of a catalyst (Chheda et al. 2007b; Huber et al. 2004; Roman-Leshkov et al. 2006). Many empirical investigations have been conducted on liquefaction and flash pyrolysis, but surprisingly few have been conducted on the chemistry involved in the liquefaction and flash pyrolysis processes.

Better control of the pyrolysis reactions is required so that biomass can be directly decomposed into a simple set of usable products such as sugars and phenolics. Many investigations of fast pyrolysis have been conducted, but only a limited number have been conducted of catalyzed fast pyrolysis. Investigations of alkali and alkaline earth metals ion-exchanged or impregnated into biomass have shown that pyrolysis mechanisms of carbohydrates are altered and that higher char yields and lower tar yields are observed (Evans and Milne 1987a, b). These catalysts do not seem to impact the degradation of lignin, and an opportunity exists to develop new selective catalysts for this process with greater control over the reaction products.

Acid hydrolysis of biomass. The efficient cleavage of targeted chemical links is a major goal in the conversion of biomass. Acid hydrolysis of the cellulosic components of biomass is one method to achieve the cleavage of targeted C–O–C bonds for glucose production. This route has been extensively investigated for sugar production, which is then used to make ethanol, by use of mineral acid catalysts (e.g., sulfuric acid). In producing ethanol, the challenge is to maximize glucose formation and minimize glucose degradation reactions, which produce HMF, furfural, and levulinic acid. This challenge is great because glucose is highly reactive, and the maximum glucose yield for acid hydrolysis with mineral acids has only approached 75 percent. In contrast, the glucose yield for enzymatic hydrolysis can approach 95 percent (Yang et al. 2007). However, acid hydrolysis may be an effective pretreatment for biomass conversion technologies that use heterogeneous catalysis, such as aqueous-phase processing (Huber and

Dumesic 2006; Mohan et al. 2006; Valenzuela et al. 2006), or technologies that use glucose degradation byproducts. Acid hydrolysis combined with other catalytic technologies is promising for production not only of sugars, but also other monomers that can serve as fuel precursors, including levulinic acid, 5-HMF, and furfural (Yang et al. 2007). These compounds are all highly reactive. The chief scientific challenges for acid hydrolysis are selectivity and maximizing yields of targeted products without further reactions. Several recent approaches have demonstrated how higher yields can be achieved for targeted monomers by acid hydrolysis. These approaches include the use of ionic liquids as lignocellulose solvents, bi-phasic catalytic systems, solid acid catalysts, supercritical treatments, and carboxylic acids (Bootsma and Shanks 2007; Huber et al. 2006; Lynd et al. 1991). Catalysts and catalytic processes need to be designed that have high reactivity for cellulose depolymerization and low subsequent reactivity toward the targeted monomer, or bi-phasic systems that can extract the targeted compounds before they react further.

Enzymatic hydrolysis of biomass. The first step in the enzymatic hydrolysis of biomass is pretreatment, which is essential to produce high glucose yields from lignocellulose by enzymatic hydrolysis. Pretreatment is typically a thermochemical treatment of the biomass with various acids, solvents, or other chemicals to induce structural and compositional changes of the biomass to make it easier for enzymes to attack. Several structural and compositional attributes of biomass are thought to influence the enzymatic hydrolysis of cellulose to glucose. These include cellulose crystallinity, lignin levels, hemicellulose removal, and the presence of acetyl groups. However, the complex biomass structure makes understanding the relative importance of these features and their roles difficult. For example, removing hemicellulose also removes acetyl groups and usually alters the form of the residual lignin (Yang and Wyman 2004). Lignin binds cellulose fibers to form structures with excellent mechanical properties and provides protection against pathogens and microorganisms. Moreover, lignin reduces the ability of catalysts or enzymes to access and cleave cellulose. Various investigators have reported improved enzymatic cellulose hydrolysis with pretreatments that solubilized and removed lignin (Liao et al. 2005), although differences have been reported in the degree of lignin removal needed (Oehgren et al. 2007). Hemicellulose is also altered in many lignin removal techniques as it is typically linked chemically to the lignin through ester bonds (Parajo et al. 1993).

To develop enzymes with these improved characteristics for processing, techniques such as directed enzyme evolution (Moore and Arnold 1997; Turner 2003) can be employed. These rely on the availability of a range of reactants, including colorimetric, fluorometric, and native molecules, for rapid characterization of enzyme-reactant specificity. Advanced spectroscopic methods are needed for rapid analysis of the products and intermediates of the action of one or more evolved enzymes on model and authentic biopolymers. Analytical methods to follow the reaction kinetics that operate on time-scales from microseconds to hours would be especially useful. A diverse set of enzymes with different substrate specificities arising from direct evolution approaches is desirable to handle the variety of hemicellulose structures produced in nature by the grasses, hardwoods, and softwoods that constitute the current and next-generation energy crops.

Understanding the mechanism of conversion of biomass-derived oxygenates to fuels

Conversion of biomass-derived oxygenates to liquid fuels can involve a number of reactions including the following: hydrolysis, isomerization, reforming (C–C bond cleavage), decarbonylation, decarboxylation, aldol condensation (and other C–C coupling reactions), hydrogenation, selective oxidation, olefin oligomerization, water-gas shift, and carbon monoxide hydrogenation (Chheda et al. 2007a). These reactions can involve many different types of catalysts. Bifunctional catalysis can also be used (Barrett et al. 2006; Huber et al. 2005). This chemistry can occur in liquid phases, organic phases, on catalytic surfaces, and in the gas phase. Developing a mechanistic understanding of the key reactions and then understanding how these reactions can be combined are important scientific challenges. Addressing these challenges would help the biofuel industry design improved catalytic materials and processes.

Catalytic processing of biomass-derived oxygenates in the liquid phase. Most biomass-derived oxygenates such as sugars have low thermal stabilities, making it difficult to process them in the gas phase. Processing biomass-derived oxygenates in the liquid phase is particularly advantageous because fuels can be produced directly without undesired coke formation (Cortright et al. 2002; Davda et al. 2005; Huber and Dumesic 2006; Huber et al. 2003). Liquid-phase processing also has higher thermal efficiencies than gas-phase processing, because the large amounts of water present in biomass-derived oxygenates do not need to be vaporized. However, several scientific challenges exist with liquid-phase catalytic processing. Most solid catalysts have been designed for gas-phase petroleum or petrochemical feedstocks. Liquid-phase conversion can cause leaching of various components as well as catalyst stability problems (Elliott et al. 1993; Shabaker et al. 2003, 2004). However, liquid-phase processing also presents many new opportunities to use chemistry that cannot be used in the gas phase. Bi-phasic systems can be designed whereby solvents can extract the desired chemical species (Chheda et al. 2007b). The ionic strength of the liquid, pH, and solvent effects can all be used to tune the chemistry. The low temperature of liquid-phase processing also allows the utilization of functionalized catalysts that are not stable in the presence of gas-phase reactants.

Catalytic processing of biomass-derived oxygenates in the gas phase. Gas-phase processing of biomass-derived oxygenates is particularly challenging because of the high levels of coke and char formation. However, catalysis can be used to minimize coke and char formation. For example, researchers have demonstrated how catalysis can be used to make clean syngas (without any coke or char formation) from biomass-derived feedstocks (Deluga et al. 2004; Salge et al. 2006). This process occurs in reactors that have residence times of milliseconds. Tomishige et al. (2004) have observed that addition of $Rh/CeO_2/SiO_2$ catalysts to a gasification reactor can reduce the coke yield (on a carbon basis) from 40 percent to less than 1 percent. Knowledge of the coke-forming mechanisms will allow the development of low-coke-forming catalysts or catalysts that can readily be regenerated for sufficient life for eventual technological deployment. The knowledge of the mechanism of coke formation will also enable the design of reactors that minimize coke formation.

Potential Scientific Impact

Understanding biomass to enable tailored deconstruction and conversion technologies for a wide range of biomass types

Development of molecular-scale understanding of the deconstruction of biomass and the conversion of the products from this process to fuels would enable the prediction of how a particular biomass source might be best processed. Similar knowledge has been developed for processing petroleum but is available for biomass processing in only a very rudimentary form. Knowledge of how catalyst structure and composition affect the kinetics of individual elementary processes will be invaluable for understanding of how these properties can be adjusted to achieve maximum performance in terms of activity and selectivity for both high- and low-temperature processing.

Multi-scale computational modeling to enable design and construction of advanced catalysts

Establishing a fundamental understanding of the mechanisms catalysts employ for the cleavage of targeted chemical moieties within biomass will increase the capacity to improve reactant specificity, turnover number, and stability in various environments. A broad array of well-understood catalysts could then be available to convert the diverse regional plant feedstocks into sugars for further processing into fuels and chemicals by application of pretreatment regimens that have variations in temperature, pH, and other properties during or after the pretreatment process. Fundamental understanding of the chemistry underlying the function of enzymes and non-enzymatic catalysts under various conditions would assist in the design of better solid, soluble, or bio-inspired synthetic catalysts.

Potential Impact on Catalysis for Energy Applications

Development of multiple product biorefineries capable of processing several feedstocks and consolidated unit operations

The United States has the potential to sustainably harvest 1.3 billion tons of biomass annually (Perlack et al. 2005), which could support ethanol production at the level of more than 60 billion gallons/year, enough to replace 30 percent of the nation’s current gasoline use. The major obstacles to commercialization, in terms of performance and cost, are found in the cellulose deconstruction process. Establishing an optimized and universally applicable pretreatment technology would dramatically decrease the costs associated with cellulosic biorefineries. Catalysts designed and engineered for the specific linkages in biomass that are the most recalcitrant to deconstruction would positively impact process yields and decrease costs. This combination of effects makes this research particularly important.

Combined advances in plant breeding and engineered deconstruction technologies

The knowledge developed in the fundamental characterization of biomass and the identification of the chemical linkages that make it difficult to convert will positively impact the development of engineered plants specifically tailored for fuel conversion. These engineered plants are envisioned to (1) contain weak links within the cell wall components that make them more amenable to deconstruction, (2) have certain chemical, genetic, and/or environmental triggers that initiate the deconstruction process, and/or (3) have been engineered so that certain structural and cross-linking elements no longer exist.

References

Avgerinos, E. S., E. Billa, and G. Koukios. 2005. “Correlating Structural and Functional Properties of Lignocellulosics and Paper by Fluorescence Spectroscopy and Chemometrics,” *Polysaccharides* **2**:267-280.

Barrett, C. J., J. N. Chheda, G. W. Huber, and J. A. Dumesic. 2006. “Single-reactor Process for Sequential Aldol-Condensation and Hydrogenation of Biomass-derived Compounds in Water,” *Applied Catalysis, B: Environmental* **66**:111-118.

Bootsma, J. A., and B. H. Shanks. 2007. “Cellobiose Hydrolysis Using Organic-Inorganic Hybrid Mesoporous Silica Catalysts,” *Applied Catalysis, A: General* **327**:44-51.

Bridgwater, A. V. 1994. “Catalysis in Thermal Biomass Conversion,” *Applied Catalysis, A: General* **116**:5-47.

Bridgwater, A. V., and G. V. C. Peacocke. 2000. “Fast Pyrolysis Processes for Biomass,” *Renewable and Sustainable Energy Reviews* **2000**(4):1-73.

Chheda, J. N., G. W. Huber, and J. A. Dumesic. 2007a. “Liquid-phase Catalytic Processing of Biomass-derived Oxygenated Hydrocarbons to Fuels and Chemicals,” *Angewandte Chemie International Edition* **46**:7164-7183.

Chheda, J. N., Y. Roman-Leshkov, and J. A. Dumesic. 2007b. “Production of 5-hydroxymethylfurfural and Furfural by Dehydration of Biomass-derived Mono- and Poly-saccharides,” *Green Chemistry* **9**:342-350.

Cortright, R. D., R. R. Davda, and J. A. Dumesic. 2002. “Hydrogen from Catalytic Reforming of Biomass-Derived Hydrocarbons in Liquid Water,” *Nature* **418**(6901):964-967.

Davda, R. R., J. W. Shabaker, G. W. Huber, R. D. Cortright, and J. A. Dumesic. 2005. “A Review of Catalytic Issues and Process Conditions for Renewable Hydrogen and Alkanes by Aqueous-Phase Reforming of Oxygenated Hydrocarbons over Supported Metal Catalysts,” *Applied Catalysis B, Environmental* **56**:171-176.

Deluga, G. A., J. R. Salge, L. D. Schmidt, and X. E. Verykios. 2004. “Renewable Hydrogen from Ethanol by Autothermal Reforming,” *Science* **303**(5660):993-997.

Donaldson, L. 2007. “Cellulose Microfibril Aggregates and Their Size Variation with Cell Wall Type,” *Wood Science and Technology* **41**(5):443-460.

Elliott, D. C., D. Beckman, A. V. Bridgwater, J. P. Diebold, S. B. Gevert, and Y. Solantausta. 1991. “Developments in Direct Thermochemical Liquefaction of Biomass: 1983-1990,” *Energy and Fuels* **5**:399.

Elliott, D. C., L. J. Sealock Jr., and E. G. Baker. 1993. “Chemical Processing in High-Pressure Aqueous Environments. 2. Development of Catalysts for Gasification,” *Industrial Engineering Chemistry Research* **32**:1542-1548.

Elliott, D. C., and A. Oasmaa. 1991. “Catalytic Hydrotreating of Black Liquor Oils,” *Energy and Fuels* **5**:102-410.

Esparza-Soto, M., and P. K. Westerhoff. 2001. “Fluorescence Spectroscopy and Molecular Weight Distribution of Extracellular Polymers from Full-Scale Activated Sludge Biomass,” *Water Science and Technology* **43**(6):87-95.

Evans, R. J., and T. A. Milne. 1987a. “Molecular Characterization of the Pyrolysis of Biomass. 1. Fundamentals,” *Energy and Fuels* **1**:123-137.

Evans, R. J., and T. A. Milne. 1987b. “Molecular Characterization of the Pyrolysis of Biomass. 2. Applications,” *Energy and Fuels* **1**:311-319.

Faulon, J. L., G. A. Carlson, and P. G. Hatcher. 1994. “A Three-Dimensional Model for Lignocellulose from Gymnospermous Wood,” *Organic Geochemistry* **21**(12):1169-1179.

Filip, D., V. I. Uricanu, M. H. G. Duits, D. Van den Ende, J. Mellema, W. G. Agterof, and F. Mugele. 2006. “Microrheology of Aggregated Emulsion Droplet Networks, Studied with AFM -CSLM,” *Langmuir* **22**(2):560-574.

Freitas, J. C. C., T. J. Bonagamba, and F. G. Emmerich. 2001. “Investigation of Biomass- and Polymer-based Carbon Materials Using ^{13}C High-resolution Solid-state NMR,” *Carbon* **39**(4):535-545.

Hamman, K. D., R. L. Williamson, E. D. Steffler, C. T. Wright, J. R. Hess, and P. A. Pryfogle. 2005. “Structural Analysis of Wheat Stems,” *Applied Biochemistry and Biotechnology* **121** (1-3):71-80.

Hashaikeh, R., I. S. Butler, and J. A. Kozinski. 2006. “Selective Promotion of Catalytic Reactions during Biomass Gasification to Hydrogen,” *Energy & Fuels* **20**(6):2743-2747.

Huber, G. W., and A. Corma. 2007. “Synergies Between Bio- and Oil Refineries for the Production of Fuels from Biomass,” *Angewandte Chemie International Edition* **46**:7184-7201.

Huber, G. W., and J. A. Dumesic. 2006. “An Overview of Aqueous-phase Catalytic Processes for Production of Hydrogen and Alkanes in a Biorefinery,” *Catalysis Today* **111**(1-2):119-132.

Huber, G. W., J. N. Chheda, C. J. Barrett, and J. A. Dumesic. 2005. “Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates,” *Science* **308**: 1446-1450

Huber, G. W., R. D. Cortright, and J. A. Dumesic. 2004. "Renewable Alkanes by Aqueous-phase Reforming of Biomass-derived Oxygenates," *Angewandte Chemie International Edition* **43**:1549-1551.

Huber, G. W., S. Iborra, and A. Corma. 2006. "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts and Engineering," *Chemical Reviews* **106**:4044-4098.

Huber, G. W., P. O'Connor, and A. Corma. 2007. "Hydrotreating of Vegetable Oils and Vegetable Oil-Vacuum Gas-Oil Mixtures," *Applied Catalysis A: General* **329**:120-129.

Huber, G. W., J. W. Shabaker, and J. A. Dumesic. 2003. "Raney Ni-Sn Catalyst for H_2 Production from Biomass-Derived Hydrocarbons," *Science* **300**:2075-2077.

Kosugi, A., T. Arai, and R. H. Doi. 2006. "Degradation of Cellulosome-produced Cello-Oligosaccharides by an Extracellular Non-cellulosomal β-glucan Glucohydrolase, BglA, from *Clostridium cellulovorans*," *Biochemical and Biophysical Research Communications* **349**(1):20-23.

Laurent, E., and B. Delmon. 1994a. "Influence of Water in the Deactivation of a Sulfided NiMo/Al_2O_3 Catalyst during Hydrodeoxygenation," *Journal of Catalysis* **146**:281-291.

Laurent, E., and B. Delmon. 1994b. "Study of the Hydrodeoxygenation of Carbonyl, Carboxylic and Guaiacyl Groups over Sulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 Catalysts. I. Catalytic Reaction Schemes," *Applied Catalysis A: General* **109**:77-96.

Liao, W. Z. Wen, S. Hurley, Y. Liu, C. Liu, and S. Chen. 2005. "Effects of Hemicellulose and Lignin on Enzymatic Hydrolysis of Cellulose from Dairy Manure," *Applied Biochemistry and Biotechnology* **124**:1017-1030.

Lee, I., B. R. Evans, and J. Woodward. 2000. "The Mechanism of Cellulase Action on Cotton Fibers: Evidence from Atomic Force Microscopy," *Ultramicroscopy* **82**, 213-221.

Lynd, L. R., J. H. Cushman, R. J. Nichols, and C. E. Wyman. 1991. "Fuel Ethanol from Cellulosic Biomass," *Science* **251**:1318-1323.

Milne, T. A., F. Agblevor, M. Davis, S. Deutch, and D. Johnson. 1997. "A Review of the Chemical Composition of Fast Pyrolysis Oils from Biomass." In *Developments in Thermalchemical Biomass Conversion,* eds. A. V. Bridgwater, D. G. B. Boocock, Blackie Academic and Professional: London, pp. 409-424.

Mohan, D., C. U. Pittman, and P. H. Steele. 2006. "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review," *Energy and Fuels* **20**:848-889.

Moharram, M. A., and O. M. Mahmoud. 2007. "X-Ray Diffraction Methods in the Study of the Effect of Microwave Heating on the Transformation of Cellulose I into Cellulose II during Mercerization," *Journal of Applied Polymer Science* **105**(5):2978-2983.

Moore, J. C., and F. H. Arnold. 1997. "Directed Evolution of Enzymes," *Proceedings from the Genetic and Molecular Biology of Industrial Microorganisms (GMBIM) Conference, Developments in Industrial Microbiology Series*, Fairfax, Virginia, Society for Industrial Microbiology **34**:67-70.

Oehgren, K., R. Bura, J. Saddler, and G. Zacchi. 2007. "Effect of Hemicellulose and Lignin Removal on Enzymatic Hydrolysis of Steam Pretreated Corn Stover," *Bioresource Technology* **98(**13):2503-2510.

Parajo, J. C., J. L. Alonso, and D. Vazquez. 1993. "On the Behavior of Lignin and Hemicelluloses During the Acetosolv Processing of Wood," *Bioresource Technology* **46**(3):233-40.

Perlack, R. D., L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, and D. C. Erbach. 2005. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at: http://www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf

Roman-Leshkov, Y., J. N. Chheda, and J. A. Dumesic. 2006. "Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose," *Science* **312**(5782):1933-1937.

Salge, J. R., B. J. Dreyer, P. J. Dauenhauer, and L. D. Schmidt. 2006. "Renewable Hydrogen from Nonvolatile Fuels by Reactive Flash Volatilization," *Science* **314**(5800):801-804.

Serp, D., M. Mueller, U. Von Stockar, and I. W. Marison. 2002. "Low-Temperature Electron Microscopy for the Study of Polysaccharide Ultrastructures in Hydrogels. I. Theoretical and Technical Considerations," *Biotechnology and Bioengineering* **79**(3):243-252.

Shabaker, J. W., G. W. Huber, R. R. Davda, R. D. Cortright, and J. A. Dumesic. 2003. "Aqueous-phase Reforming of Ethylene Glycol over Supported Platinum Catalysts," *Catalysis Letters* **88**:1-8.

Shabaker, J. W., G. W. Huber, and J. A. Dumesic. 2004. "Aqueous-phase Reforming of Oxygenated Hydrocarbons Over Sn-Modified Ni Catalysts," *Journal of Catalysis* **222**:180-191.

Stuhler, S. L., and C. E. Wyman. 2003. "Estimation of Temperature Transients for Biomass Pretreatment in Tubular Batch Reactors and Impact on Xylan Hydrolysis Kinetics," *Applied Biochemistry and Biotechnology* **105**(1-3):101-114.

Timlin, J. A., L. T. Nieman, H. D. T. Jones, M. B. Sinclair, D. M. Haaland, and J. F. Guzowski. 2006. "Imaging Multiple Endogenous and Exogenous Fluorescent Species in Cells and Tissues," *Proceedings of SPIE-The International Society for Optical Engineering*, 6088 (Imaging, Manipulation, and Analysis of Biomolecules, Cells, and Tissues IV), 608805/1-608805/10.

Tomishige, K., M. Asadullah, and K. Kunimori. 2004. "Syngas Production by Biomass Gasification Using Rh/CeO_2/SiO_2 Catalysts and Fluidized Bed Reactor," *Catalysis Today* **89**(4):389-403.

Turner, N. J. 2003. "Directed Evolution of Enzymes for Applied Biocatalysis," *Trends in Biotechnology* **21**(11):474-8.

Valenzuela, M. B., C. W. Jones, and P. K. Agrawal. 2006. "Batch Aqueous-Phase Reforming of Woody Biomass," *Energy and Fuels* **20**(4):1744-1752.

Wyman, C. E., B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, and Y. Y. Lee. 2005a. "Coordinated Development of Leading Biomass Pretreatment Technologies," *Bioresource Technology* **96**:1959-1966.

Wyman, C. E., S. R. Decker, M. E. Himmel, J. W. Brady, C. E. Skopec, and L. Viikari. 2005b. “Hydrolysis of Cellulose and Hemicellulose.” In *Polysaccharides,* 2nd ed., ed. S. Dumitriu, Marcel Dekker, Inc.: New York, pp. 995-1035.

Yang, B., and C. E. Wyman. 2004. “Effect of Xylan and Lignin Removal by Batch and Flowthrough Pretreatment on the Enzymatic Digestibility of Corn Stover Cellulose,” *Biotechnology and Bioengineering* **86**(1):88-98.

Yang, H., R. Yan, H. Chen, L. Hanping, H. Dong, and C. Zheng. 2007. “Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis,” *Fuel* **86**(12-13):1781-1788.

Zhang, L. J., Y. Zhang, R. J. Zhang, and X. S. Feng. 2007. “In Situ AFM Investigations on Degradation of Self-Assembled Monolayers on Mica: Effect of Humidity,” *Colloids and Surfaces A, Physicochemical and Engineering Aspects* **293**(1-3):195-200.

Zhao, H., J. E. Holladay, H. Brown, and Z. C. Zhang. 2007. “Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural,” *Science* **316**:1597-1600.

PHOTO- AND ELECTRO-DRIVEN CONVERSION OF CARBON DIOXIDE AND WATER

Abstract

Catalysis to convert carbon dioxide to liquid fuels using solar and electrical energy is a critical global challenge. Meeting this challenge will positively impact the earth's carbon balance by allowing recycle of carbon dioxide as fuel. Practical electrical or solar conversion to chemical energy necessarily awaits the development of efficient catalysts for the reduction of carbon dioxide and the oxidation of water to oxygen. New catalysts must employ durable and abundant materials, as the best catalysts today often use expensive and rare metals such as platinum or iridium. New catalysts will involve multiple site structures and will drive the multiple electron- and hydrogen-transfer reactions required to make fuels from carbon dioxide and water. Detailed theoretical and physical knowledge must be developed as the new synthetic and mechanistic investigations proceed toward their ultimate goals of making available scalable catalysts to convert carbon dioxide and water. The influences of complex reaction environments, site-to-site communication, and catalyst regeneration will figure prominently in catalyst development. Advances in artificial systems can be expected to be influenced by knowledge gained from the biology of photosynthesis.

Executive Summary

Efficient conversion of carbon dioxide to fuels and useful chemicals using energy from renewable sources is a major challenge to the catalysis science community. Impediments to realizing viable technologies lie not only in the absence of scientific knowledge about carbon dioxide catalytic conversion, but also in challenges associated with driving such thermodynamically uphill reactions with "non-sacrificial" electron donors such as water. Major scientific challenges to the realization of this goal include the following:

1. developing efficient, inexpensive, and durable catalytic systems for carbon dioxide reduction and water oxidation using electrical and solar energy
2. establishing design principles to synthesize catalytic assemblies and molecular systems that facilitate complex, multi-electron and atom/ion transfer events
3. determining detailed knowledge of the free energy landscapes for these coupled thermal and non-thermal catalytic reactions.

Basic science aimed at these challenges is expected to result in new fundamental knowledge and expertise crucial for the eventual development of efficient, durable, and scalable catalyst systems to convert carbon dioxide into fuels and useful chemicals.

Scientific Challenges

Control of multi-electron and atom/ion transfer events

Multi-electron reduction of carbon dioxide producing highly reduced organic molecules such as methanol (CH_3OH) and methane (CH_4) is a critical goal. The coupling of carbon dioxide reduction catalysts to catalysts that can homologate reduced carbon and produce higher-molecular-weight fuels (such as butanol that can be transported via the nation's present infrastructure for liquid fuel delivery) is a priority research area. Understanding and controlling the details of the stepwise multi-electron multi-H atom transfer conversion of carbon dioxide to methanol or methane is essential (e.g., as in: $M\text{-}CO_2 \rightarrow [M\text{-}COOH]^+ \rightarrow [M\text{-}CO]^{2+} \rightarrow [M\text{-}CHO]^+ \rightarrow [M\text{-}CH_2OH]^+$). The energy-efficient reduction of carbon dioxide will demand catalysts that operate near thermodynamic potentials with high rates of chemical and electrochemical reactions. The multiple electron and H-atom transfers involved in the reduction of carbon dioxide to fuels will require complex catalysts and catalyst assemblies including hybrid catalysts, hierarchal nanostructured systems, and multiple-site catalysts that work in concert to achieve the overall carbon dioxide reduction process. The development of new catalysts and mechanistic knowledge required for the reduction of carbon dioxide to fuels will also benefit from understanding of biology. The production of carbohydrates from carbon dioxide in natural photosynthesis involves dark (thermal) reactions, and many of the details of catalysis of these processes are directly relevant to artificial systems. Nature's carbon monoxide dehydrogenases are the only catalysts known that are efficient in catalyzing the reduction of carbon dioxide to carbon monoxide. This fact underscores the importance of developing catalysts that operate at the thermodynamic potentials for the processes involved.

Understanding how to achieve and control water oxidation to oxygen is a great challenge in science and equally relevant to carbon dioxide conversion. Because the ultimate products of fossil fuel combustion are carbon dioxide and water, the conversion of these stable molecules back into fuels involves thermodynamically uphill reactions that remove the oxygen atoms. The oxidative side of the simplest reactions for converting carbon dioxide and water into fuels consists of oxygen generation from water. The 4-electron, 4-proton oxidation of water to oxygen is also the oxidative side of biological photosynthesis. The specific details of the multiple electron and proton transfers and the O–O bond forming reaction in either natural or artificial systems are subjects in need of intense investigation. The realization of efficient systems for either carbon dioxide conversion or water oxidation must await the solution of this problem.

Catalysts for efficient carbon dioxide reduction coupled to electrical and solar energy

The design and synthesis of catalyst systems for efficient carbon dioxide reduction are major scientific challenges. Because multiple electron and H-atom or ion transfers are required, the catalysts are likely to have complex topologies that are hybrids of molecular and solid-state materials, hierarchal architectures, and multiple sites that work in concert to achieve the overall carbon dioxide reduction process. In photochemical systems, efficiency requires a vectorial arrangement of the oxidation and reduction units across a barrier or membrane to prevent destructive cross and back reactions. This arrangement can be considered a first-order example of the hierarchical architecture (see sidebar). Ultimately, an efficient catalyst system may require positioning active centers and reactive species over a range of length scales from sub-nanometer

Conceptual Model of a Multifunctional Photocatalyst for the Reduction of Carbon Dioxide to Methanol Using Water as the Electron Donor

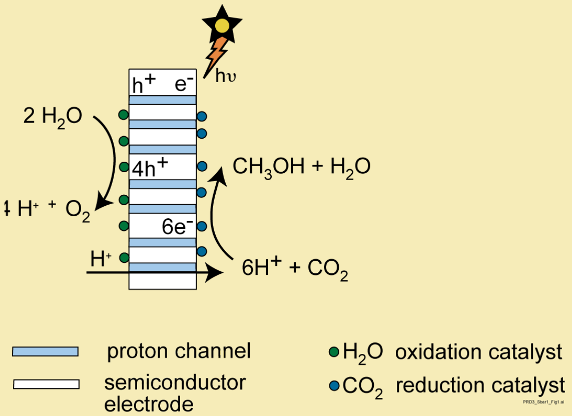

Figure 38: Conceptual model of photocatalyst to reduce carbon dioxide to methanol. (Model courtesy of Dr. Dan L. Dubois, Pacific Northwest National Laboratory).

The reduction of carbon dioxide to simple fuels is a multi-electron transfer process that requires a kinetically balanced oxidation half reaction to achieve efficiency. In this conceptual model (Figure 38), a semiconducting electrode is synthesized with channels that permit proton communication between cells containing half-reaction catalysts, but do not permit reactants or products through. Molecular catalysts for water oxidation and carbon dioxide reduction are anchored to opposite sides of the electrode. The electrode is designed to absorb solar radiation and facilitate diffusion of resulting point charges to the respective molecular catalysts responsible for the carbon dioxide reduction and water oxidation chemistry. Although this catalytic system is conceptually simple, there are significant scientific challenges hindering the achievement of high activity with molecular systems anchored to a porous semiconductor material that absorbs visible light and permits only proton communication through its pores.

to microns. The stability of catalysts is also a critical issue, because inherently reactive, and hence potentially destructive, species are required for the activation of the ultra-stable carbon dioxide molecule. These design principles have their inspiration in biology. However, in biology, the catalytic centers are also embedded in dynamic media, which adapt almost perfectly to the series of changes in the reacting molecule to facilitate the transformation under near-equilibrium conditions. In electrocatalytic terms, this is equivalent to operating at very low overpotential and, thus, very high efficiency. The successful construction of such complex, organized catalytic systems using robust, abundant, and inexpensive reagents will require the development of approaches beyond the current state of synthesis capabilities.

Detailed knowledge of free-energy landscapes for coupled thermal and non-thermal catalytic reactions

The ability to rationally design scalable and durable catalysts that efficiently carry out the photo- and electro-chemical conversion of carbon dioxide and water into fuels and chemicals will require fundamental understanding of the mechanisms that control carbon dioxide reduction and water oxidation. Very little, however, is known about the elementary pathways, their corresponding kinetics, or how they control the reaction chemistry. Detailed knowledge about the overall potential energy surface is obscured because of the complexity of the reaction environment and because many of the bond-forming and -breaking processes involve simultaneous proton- and electron-transfer steps. Controlling these steps will require the specific delivery of charge at a specific potential into the reactant states of the catalytic reaction. The spectroscopic resolution of the transient catalytic intermediates involved in the mechanisms that control photo- and electro-chemical activation has not been possible because of their very short lifetimes and low concentrations as well as difficulty in resolving intermediates spectroscopically. The characterization of surface intermediates under working conditions will require the development and application of sensitive ultrafast spectroscopic and pump-probe scattering methods.

Although in-situ spectroscopy can be used to begin to establish the intermediates that form and their possible reaction paths, the full realization of the potential energy surface will require a close coupling and integration with theory. Ab-initio methods can be used to calculate the overall reaction energies and activation barriers for important reactions that occur for gas-phase model catalytic systems. Subsequently, these methods can be used to construct overall potential energy surfaces. Simulating reaction conditions that explicitly treat the effects of surface coverage, solution, electrolyte, electrochemical potential, and appropriate nanoscale environments, including the effects of ligands, particle size, and morphology, presents significant challenges. The ability to establish free-energy landscapes for excited state systems presents significant challenges for theory as well as experiment. Ultrafast in-situ techniques and high-level ab-initio methods exist that can begin to probe excited states; however, the need to follow the dynamics and establish excited state potential energy surfaces presents a tremendous challenge.

Multidisciplinary approach needed to realize catalytic systems

The ability to replace existing energy-production methods with renewable and other carbon-neutral processes on a global scale is likely to be one of the greatest challenges facing humanity in the 21st century. In this context, scientific activities that support the discovery of new catalysts and catalytic structures for carbon dioxide reduction and water oxidation are prototypical examples of basic science directed at meeting a critical human need.

It is encouraging that natural photosynthetic systems accomplish photo-driven conversion of carbon dioxide and water, albeit at low solar efficiencies. Furthermore, many aspects of photosynthesis have been mimicked in both homogeneous and heterogeneous artificial systems. However, mimicking nature in a cost-effective artificial system that can be applied on a global scale is a complex and unmet scientific challenge. Researchers working on this problem are in agreement that progress in developing catalysts for the multi-electron, multi-proton transformation of carbon dioxide and water into stable yet energy-rich molecules is absolutely critical. Moreover, basic understanding of how to embed catalytic centers effectively into energy conversion systems is lacking.

Because of the inherent complexity of photo- and electro-chemical energy conversion, progress in catalyst development will require involvement of researchers from many disciplines. Cooperation between experimental and theoretical approaches is needed in the areas of photobiology, molecular, polymer and materials synthesis, electrochemistry, surface science, (photo)chemical dynamics, etc. Realization of the goal of providing inexpensive and renewable energy to humanity in the twenty-first century will require cross-fertilization between these disciplines and, more important follow-up synergistic activities that maintain a focus on the essential scientific and technical issues.

Summary of Research Directions

To increase scientific understanding of the photo- and electro-chemical conversion of carbon dioxide and the potential use of this understanding, new and improved experimental and theoretical methods are needed that can elucidate the kinetics, mechanisms, and thermodynamics associated with redox and charge transfer reactions of carbon dioxide and water under typical catalyst operating conditions. The needs include methods for examining catalysts on a site-specific basis at time scales relevant to electron- and atom-transfer events. Understanding the complex potential energy surfaces relevant to multi-step, multi-electron, and excited-state-related chemical transformations will require the development of new theoretical methods.

Research is needed toward understanding the influence of the complex reaction environments, site-to-site communication, deactivation processes, and regeneration mechanisms in multi-electron processes. The roles that long-range interactions, second coordination sphere influences, and electrical double layer—solvent dynamics play in stabilizing key intermediates and promoting desired reactions need to be investigated.

New design principles and synthetic methods are needed that facilitate assembly of novel multifunctional molecular and nanostructured catalysts employing photo- and electro-chemical energy that efficiently promote conversions of carbon dioxide to fuels and useful chemicals using non-sacrificial electron donors. In particular, multifunctional catalysts are needed that efficiently drive carbon dioxide reduction to products containing C–C bonds using water oxidation as the electron source. These new catalysts should require minimal preparation costs, use abundant materials, and have long lifetimes under typical operational conditions.

Scientific impact

The development of catalysts for the photo- and electro-driven conversion of carbon dioxide would advance basic science in a number of ways. The potential for the development of new synthetic methods and materials would be significant, given the challenges inherent in this priority research direction. Knowledge about the factors that determine kinetics and mechanisms will lead to strategies for improving the efficiency of photo- and/or electro-chemical transformations. Advances in computational methods will make it possible to include electron transfer and excited states in quantum mechanical simulations. The combination of these advances will provide design principles for efficient catalysis of thermodynamically uphill chemistry at ambient temperatures.

Technology impact

The development of successful catalysts for the photo- and electro-driven conversion of carbon dioxide and water could lead to vital chemical energy resources. The development of new commercial processes for the reduction of carbon dioxide to C_1 and higher-molecular-weight fuels (e.g., butanol) would positively impact the earth's carbon balance by recycling carbon dioxide. Furthermore, such fuel products would in prospect fit well with the current U.S. liquid fuel infrastructure.

APPENDICES

APPENDIX 1 • TECHNICAL PERSPECTIVES RESOURCE DOCUMENT

APPENDIX 2 • WORKSHOP PROGRAM

APPENDIX 3 • WORKSHOP PARTICIPANTS

APPENDIX 1

TECHNICAL PERSPECTIVES RESOURCE DOCUMENT

APPENDIX 1 • CONVERSION OF ENERGY FEEDSTOCKS TO LIQUID TRANSPORTATION FUELS

MOTIVATION AND SCOPE

Our nation requires a secure, economical, and environmentally acceptable energy supply to uphold our standard of living, ensure national security, and maintain economic competitiveness. Transportation accounts for about 40 percent of all energy consumption in the United States, and except for electrified railroads, virtually all transportation energy involves liquid fuels derived from petroleum, with more than 60 percent of that petroleum requirement currently being imported.

The basic processes for refining petroleum into liquid transportation fuels (including gasoline, diesel, aviation, and marine fuel), as well as into non-transportation fuel (such as liquefied petroleum gas and heating oil) and chemical feedstocks, are well established and widely distributed. The processes involve removing contaminants from the raw crude oil, fractionating, cracking higher-molecular-weight fractions, combining lower-molecular-weight fractions, rearranging, reforming, and other chemical transformations to produce fuel components with specific desirable properties. Many of these processes involve reactions with hydrogen. Virtually all of the chemical reaction processes involve catalysts, and many of the separations involve solvents, sorbents, and other specialized mass separation agents. The performance of these catalysts and materials is critical to the economics of liquid transportation fuel production.

Some crude oil feedstocks contain high proportions of relatively low-molecular-weight components and few contaminants (such as compounds of sulfur). These are known as light sweet crudes. They are particularly desirable, and their prices are widely quoted. However, transportation fuel demand exceeds the current productive capacity of light sweet crude, forcing refiners to process increasingly heavier and more contaminated feedstocks. Furthermore, stricter environmental regulations are allowing lesser amounts of contaminants, especially sulfur, in fuel products. Processing conditions, hydrogen requirements, and catalytic performance are constantly changing in response to the need to process heavier, more highly contaminated crudes.

Worldwide economic growth continues to result in accelerated energy demand in all sectors. This demand is a challenge to the world's capacity to produce and process ever-heavier crude oils; this challenge results in increased prices for transportation fuels. Furthermore, security and sustainability concerns are related to the increasing proportion of imported feedstocks, especially from politically unstable or unfriendly regions. Both of these forces suggest that alternative domestic sources must be considered for transportation fuel production. Alternative feedstocks include tar sand, oil shale, coal, biomass, natural gas, and even carbon dioxide. This assessment provides a basis for identifying catalysis needs and challenges to the utilization of these alternative energy feedstocks.

Compressed and liquefied gases such as methane and propane are used for fuel in specialized situations, including large short-range fleet vehicles (e.g., urban buses) and small mobile devices (e.g., forklifts). Because of limited transportation applicability, the production and use of such fuels are not discussed in depth here. Likewise, the production, storage, and use of gaseous or liquid hydrogen as a fuel for combustion engines or fuel cells are omitted here (see *Basic Research Needs for the Hydrogen Economy,* Dresselhaus et al. 2003). However, challenges related to hydrogen production and reactions in the context of alternative carbon-containing liquid fuels will be discussed.

Fossil Fuel Feedstocks

This section summarizes alternative fossil raw materials for transportation fuels, especially the hydrogen consumption and catalytic implications of higher-molecular-weight and higher-sulfur crude oils in refining processes. These challenges are then extended to alternative feedstocks, including bitumen from tar sands and kerogen from oil shale.

Coal is also considered an alternative fossil feedstock that can be processed into liquid fuels in either of two basic ways. The first is direct reaction with hydrogen or a hydrogen-donating solvent (coal liquefaction) to make a synthetic crude oil feedstock suitable for conventional refining. The second is reaction with water at high temperature to form hydrogen and carbon monoxide (coal gasification). Hydrogen/carbon monoxide mixtures (known as synthesis gas or syngas), in turn, can be converted either to form a) primarily hydrocarbons (Fischer-Tropsch technology) similar to crude oil for refining, or b) specific organic compounds including methanol or other oxygenated species that could be used as alternative liquid fuels or as fuel additives.

Methane can also be reformed with water to a syngas that, like syngas from coal, is suitable for further processing to hydrocarbons or oxygenates (gas-to-liquids technology). This alternative is being implemented in locations with significant methane resources but with insufficient infrastructure to move methane to other markets (stranded gas) such as Trinidad, Chile, Nigeria, Siberia, and the Persian Gulf. This alternative will not likely be practiced in the United States, although implementing this technology has economic implications. All of these alternative fossil feedstock processes involve important catalysis challenges.

Biological Fuel Feedstocks

There is increasing interest in considering biomass as an alternative raw material for transportation fuels. Biomass consumes carbon dioxide from the atmosphere by photosynthesis, and therefore, biomass growth can potentially offset carbon dioxide emissions to the environment that are the products of combustion. Biomass contains many classes of components, including carbohydrates, lignin, and lipids. Similar to coal, biomass may be processed (pyrolyzed or gasified) to make syngas (which in turn can be processed to hydrocarbons or oxygenates, as in the case of syngas from fossil feedstocks), or it may be processed chemically or biochemically to make specific fuel compounds. An example of such a chemical process is the methanol esterification of vegetable oils to produce biodiesel fuel. Examples of biological processes include the fermentation of sugar, starch, or cellulosic carbohydrates to produce ethanol or butanol. Again, all of these processes involve catalysis, and some include enzymatic catalysis.

Carbon Dioxide as a Fuel Feedstock

Processing heavier crude oils and other alternative fossil or biological raw materials will require incorporating increasing amounts of hydrogen. Initially, this hydrogen is likely to be generated either directly from fossil raw materials (through gasification or reforming) or indirectly as reducing equivalents within a biological pathway. In either case, it will be accompanied by additional carbon dioxide production and emission to the environment (unless the carbon dioxide is sequestered).

In the longer term, developing non-carbonaceous sources for hydrogen production is desirable. Nuclear or solar power, for example, may be used for water electrolysis or other catalytic water-splitting technology, as discussed in *Basic Research Needs for the Hydrogen Economy* (Dresselhaus et al. 2003). With non-fossil sources of hydrogen, it may also be appropriate to chemically or electrochemically reduce carbon dioxide captured from fossil-burning facilities or from the atmosphere itself to form liquid transportation fuels or other products. These processes also involve significant catalysis and materials challenges.

FOSSIL FUEL FEEDSTOCKS

Introduction

The primary source of transportation fuels is petroleum or crude oil. Oil has become the most important energy source in the world because of its high energy density, easy transportability, and relative abundance. Crude oil supplies more than 40 percent of our total energy demands and more than 99 percent of transportation fuels. Crude oil is a convenient energy source because it can be pumped out of the ground and transported via pipelines or shipped to refineries for processing. This section summarizes catalytic processes for converting fossil feedstocks into transportation fuels, with an emphasis on established petroleum refining processes. Other fossil sources (e.g., tar sand, shale, coal, and natural gas) are placed in this context, with summaries of how they are converted into transportation fuel in comparison with petroleum. A foundation is built in this section to anticipate catalytic processing of biomass-derived feedstocks to be discussed later.

Fossil Resources and Compositions

The majority of U.S. fuels come from fossil hydrocarbon sources, primarily crude oil. The representative compositions of fossil feedstocks are summarized in Table 1.

Table 1: Comparison of compositions of various fossil fuel feedstocks.

Feedstock	**Composition (wt%)**						**Specific Gravity (g/mL)**	**Boiling Range (°C)**
	C	**H**	**S**	**N**	**O**	**Metals**		
Natural gas	74-75	24-25	<1.0	nil	nil	–	–	–
Crude petroleum (Arabian light)[a]	~85	~13		~0.1	<0.1	0.03	~0.86	40-500
Bitumen	80- 93	2.5- 5.6	<5.0	0.9- 1.9	2.1- 11.1		–	–
Petroleum residuum[b]	80-90	7-12	1-4	1-2	0.4-1	0.08-0.20	<0.93	540+
Coal-derived oil	86-88	10-13	0.04-0.2	0.05-0.5	0.2-3.0	<0.005	0.85-0.93	10-425
Shale oil (Paraho)[c]	84	11	~0.7	~2.2	~1.1	0.005-0.01	~0.94	95-450+
Tar sands oil[d]	83.2	10.4	4.7	0.4	1.3	~0.07	1.02	

a) U.S. Department of Energy (DOE) Coal Liquefaction Research Needs (COLIRN) Assessment Panel. 1989. *Coal Liquefaction: A Research & Development Research Needs Assessment: Final Report*, Vol. II. DOE/ER-0400. U.S. Department of Energy, Washington, D.C.

b) K. H. Altgelt and M. M. Boduszynski. 1994. *Composition and Analysis of Heavy Petroleum Fractions.* Marcel Dekker: New York.

c) S. A. Newman, ed. 1983. *Shale Oil Upgrading and Refining.* Butterworth: Boston (Chapters 1 and 5).

d) J. B. Jones, ed. 1965. *Hydrocarbons from Oil Shale, Oil Sands and Coal,* CEP. Symp. Series 54, Vol. 61, Chapter 1.

Petroleum

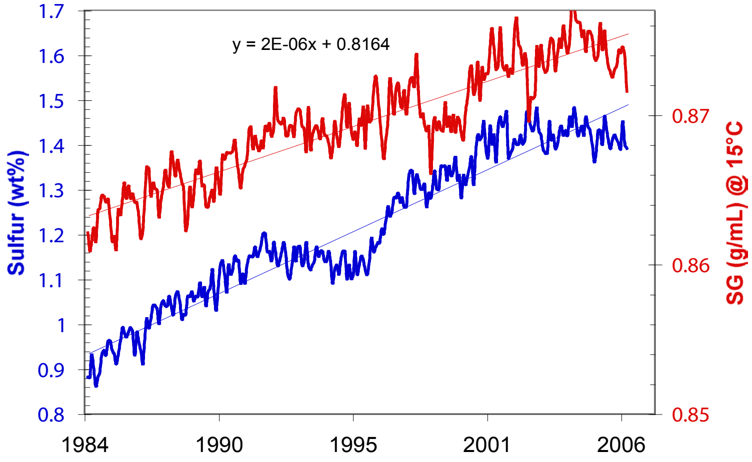

Figure 1: Recent crude oil sulfur and density trends.

Crude oil (petroleum) is found in underground formations in many locations. It consists primarily of complex mixtures of hydrocarbons (mostly alkanes and aromatics) of various molecular weights, most in the range of C_5-C_{25}. Lighter compounds are gases at ambient temperature, and heavier gases are solids or semisolids. Besides hydrocarbons, crude oil contains compounds involving heteroatoms such as sulfur, nitrogen, and metals.

The highest-quality crude oils are relatively light and low in heteroatom contents. These have been used preferentially and are becoming relatively scarce and expensive. The average molecular weight (reflected in specific gravity) and sulfur content of both domestic and imported crude oils have been rising (Figure 1).

Simultaneously, the permitted sulfur content in refined products (gasoline and diesel fuel) has become increasingly lower to protect the environment. In 1980, the average sulfur content in U.S. diesel fuel was 1000 ppm, whereas the 2007 U.S. Environmental Protection Agency specification for low-sulfur diesel fuel is 15 ppm. Because removing sulfur from petroleum results from catalytic hydroprocessing, hydrogen needs are increasing.

Tar sands

Tar sands (also referred to as oil sands or bituminous sands) are combinations of clay, sand, water, and bitumen. Large deposits of tar sands are found in Alberta, Canada. The deposits are strip mined or made to flow into producing wells by in situ techniques that reduce the viscosity of bitumen with steam and/or solvents. The processes make heavy use of water. This presents a challenge because the largest deposits are located in areas with limited water resources.

Bitumen is oil-like and is refined in processes comparable to those used in petroleum processing. Major processing challenges are associated with the high average molecular weights and high heteroatom contents (Table 1). Large amounts of hydrogen must be added to reduce the bitumen molecular weight (to make it suitable for pipeline transport) and heteroatom content. Most refineries can handle only about 10-15 percent of their input from these heavy oil sources.

Shale oil

Oil shale is sedimentary rock containing enough organic material (kerogen) to yield oil and combustible gas upon distillation. It is found in massive amounts in the western United States, primarily in Utah and Wyoming. Worldwide deposits are estimated to contain 30 trillion barrels of shale oil. Kerogen contains high concentrations of heteroatoms (primarily nitrogen and oxygen, Table 1). When upgrading to fuels, kerogen must be depolymerized, separated from inorganic material, and then processed into fuels using refinery processes comparable to those for petroleum.

Mining and processing of kerogen-containing rock are expensive, consume significant amounts of water, and have not been applied on a significant scale. A potentially more economical alternative, described in patents, is in situ conversion of the kerogen. This alternative uses electrical resistance heaters placed into holes drilled in the shale deposit to slowly warm the rock to temperatures above 300 °C, turning some of the trapped kerogen into light hydrocarbon liquids and gas.

Coal

A mixture of organic and mineral matter, coal is extracted by underground or surface mining. Technology used to convert coal to liquid fuels has been applied on an industrial scale for decades. The processes, described in a later section, involve either direct liquefaction of coal with hydrogen to produce hydrocarbon-rich liquid fuel feedstocks or indirect gasification of the coal followed by conversion of the resultant synthesis gas (hydrogen and carbon monoxide) into liquid fuels.

The C:H ratio increases with increasing coal rank. The atomic C:H ratios of lignite, sub-bituminous, and bituminous coals are typically 1.0-1.3, whereas that of anthracite is typically greater than 2.5. The hydrogen contents are lower than the contents of typical liquid fuels (Tables 2 and 3).

Natural gas

Natural gas consists primarily of methane but also contains ethane, propane, butane, and sulfur-containing compounds. Natural gas can be compressed or liquefied and used directly as a transportation fuel. In addition, it can be converted by catalytic steam reforming into synthesis gas and then into Fischer-Tropsch products.

Classification of Coals

Coal exists in a variety of grades, or ranks, ranging from lignite, sub-bituminous and bituminous coal, to anthracite. In this sequence, the content of carbon in the coal increases, and the contents of oxygen and hydrogen decrease. Thus, anthracite has more highly condensed aromatic structures than the other coals, and lignite has the highest fraction of functional groups. Figure 2 shows for the various types of coal how hydrogen and oxygen contents are interrelated (Wasaka et al. 2002). Figure 3 shows the uses of various types of coal.

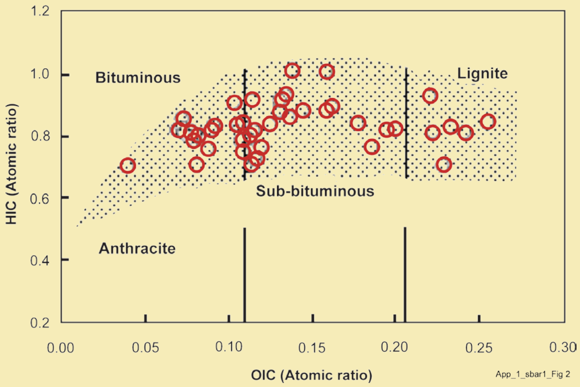

Figure 2: H:C and O:C ratios in various coals. Reprinted from Wasaka et al. (2002) with permission from Elsevier.

Lignite coal consists of small, largely single-ring systems, extensively substituted with oxygen-containing functional groups (-COOH, $-OCH_3$, OH), with one oxygen atom per 3-4 carbon atoms. Cross linking occurs via hydrogen bonds, salt bonds as in COO-Ca-OOC, and a few aliphatic links. Water is an important structural component of this rather hydrophilic coal.

Sub-bituminous coal, containing roughly 60 percent aromatics, has mostly single rings, with some larger rings. With one oxygen atom per 5-6 carbon atoms, oxygen-containing groups (-OH, -COOH) are present on almost all of the rings, but in lower concentrations than in lignite. Cross linking increasingly occurs via ether and some C-C bonds.

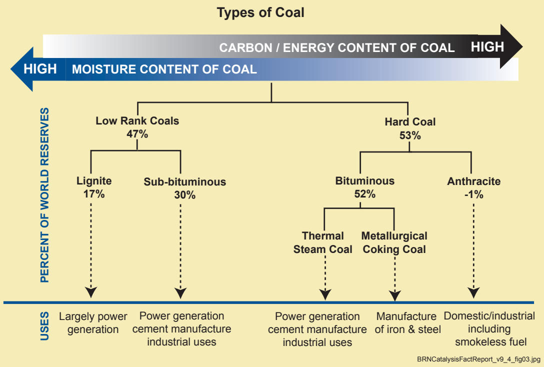

Figure 3: Types of coals and their uses. From http://geo-tec.net/coal_outlook.htm.

Bituminous coal contains about 70-80 percent aromatic moieties, but with a greater degree of condensation in the aromatic moieties and a greater density of C-C bonds than sub-bituminous coal. The concentration of oxygen is lower than in lignite and sub-bituminous coal; with increasing aromatic content, oxygen exists more in the form of OH groups and ether linkages.

Anthracite coal consists almost completely of condensed aromatic structures with few remaining C-C single bonds and roughly 1 percent ether bridge bonds.

The heating value of coal increases in the sequence mentioned, and the chemical reactivity decreases. Thus, the cheaper, low-rank coals, including lignite and sub-bituminous coal, might be targeted for conversion into fuels by processes such as liquefaction and gasification.

Lignite and sub-bituminous coals contain sulfur and nitrogen directly bound to organic units as well as a number of inorganic components that include sulfur and metals (salts, aluminosilicates, alkalis, alkaline earths, and heavy metals). During coal conversion, these heteroatoms and mineral components become important as potential catalyst poisons.

Table 2: Analyses of coal samples from the Argonne Premium Coal Sample Bank (http://www.anl.gov/PCS/pcshome.html).

Coal	As Received						Moisture and Ash						Dry Ash Free				
	H^2O	Mineral Matter	Volatile Matter	S	Btu	Dry Btu	C	H	N	Pyritic S	Sulfate S	Organic S	C	H	N	O	Btu
UF	1.13	13.03	27.14	2.29	13315	13467	74.23	4.08	1.35	1.77	0.01	0.54	88.08	4.84	1.60	4.72	15980
WY	28.09	6.31	32.17	0.45	8426	11717	68.43	4.88	1.02	0.17	0.03	0.43	76.04	5.42	1.13	16.90	13020
IL	7.97	14.25	36.86	4.45	10999	11951	65.65	4.23	1.16	2.81	0.01	2.01	80.73	5.20	1.43	10.11	14696
PITT	1.65	9.10	37.20	2.15	13404	13629	75.50	4.83	1.49	1.37	0.01	0.81	84.95	5.43	1.68	6.90	15336
POC	0.65	4.74	18.48	0.66	14926	15024	86.71	4.23	1.27	0.15	0.03	0.48	91.81	4.48	1.34	1.66	15908
UT	4.63	4.49	43.72	0.59	13280	13925	76.89	5.49	1.50	0.24	0.03	0.35	81.32	5.81	1.59	10.88	14728
WV	2.42	19.36	29.44	0.69	11524	11810	66.20	4.21	1.25	0.16	0.03	0.52	85.47	5.44	1.61	6.68	15247
ND	32.24	6.59	30.45	0.54	7454	11000	65.85	4.36	1.04	0.14	0.03	0.63	74.05	4.90	1.17	19.13	12370

IL = Illinois #6 seam (high volatility bituminous)
ND = Beulah-Zap seam (lignite) (Argonne Premium Coal Database, http://www.anl.gov/PCS/)
PITT = Pittsburgh seam (high volatility bituminous)
POC = Pocahontas #3 seam (low volatility bituminous)
UF = Upper Freeport seam (medium volatility bituminous)
UT = Blind Canyon seam (high volatility bituminous)
WV = Lewiston-Stockton seam (high volatility bituminous)
WY = Wyodak Anderson seam (sub-bituminous)

Table 3: Analyses of coals (Argonne Premium Coal Database, http://www.anl.gov/PCS).

Seam	State	Rank	Composition (% by wt)				Mineral Matter
			C	H	O	S	
Upper Freeport	PA	Medium Volatility Bituminous	86	4.7	8	2.3	13
Wyodak-Anderson	WY	Sub-bituminous	75	5.4	18	0.6	9
Illinois #6	IL	High Volatility Bituminous	78	5.0	14	4.8	15
Pittsburgh #8	PA	High Volatility Bituminous	83	5.3	9	2.2	9
Pocahontas #3	VA	Low Volatility Bituminous	91	4.4	2	0.7	5
Blind Canyon	UT	High Volatility Bituminous	81	5.8	12	0.6	5
Lewiston-Stockton	WV	High Volatility Bituminous	83	5.3	10	0.7	20
Beulah-Zap	ND	Lignite	73	4.8	20	0.8	10

Catalytic Processes for Fuel Upgrading

The modern oil refinery is an integrated industrial processing plant in which crude oil is distilled into fractions and refined in catalytic conversion processes into liquid fuel products, such as gasoline, diesel fuel, aviation fuel, and heating oil. Figure 4 shows schematically how the processing units are linked.

The various conversion processes change the sizes and/or structures of the organic molecules. These conversion processes are classified into four primary categories:

- decomposition (division), including fluidized catalytic cracking (FCC) and hydrocracking
- unification (combination), including alkylation and polymerization
- alteration (rearrangement), including isomerization and reforming
- treatment processes (removal of undesirable components), including hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetalization.

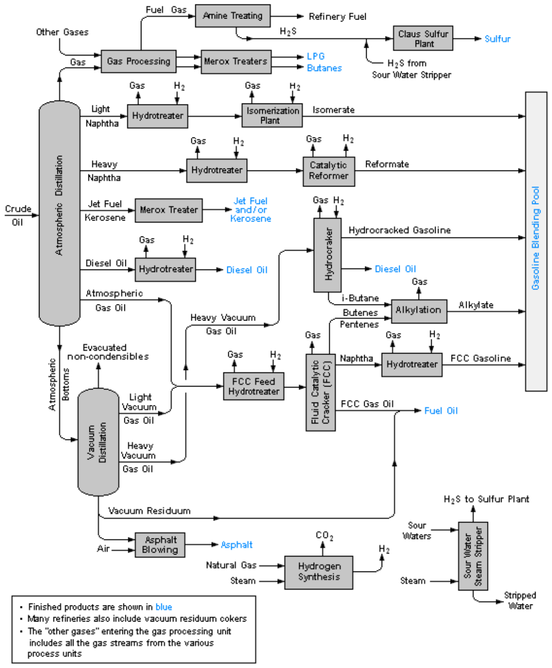

Figure 4: Flow diagram of a typical oil refinery.

Changes in one process or catalyst can have far-reaching effects on the entire refinery because the operation of each unit in a petroleum refinery is dependent on the operation of the others. The FCC unit, for example, may be the workhorse providing most of the high-octane-number gasoline, but its success requires HDS units to provide low-sulfur feeds that can be cracked into gasoline fractions. Without the HDS pretreatment, the catalyst in the FCC unit would produce too much coke, leading to energy balance problems and low selectivity to gasoline. The HDS unit is a major consumer of hydrogen, which has traditionally come from the reforming unit. Because gasoline is no longer permitted to contain large quantities of aromatic compounds, the use of reformers to supply hydrogen is greatly diminished. To keep the HDS unit supplied requires supplemental sources of hydrogen, such as steam reforming of methane.

Catalytic cracking

The catalytic cracking process converts oil into valuable fuel products and petrochemical feedstocks. The process is referred to as FCC because the heterogeneous cracking catalyst is implemented in fluidized bed reactors. FCC is the basic gasoline-making process in refineries, and in U.S. refineries it is typically the largest unit and the most important catalytic process in terms of economics. Figure 5 shows a schematic diagram of a typical FCC unit. Worldwide, more than 14 million barrels per day of feed are processed in these units, consuming some 1500 tons per day of catalyst.

Table 4: Products of catalytic cracking (Venuto and Habib 1979).

Reactant	**Characteristics of Reactions in Catalytic Cracking**
n-Alkanes	C_3 to C_6 is a major product; very few α-olefins larger than C_4; extensive branching
Olefins	Rapid double bond shifts, extensive skeletal isomerization; hydrogen-transfer is major and selective for tertiary olefins; large amount of aromatics formed from aliphatics
Naphthenes (cycloalkanes)	Crack at about the same rate as *n*-alkanes
Alkylaromatics	Cracked, breaking bond between substituent and ring

In the process, C-C bonds in hydrocarbons produce smaller molecules, many in the gasoline boiling range (C_6-C_{12}). This conversion is catalyzed by Brønsted acid sites, primarily in the zeolite. The important classes of reactions are summarized in Table 4. Cracking is favored thermodynamically at high temperatures, and the reactors typically operate at about 500 °C and near atmospheric pressures. Cracking catalysts are solid acids and work by forming carbocation intermediates that undergo β-scission to produce alkanes and alkenes.

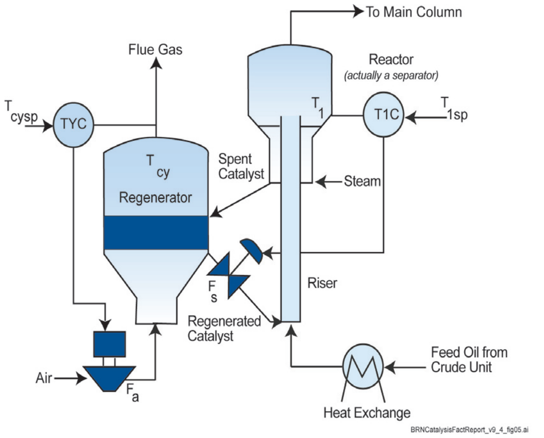

Figure 5: Schematic diagram of a fluidized catalytic cracking unit. Reprinted with permission from B. W. Bequette from http://www.rpi.edu/dept/chem-eng/WWW/faculty/bequette/courses/.

The FCC unit continuously cycles catalyst particles from a riser reactor (in which the catalyst is entrained in the flowing reactant gas stream) to the fluidized-bed catalyst regeneration reactor and back (Figure 5). Preheated oil from the crude distillation unit is sprayed into the base of the riser through feed nozzles, encountering hot, freshly regenerated catalyst from the regenerator at a temperature in the range of 665-760 °C. The hot catalyst instantly vaporizes the feed and, within the few seconds that it resides in the reactor, catalyzes cracking and related reactions, breaking down the high-molecular-weight oil into lighter components. The exothermic combustion of the coke in the regenerator heats the catalyst that is recirculated to the riser reactor, facilitating the vaporization of the oil and the endothermic cracking reaction. If not enough heat is provided because of low coke yields or improper combustion, the conversion in the riser drops and the gasoline yield suffers. On the other hand, if the coke yield is too high, the coke burnoff generates too much heat. This results in cracking reaction temperatures that are too high, decreased gasoline yields, and increased dry gas yields. To compensate for heat-balance problems, the operator can lower or raise the catalyst recirculation rate, change the rate of feed of steam to the stripper, or add various amounts of relatively unreactive heavy oils to the feed. High temperatures in the regenerator caused by too much coking lead to high-temperature steam formed by combustion. This leads to the loss of crystallinity of the zeolite catalyst and to dealumination of the zeolite, with removal of acidic sites and loss of catalytic activity.

Steam is used to strip the catalyst of volatile products, and the deactivated catalyst, containing coke that partially fills the pores and blocks the active sites, is transferred to the regenerator. In the regenerator, the catalyst is mixed with air that burns off the coke and prepares the catalyst for its return to the riser to begin the process again. A portion of the catalyst is withdrawn from the reactor inventory and replaced with fresh material, so the catalyst inventory is a mixture with a distribution of ages.

FCC catalysts are complex, multicomponent solids that are tailored to specific feedstocks and applications. As essential components, cracking catalysts include acidic crystalline zeolites (faujasite, zeolite Y) embedded in an amorphous silica-alumina matrix. The matrix contributes significantly to the overall performance of a catalyst, especially for converting the heaviest fraction of the feed.

Within the zeolite's aluminosilicate framework, aluminum atoms with a +3 charge (in contrast to the +4 charge of silicon) are associated with a charge imbalance that requires compensation by a cation. In the as-synthesized zeolite, this cation is normally sodium. It is replaced by H+ to create the acidity and the catalytic activity. Figure 6 illustrates the principal mechanism of the cracking of an alkane. A carbenium ion carries this chain reaction; the representation of the carbenium ion as free in this depiction is simplified, and the true intermediate is instead bonded to the zeolite surface. Key steps in the mechanism are hydride transfer and β-scission, generating an alkane and a smaller carbenium ion. The chain is terminated when the carbenium ion donates a proton back to the zeolite surface. Several possible mechanisms for initiating the cycle are shown in Figure 6. One involves another mechanism of cracking (protolytic cracking), whereby the catalyst donates a proton to the alkane reactant, generating a pentavalent carbonium ion (a transition state, which is actually bonded to the catalyst surface). The carbonium ion can undergo conversion to produce hydrogen and a carbenium or an alkane and a carbenium ion. The carbenium ion may return a proton to the catalyst, generating an alkene.

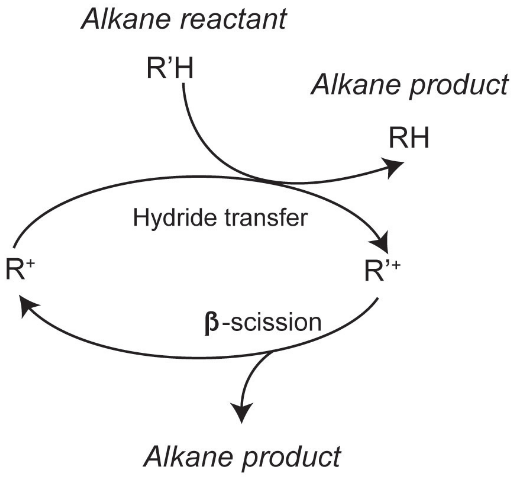

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Figure 6: Mechanism of acid-catalyzed cracking catalyzed by solid acids such as zeolites.

Protonation of an alkene or abstraction of a hydride by a Lewis acid site of the catalyst may cause the carbenium ion to initiate the cycle shown in Figure 6.

In addition to the zeolite and the silica-alumina matrix, cracking catalysts incorporate components to meet specific processing needs. Clays may be added for cracking heavy feed components and adding physical strength to the ~70-µm-diameter catalyst particles. Nickel in the catalyst's feed deposits catalyzes dehydrogenation reactions that lead to high yields of light gas and coke. To passivate the nickel, organometallic compounds of antimony and bismuth may be added to the feed to bind with the nickel. Vanadium in the feed reacts with the zeolite in the FCC catalyst by destroying it and lowering the overall activity. The attack of vanadium on the zeolite may be counteracted by adding basic trapping materials such as magnesium oxide into the catalyst. Furthermore, small amounts (2-3 percent) of the zeolite HZSM-5 may be added to the FCC catalyst to improve yield of high-octane number products. HZSM-5 selectively cracks the straight-chain, low-octane-number hydrocarbons because of transition-state shape selectivity. Many catalysts also have small amounts of platinum added to catalyze the oxidation of carbon monoxide in the regenerator to improve air quality. This platinum is also useful in catalyzing the oxidation of sulfur dioxide into sulfur trioxide in the regenerator. The sulfur trioxide can then react with a cerium dioxide additive in the catalyst that carries the sulfur trioxide back to the reactor where it can be reduced to hydrogen sulfide. The hydrogen sulfide is then converted in a Claus unit into elemental sulfur.

Because refineries are processing heavier feeds, FCC units are increasingly being required to handle materials with higher molecular weights and higher concentrations of sulfur and metals. The higher molecular weights normally lead to more coke formation and catalyst deactivation.

Alkylation

Some molecules formed in the cracking process are too small to be used in gasoline, and there is an incentive to put them back together. Thus, in the alkylation process, small hydrocarbons such as isobutane and C_3-C_5 alkenes are combined. Again, the catalyst is an acid, and the temperature is low to favor the equilibrium formation of products, which are a complex mixture of branched alkanes, called alkylate. Alkylate is an excellent blending component for gasoline, having a high octane number and low Reid vapor pressure, and being free of aromatics, alkenes, and sulfur.

Liquid hydrofluoric acid and sulfuric acid are used as catalysts for alkylation. Each is nearly immiscible with hydrocarbons. Thus, the processes require intensive mixing of acid and hydrocarbon phases to form emulsions. The alkylation reaction is highly exothermic (82-93 kJ/mol of reacted isobutane). Cooling is achieved with water in the hydrofluoric acid processes (operating at temperatures between 16-40 °C), and with refrigeration in the sulfuric acid processes.

In the product purification, the acid and hydrocarbon phases are typically separated in a settler. The hydrocarbon stream is fractionated to separate the alkylate from recycled isobutane as well as from propane, *n*-butane, and (sometimes) isopentane. All hydrocarbon streams have to be treated to remove impurity acids and acid esters. Corrosion of process equipment and environmental liability associated with the disposal of spent acid are issues with both hydrofluoric- and sulfuric acid-catalyzed processes.

Consequently, substantial research has been done in attempts to replace these liquid catalysts with solid acids. In one process, a supported liquid-phase catalyst is used, consisting of triflic (trifluoromethanesulfonic) acid supported on a porous support. The acid in the bed is concentrated in a well-defined zone in which the alkylation takes place. At the upstream end of the catalyst zone, ester intermediates are formed, which are soluble in the hydrocarbons and are transported into the acid zone. Here, they react to form the products and free acid. Thus, the active zone slowly migrates through the bed in the direction of the hydrocarbon flow. The spent acid can be withdrawn from the reactor without interrupting the production. Reaction temperature is in the range of 0-20 °C. The reactor is operated adiabatically, and the reaction heat is removed by a cooled reactor effluent recycle.

In another process, the pretreated alkene feed is mixed with recycle isobutane and injected into a vertical riser reactor with a freshly reactivated catalyst operating at 10-40 °C. The two flow concurrently upwards through the riser, where the reaction takes place. The catalyst particles are separated from the effluent at the top and then sink into the reactivation zone. The reactivation zone is a packed bed with the catalyst slowly moving downward in a low-temperature stream of isobutane saturated with hydrogen. The reactivation zone leads to the bottom of the riser, where the cycle starts again. The catalyst is an alumina-supported aluminum chloride modified with alkali metal ions with nickel, palladium, or platinum hydrogenation functionality.

Hydroprocessing

Hydroprocessing is the term used for the catalytic reactions of hydrogen with process streams to remove the heteroatoms sulfur, nitrogen, oxygen, and metals, and for the saturation of aromatic structures. Hydroprocessing can also refer to hydrogenation of olefins or other unsaturated species. HDS refers to hydroprocessing for sulfur removal, breaking C-S bonds and forming hydrogen sulfide. HDN, hydrodeoxygenation (HDO), and hydrodemetalization are processes targeting the removal of nitrogen (as ammonia), oxygen (as water), and metals (typically as metal sulfides), respectively. Hydroprocessing is carried out in fixed-bed reactors at high pressures, with the severity of the reaction conditions generally increasing with the heaviness of the feed. Reactors used with the heavier feeds are trickle beds, in which the liquid oil trickles through the catalyst bed, with hydrogen concentrated in the gas phase. Slurry reactors have also been used for heavy feedstocks.

Heavy petroleum fractions, such as residua, incorporate relatively large amounts of organosulfur and multi-ring organonitrogen compounds. Shale oils contain substantial nitrogen as well, and these feedstocks require large amounts of hydrogen in their conversion; coal conversion requires even more (Table 5).

Hydrogen consumption is about 70 standard ft^3/bbl of feed per percent sulfur, 320 standard ft^3/bbl per percent nitrogen, and 180 standard ft^3/bbl per percent oxygen removed. Hydrogen consumption for olefin and aromatics reduction can be estimated from the stoichiometric amounts required. If operating conditions are severe enough that a significant amount of hydrocracking occurs, hydrogen consumption rises rapidly.

Hydrodesulfurization. HDS is the most widely used hydrotreatment process, being required to produce fuels meeting government-mandated sulfur specifications for reformulated gasoline, diesel fuel, and heating oil. Organosulfur compounds are present in most refinery streams and

Table 5: Hydrogen consumption in hydroprocessing.

Feedstock	H_2 Consumption (std ft^3/bbl)
Khafji Residuum (giving 1.0wt% S in product)[a]	580
West Texas Sour Residuum (giving 1.0wt% S in product)[a]	420
West Texas Sour (giving 0.3wt% S in product)[a]	600
Tar sands[b]	2200
Coal[b]	5000

a) B. C. Gates, J. R. Katzer, and G. C. A. Schuit. 1979. *Chemistry of Catalytic Processes.* McGraw-Hill: New York, pp 429.
b) J. L. Skinner. 1980. “Hydrogen Requirements in Shale Oil and Synthetic Crude from Coal,” *ACS Symposium Series* **116** (Hydrogen: Prod. Mark.), 279-291.

present in tar sand oil and other fossil fuel liquids (Table 1). The primary HDS catalyst is cobalt-promoted molybdenum disulfide supported on amorphous alumina (Figures 7 and 8). Temperatures of HDS are typically in the range of 300-425 °C, with high partial pressures of hydrogen (35-170 atm).

Beyond catalytic HDS, several non-hydrotreating processes for sulfur removal have been commercialized. Adsorbents can be used to remove selected sulfur-containing species directly from the FCC gasoline; alternatively, some sulfur-containing compounds can be converted to more readily adsorbed compounds. In one process, sulfur-containing species react with olefins in the FCC gasoline, producing heavier sulfur species that may be removed by distillation. In another process, the compounds are oxidized so that they may be removed by water washing.

Limitations in hydrogen availability in refineries and the high cost of hydrogen from methane steam reforming have provided part of the motivation to develop selective HDS catalysts. Specifically, there is interest in catalysts that remove sulfur from aromatics with the least amount on concurrent ring saturation. Such catalysts, for example, convert dibenzothiophene, which is present in heavy petroleum fractions, primarily by direct breaking of C-S bonds. This conversion produces hydrogen sulfide with minimum hydrogen consumption (hydrogenolysis). Accompanying the bond cleavage is some aromatic ring saturation occurring before C-S bond breaking (Figures 9 and 10). The selective route is referred to as the direct desulfurization (DDS) pathway.

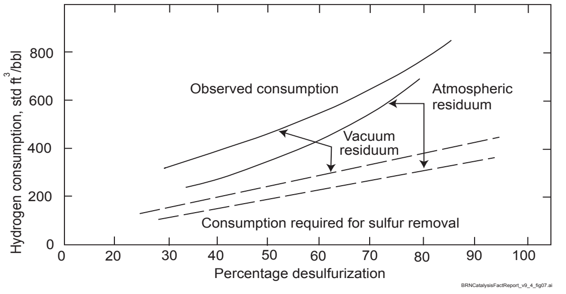

Figure 7: Dependence of hydrogen consumption on the degree of desulfurization of Kuwait residuum (Reprinted from Gates et al. (1979) with permission from McGraw-Hill). Adapted from Beuther and Schmid (1963).)

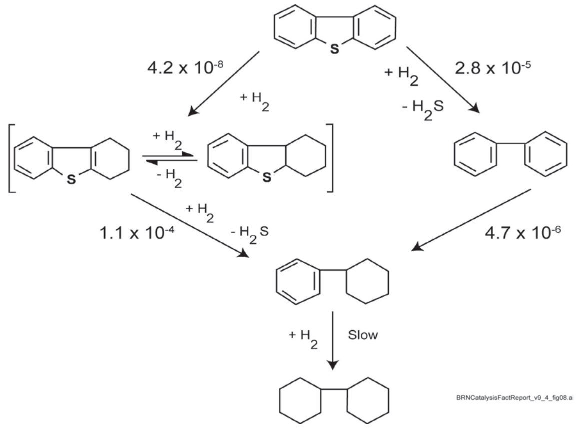

Figure 8: Reaction network for hydrodesulfurization of dibenzothiophene catalyzed by sulfided CoMo/ Al_2O_3 at 300 °C and 102 atm. Pseudo-first-order rate constants in units of L/(g of catalyst t × s) are indicated next to each of the arrows. From Houlla et al. (1978). Reprinted with permission of John Wiley & Sons, Inc.

Hydrodenitrogenation. HDN is required primarily to remove basic organonitrogen compounds from refinery streams, such as feeds to catalytic crackers. The organonitrogen compounds are not only strong inhibitors of the acidic FCC catalysts, they are also a major cause of coke formation in cracking. Nitrogen removal may also be needed to meet product specifications, such as stability, or to meet NO_x emission standards upon combustion of the resultant fuels.

Hydrodesulfurization Catalysts

Decades of fundamental research have guided the development of improved HDS catalysts. Mounting evidence from model systems suggests that the catalytically active species are nanoclusters of molybdenum disulfide only a few layers thick (Figure 9). These nanoclusters have metal-like reactivity and expose edges of sulfur atoms that are paired and not separated by equal distances and edges of molybdenum atoms (Figures 9 and 10). Incorporation of promoter cobalt or nickel atoms at the edges improves the activities of the catalysts. Activity for DDS reactions is associated with molybdenum sites on the cluster edges; activity for hydrogenation reactions is associated with promoter cobalt or nickel sites on cluster edges. The promoters work by controlling the local phase, with paired sulfur atoms, exposed cobalt and nickel centers, and providing metal-like edge electronic states.

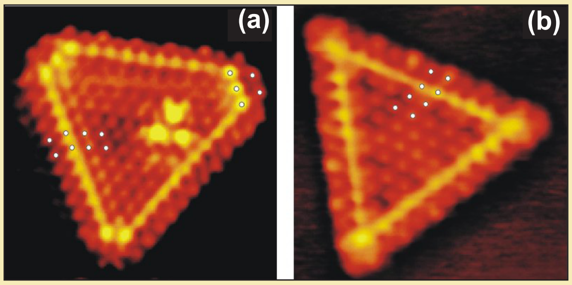

Figure 9: Model hydrodesulfurization catalyst. (a) STM image of a hydrodesulfurization catalyst, a molybdenum disulfide layer with cobalt incorporated at the edges between the molybdenum and sulfur layers; these nanoclusters are supported on gold. (b) A triangular single-layer molybdenum disulfide nanocluster. The brightest regions around the perimeter are images associated with metal-like electronic states that are considered important contributors to the catalytic activity. Reprinted from Lauritsen et al. (2002) with permission from Elsevier.

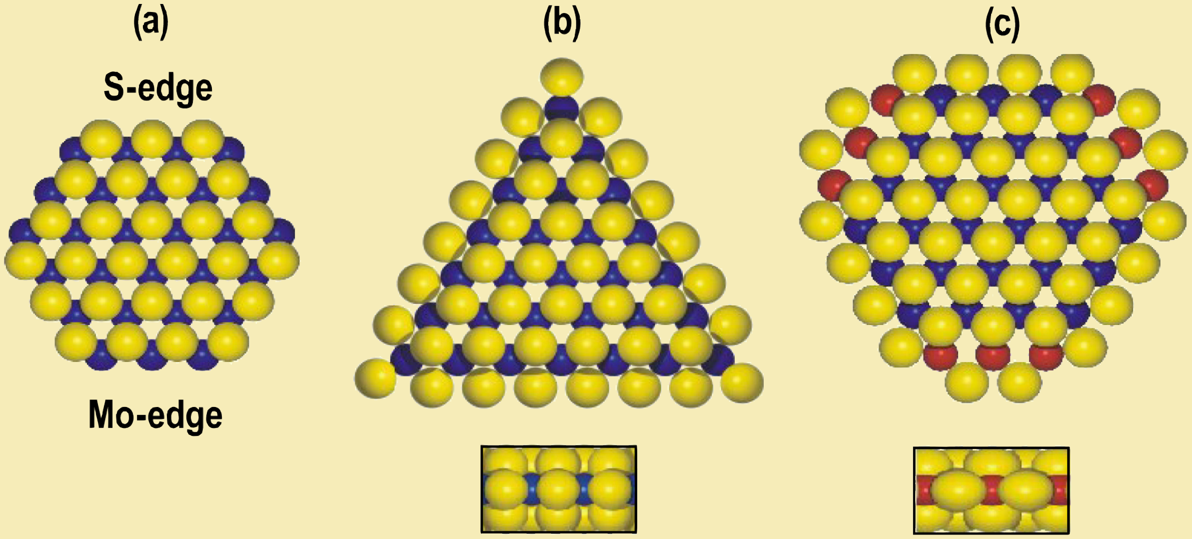

Figure 10: Configurations for the molybdenum disulfide catalyst. (a) Model (top view) of a hypothetical bulk truncated molybdenum disulfide hexagon exposing both the molybdenum and the sulfur edge. (b) A triangular molybdenum disulfide cluster exposing molybdenum edges with edge sulfur atoms located out of registry with the basal plane. (c) Model of the proposed hexagonally truncated cobalt-molybdenum-sulfur structures. Molybdenum (blue), sulfur (yellow), cobalt (red). Reprinted from Lauritsen et al. (2002) with permission from Elsevier.

In contrast to HDS, HDN is generally unselective, with ring hydrogenation predominating over direct C-N bond breaking, as illustrated by the reaction network for quinoline shown in Figure 11. Concomitant hydrogenation of multi-ring aromatics in feeds to FCC units increases their susceptibility to cracking to produce gasoline-range products. Nickel-promoted molybdenum disulfide catalysts have been found to have higher activities for aromatic ring hydrogenation than cobalt-promoted molybdenum disulfide catalysts, and so they are more active for HDN as well.

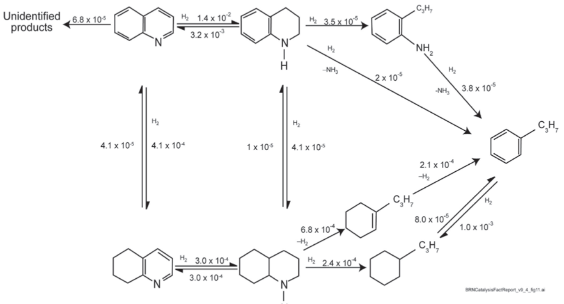

Figure 11: Reaction network for hydrodenitrogenation mechanism for quinoline with a Ni-Mo/ γ-Al_2O_3 catalyst at 350 °C and 35 atm. The numbers next to the arrows indicate the pseudo first-order rate constants of the reactions in units of L/(g of catalyst × s) (Sundaram et al. 1988).

Hydrodeoxygenation. HDO has not been as well investigated as HDS and HDN, because there are hardly any organooxygen compounds in crude oil. Some attention has been paid to HDO because of the presence of organooxygen compounds in coal liquefaction products, and they are likely to gain increasing attention because of their presence in biomass-derived liquids. The catalysts most investigated for HDO are those that have been used for HDS and HDN, namely, supported, promoted molybdenum disulfide on alumina. In investigations of HDO of individual compounds, sulfur-containing compounds have been added to the feeds to maintain the catalysts in the sulfided state.

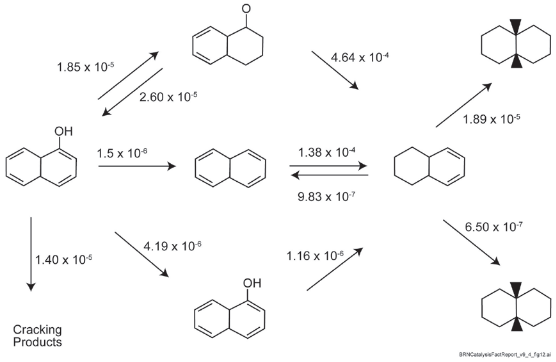

Figure 12: Reaction network for 1-naphthol proposed by Li et al. (1985). The numbers next to the arrows are pseudo-first-order rate constants in L/(g of catalyst × s) at 200 °C. From Li et al. (1985). Reprinted with permission of John Wiley & Sons, Inc.

The reaction network characterizing HDO of 1-naphthol (and of benzofurans) involves parallel hydrogenation and hydrogenolysis, similar to the reactions of analogous compounds that contain nitrogen. Figure 12 shows an approximate reaction network for HDO of 1-naphthol. This compound may be representative of compounds occurring in the liquids formed from biomass. The selectivity for C-O bond breaking is not high.

Hydrodemetalization. Some forms of crude oil contain substantial quantities of metals (Table 1), especially vanadium and nickel, bonded in porphyrin-like structures in the asphaltenes, which are concentrated in the heaviest cut (vacuum residuum). In catalytic hydroprocessing, the reaction of these metal-containing components with hydrogen is called hydrodemetalization, and it yields organic fragments and solid deposits (mostly metal sulfides) in the sulfur-containing atmospheres of the reactors. These deposits clog the pores of the catalysts and the interstices of the fixed-bed reactors. In contrast to coke, these deposits cannot be removed by burning, and they foul the catalyst irreversibly. Effectiveness factors for hydrodemetalization are typically small, so that the deposits form preferentially near the catalyst pore mouths, fouling the catalysts quickly; deposits also form preferentially near the upstream ends of fixed-bed reactors.

Processes designed for heavy feeds with substantial metal contents often include guard beds upstream of the main reactor for the removal of metal. Feeds with the highest metal contents require catalysts designed specifically for hydrodemetalization, having high pore volumes and optimal pore-size distributions to accommodate the metals. These catalysts may be used for short periods and then replaced. Metal removal, whether by hydrodemetalization or another process, will increase in importance as liquids derived from shale and tar sands enter the refinery mix; for example, arsenic is present in high concentrations in shale oils.

Aromatic saturation. Saturation of aromatics may be deliberate and desirable for lowering the aromatic content in FCC feed to increase conversion or to meet product specifications in diesel fuel. However, it may be undesirable, as in the concomitant saturation of aromatics when only HDS is desired. Government regulations stipulating lower aromatic content in fuels have led to the development of sulfur-tolerant, supported noble metal catalysts that typically incorporate zeolites as supports. These catalysts may also be used in finishing steps that remove almost the last traces of sulfur from heavy feeds, because the products that have undergone such a high degree of desulfurization do not inhibit the action of noble metals nearly as much as the untreated feedstocks do.

Hydrocracking

In hydrocracking, bifunctional catalysts combine the characteristics of acids, as in cracking, and metals or metal sulfides, as in aromatic hydrogenation. The functions work together to produce products that are reduced in molecular weight (cracked) and hydrogenated. Straight-chain alkanes are cracked to produce shorter-chain alkanes. Multi-ring aromatics are cracked to produce substituted benzenes and substituted cycloalkanes; additional hydrocracking leads to side-chain cracking and isomerization. Typical products of hydrocracking are saturated hydrocarbons which, depending on the reaction conditions (temperature, pressure, catalyst activity), include components of jet fuel, diesel fuel, and relatively high-octane-number gasoline. Other hydroprocessing reactions accompany hydrocracking so that the products have reduced contents of sulfur and other heteroatoms. Hydrogen consumptions may be high.

The choice of catalyst depends on the nature of the feed and the desired product distribution. Platinum or palladium supported on zeolites such as zeolite Y, mordenite, or ZSM-5 is used primarily with light feeds containing almost no sulfur or nitrogen and is highly selective for the production of gasoline-range hydrocarbons. Catalysts containing noble metals on zeolite Y are apparently more sulfur-tolerant and long-lived than catalysts containing the same metals on amorphous supports. As mentioned in previous sections, catalysts typically applied in the hydroprocessing reactions and commonly used with heavier feeds contain cobalt or nickel promoters and molybdenum sulfide or tungsten sulfide supported on acidic, amorphous oxides such as acid-treated aluminum oxide, silica-alumina, or a zeolite. These catalysts produce lubricating oils, diesel fuel, and middle or heavy distillate fuels. Hydrocracking catalysts are also used to convert waxy Fischer-Tropsch liquids into diesel fuel. Typical catalyst compositions are 2-8 percent cobalt or nickel and 10 percent molybdenum or 20 percent tungsten as oxides on alumina or silica-alumina (these oxides are converted into sulfides when sulfur-containing species are present) or 0.5 percent platinum or palladium on zeolites.

Hydrocracking temperatures are typically in the range of 345-425 °C, with partial pressures of hydrogen that may be high (100-200 atm). Hydrocracking units may be single-stage or two-stage reactors.

Naphtha reforming

Catalytic reforming of naphtha increases the octane numbers, typically from about 60 to as much as 120. The principal reactions are rearrangements, such as branching of alkanes and dehydrocyclization reactions, producing aromatics. Some hydrocracking also occurs, selectively removing low-octane-number, straight-chain alkanes. Catalytic reforming is a net hydrogen producer and has been a major source of refinery hydrogen for applications such as hydroprocessing. However, the reforming process is of declining importance because of requirements to minimize environmentally harmful gasoline components such as benzene. Reforming is still a major process, however, for producing aromatic feedstocks for the petrochemical industry.

Naphtha reforming catalysts for years have been platinum supported on various types of high-area aluminas. However, in recent decades, bimetallics have become the norm, including platinum with rhenium, tin, or iridium. Chloride is an important catalyst component and adds acidity to facilitate reactions such as isomerization. The chloride content is controlled to balance the reactions, including coke formation and metal dispersion. Reforming catalysts used for selective manufacture of aromatics consist of platinum clusters in a basic zeolite.

Since its discovery almost 70 years ago, catalytic reforming has been conducted in fixed-bed reactors, with periodic catalyst regeneration by burning off coke and treating the catalyst (e.g., with chloride compounds) to redisperse the precious metal. Water in the feedstock and recycle gas must be carefully monitored to prevent excessive loss of chloride and to control any loss of catalyst surface area at high temperatures, especially during regeneration. Because sulfur and nitrogen compounds are catalyst poisons, the reformer feedstock must contain low concentrations of these compounds (less than 1 ppm).

Catalytic reformers operate at temperatures in the range of approximately 425-525 °C (with substantial temperature gradients, because the principal reactions are endothermic) and at various pressures, from about 15-70 atm. Considerations of reaction equilibria and kinetics indicate that octane numbers and yields are maximized at low hydrogen partial pressures, but coke formation is favored at these low pressures. The tradeoffs have dictated high-pressure operations, but developments of bimetallic catalysts have allowed operations at lower pressures, with the relatively rapid catalyst deactivation being handled by almost continuous catalyst regeneration facilitated by moving bed reactors and clever reactor designs.

Reforming reaction chemistry has been well investigated and is the classic illustration of bifunctional catalysis. *n*-heptane, for example, is dehydrogenated on a metal surface, giving *n*-heptene, which is transported to an acidic site on the support surface, where it is protonated and converted into isoheptene. Isoheptene is then transported to the metal, where it is hydrogenated to produce isoheptane, a branched product with a higher octane number than the reactant *n*-heptane. The important reactions are summarized in Figure 13, which represents the conversion of various lumps—classes of compounds. Determining the

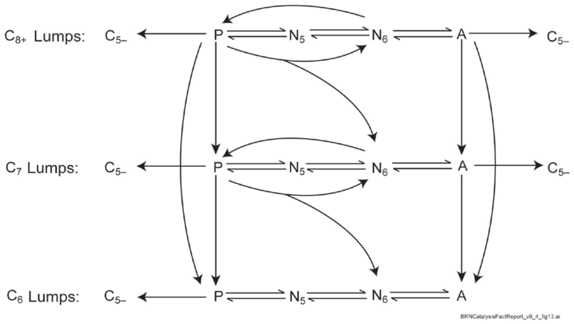

Figure 13: Lumped reaction network for catalytic reforming of naphtha. N represents naphthenes; P, paraffins; A, aromatics; and C_{5-}, pentane and lighter compounds. Reprinted from Ramage et al. (1987) with permission from Elseiver.

reactivities of the characteristic lumps is valuable in predicting the performance of feedstocks of various compositions and as a basis for comparing the performances of various catalysts.

Hydrogen production

Converting heavier feedstocks by hydrocracking and removing heteroatoms by hydroprocessing require hydrogen in increasing amounts. Hydrogen is produced in naphtha reforming and in alkane thermal cracking processes to produce olefins for the petrochemical industry. With heavier feedstocks and lower limits on sulfur placing greater demands on hydrocracking and hydroprocessing operations, refineries now require supplemental sources of hydrogen, which is generally supplied by steam reforming of methane, and sometimes by the gasification of petroleum coke.

Steam reforming of methane. In steam reforming of methane, high-temperature steam (700-1000 °C) at pressures in the range of 3-25 atm in the presence of a catalyst is used to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide from a methane source such as natural gas. The reaction is endothermic, and the required energy is usually supplied by burning some of the methane feedstocks. The catalysts are typically rare-earth-promoted nickel and calcium oxides on alumina supports.

Subsequently, in the water-gas shift reaction (discussed later), the carbon monoxide and additional steam are converted further in the presence of a catalyst to produce carbon dioxide and more hydrogen. Absorption in a solvent or pressure-swing adsorption is used to separate carbon dioxide and other impurities, leaving essentially pure hydrogen.

Partial oxidation. In partial oxidation (POX), the methane and other hydrocarbons in natural gas react with a limited amount of oxygen (typically from air). With less than the stoichiometric amount of oxygen available for the reaction, the reaction products contain primarily carbon monoxide and water (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide. Subsequently, again by application of the water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and hydrogen.

POX is exothermic and a much faster process than steam reforming. This process requires a smaller reactor and is generally operated without catalysts, although catalytic POX using, for example, rhodium catalysts has been investigated for low-volume hydrogen production. POX produces less hydrogen per unit of natural gas than is obtained by steam reforming of the same feedstock.

Autothermal reforming. Autothermal reforming is essentially a heat-balanced combination of exothermic POX and endothermic steam reforming of methane in a single reactor. Under ideal operating conditions with precise amounts of air, methane, and steam, the heat produced from the POX reaction is directly used by the steam reforming reaction. Autothermal reforming processes are characterized by smaller reactors, lower cost, and faster startup times than POX and steam reforming. With newly developed catalysts (rhodium and calcium oxide on silica), autoreforming temperatures have been reduced from 1200 °C to 650-900 °C.

Unconventional methods. In principle, carbon dioxide and water can be used to reform methane. In some processes for steam reforming methane, carbon dioxide from the furnace section is recovered and so used. The overall stoichiometry is then similar to that of autothermal reforming. Carbon dioxide-methane reforming can also be accomplished in a plasma discharge, but no commercial applications exist.

Catalytic challenges related to several other unconventional methods of large-scale hydrogen generation (including electrolysis, thermal water splitting, and photobiological water splitting) were examined in detail in *Basic Research Needs for the Hydrogen Economy* (Dresselhaus et al. 2003).

Coal Conversion Processes

Direct coal liquefaction

In direct coal liquefaction, hydrogen is added to coal at elevated temperatures and pressures, sometimes in the presence of an added catalyst. Direct liquefaction of coal to make liquid fuels is technologically feasible, as shown by the performance of demonstration plants, but at present it is not economically attractive. After a century of effort beginning in Europe and continuing to North America and China, none of the versions of direct liquefaction is practiced today at the scale of even a small petroleum refinery.

Direct liquefaction has evolved to the point that capital costs are about one-third less than indirect gasification/Fischer-Tropsch synthesis, with operating cost being about 40 percent less, largely because of higher product yields. However, the diesel fuel product of direct liquefaction technology is of lower quality (45 cetane number) than that produced by Fischer-Tropsch technology. The direct liquefaction processes also offer less potential for specialty chemicals production. The technological development of these processes is much less mature than that of the gasification-based alternatives.

Direct coal liquefaction research and development have identified three main goals for the chemistry:

- cleave strategic bonds in the macromolecular organic network structure of coal to liberate fragments of low to moderate molecular weight that have boiling points that are acceptable for transportation fuels.
- remove toxic, noxious, and/or troublesome components: mineral matter, sulfur, nitrogen, and oxygen.
- increase the atomic H:C ratio from about 0.8 (typical for a coal with 6 wt% hydrogen) to values of 1.3-1.8, more typical of petroleum feedstock.

Attempts to make distillable liquid fuels from coal have taken one of three main tracks:

- pyrolysis, which yields mostly coke (char) with only 15-35 percent liquids (coal tar, creosote oil).
- catalytic liquefaction/hydroprocessing, generally carried out in the presence of a heavy solvent at high temperature.
- solvent extraction, generally at high temperature under high hydrogen partial pressure, which produces a product slate with a wide boiling range.

Pyrolysis. Liquid yields are low, and coal pyrolysis methods are mentioned only because they have some rough comparability to those used for pyrolysis of biomass.

Catalytic liquefaction/hydroprocessing. In early versions of this process, coal was slurried in a heavy solvent with an iron oxide catalyst and hydroprocessed at pressures up to about 700 atm. Liquid yields were high, but so were costs.

Work that is more recent has focused on better catalysts to enhance both cracking of the nonvolatile macromolecular coal structure and stabilization of the resulting fragments as low molecular weight compounds that can be distilled. Data characterizing some coal liquefaction processes are collected in Table 6.

Table 6: Summary of catalytic liquefaction processes (Speight 1983).

Process	Reactor	Catalyst	Temperature (˚C)	Pressure (atm)
Bergius	Plug flow	$Co\text{-}Mo/Al_2O_3$	480	200-700
University of Utah	Entrained	$ZnCl_2$, $SnCl_2$	500-550	100-170
Schroeder	Entrained	$(NH_4)_2MoO_4$	500	135
DOW	Entrained	Aqueous salts	450-460	135
H-coal	Ebullated bed	$Co\text{-}Mo/Al_2O_3$	450	150-200
Synthoil	Fixed bed	$Co\text{-}Mo/Al_2O_3$	450	135-275
CCL	Fixed bed	$Co\text{-}Mo/Al_2O_3$	400	135
Multistage	Expanded bed	$Co\text{-}Mo/Al_2O_3$	400-430	70
Zinc chloride	Liquid phase	$ZnCl_2$	360-440	100-240

Coal conversion in these processes initially proceeds by thermal conversion that breaks bonds in the organic coal structure via radical intermediates. Dihydroaromatics like dihydrophenanthrene or tetrahydroaromatics like tetralin react with the highly reactive radical fragments to prevent “retrograde reactions” that lead to undesirable increased molecular weight. Relatively stable radicals derived from the donor solvent live long enough to donate additional hydrogen driven by aromatic stabilization. Catalysts and added hydrogen can replenish the “donor solvents” in the reactor where the initial fragmentation reactions occur or in separate reactors. Solvent rehydrogenation in a separate reactor resembles conventional fixed-bed oil hydroprocessing.

Solvent extraction methods. Solvent extraction conducted at temperatures high enough to achieve thermal cracking of the coal structure offers one way to avoid the high catalyst makeup requirements of the previously described liquefaction methods. Researchers found that solvent quality was important, and that high hydrogen partial pressures helped maintain solvent quality and did some upgrading of the products, even without an added catalyst.

The “liquid” product from coal liquefaction may be a solid at room temperature and contains significant concentrations of sulfur, oxygen, and nitrogen. Moreover, it is likely to be very unstable with respect to the formation of gum and sludge and often contains intractable deposits that would disrupt petroleum refinery operations. Few coal liquids are ready to blend with petroleum refinery streams of comparable boiling point.

Coal gasification

Gasification is a thermochemical process that converts water and almost any carbon-containing feedstock, such as coal, petroleum coke, biomass, and hydrocarbons, into a gaseous product containing hydrogen, carbon monoxide, and carbon dioxide, known as synthesis gas (syngas). Syngas can be used as a fuel directly, or it can be processed further into liquid fuels or chemicals. Gasification is typically conducted at temperatures of 850-1500 ºC and pressures from 1 to 70 atm in the presence of carefully controlled amounts of air or oxygen. Gasification involves a complex combination of reactions in the solid, liquid, and gas phases, including partial oxidation and steam reforming. Partial oxidation processes use less than the stoichiometric amount of oxygen required for complete combustion. Steam reforming involves the reaction of water with the carbon-containing feedstocks to produce syngas. Many of the reactions are reversible. The water-gas shift reaction and methanation are two other important reactions that may occur during gasification.

Heat to bring reactants to gasification temperatures can be provided in several ways. In air- and oxygen-blown gasifiers, heat is provided directly by partially oxidizing a portion of the carbon-containing feedstock. In air-blown gasifiers, the nitrogen in the air dilutes the product gas, and the resulting syngas product is referred to as low-energy or low-Btu gas (the water gas or town gas formerly used for illumination before the availability of electricity). Low-energy gas may be suitable for limited heat and power applications, but it is not suitable for producing liquid fuels. Oxygen-blown gasifiers use purified oxygen instead of air to partially oxidize part of the feedstock, producing a medium-energy-content gas containing mostly hydrogen and carbon monoxide and some carbon dioxide. This product is suitable for both heat and power applications and can also be used for fuel or chemical synthesis. Indirectly fired gasifiers use normal air for combustion physically separate from the gasification reactor and use heat-exchange tubes, circulating beds of hot materials, or other configurations to reach gasification temperatures to produce a medium-Btu syngas without nitrogen dilution.

Many gasifier designs exist, including fixed beds, moving circulating and fluidized beds, and entrained flow reactors. The outlet gas composition from the gasification reactor depends on the feedstock composition, gasification process, gasifying agent, and temperature. If the feedstock is a solid, transferring the feed into high-pressure gasifiers can be a challenge. Inorganic contaminants in the feedstock lead to ash, and ash handling is another significant technical challenge. Some slagging designs keep the ash molten in the gasifier section but quench the products in water for easier ash separation.

Technology developed for coal gasification has also been adapted for the gasification of similar materials such as petroleum coke and residual oil. Gasification of other hydrocarbons, especially methane, is more generally referred to as steam reforming and is performed at lower temperatures with catalysts. Biomass gasification is discussed later in this report.

Syngas cleaning

Before conversion to liquid fuels, contaminants in the syngas must be cleaned. The impurities may include tars, metals, chlorine- and sulfur-containing compounds, and particulates that cannot be tolerated by catalysts in subsequent steps. The ratio of H_2:CO must also be adjusted to a value suitable for the downstream fuel synthesis.

Unwanted syngas impurities that must be removed include carbon dioxide, hydrogen sulfide, carbonyl sulfide (COS), ammonia, and heavy metals including mercury. Without such a cleanup, downstream catalyst systems could be poisoned. If the syngas is to be used at low temperatures, some form of wet scrubbing may be used. Methanol and dimethyl ethers of polyethylene glycol have been used to dissolve the acid gases carbon dioxide, COS, and hydrogen sulfide at high pressure. The rich solvent containing the acid gases is then let down in pressure and/or steam or nitrogen stripped to release and recover the acid gases. Amine-based acid gas removal involving chemical reactions is also possible, but regeneration generally requires greater energy.

If the syngas is to be used at a high temperature, some method of hot gas cleaning is desirable, because cooling and reheating the gas, as would be required with wet scrubbing, decreases overall process thermal efficiency. Two main types of catalysts are used for hot gas conditioning for carbon dioxide and hydrogen sulfide removal: nonmetallic mixed oxide catalysts and metal-containing catalysts. The principal nonmetallic mixed oxide catalyst that has been used is a mixed MgO-CaO, which is formed by calcining dolomite at a temperature of 800-900 °C. The operating conditions for using dolomite adsorbents are temperatures from 700 to 1000 °C and space times from 0.007 to 7 s. Other oxide adsorbents proposed for this reaction include magnesium oxide, calcium oxide, and olivine (a magnesium silicate). Dolomite is not a good catalyst when the syngas is highly pressurized because the calcination reaction is reversible and an inactive dolomite phase will form if the carbon dioxide partial pressure is too high. Other problems with dolomite include severe catalyst attrition and the production of fine particulate material in fluidized-bed reactors.

Another contaminant that must be removed from the synthesis gas is mercury. Some coals contain significant amounts of mercury, which is both an environmental pollutant and detrimental to downstream catalyst life. Therefore, sulfur-impregnated activated carbon is commonly used as a mercury adsorbent in packed beds operated at 30 °C and 60 atm. In typical operations, a 90-95 percent mercury removal has been reported with a bed life of 18-24 months.

Water-gas shift reaction

As in steam reforming of methane, the syngas H_2:CO ratio may be adjusted for subsequent reactions by the water-gas shift reaction. Carbon monoxide is reformed with water to form carbon dioxide and hydrogen in this moderately exothermic, reversible reaction (Equation 1):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mol} \tag{1}$$

The water-gas shift reaction is not thermodynamically favorable at elevated temperatures because the equilibrium carbon monoxide conversion decreases with increasing reaction temperature; higher overall conversions are obtained at lower temperatures. Because of this equilibrium limitation, the water-gas shift reaction is typically conducted in two adiabatic temperature regimes separated by interstage cooling: high-temperature shift and low-temperature shift. Although the reaction pressure has little effect on the equilibrium, high-temperature shift typically operates at 10-60 atm, whereas low-temperature shift operates at 3-14 atm. If the objective is to make as much hydrogen as possible, the high-temperature shift converter can operate within the range of 315-500 °C, and lower carbon monoxide content to 1-5 percent. The low-temperature shift reactor operating in the range of 200-270 °C can reduce the final carbon monoxide content to between 0.2 and 1 percent.

Ferrochrome catalysts are used extensively for the high-temperature shift. The reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4) in the high-temperature shift process is necessary because magnetite is believed to be the catalytically active material. Chromium(III) oxide is a textural promoter that inhibits sintering but itself does not catalyze the water-gas shift reaction. A major drawback of the ferrochrome catalyst is that it may contain hexavalent chromium, a severe toxicological hazard. The catalyst formulation is copper/zinc oxide/alumina for low-temperature shift. These catalysts have higher intrinsic activity than ferrochrome, but they are unstable at temperatures greater than 300 °C. Copper is the active species; zinc oxide enhances activity of the copper and also improves thermal stability; aluminum oxide is the support. Deactivation occurs by sintering and poisoning by sulfur.

Many development efforts are underway to create water-gas shift catalysts that can lead to compact shift reactors, catalysts that do not require in situ activation, or catalysts that are not pyrophoric in air. These include the transition metal carbides and nitrides, gold/cerium (IV) oxide, bimetallic and multimetallic oxide mixtures, platinum on mixed metal oxides, and various noble metals with molybdenum. Integrated reactor-separator configurations are also being explored to drive shift reactions toward completion.

Fischer-Tropsch synthesis

Fischer-Tropsch technology enables the catalytic conversion of synthesis gas to hydrocarbons and hydrocarbon derivatives containing more than one carbon atom. The syngas may come from almost any carbon source, such as methane, heavy oil, coal, coke, and biomass. The hydrocarbon products are mostly straight-chain alkanes (paraffins) or alkenes (olefins), especially the normal 1-alkenes (α-olefins). Straight-chain primary alcohols are the most common derivative product. Aromatics can be nearly absent from Fischer-Tropsch products, but they can be made at higher temperatures.

Today, Fischer-Tropsch technology is practiced on an industrial scale in South Africa, the Middle East, and Malaysia. These plants employ several different options for feedstocks, syngas generation, Fischer-Tropsch reactor type, catalyst, reaction conditions, and post Fischer-Tropsch product treatment.

Catalytic chemistry. Equation (2) represents the simplest of Fischer-Tropsch chemistry—alkane formation. Olefins and alcohols are formed by similar routes.

$$(2n + 1)\,H_2 \;+\; n\,CO \;\rightarrow\; C_nH_{(2n+2)} \;+\; n\,H_2O \;+\; \text{heat} \qquad (2)$$

The three types of Fischer-Tropsch catalysts are fused iron, precipitated iron, and supported cobalt. The iron catalysts have lower activity and are used at higher temperatures, generally with gas-phase reactants to make products of lower molecular weight or containing more olefins. Cobalt catalysts afford higher activity and are generally used at lower temperatures, resulting in products that may contain significant amounts of alcohols, in addition to alkanes.

High levels of the alkali promoter help control methane formation, but the potential to form heavy hydrocarbons puts a limit on this approach in the reactors with gas-phase reactants. The best fused-iron catalysts generally limit methane to about 7 percent of the total carbon in the product slate.

Cobalt catalysts for slurry-phase Fischer-Tropsch synthesis are generally supported on a spray-dried refractory support. The support would be an extrudate for a fixed-bed Fischer-Tropsch unit. Promoter metals, such as lanthanum, platinum, palladium, rhodium, and ruthenium, are typically added by impregnation, along with the cobalt. Small cobalt crystallite size is important for high activity, especially for fixed-bed units, for which continuous catalyst rejuvenation is not practical, and cobalt catalysts are designed for long life. The best cobalt catalysts produce less than 5 percent methane in the product slate.

Fluidized-bed Fischer-Tropsch reactors operate at 320-350 °C, whereas slurry reactors operate at 220-250 °C. A key difference is that there is no liquid in the high-temperature reactor outside of the catalyst particles. Were any free liquid present, it would cause catalyst agglomeration and loss of fluidization.

Product distribution. Polymethylene chain growth in Fischer-Tropsch synthesis leads to a complex product slate that not only contains different types of products—alkanes, alkenes, alcohols, and more—but also a distribution of alkyl chain lengths in each product family. The chain-length distribution for ideal growth is described by the Anderson-Schulz-Flory distribution, as shown in Figure 14.

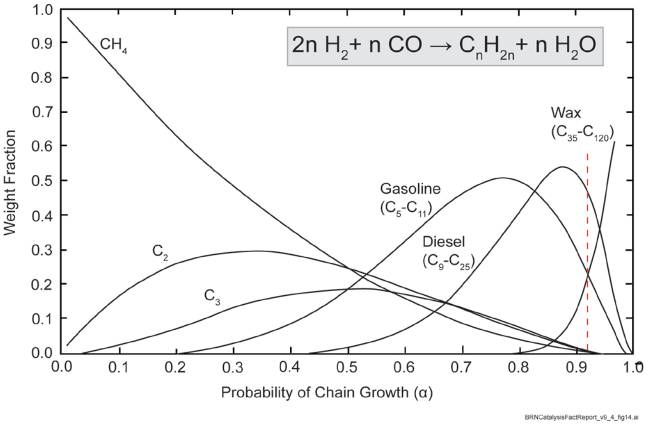

Figure 14: Product composition as a function of chain growth probability, assuming ideal Anderson-Schulz-Flory kinetics. Reprinted from Steynberg and Dry (2004) with permission from Elsevier.

Fischer-Tropsch product refining

The majority of the product from a Fischer-Tropsch plant is straight-chain aliphatic hydrocarbons. These waxy materials are easily hydrocracked to diesel fractions.

The oxygenated products, however, are more problematic materials for use within a refinery. By molecular weight, they would mostly fit in with the feed to the FCC unit. However, the resulting water would deactivate the zeolite material in the FCC unit and lead to a loss in overall activity. Furthermore, at least some of the product from the FCC unit continues on to the naphtha-reforming unit, and the reforming catalyst is extremely sensitive to water.

Alternatively, Fischer-Tropsch oxygenated species (perhaps comparable to oxygenated species from biological feedstocks) may be used as blend stocks for refinery products. Alcohols (e.g., ethanol and butanol) have high octane numbers and are used today in motor fuels. Alternatively, there are opportunities for converting the alcohols into hydrocarbon feedstocks that are compatible with current refinery processes. The available data suggest the possibilities of acid-catalyzed reactions such as alcohol dehydration and hydroprocessing reactions such as HDO, perhaps occurring in combination.

Alcohol synthesis

Syngas can be converted selectively to methanol and to higher alcohols. These alcohols can be used either as neat fuels or as fuel additives. Indeed, most gasoline sold today in the United States contains up to 10 percent by volume ethanol, and the blend E85 is 85 percent ethanol and 15 percent gasoline.

The chemical industry for decades has been using catalytic processes for the conversion of syngas to methanol. This reaction takes place at high rates and produces high yields. Catalysts incorporating copper-zinc oxides with alumina can produce selectivities to methanol as high as 99 percent.

The present fermentation route for producing ethanol is limited to using sugars and starch from parts of certain cultivated plants such as sugarcane and cereals. Corn is the principal feedstock for fermentation in the United States. By contrast, the United States has large reserves of coal that could be used for the production of ethanol through a chemical pathway. In this approach, the coal is first transformed by gasification into syngas. The syngas is either converted to methanol, which is then homologated to ethanol with additional syngas, or converted to methanol, which is then carbonylated to produce acetic acid and reduced to ethanol with separated syngas (or, in principle, the syngas could be converted directly to ethanol). Catalysts have been developed to directly convert syngas into ethanol and higher alcohols, but they suffer from low activity and poor selectivity.

Liquid Fuels from Natural Gas

Natural gas can be refrigerated and liquefied for transport or use as a cryogenic fuel. It can also be converted into liquid fuels, mainly diesel, by using the Fischer-Tropsch technology discussed in the previous sections. Gas-to-liquids technology is becoming an attractive alternative for methane resources lacking transport infrastructure (stranded gas). In most cases, distillate for diesel, turbine, and heating fuels is the most desired product, with naphtha as a lower-value gasoline-range feedstock that could be steam cracked to make olefins. Gas-to-liquid conversion of remote gas would be more widely applicable if it were efficient for small gas fields or for small amounts of associated gas (co-produced with crude oil). Such gas is often flared, putting carbon dioxide and SO_x into the atmosphere. The key influences on gas-to-liquid competitiveness are the cost of capital, operating costs of the plant, feedstock costs, scale, and ability to achieve high utilization rates in production.

References

Altgelt, K. H., and M. M. Boduszynski. 1994. C*omposition and Analysis of Heavy Petroleum Fractions.* Marcel Dekker: New York.

Argonne National Laboratory. “Argonne Premium Coal Samples.” U.S. Department of Energy, Office of Fossil Energy. Available at: http://www.anl.gov/PCS/.

Beuther, H. and B. K. Schmid. 1963. “Reaction Mechanisms and Rates in Residue Hydrodesulfurization,” *6th World Petroleum Congress, Verein zur Forderung des 6.* Welt-Erold-Kongress: Hamburg, Section 3, 297-310.

Dresselhaus, M., G. Crabtree, and M. Buchanan. 2003. *Basic Research Needs for the Hydrogen Economy.* U.S. Department of Energy, Washington, D.C. Available at: http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf.

Gates, B. C., J. R. Katzer, and G. C. A. Schuit. 1979. *Chemistry of Catalytic Processes.* McGraw-Hill: New York.

Houalla, M., N. K. Nag, A. V. Sapre, D. H. Broderick, and B. C. Gates. 1978. “Hydrodesulfurization of Dibenzothiophene Catalyzed by Sulfided $CoO-MoO_3/\gamma$- Al_2O_3: The Reaction Network,” *AIChE Journal* **24**(6), 1015-1020.

Jones, J. B. ed. 1965. *Hydrocarbons from Oil Shale, Oil Sands and Coal, Chemical Engineering Progress Symposium Series,* Vol. 54, Chapter 1, American Institute of Chemical Engineers: New York.

Lauritsen, J. V., S. Helveg, E. Lægsgaard, I. Stensgaard, B. S. Clausen, H. Topsøe, and F. Besenbacher. 2001. “Atomic-Scale Structure of Co-Mo-S Nanoclusters in Hydrotreating Catalysts,” *Journal of Catalysis* **197**, 1-5.

Li, C. L., Z. R. Xu, Z. A. Cao, B. C. Gates, and L. Petrakis. 1985. “Hydrodeoxygenation of 1-Naphthol Catalyzed by Sulfided $Ni-Mo/\gamma-Al_2O_3$: The Reaction Network,” *AIChE Journal* **31**, 170.

Newman, S. A., ed. 1983. *Shale Oil Upgrading and Refining.* Butterworth: Boston.

Ramage, M. P., K. R. Graziani, P. H. Schipper, F. J. Krambeck, and B. C. Choi. 1987. "KINPTR (Mobil's Kinetic Reforming Model): A Review of Mobil's Industrial Process Modeling Philosophy," *Advances in Chemical Engineering* **13**, 193-266.

Skinner, J. L. 1980. "Hydrogen Requirements in Shale Oil and Synthetic Crude from Coal." *ACS Symposium Series* **116** (Hydrogen: Prod. Mark.), 279-91.

Speight, J. G., ed. 1983. *The Chemistry and Technology of Coal.* Chemical Industries, Vol. 12. Marcel Dekker: New York.

Steynberg, A. P., and M. E. Dry, eds. 2004. *Fischer-Tropsch Technology*. Elsevier: Amsterdam.

Sundaram, K. M., J. R. Katzer, and K. B. Bischoff. 1988. "Modeling of Hydroprocessing Reactions," *Chemical Engineering Communications* **71**(1), 53-71.

U.S. Department of Energy (DOE) Coal Liquefaction Research Needs (COLIRN) Assessment Panel. 1989. *Coal Liquefaction: A Research & Development Research Needs Assessment: Final Report,* Vol. II. DOE/ER-0400, U.S. Department of Energy, Washington, D.C.

Venuto, P. B. and T. E. Habib. 1979. *Fluid Catalytic Cracking with Zeolite Catalysts, Chemical Industries,* Vol. 1. Marcel Dekker: New York.

Wasaka, S., S. Ibaragi, T. Hashimoto, Y. Tsukui, T. Katsuyama, and S. Shidong. 2002. "Study on Coal Liquification Characteristics of Chinese Coals," *Fuel* **81**, 1551-1557.

BIOLOGICAL FUEL FEEDSTOCKS

Introduction

Plants convert carbon dioxide with solar energy into a low-cost carbon source that can be used as feedstocks to make liquid transportation fuels. Biomass can also be part of an offset solution to the problem of carbon dioxide emissions from the transportation sector.

As much as 1.3 billion metric tons of non-food dry biomass could be sustainably produced in the United States each year. This has the energy content of 3.8 billion barrels of oil equivalent (boe). The United States currently consumes about 5 billion barrels of oil per year in the transportation sector. Therefore, biomass feedstocks cannot meet all the transportation energy needs without breakthroughs in conversion technologies or a significant increase in biomass growth area and/or biomass growth rate. However, new biomass conversion process concepts such as the Agrawal hybrid hydrogen-carbon process suggest that the needs of the total U.S. transportation sector could be met using available biomass if hydrogen from carbon-free primary energy sources such as solar, wind, or nuclear were used to chemically reduce the biomass and also to provide all process energy.

Biomass Resources

Biomass sources include forest resources, agricultural resources, municipal solid waste, and animal waste. Forest resources include logging and other removal residues, harvested biomass from timber management practices, fuel wood, forest products, wood residues, and black liquor (from paper pulp manufacture). Agriculture residues include corn stover, wheat straw, and other crop residues, grains used for ethanol synthesis, and vegetable oils. Not included in agricultural residues are animal manures and food processing wastes. Table 7 summarizes the currently used and unused resources as well as the potential resources for various subcategories of forest and agricultural resources in the United States.

Table 7: Current and potential availability of various biomass resources for fuel applications (Perelack et al. 2005).

Resource	Currently Used (Million Dry Tons)	Unused Current Availability (Million Dry Tons)	Potential Additional Availability (Million Dry Tons)	Total Resource (Million Dry Tons)
Forest Resources				
Woody residues	89	137	66	292
Black liquor	52	0	22	74
Total	141	137	88	366
Agricultural Resources				
Corn stover	0	75	95-181	170-256
Wheat straw	0	11	24-41	35-52
Other crop residues	0	58	51-76	109-134
Perennial crops	0	0	146-367	146-367
Fuel and bioproduct grains	15	0	41-72	56-87
Vegetable oil	<1	0	13-48	13-48
Total	15	144	370-785	529-944
Total	156	281	458-873	895-1310

The three main classes of biomass feedstocks currently being exploited for transportation fuels are lignocellulosics, amorphous sugars (starches, simple sugars, etc.), and triglycerides (vegetable oils and animal fats). The cost of biomass is highly dependent on biomass growth location. However, it typically decreases in the following sequence:

triglycerides > amorphous sugars > lignocellulosics

The ease of conversion of biomass to liquid fuel likewise decreases in the following sequence:

triglycerides > amorphous sugars > lignocellulosics

Advances in biotechnology are focusing on the development of high-yield growth crops including energy cane, miscanthus, switchgrass, and hybrid poplar. In terms of yield of biomass on an energy basis, lignocellulosic biomass (approximate yield of lignocellulosic biomass: 40-70 boe/ha-yr) is by far greater than amorphous sugars (20 boe/ha-yr) or triglycerides (7-14 boe/ha-yr). Lignocellulosic biomass is the cheapest, fastest growing, and most abundant form of biomass.

Carbohydrates

The primary biomass feedstock for producing ethanol in the United States is starch-rich corn grain, although other grains would be suitable if their prices were competitive.

Starch is a polysaccharide consisting of amylose and amylopectin. Amylose is an α-(1,4) linear polymer of glucose and can contain several thousand glucose units. Amylopectin is a highly branched polymer of glucose and typically contains 300-3000 glucose units.

Cellulose is a natural linear polymer consisting of β-1,4 linkages of the six-carbon sugar, D-glucose. Cellulose typically contains between 200 and 10,000 glucose molecules in the chain.

Hemicellulose is a branched polymer made up of a mixture of the five-carbon sugars xylose and arabinose (in hardwoods) and six-carbon sugars including glucose, mannose, and rhamnose (in softwoods). Sugar acids such as mannuronic and glacturonic acids are also found in hemicellulose. Hemicellulose molecules typically contain between 50 and 200 sugar units.

Table 8 compares the nominal concentrations of cellulose, hemicellulose, and lignin in wood and selected herbaceous crops. There can be considerable variation in the concentrations of these components depending on the plant species and the specific portion of the plant of interest. Both wood and herbaceous crops have between 60 and 68 percent (dry basis) cellulose plus hemicellulose, which can be hydrolyzed into their basic sugar monomers, such as glucose, xylose and arabinose, and other five- and six-carbon sugars.

Table 8: Nominal cellulose, hemicellulose, and lignin in wood and selected herbaceous crops, dry basis (PHYLLIS: ECN database on composition of biomass and waste, available at http://www.ecn.nl/phyllis/).

Biomass Source	Composition (wt%)		
	Cellulose	Hemicellulose	Lignin
Wood	39.8	23.3	24.8
Corn stover	35.3	25.3	10.8
Switchgrass	36.9	30.6	9.6
Wheat straw	37.8	26.5	17.55

Lignin

Lignin is a large, randomly constructed, highly aromatic, cross-linked macromolecule. It has molecular weights greater than 10,000 amu. Lignin is constructed mainly from a mixture of the three monolignols: coniferyl alcohol (in hardwoods), sinapyl alcohol (in softwoods), and paracoumaryl alcohol. Other monolignols may also be present depending on the plant species.

Black liquor is produced during the manufacture of wood pulp. It is a highly alkaline aqueous solution, rich in lignin and sodium salts. Table 9 provides a typical composition of Kraft black liquor. It is burned in the pulp and paper industry to recover the alkali and as a fuel, providing a substantial portion of the energy needs of a pulp plant.

Table 9: Percentage of chemical species in Kraft black liquor (Adams 1997).

Chemical Species	Nominal Concentration (wt%)
Alkali lignin	30-45
Hydroxy acids	25-35
Extractives	3-5
Acetic acid	5
Formic acid	3
Methanol	1
Sulfur	5
Sodium	15

Oil seeds

Soybeans, which are rich in vegetable oil, are the principal resource for producing biodiesel fuel in the United States, although other oil seed crops such as rape (canola), mustard, flax, sunflower, palm, and coconut are also used. Waste cooking oil is also a currently important source of vegetable oils for biodiesel and includes cooking oils derived from animal fats.

Vegetable oils are triglyceride lipids, esters consisting of glycerol and three fatty acids. The triglycerides in vegetable oils typically contain a mixture of fatty acids. Soybean oil, for example, typically contains 7 percent linolenic acid, 51 percent linoleic acid, 23 percent oleic acid, 4 percent stearic acid, and 10 percent palmitic acid.

Both grains and oil seeds contain significant quantities of carbohydrates, vegetable oil, and proteins. Table 10 summarizes the nominal amounts of all three components in various grain and oil seed crops.

Biomass as a fuel feedstock

Biomass-derived feedstocks contain highly oxygenated compounds that have a high degree of functionality and low thermal stability. In contrast, petroleum-derived feedstocks have a high degree of thermal stability and low functionality. The grand challenge with biomass conversion strategies is how to remove oxygen efficiently from hydrophilic biomass-derived feedstocks and produce liquid fuel products with good combustion and thermochemical properties. Oxygen can be removed as carbon monoxide, carbon dioxide, or water. Reactions, catalysts, and processes must be developed and optimized for a new class of feedstocks: those derived from plant biomass.

Table 10: Nominal ranges of starch oil and protein from selected seed crops.

Seed	Starch (wt%)	Sugars (wt%)	Oil (wt%)	Protein (wt%)
Corn[a,b]	64-72	NR	4-5	8-14
	68-74	2	4-6	8-12
Soybean[c,d]	NR	NR	16-20	31-43
	5	10	22	42
Sunflower[e]	NR	NR	25-38	26-28
Rapeseed[f]	~3	~5	42-44	~22
Flaxseed[g]			41	20
Mustard seed[h]			35	38

a) Borás, L., J. A. Curá, and M. E. Otegui. 2002. “Maize Kernal Composition and Post-flowering Source Sink Ratio.” *Crop Science* **42**, 781-790.
b) Watson, A., and P. E. Ramstad. 1987. *Corn: Chemistry and Technology.* American Association of Cereal Chemists, Inc.: St. Paul, Minnesota.
c) Maier, D. E., J. L. Briggs, and R. W. Gann. 1997. 1*996 Indiana Soybean Composition Data*. Grain Quality Task Force #31. Purdue University Cooperative Extension Service, West Lafayette, Indiana. Available at http://www.ces.purdue.edu/extmedia/GQ/GQ-31.html.
d) Sale, P. W. G., and L. C. Campbell. 1986. “Yield and Composition of Soybean Seed as a Function of Potassium Supply,” *Plant Soil* **96**, 317-325.
e) de Rodriguez, D. J., B. S. Phillips, R. Rodriguez-García, and J. L. Angulo-Sánchez. 2002. “Grain Yield and Fatty Acid Composition of Sunflower Seed for Cultivars Developed under Dry Land Conditions.” *Trends in New Crops and New Uses*, ed. J. Janick and A. Whipkey. The American Society for Horticultural Science (ASHS) Press: Alexandria, Virginia.
f) Canola Council of Canada. Available at http://www.canola-council.org/PDF/canolamealnutrientcom.pdf#zoom=100.
g) Thiessen, D. L. 2004. “Optimization of Feed Peas, Canola and Flaxseed for Aqua Feeds: the Canadian Prairie Perspective.” *Avances en Nutrición Acuicola VII. Memorias del VII Simposium Internacional de Nutrición Acíucola,* ed. L. E. Suárez, M. D. Ricque, M. G. Nieto López, D. Villarreal, U. Scholz, and M. González. Hermosillo: Sonora, México.
h) Sengupta, R., and D. K. Bhattacharyya. 1996. “Enzymatic Extraction of Mustard Seed and Rice Bran,” *Journal of the American Oil Chemists’ Society* **73**(6), 687-692.

Lignocellulosic biomass is a low-energy-density feedstock; thus, costs for transportation of the feedstock are high. This means that it would be desirable to have dispersed processes that are built close to the locations of the biomass sources. However, because of economies of scale, the costs to produce commodities typically decrease with increased size of the production unit. Thus, it would be desirable to have large biorefineries to take advantage of the benefits of economy of scale. Consequently, in biomass conversion, there is a tradeoff between economies of scale and transportation costs. These are typical of the practical engineering challenges in the exploitation of biomass for transportation fuels.

Biomass is amenable to both chemical and biological conversion. Chemical catalysts convert biomass-derived feedstock to liquid products over a wide range of conditions ranging from 100 to 1000 °C and ranging from 1 to 200 atm. These temperatures are higher than the operating temperatures of biological catalysts (enzymes). Thus, chemical conversion processes have shorter residence times and smaller reactor volumes than typical biological conversion processes exploiting enzymatic catalysis. Processes that use heterogeneous chemical catalysis may also be attractive if the catalysts are easily recoverable or cost less than biological catalysts. In both chemical and biological conversion processes, developing improved catalysts is a major challenge.

Producing biofuels is also directly related to the challenge of developing low-cost hydrogen. Like coal, biomass is generally hydrogen-deficient compared to petroleum-derived feedstocks and typical liquid fuels. The required hydrogen can be produced from biomass or fossil sources with co-product carbon dioxide production, or possibly from water using nuclear or solar energy, as mentioned previously.

Indirect Biofuel Production

A range of processes is available for converting lignocellulosic biomass into liquid fuels; the conversion processes fall into three general classes:

- high temperature for syngas production
- intermediate temperature for bio-oil production
- low temperature for aqueous sugar production.

These approaches have been investigated at an applied level with a focus on process development; however, for these processes to become truly economical, the basic chemistry, biochemistry, and associated catalysis must be understood on a fundamental level. Efficient catalysts and enzymes that are selective, stable, and active are lacking for biomass-derived feedstocks.

Biomass gasification

As summarized previously, thermochemical gasification converts carbon-containing feedstocks, including biomass, into gaseous products (carbon monoxide and hydrogen) that can potentially be used to produce liquid fuels or heat and power. However, biomass contains significant potassium, sodium, and other alkali metals that can cause slagging and fouling problems in conventional gasification equipment. Therefore, biomass gasification is typically conducted at lower temperatures (850-1000 °C) in the presence of air, oxygen, or steam, resulting in a complex combination of reactions in the solid, liquid, and gas phases including pyrolysis, partial oxidation, and steam reforming.

Pyrolysis is the thermal decomposition of the feedstock into gaseous, liquid, and solid products without oxygen or steam. Partial oxidation processes use less than the stoichiometric amount of oxygen required for complete combustion to increase temperature. Steam reforming involves the reaction of water with the biomass-derived feedstock to produce syngas. Again, the water-gas shift reaction and methanation can also occur during gasification.

As with coal gasification, heat to drive the gasification reactions can be provided directly or indirectly. In air- and oxygen-blown gasifiers, heat is provided by partially oxidizing the biomass feedstock. In air-blown gasifiers, the nitrogen in the air dilutes the product gas, resulting in a low-energy product suitable for heat and power applications, but not suitable for producing liquid fuels. Oxygen-blown gasifiers use purified oxygen instead of air to partially oxidize the biomass, producing medium-energy-content gas that is suitable for both heat and power applications. The gas can also be used for fuel synthesis after cleanup and conditioning. Biomass is sufficiently reactive so that heat for the gasification reaction can also be provided by indirect methods, usually with the addition of steam to improve the char gasification reactions. Indirectly fired gasifiers produce a medium-energy gas suitable for fuels synthesis or heat applications.

Because of generally lower gasification temperatures in biomass conversion, higher-molecular-weight hydrocarbon tars can be formed. They condense in exit pipes and on particulate filters, leading to blockages. Tars also cause further downstream problems by clogging fuel lines and injectors in internal combustion engines. Tar removal, conversion, or destruction is a major technical challenge for the successful development of commercial biomass gasification. One approach to decrease the tar concentration is to add solid catalysts such as palladium, platinum, ruthenium, or nickel supported on CeO_2/SiO_2, inside the gasification reactors.

Nickel-containing catalysts have high activities for tar destruction and methane reforming. In addition, these catalysts have some water-gas shift activity. The reaction conditions required for nickel-containing catalysts are temperatures of 600-900 °C and contact times of 0.01-3 s. Most of the nickel catalysts were supported on low-surface-area aluminas. Magnesium oxide, calcium oxide, silicon dioxide, potassium oxide, and copper(II) oxide have been added to nickel-containing catalysts. Several novel catalyst compositions have been tried as well for this reaction, including Ni/dolomite, Co/MgO, Ni/MgO, $LaNi_{0.3}Fe_{0.7}O_3$, and $Ni/LaO/Al_2O_3$. Several deactivation mechanisms occur with nickel-containing catalysts. These mechanisms include poisoning by sulfur, chlorine, alkali metals, and coke formation. The coke can be removed by oxidation; however, repeated high-temperature regenerations of these catalysts lead to sintering, phase transformations, and volatilization of the nickel. Effective hot gas conditioning requires developing new catalysts that are effective in tar removal, resistant to deactivation because of carbon fouling, capable of providing suitable H_2:CO ratios for downstream processing, resistant to attrition, easily regenerated, and inexpensive.

Alkali metal catalysts (such as K_2CO_3, Na_2CO_3, $Na_3H(CO_3)_2$, $Na_2B_4O_7 \cdot 10H_2O$, $CsCO_3$, NaCl, KCl) as well as well as ZnC_{l2} and $AlC_{l3} \cdot 6H_2O$ have been added to biomass feedstocks by using dry mixing or wet impregnation. Although alkali metal salts decrease tar formation, they also enhance char yields. Alkali metals may not be attractive as commercial gasification catalysts because of poor carbon conversion and difficulty of removal from products. They also lead to increased rates of mineral product production.

At present, numerous biomass gasifiers produce gases for heat and power applications. Most are air-blown gasifiers producing a low-energy syngas. Examples include a large-scale (~100 MWt) fluidized-bed gasifier in Lahti, Finland, that provides fuel gas to co-fire a coal combustor, smaller gasifiers in Denmark that use straw for combined heat and electricity generation in district heating systems, and others in applications where the quality of the product gas need not be high. Limited amounts of biofuels are also produced via gasification at present. In Germany, biomass is co-gasified with coal and other hydrocarbon resources to produce a syngas that is converted to methanol and sometimes Fischer-Tropsch liquids. Several smaller demonstrations of biomass gasification for liquid fuels are active in Europe where Fischer-Tropsch liquids are favored because of the large demands for diesel fuel. No commercial biomass gasification facilities are currently operating in the United States.

Biosyngas utilization

Syngas produced from biomass gasification can be used to produce fuels. These fuels can be produced by applying many of the processes available to use coal-derived syngas and natural gas. These processes include hydrogen production by the water-gas shift reaction, gasoline or diesel fuels by Fischer-Tropsch synthesis, and methanol or other alcohols for fuel or fuel additives. See previous sections.

Although proven catalysts exist for manufacturing Fischer-Tropsch liquids, methanol, and other products, they are best suited to large-scale facilities where economies of scale make multiple-pass conversion systems economically feasible. The known catalysts are much less active and selective for other products, including ethanol. Highly active and selective catalysts for fuel synthesis with improved tolerance to syngas impurities from biomass feedstocks might enable cost-effective production of liquid fuels on relatively small scales.

Direct Biofuel Production

Bio-oil fuels

The chemical production of liquid fuels from biomass typically involves a two-step process. In the initial step, biomass solids are liquefied and deoxygenated to varying degrees. In the upgrading step, crude bio-oil is sufficiently deoxygenated and the molecular weight reduced sufficiently to produce useable liquid fuel. The process development work on the liquefaction step has moved away from the use of catalysts to less-demanding, non-catalytic processes. In all cases, the upgrading step has required the use of a catalyst to achieve high degrees of deoxygenation and molecular-weight reduction.

The initial liquefaction processes can be categorized into simple pyrolytic processes (usually performed at near atmospheric pressure) or solvent-based liquefaction processes, usually requiring a high operating pressure.

Pyrolysis. Simple thermal decomposition processes performed in a fluidized bed are called pyrolysis to distinguish the processes from gasification processes, which often incorporate partial oxidation and steam reforming chemistry. Pyrolysis at lower temperature (500 °C vs. 700-1000 °C) will produce less gas product. Performing the pyrolysis process with a short residence time (less than a second, called fast or flash pyrolysis) maximizes liquid product yield. Extended time at higher temperatures or operation at elevated pressure in fixed beds tends to maximize solid (char) product formation. There has been limited investigation of catalysts in simple pyrolysis systems. The introduction of acid or base catalysts by impregnating the biomass feedstock has been investigated as a means to change the product oil composition. Improved yields of levoglucosan or hydroxyacetaldehyde, for example, have been claimed. Other catalytic processing has mimicked the catalytic cracking of petroleum with the use of heterogeneous acid catalysts. This processing usually leads to high levels of coking on the catalyst with deactivation after short periods. There have been only preliminary investigations of the use of catalysts and a reducing gas atmosphere. The potential use of catalysts for redirecting the pyrolytic pathways to favor liquid products over gas or char is a challenge.

Liquefaction. Biomass liquefaction is accomplished in slurry-feed reactors operated at elevated pressure. Water has been most commonly used as a solvent (known as hydrothermal liquefaction), but the use of the recycled oil product or other organic carriers has also been tested. Use of catalysts has been more common in this type of process than pyrolysis. Alkali has been found to be useful in promoting reactions leading to oil products, which more readily separate from water. In combination with carbon monoxide or syngas, alkali is thought to form active reducing agents variously suggested to be nascent hydrogen or formate. Heterogeneous and homogeneous metal catalysts have also been investigated. The heterogeneous metals are most commonly used in combination with hydrogen gas. The mechanisms of the homogenous catalysts similarly used are not completely understood, but they appear to be a combination of the base-promoted chemistry and metal-catalyzed hydrogenation. The use of hydrogen-donor solvents has also been reported.

The crude products from these liquefaction processes are complex mixtures of oxygenates derived from the lingocellulosic biopolymer structures. As such, the bio-oils can be used for direct firing for heat and power production but cannot be used for transportation fuels. The main concerns for bio-oils as a fuel are difficult ignition (because of low heating value and high water content), poor volatility, high viscosity, coking, corrosiveness, and cold flow problems. More specifically, bio-oils have lower energy densities than hydrocarbons and can be thermally unstable in the case of pyrolysis products or highly viscous in the case of the liquefaction products, and must be upgraded or blended. Further upgrading of the crude bio-oils has been investigated using various catalytic methods to attempt to produce a hydrocarbon product compatible with petroleum refinery processes, products, and distribution systems as well as being useful in existing engine systems. Two general tactics have been pursued: catalytic hydroprocessing and catalytic cracking.

Hydrodeoxygenation. Hydrodeoxygenation of bio-oils involves treating the oils at moderate temperatures (300-600 °C) with high-pressure hydrogen in the presence of heterogeneous catalysts. It is desirable to avoid hydrogenation of aromatics in the bio-oils, because this would decrease the octane number and increase hydrogen consumption. Hydrodeoxygenation, similar to hydrodesulfurization used in petroleum processing, has been developed for bio-oils. This type of technology using the same types of catalysts (e.g., sulfided Co-Mo or Ni-Mo) has been found to be directly applicable to the biomass liquefaction products. Its application to pyrolysis bio-oils is not straightforward because of the thermal instability of the pyrolysis product. An additional step is required to produce a stabilized pyrolysis bio-oil product before finishing the hydrodeoxygenation process. High levels of oxygen removal are possible with this method but require low space velocities. Other reports describe the use of more active precious metal catalysts as another option. A range of oxygenate and hydrocarbon products is possible with these catalysts depending on the processing conditions.

The long-term stability of these catalyst systems remains unknown. Adding sulfur (dimethyl disulfide) to the feed is needed to keep the sulfided cobalt-molybdenum or nickel-molybdenum catalysts from deactivating. Stability of the support material is a key issue related to the high level of water in the system. Coke formation on the catalyst is also a challenge. The use of gamma-alumina supports has been implicated as a contributor to both problems, while catalyst formulations based on activated carbon supports have been shown to be useful. Future work in hydrodeoxygenation could focus on developing non-sulfur-based catalysts with enhanced stability that do not require high-pressure hydrogen.

Catalytic cracking. Non-hydrogenation methods for upgrading bio-oils have been investigated. The acidic materials such as zeolite catalysts used in petroleum catalytic cracking have been tested to reduce oxygen content and improve thermal stability of bio-oils. The advantages of using a zeolite catalyst are that no hydrogen is required, processes are operated at atmospheric pressure, and temperatures are similar to those for bio-oil production. Although catalytic cracking of biomass liquefaction products has not been useful, the application of catalytic cracking to pyrolysis bio-oils has yielded better results. The problems are the same as in the direct use of the catalyst in the pyrolytic reactor, namely high coke formation rates on the catalyst and rapid deactivation. Feedstocks containing phospholipids are particularly problematic. The liquid hydrocarbon product produced is typically highly aromatic.

Steam reforming. Steam reforming of bio-oils can be used for syngas or hydrogen production. In particular, for distributed hydrogen production, transporting the dense bio-oil is cheaper than transporting biomass. Although steam reforming of bio-oils is an extension of well-established steam reforming of hydrocarbons, some bio-oil components are thermally unstable and can cause severe catalyst deactivation problems because of coke formation. A potential means to mitigate this problem is to partially hydrogenate the bio-oils before the steam reforming section. Partial hydrotreating of bio-oils at lower temperatures will improve thermal stability and should decrease the amount of coking on the catalyst.

Bioethanol from fermentation of sugars

Carbohydrate biomass can be converted into sugars by low-temperature reactions involving hydrolysis. Sugars can then be fermented selectively into targeted fuels such as ethanol or butanol. Biomass conversion into sugar monomer units is a function of the biomass type. Some plant materials, such as sugarcane and cornstarch, are easily converted into monomer units. Lignocellulose is difficult to break up into monomer units because of its nature, and a significant amount of research has been done to selectively convert this low-cost material into monomer units.

Sugar and starch processes. In Brazil, sugarcane, which grows in tropical climates, is an economical source of fermentable sugar. In the sugarcane process, the disaccharide sucrose is simply expressed from crushed raw sugarcane plants and used for fermentation. In the United States, cornstarch is the major carbohydrate used for ethanol production. In this process, enzymes are used to liquefy and saccharify starch into a glucose monomer stream for subsequent fermentation.

The predominant corn processing method in the United States is dry grinding, which accounts for about two-thirds of the total ethanol production. In dry grinding, whole corn is ground into flour that is subsequently combined with water to form “mash.” To hydrolyze into soluble dextrins and liquefy the starch in the mash, a combination of alpha amylase and heat is used. The mash is then cooled and treated with a second enzyme, glucoamylase, to release glucose.

Wet mills separate corn into streams that include fiber, gluten, germ, and starch. In turn, these components are converted into valuable products, including ethanol. The starch fraction is processed in a similar method (enzymatic deconstruction) as the dry grind process. Wet mills are responsible for roughly a third of the ethanol production in the United States. Approximately 2.5 gallons of ethanol are produced per bushel of corn by the wet mill process compared to 2.8 gallons for the dry grind process. Wet mill ethanol plants are 2-4 times more expensive to build than are dry grind plants.

Cellulose pretreatment. With ethanol production on the rise in the United States, the demand for cornstarch for fermentation will seriously conflict with other demands for corn. Current production capacity is greater than 5 billion gallons per year, and the maximum from cornstarch is 12-15 billion gallons per year. With the presidential goals of 35 billion gallons per year by 2017 and 60 billion gallons per year by 2030, it is clear that alternative sources of fermentable sugars must be utilized to increase bioethanol output. The hydrolysis of cellulose and hemicellulose from lignocellulosic feedstock is intended to fill the gap between cornstarch ethanol output and bioethanol demand.

Lignocellulose sources require preliminary processing to decrease the crystallinity of cellulose, increase biomass surface area, remove hemicellulose, and break the lignin matrix. This pretreatment changes the biomass structure and improves later processing. Pretreatment methods include physical, chemical, thermal, or combinations of these three methods. The most cost-effective and promising pretreatment methods are dilute acid hydrolysis, uncatalyzed steam explosion, pH-controlled hot water, treatment with lime, and treatment with ammonia. Pretreatment is one of the most expensive processing steps for producing sugars from cellulosic biomass and is one of the least understood processing operations.

To increase the rate of hydrolysis, biomass must be thermochemically and/or mechanically pretreated to increase enzyme access to the substrate. Although low pH thermochemical pretreatments hydrolyze hemicellulose and leave cellulose and lignin intact, high pH thermochemical pretreatments remove lignin leaving cellulose and hemicellulose. Thermochemical pretreatments are problematic because of chemical and energy costs and waste stream issues. In addition, the heat and acid often generate byproducts such as acetate and furfurals that inhibit the yeast or other microbial ethanologen. Mechanical pretreatment is costly from an energy input standpoint because energy must be used to physically break the biomass into smaller pieces to make it more accessible to enzymes.

Some of the more common pretreatment methods are catalytic (dilute acid) or physical (ammonia fiber explosion) processes. Typical sugar recovery yields are shown in Table 11. The technologies are capital-intensive, requiring expensive reactors and/or expensive catalyst recovery schemes.

Table 11: Cellulose pretreatment process yields (Eggeman et al. 2005).

Pretreatment	**Xylose Yields (% Theoretical)***		**Glucose Yields (% Theoretical)***	
	After Pretreatment	**After Enzymatic Hydrolysis**	**After Pretreatment**	**After Enzymatic Hydrolysis**
Dilute acid	90.2/89.7	95.6/95.1	8.0/7.5	85.1/84.6
Hot water	50.8/7.3	81.8/38.3	4.5/2.0	90.5/88.0
Ammonia fiber explosion	0/0	92.7/77.6	0/0	95.9
Ammonia recycle percolation	47.2/0	88.3/41.1	1.4	90.1
Lime	24.3/0.8	75.3/51.8	1.6/0.5	92.4/91.3
No pretreatment	0	8.5	0	15.7
Ideal pretreatment	–	100	–	100
* Soluble sugar yields = (oligomer + monomer)/monomer; single number = monomer				

Alternate technologies are emerging. It has been known for some time that cellulose is soluble in certain ionic liquids at levels up to 5 percent. More recently, this has been extended to whole biomass. Other solvent systems show interesting results as well. Trifluoroacetic acid is effective at decrystallizing cellulose at low temperatures. Fundamental understanding of the nature of hydrated cellulose in biomass and of disrupting cellulose crystallinity could lead to improved enzymatic access and lower cost fermentable sugars.

Cellulose hydrolysis. Cellulose and hemicellulose hydrolysis to sugars can be catalyzed by acids or enzymes. The acid hydrolysis reactions are heterogeneous and mass transfer limitations can be an issue. Undesired byproducts of acid hydrolysis include 5-hydroxymethylfurfural (HMF) and levulinic acid, which are produced by acid catalyzed degradation of sugars. In addition, modified cellulose could be formed during acid hydrolysis that cannot be further hydrolyzed to glucose. The maximum yield of glucose is typically less than 70 percent.

Heterogeneous reactions occur during cellulose hydrolysis in biomass where the acid first penetrates into amorphous cellulose regions leading to an initial rapid decrease in the degree of polymerization. Oxidation of cellulose (with oxidizing agents such as H_2O_2, $NaClO_2$, O_3, $KBrO_3$) before hydrolysis or during progressive hydrolysis reduces the degree of polymerization of partially hydrolyzed residues. This treatment decreases the aldehyde concentration and increases the carboxyaldehyde concentration, which prevents recrystallization. Recrystallization can occur during acid or enzymatic hydrolysis.

Of the three major plant biomass polymers, cellulose with its uniform polymeric glucose structure is the simplest target for biocatalytic deconstruction. Only three enzyme activities are needed for degradation of cellulose: endo-β-1,4-glucanase, exo-β-1,4-glucanase, and β-glucosidase. Endo-β-1,4-glucanases cleave cellulose in the middle of the chain, creating more reducing and non-reducing ends. Exo-β-1,4-glucanases liberate cellobiose, two-glucose oligomers. Depending on the enzyme, cellobiose is generated specifically from either the cellulose-reducing end or the non-reducing end. β-glucosidases cleave glucose from the non-reducing ends of glucose oligomers, predominantly cellobiose.

In contrast to cellulose, the enzymes needed for deconstruction of hemicellulose are less well-defined because of the heterogeneous nature of the polymer across the plant kingdom. Hemicellulose derived from corn, for example, consists of a xylan backbone with side chain constituents—arabinose, acetate, xylose, glucuronic acid, and ferulic acid. Enzymatic deconstruction of the xylan backbone is similar to cellulose deconstruction with endo-xylanases, exo-xylanases, and β-xylosidases performing functions analogous to endo-β-1,4-glucanases, exo-β-1,4-glucanases, and β-glucosidases, respectively. The action of these enzymes is effectively inhibited when side chains are encountered. Thus, α-arabinofuranosidase, α-glucuronidase, and a variety of esterase activities are needed to denude the xylan backbone for efficient enzymatic deconstruction.

Ethanol production by fermentation. Sucrose from sugarcane or glucose from cornstarch or cellulose hydrolysis is fermented by *Saccharomyces cerevisiae* and related yeasts into ethanol with carbon dioxide co-production. The ethanol concentration can reach the range of 10-12 percent after 48-72 h of fermentation. The ethanol is then distilled to 95 percent purity. Azeotropic distillation, pervaporation, molecular sieves, or adsorption is used to remove the remaining 5 percent of water. Material that remains in the still after distillation is converted into animal feed.

The vast majority of ethanol processes utilize the yeast *S. cerevisiae* in an anaerobic fermentation of hexoses to ethanol. In some processes, yeast can be separated from the fermentation broth, washed, and then reused. Other, older batch ethanol processes do not reuse the yeast. Ethanol is produced via the glycolytic pathway. Glucose, fructose, and mannose are able to enter the cell by passive transport using a variety of hexose transporters. Galactose is another hexose, which can be utilized by *S. cerevisiae* for ethanol production, but it requires a specific transporter and is often not utilized simultaneously with glucose. The conversion of galactose involves more steps than the other sugars. Once inside the cell, glucose, fructose, mannose, and galactose enter the glycolytic pathway via enzymatic epimerization and phosphorylation to fructose-6-phosphate. One major limitation of *S. cerevisiae* is its inability to utilize pentoses, such as xylose and arabinose.

Enzyme production. Current processes for degradation of lignocellulosic biomass primarily use fungi as both the source and production host for biomass degrading enzymes. In 2000, the U.S. Department of Energy sponsored projects to reduce the costs of cellulose-degrading enzymes by ten times. Although this target was exceeded, enzyme costs remain a bottleneck for cellulosic ethanol.

One way in which costs can be lowered is through more efficient production of enzymes. This may be achieved by a combination of bioprocess optimization and genetic methods. Enzyme secretion is a complex cellular process. Regulation of enzyme production occurs at many levels: transcription, translation, post-translational modification, and the cellular secretion pathway. Modifying bioprocessing methods such as medium composition, aeration, and mixing can affect all biological machinery involved in cell growth and protein secretion. Exploring bioprocess parameter space for optimal protein secretion is a necessary component of any program to improve protein secretion.

Genetic modification of protein secretion organisms is another powerful method to improve secretion of enzymes. Classical forward genetic methods involve chemical or radiological treatment that randomly mutates an organism’s genome. The random nature of this type of mutagenesis results in positive phenotypes such as decreased protease secretion as well as negative phenotypes such as reduced sporulation. A combination of genome sequence and molecular tractability of an organism leads to the ability to perform reverse genetic screens for improved enzyme secretion. In these situations, genes are selectively deleted or overexpressed and then assayed for improved protein secretion. Large functional genomic projects that “scan” the genome have the potential to identify large numbers of genes with roles in protein secretion. Once identified, multiple gene deletion and overexpression mutations can be “stacked” into a single strain. While classical mutagenesis has been used for many decades, few large-scale functional genomic programs have been implemented.

Enzyme discovery and engineering. Although the activities needed for deconstruction of cellulose and, to a lesser extent, hemicellulose are known, significant room for improvement exists. Microbes use one of two strategies for enzymatic degradation of biomass: cellulosomes and mixed individual enzymes. Cellulosomes are secreted protein complexes wherein a number of individual enzymes with a variety of activities are attached to a common scaffold. Cellulosomes have been thoroughly investigated in bacteria and are thought to exist in anaerobic rumen chytrid fungi. The more common microbial strategy is the secretion of a mixture containing individual enzymes that do not form a single complex. The combination of enzyme activities constitutes a biomass-degrading cocktail. A majority of fungi and other microbes use this mixed-enzyme strategy for digestion of plant biomass.

The catalog of known and characterized biomass-degrading enzymes derived from microbes remains small when compared to the potential that is present in nature. Any particular enzyme has a narrow range of activity and stability optima. Thus, product inhibition, range of pH, temperature, and stability optima for available enzymes are limited by the small number of enzymes known to be active. One strategy to expand the range of optimal enzyme activity conditions involves random or directed mutation of well-characterized, biomass-degrading enzymes with the goal of improving a desired property, such as thermostability. An alternative approach is the implementation of aggressive genome-sequencing projects for phylogenetically diverse groups of fungi and other biomass-degrading microbes with the goal of expanding the catalog of genes that encode for biomass-degrading enzymes. In parallel to enzyme improvement and discovery projects, molecular genetic methods are being used to engineer custom cellulosome scaffolds that bind specific sets of enzymes.

Ethanologens. Because *S. cerevisiae* lacks the ability to utilize pentoses and because this microbe is used to ferment both cornstarch and sugarcane ethanol, using pentoses for ethanol production is problematic. A large body of research and development has gone into metabolic engineering of microbes to use pentoses efficiently. Although industry uses the processes that use these strains, they perform at levels lower than optimized *S. cerevisiae* hexose fermentations. An example of such a situation is the use of the bacteria *Escherichia coli* that has been engineered for mixed sugar fermentation. The ethanol tolerance of this organism is less than half that of *S. cerevisiae,* resulting in lower final concentrations of ethanol. Research and development has not been limited to organisms that require genetic modification to utilize a mix of sugars. Indeed, a number of microbes are able to utilize pentoses to produce ethanol without metabolic engineering, albeit at a slower rate and lower final product concentration.

A major challenge for all ethanologens is non-simultaneous use of sugars. In a mixed glucose, xylose, and arabinose fermentation, for example, many microbes will ferment glucose before xylose and xylose before arabinose. This results in decreased economic viability of a process because of the extended fermentation time. Even organisms with endogenous machinery for mixed hexose and pentose ethanol production are candidates for metabolic engineering to increase the rate of ethanol production, percent yield, and final titers.

Consolidated bioprocessing. Processing regimes have been explored for producing biofuels from cellulosic and hemicellulosic biomass (Table 12). The most economical approach may be the consolidated bioprocess because each additional bioreactor and/or bioprocess step adds capital cost. Consolidated bioprocesses involving single organisms or co-cultures of two or more organisms are possible. Whether one or many organisms, it is likely that genetic manipulation and metabolic engineering will need to be performed to make a consolidated bioprocess scheme efficient and economical.

Table 12: Cellulosic and hemicellulosic bioprocessing schemes.

Process Name	**Summary of Process**
Separate hydrolysis and fermentation	Production of biomass-degrading enzymes, biomass deconstruction, hexose fermentation, and pentose fermentation are performed as four discrete processes.
Simultaneous saccharification and fermentation	Production of biomass-degrading enzymes, biomass deconstruction combined with hexose fermentation, and pentose fermentation are performed as three discrete processes.
Simultaneous saccharification and cofermentation	Production of biomass-degrading enzymes and biomass deconstruction combined with hexose/pentose fermentation are performed as two discrete processes.
Consolidated bioprocess	Production of biomass-degrading enzymes, biomass deconstruction, hexose fermentation, and pentose fermentation are performed as a single process.

Current research in this field is focused on engineering and improvements into anaerobic bacterial strains that secrete cellulosomes and ferment sugars to ethanol. Research is also focused on engineering yeast to secrete cellulases for single-process ethanol production from cellulose. One promising area where currently there is a paucity of research is in the optimization of consolidated bioprocesses for ethanol production from filamentous fungi. Filamentous fungi have the capacity to degrade biomass, metabolize hexose and pentose sugars efficiently, and produce ethanol under anaerobic growth conditions. Challenges facing all bioprocessing schemes, whether four steps or one, include organism growth inhibition by non-sugar contaminants and byproducts of lignocellulose deconstruction, substrate accessibility, product inhibition by both biomass hydrolysis and fermentation products, and separation of sugars and/or products from unhydrolyzed biomass and contaminants.

Biobutanol

The United States has a dedicated effort to produce massive amounts of fermentation ethanol to replace imported oil for transportation fuel. *n*-Butanol has properties that also make it attractive as a fuel (Table 13). Like ethanol, it can be made via fermentation. Its octane value is lower than that of ethanol, but its energy content is higher, both on a volume and weight basis, and it has a higher density but lower Reid vapor pressure than ethanol. *n*-Butanol is more widely miscible with gasoline, is less affected by moisture than is ethanol, and its stoichiometric air:fuel ratio is closer to gasoline than ethanol.

Recently, plans have been announced to produce *n*-butanol, from sugar beets, as a transportation fuel. It has been claimed that advances in organism genetic engineering have drastically improved the yields of *n*-butanol and process-engineering improvements have reduced overall complexity and costs. Plants are reported to be producing about 30,000 mt/yr of *n*-butanol and is expected to be producing renewable fuel by the end of 2007.

Table 13: Comparison of alcohol and gasoline fuels.

Property	Ethanol	*n*-Butanol	Gasoline
Btu/gal	76,100	96,100	114,800
Reid vapor pressure at 100 °F	2.0 psi	0.33 psi	2-4.5 psi
Density (lb/gal)	6.59	6.76	6.1-6.2
Research octane	130	96	91-99
Motor octane	96	78	81-89
Energy density (MJ/L)	19.6	29.2	32
Air:fuel ratio	9	11.2	14.6

Aqueous phase reforming

Dumesic Research Group, led by James Dumesic, University of Wisconsin, Madison, Department of Chemical Engineering, has recently developed aqueous-phase catalytic processes for the conversion of sugars, sugar alcohols, and polyols into hydrogen or alkanes ranging from C_1 to C_{15}. Hydrogen as well as carbon dioxide, carbon monoxide, and light alkanes are produced by aqueous-phase reforming (APR) of the sugar or sugar-derived feed with liquid water using a heterogeneous catalyst at low temperatures (200-260 °C) in the aqueous phase (10-50 bar). One of the advantages of APR is eliminating of the need to vaporize both water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen. Another potential advantage is that APR produces hydrogen with low levels of carbon monoxide (100-1000 ppm). This makes it ideal for polymer electrolyte membrane (PEM) fuel cells) in a single reactor, whereas conventional gasification or steam reforming requires multiple water-gas shift reactors and other processing to reduce carbon monoxide levels.

The catalytic pathways for hydrogen and carbon dioxide production by APR involve cleavage of C-C, C-H, and O-H bonds to form adsorbed species on the catalyst surface. A good catalyst for production of hydrogen by APR must facilitate C-C bond cleavage and promote removal of adsorbed carbon monoxide species by the water-gas shift reaction, but the catalyst must not facilitate C-O bond cleavage and hydrogenation of carbon monoxide or carbon dioxide. The product selectivity is a function of the feed molecules, the catalyst, and the reaction conditions. As the size of the feed molecule increases, the hydrogen selectivity decreases and the alkane selectivity increases. The overall catalytic activity for APR of ethylene glycol (as measured by the rate of carbon dioxide production per surface site at 483K) decreases in the following order for silica-supported metals:

platinum ~ nickel > ruthenium > rhodium ~ palladium > iridium

The activity of platinum catalysts can be improved further by adding nickel, cobalt, or iron to a Pt/Al_2O_3 catalyst. Nickel-based catalysts are active for APR; however, they have poor selectivity and stability. The hydrogen selectivity of nickel-based catalysts can be improved by adding tin to the nickel catalyst. In particular, Raney-nickel/tin catalysts have good activity, selectivity, and stability for hydrogen production by APR of biomass-derived oxygenated hydrocarbons. This inexpensive material has catalytic properties (activity, selectivity, and stability) that are comparable to those of Pt/Al_2O_3 for production of hydrogen from small oxygenates, such as ethylene glycol, glycerol, and sorbitol. Hydrogen production rates by APR of ethylene glycol using Raney-nickel/tin catalysts with Ni:Sn atomic ratios of up to 14:1 are comparable to 3 wt% Pt/Al_2O_3, based on reactor volume.

The alkane selectivity can be increased by changing the catalyst and reaction conditions. Alkanes are produced by aqueous-phase dehydration/hydrogenation (APD/H) of sorbitol with a catalyst containing metal (e.g., platinum or palladium) and acid (e.g., SiO_2-Al_2O_3) sites to catalyze dehydration and hydrogenation reactions, respectively. Alkanes produced by the APD/H of carbohydrates would provide a renewable source of transportation fuel that could fit into the current infrastructure. Unfortunately, the largest compound produced by APD/H of carbohydrates is hexane, which has a low value as a fuel additive because of its high volatility.

This limitation has been overcome by combining the APD/H process with a base-catalyzed aldol condensation step. This step links carbohydrate-derived moieties through the formation of C-C bonds to produce larger liquid alkanes ranging from C_7 to C_{15}. Aqueous-phase processing, because of its high thermal efficiency and selectivities, appears to be a promising method for converting biomass-derived sugars into alkanes and hydrogen. Previous aqueous-phase processing research has been used primarily with clean feeds, and future work should focus on using real biomass-derived feedstock.

Producing diesel fuel by APP requires that lignocellulose be converted selectively into HMF and furfural. Furfural is commercially produced selectively from xylose; however, HMF production from glucose is not currently possible with high yields. Recently, chromium dichloride in 1-alkyl-3-methylimidazolium chloride solvent was reported effective for the selective conversion of glucose to HMF, with yields of ~70 percent.

Biodiesel

Triglyceride lipids are the major component of vegetable oils and animals fats. Vegetable oils can be used directly in diesel (compression ignition) engines; however, there are disadvantages of pure vegetable oils, including high viscosity, low volatility, and engine problems (including coking on the injectors, carbon deposits, oil ring sticking, and thickening of lubricating oils). These problems require that vegetable oils be upgraded if they are to be used as transportation fuel.

Triglyceride transesterification. Transesterification is the reaction of triglycerides with alcohols to produce alkyl esters (biodiesel) and glycerol, typically mediated by acid or base catalysts. Although other alcohols including ethanol or isopropanol can produce biodiesel with better fuel characteristics, methanol is most commonly used because of its low cost. Transesterification consists of several consecutive, reversible reactions with diglycerides and monoglycerides as intermediates. Excess alcohol is used (typically 50-200 percent excess) to drive the reaction to completion with yields of alkyl esters as high as 99.7 percent. The alkyl esters also separate from the alcohol-catalyst phase during the reaction, further decreasing the reverse reaction rate. Alkyl esters can be used directly in diesel engines with minor engine modifications; they are sold in the United States as a fuel called B100. Alkyl esters can be blended with traditional diesel fuel in up to 20 vol%, with no engine modification.

Triglycerides only have a limited solubility in the methanol. Mechanical mixing of the two phases is important for improving the mass transfer between the two phases. The addition of solvents that increase the solubility of methanol and triglycerides, such as tetrahydrofuran, can significantly increase the reaction rate. Water has a negative effect on the reaction because alkyl esters, triglycerides, diglycerides, and monoglycerides can react with water to form free fatty acids. Free fatty acids react with base catalysts to form soap, which causes downstream problems such as plugging, gel formation, an increase in viscosity, and problems with product separation.

Both acid and base catalysts can be used for transesterification; however, base catalysts are 4000 times more active and cause fewer corrosion problems than acid catalysts. Most biodiesel processes use mineral acid catalysts for esterification of free fatty acids and alkali base catalysts for transesterification, including sodium hydroxide, potassium hydroxide, and sodium methoxide. Sodium methoxide is the most widely used biodiesel catalyst with more than 60 percent of manufacturing plants using this catalyst. Sodium methoxide is the most active but also the most expensive transesterification catalyst.

Research is ongoing to develop heterogeneous and enzymatic catalysts for esterification and transesterification because removal of homogeneous catalysts requires further downstream processing, increasing biodiesel production cost. Heterogeneous catalysts have the advantage that they can be easily removed from the product and recycled. Preliminary economic analyses suggest that the cash cost of biodiesel production can be reduced by ~5 percent or more with the development of a heterogeneous catalyst. Challenges with current heterogeneous catalysts include lower activity compared to homogeneous catalysts and higher reaction temperatures (200-250 °C) and pressures. Catalysts such as mixed magnesium-aluminum oxides, magnesium oxide, Amberlyst, Nafion®, SO_x/ZrO_2, WO_x/ZrO_2, NaX faujasite zeolite, and ETS-10 (sodium, potassium) have been investigated for the transesterification reaction. However, leaching of sodium occurred with ETS-10 catalyst, whereas the deactivation rate for WO_x/ZrO_2, Nafion®, and Amberlyst® was low. WO_x/ZrO_2 and SO_x/ZrO_2 had activities on a per-site basis, similar to sulfuric acid; however, these catalysts are less active on a mass basis than sulfuric acid because they do not have the same number of sites. Development of future highly active, selective, and stable heterogeneous catalysts for transesterification reaction promises to decrease biodiesel production cost.

The presence of free fatty acid in the feed will strongly poison solid base catalysts. Thus, special care should be taken to remove free fatty acid before they encounter the fixed-bed reactor containing the solid base catalyst. An alternative approach is an integrated “acid-base” calcium silicate mixed oxide catalyst. This catalyst uses the acidic sites to catalyze the efficient esterification of free fatty acids to biodiesel while using the basic sites to catalyze the transesterification of triglyceride to biodiesel.

Enzymatic catalysts like lipase can also catalyze esterification reactions. The advantages of lipase catalysts include the following:

- ability to catalyze both transesterification and esterification of free fatty acids in one step
- production of glycerol side stream with minimal water content and little or no inorganic material
- ability to recycle catalysts.

Enzymatic catalysts have high costs and deactivate because of feed impurities.

Glycerol utilization. Glycerol is becoming an economic choice for fuel because the price has dropped significantly. This price drop was caused by increased biodiesel production; for every gallon of biodiesel, 0.77 lb of glycerol byproduct is produced. Glycerol can then undergo aqueous-phase reforming and gas-phase steam reforming to produce hydrogen. The hydrogen can be used to convert biomass to fuels, which requires a higher level of hydrodeoxygenation compared to the conversion of fossil feedstocks to fuels. Another process for fuel production from glycerol is the etherification of glycerol with isobutylene and ion-exchange resin catalyst to produce butyl ethers of glycerol, which could be used as an oxygenated diesel fuel additive. As mentioned previously, APR can be applied to glycerol. Byproduct glycerol can also be used as a chemical or biochemical feedstock; for example, for 1,3-propanediol, propylene glycol, or acrolein production.

Green diesel. “Green diesel” refers to an acceptable diesel pool blend component produced from a suitable biofeedstock. Green diesel can be produced by either hydrodeoxygenation or decarboxylation of plant oils and greases with propane as a co-product. Although hydrodeoxygenation removes oxygen from a triglyceride or free fatty acid by reaction with hydrogen to form water and an *n*-paraffin, decarboxylation removes oxygen in the biomass carboxy groups to form carbon dioxide and a shorter *n*-paraffin. In contrast to biodiesel, green diesel hydrocarbons do not contain oxygen in their molecular structure, leading to high heating value and high density. Green diesel also has extremely higher cetane number (80-90 vs 50 for biodiesel) and lower NO_x emissions. Table 14 compares the processes by which biodiesel and green diesel are produced.

Table 14: Comparison of biodiesel and green diesel production processes.

	Biodiesel	**Green Diesel**
Complexity	High-multistages	Low
Feedstock	Sensitive to level of free fatty acid	No sensitivity to free fatty acid
Requirement	Methanol -10%	H_2 -2-3%
Byproduct	Glycerol	Propane
Catalyst	Homogeneous	Heterogeneous

The biodiesel process is complicated, requiring multiple distillations and purifications. Green diesel is feed-flexible and can handle low-cost feedstocks like brown grease with high free fatty acid content. Biodiesel requires methanol as feed and produces glycerol as a byproduct. Green diesel only requires hydrogen as a feed and produces only diesel hydrocarbons and propane as products; therefore, its value is not affected by prices of methanol or glycerol. Biodiesel requires a homogeneous catalyst, resulting in higher chemical and separation costs. Biodiesel does have an advantage in the yield of diesel product per pound of vegetable oil feed. This is because the oxygen in vegetable oil is retained in the biodiesel product, whereas the oxygen is rejected in the green diesel as water or carbon dioxide. Depending on the availability and cost of hydrogen, the overall cost of green diesel production is projected to be half that of biodiesel diesel and overall green diesel may be a superior product.

Standard hydrotreating catalysts, such as NiMo, CoMo, and palladium have been tested, and both hydrodeoxygenation and decarboxylation reactions occur with greater than 85 percent deoxygenation. Decarboxylation is favored at lower pressures and hydrodeoxygenation increased with increasing pressure. There are several clear advantages for decarboxylation over hydrodeoxygenation:

1) Chemical hydrogen consumption is limited to olefin saturation; therefore, hydrogen consumption is lower, reducing hydrogen plant capital or hydrogen purchases and the size of the makeup hydrogen compressor.

2) Water is not produced as a reaction product, thereby increasing catalyst stability because of fewer concerns with its hydrothermal stability.

3) Rejected carbon dioxide can be captured in a relatively pure state as a product, potentially producing additional carbon dioxide credits.

Developments in green diesel production have been limited to proof-of-principle. Further understanding the requirement in catalyst composition, particularly the roles of hydrotreating catalysts, and the optimization of reaction conditions are needed to improve the green diesel process.

Biohydrogen production

Effective hydrogen production from biomass may be important in future biorefineries. In addition to the processes discussed in the preceding sections, there are processes for hydrogen production by dark fermentation processes using anaerobic and facultative anaerobic chemohetrotrophs, which also produce acetic and butyric acids. Glucose, cellulose, starches, and several different waste materials can be used for hydrogen fermentation. The maximum amount of hydrogen that can be produced from these routes is 4 moles of hydrogen per mole of glucose, because acetic and butyric acids are also formed. Reported yields of hydrogen production range from 0.5-3.8 mol H_2/mol feed. Hydrogen production is highly dependent on the pH, retention time, and gas partial pressure. The reaction is inhibited by hydrogen. To achieve high yields, the hydrogen must be diluted, removed, or retained for long residence times. The organic acids produced must be sold or converted into other products.

Higher yields of hydrogen from glucose are possible with APR or supercritical reforming. The specific biological hydrogen production rate ranges from 8 to 121 mmol H_2 /(L × h). A biological reactor, for example, with a volume of approximately 1000-15,000 L, would be necessary to provide enough hydrogen to power a 5.0-kW PEM fuel cell. If fermentation technology methods are to become commercially competitive, methods must be developed to synthesize hydrogen at significantly higher rates. Challenges to improve biological production of hydrogen include optimization of bioreactor designs, rapid removal and purification of gases, and genetic modification of enzyme pathways.

References

Adams, T., ed. 1997. *Kraft Recovery Boilers.* Tappi Press: Atlanta, Georgia.

Borás, L., J. A. Curá, and M. E. Otegui. 2002. "Maize Kernal Composition and Post-flowering Source Sink Ratio." *Crop Science* **42**, 781-790.

Canola Council of Canada. Available at http://www.canola-council.org/PDF/canolamealnutrientcom.pdf#zoom=100.

de Rodriguez, D. J., B. S. Phillips, R. Rodriguez-García, and J. L. Angulo-Sánchez. 2002. "Grain Yield and Fatty Acid Composition of Sunflower Seed for Cultivars Developed under Dry Land Conditions." *Trends in New Crops and New Uses*, ed. J. Janick and A. Whipkey. The American Society for Horticultural Science (ASHS) Press: Alexandria, Virginia.

Eggeman, T., and R. T. Elander. 2005. "Process and Economic Analysis of Pretreatment Technologies," *Bioresource Technology* **96**, 2019-2025.

Maier, D. E., J. L. Briggs, and R. W. Gann. 1997. 1*996 Indiana Soybean Composition Data*. Grain Quality Task Force #31. Purdue University Cooperative Extension Service, West Lafayette, Indiana. Available at http://www.ces.purdue.edu/extmedia/GQ/GQ-31.html.

Perelack, R. D., L. L Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, and D. C. Erbach. 2005. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion Ton Annual Supply.* ORNL/TM-2005/66, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at http://www.osti.gov/bridge.

Sale, P. W. G., and L. C. Campbell. 1986. "Yield and Composition of Soybean Seed as a Function of Potassium Supply," *Plant Soil* **96**, 317-325.

Sengupta, R., and D. K. Bhattacharyya. 1996. "Enzymatic Extraction of Mustard Seed and Rice Bran," *Journal of the American Oil Chemists' Society* **73**(6), 687-692.

Sovero, M. 1993. "Rapeseed, a new oilseed crop for the United States." In J. Janick and J. E. Simon, eds. *New Crops.* Wiley, New York, pp. 302-307. Available online at http://www.hort.purdue.edu/newcrop/proceedings1993/V2-302.html.

Thiessen, D. L. 2004. "Optimization of Feed Peas, Canola and Flaxseed for Aqua Feeds: the Canadian Prairie Perspective." *Avances en Nutrición Acuicola VII. Memorias del VII Simposium Internacional de Nutrición Acíucola,* ed. L. E. Suárez, M. D. Ricque, M. G. Nieto López, D. Villarreal, U. Scholz, and M. González. Hermosillo: Sonora, México.

Watson, A., and P. E. Ramstad. 1987. *Corn: Chemistry and Technology.* American Association of Cereal Chemists, Inc.: St. Paul, Minnesota.

CARBON DIOXIDE AS A FUEL FEEDSTOCK

Introduction

In addition to being a product of fuel combustion, carbon dioxide is a byproduct of numerous fuel production processes, as described previously. Most notable is the water-gas shift reaction, applied to adjust H_2:CO ratios in syngas produced from coal or biomass, and the fermentation of sugars to alcohols.

Hydrogen is required for heavy fossil feedstock hydroprocessing, coal liquefaction, bio-oil deoxygenation, and similar reactions. This increasing hydrogen demand is being met by steam reforming of methane or other hydrocarbons and the gasification of petroleum coke or other carbonaceous materials, all of which also co-produce carbon dioxide.

As the quality of fossil fuel feedstocks declines, the amount of carbon dioxide rejected in the production of transportation fuels rises. If coal is substituted for petroleum, the amount of carbon dioxide rejected will rise significantly. With biological fuel feedstocks, although the carbon dioxide released in fermentation and in combustion is offset by the atmospheric carbon dioxide adsorbed in photosynthesis, the energy consumed in the biomass production and conversion processes derived from non-biological sources results in a net generation of carbon dioxide.

To avoid increasing carbon dioxide concentrations in the atmosphere, carbon dioxide may be captured and sequestered in permanent reservoirs, for example, in saline water formations, unminable coal seams, or depleted petroleum reservoirs. Alternatively, captured carbon dioxide could be recycled as a fuel feedstock, assuming the availability of a carbon-free source of hydrogen.

The sustainable hydrogen economy concept proposes conversion of electrons to hydrogen by electrolysis of water. Carbon-free power may be available from a portfolio of new energy technologies using both non-renewable and renewable sources such as nuclear, wind, solar-thermal/Stirling generators, and solar photovoltaic cells. However, the distribution and storage of hydrogen, especially the storage of hydrogen on-board a vehicle, are major barriers to the practical implementation of the hydrogen economy in competition with other concepts.

Carbon Dioxide Recycle

To compare all concepts for electrons-to-fuels in the same context, it is useful to consider the entire system as a thermodynamic black box. In general, carbon dioxide and water are provided as feedstocks to a series of processes that produce a carbonaceous fuel: for example, methane, methanol, dimethyl ether, ethanol, Fischer-Tropsch liquids, and oxygen. Numerous chemical processes could be put into the black box. Only the non-biological processes are considered in this section, although biomass as a product is thermodynamically equivalent to the other processes considered. Direct photochemical processes will also not be considered, as these were covered in the 2005 report *Basic Research Needs for Solar Energy Utilization* (Lewis and Crabtree 2005).

The chemical processes to produce fuels from carbon dioxide and water are all endothermic, requiring the input (at a minimum) of the energy of combustion of the fuel. Thermochemical data for a number of potential fuel products from carbon dioxide and water feedstocks are given in Table 15.

Table 15: Energy requirements for regenerating fuels from carbon dioxide and water.

Reaction	$\Delta\Delta_f H^\circ$ (kJ mol $^{-1}$)	ΔE_H (V)	$\Delta\Delta_f G^\circ$ (kJ mol $^{-1}$)	ΔE_{rev} (V)
$CO_2 \rightarrow CO + 1/2O_2$	283	1.466	257	1.333
$CO_2 + H_2O \rightarrow HCOOH + 1/2O_2$	255	1.319	270	1.400
$CO_2 + H_2O \rightarrow HCHO + O_2$	571	1.479	529	1.371
$CO_2 + 2H_2O \rightarrow CH_3OH + 1/2O_2$	727	1.255	702	1.212
$CO_2 + 2H_2O \rightarrow CH_4 + 3/2O_2$	890	1.153	818	1.060
$H_2O \rightarrow H_2 + 1/2O_2$	286	1.481	237	1.229
$CO_2 + H_2O \rightarrow CO + H_2 + O_2$	569	1.474	494	1.281

The values for H_2O, HCOOH, CH_3COOH are for the liquid state; others: gas, 1 bar pressure. Abbreviations: $\Delta\Delta_f H^\circ$, change in standard enthalpy of formation; $\Delta\Delta_f G^\circ$, change in standard free energy of formation; ΔE_H, enthalpic cell voltage; ΔE_{rev} reversible cell voltage.

Much of the energy required for regenerating fuels from carbon dioxide and water may come from non-fossil sources: nuclear, solar, and wind. Hence, this may be referred to as a "carbon dioxide recycling" system.

Some of these carbon dioxide recycling systems have already been investigated in some detail, whereas others are only conceptual. In one detailed investigation, electricity from solar photovoltaic arrays was used to electrolyze seawater to produce hydrogen without the production of chlorine as a byproduct. The hydrogen was fed to a catalytic reactor for hydrogenation of carbon dioxide to methane. A complete system was constructed at the pilot scale and operated for several years. The choice of seawater as feedstock was central to the concept that the photovoltaic arrays would be located in a desert inland from a coastal area (e.g., North Africa). The challenges focused on the development of three catalytic materials needed for the chemical processes, the anodic and cathodic electrocatalysts for brine electrolysis, and the methanation catalyst needed for highly selective hydrogenation of carbon dioxide to methane. Although catalytic materials were found that enabled the entire system to operate successfully over several years, more selective hydrogenation catalysts are needed for optimum efficiency. One of the conclusions with larger implications was the cost analysis, which showed that the photovoltaic arrays were the most costly element, and that the projected cost of "solar methane" was more than an order of magnitude higher than the cost of natural gas.

A similar conclusion can be drawn for all other carbon dioxide recycling concepts. Each one requires a significant shift in the relative cost of electricity versus the value/cost of the fuel to be economically viable.

Methanol economy concept

Olah (2005) proposed a variation on the hydrogen economy concept, termed "the methanol economy," which utilizes methanol as a sustainable "carbon dioxide neutral" hydrogen carrier. A central feature of the concept is a regenerable direct methanol fuel cell, capable of either generating methanol by electrolytic reduction of carbon dioxide or generating electricity from methanol electrooxidation. At present, only the direct methanol fuel cell has been shown to have any technological feasibility. Although similar to other polymer electrolyte membrane (PEM) fuel cell technologies, the efficiency remains rather poor (e.g., less than 40 percent), the cost quite high (greater than $5000/kW), and the principal application limited to small, portable power applications for which the tolerance for lower efficiency and higher cost is greater.

The electrochemical reduction of carbon dioxide to methanol with high selectivity has not been demonstrated. However, a modified version of the Olah concept (Figure 15) can be considered. In this case, syngas is the primary product of carbon dioxide reduction by either an electrochemical or a non-electrochemical catalytic process. In each case, solar photovoltaic electricity is the sustainable energy input, although other non-carbon electricity sources (e.g., wind and nuclear energy) could also be used. Conversion of synthesis gas to liquid fuels such as methanol or Fischer-Tropsch liquids has been discussed in previous sections of this report, Methanol may be used as the example for specific quantitative statements when comparing with other solar energy concepts, including biorefineries.

The catalytic conversion of carbon dioxide to syngas is the well-known reverse water-gas shift reaction. This reaction is used commercially when carbon dioxide and excess hydrogen from methane autothermal reforming are available for methanol production. A key challenge is to develop an efficient electrochemical process for the reduction of carbon dioxide to syngas.

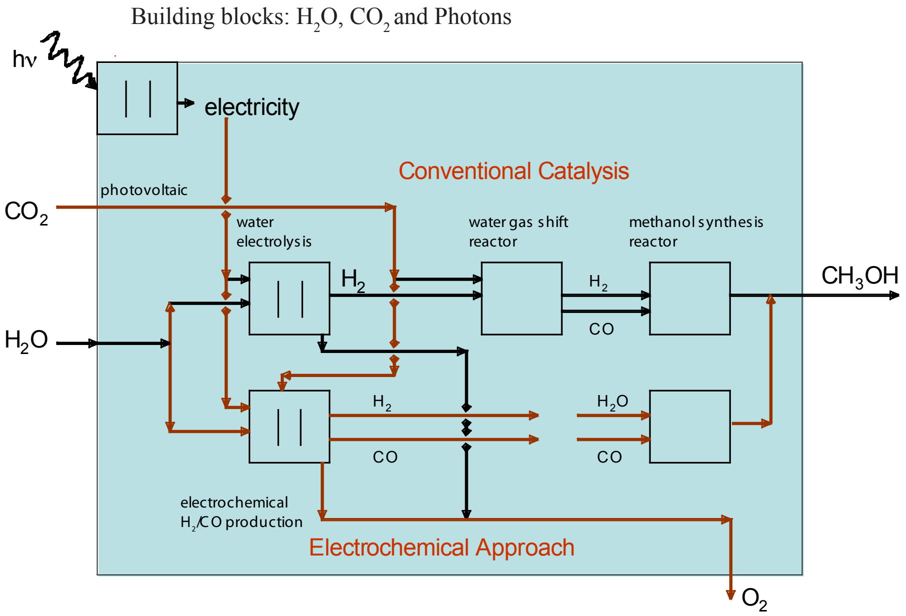

Figure 15: Photon to fuels – electrochemical vs. non-electrochemical (conventional catalytic) approaches.

Electrochemical reduction of carbon dioxide to syngas

Although the electrochemical reduction of carbon dioxide is simple, the actual reduction in practice is not. All known efforts are still at the laboratory or bench scale, and clearly the concept has not been developed as a serious production process. There are many parameters to examine, and in principle, there are significant opportunities to improve the concept. Most work has been done with metallic electrodes such as copper, nickel, silver, ruthenium, and platinum, and electrolytes such as potassium hydroxide or potassium bicarbonate. Cell designs have been quite similar to those of conventional water electrolyzers, which also employ potassium hydroxide as electrolyte.

Although there are a few reports of either methane or methanol as a primary product of the reduction, it is clear that syngas mixtures are the product easiest to produce with high thermal efficiency. One such cell design and some key results are shown in Figure 16 and Table 16. Energy efficiencies (defined as the ratio of the energy content of the products to the electrical energy input) for the production of 2:1 molar (H_2:CO) syngas as high as 45 percent are reported for the use of conventional nickel electrocatalysts. However, the current density, about 50 mA/cm², is about 20 percent of that in a conventional water electrolyzer which, if not improved, could make the electrochemical approach likely uncompetitive with the catalytic reduction approach using electrolysis-produced hydrogen.

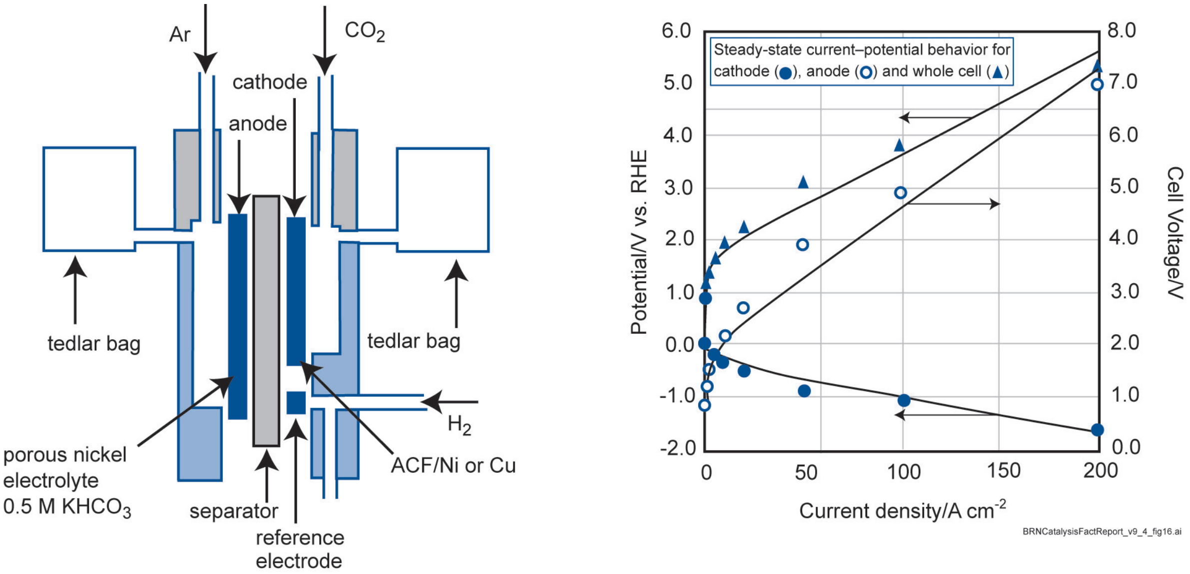

Figure 16: Electrochemical carbon dioxide reduction to syngas. Reprinted from Yamamoto et al. (2002) with permission from Elsevier.

Table 16: Literature reports on electrochemical carbon dioxide reduction.

Catalyst	Electroyte	P, atm	Product	Current Efficiency %	Potential V. *vs.* NHE	Author[a]	Year
Cu	KOH	1	C_2H_4	69	-2.8	Cook	1990
Pt	$KHCO_3$	30	CO	35	-1.02	Hara	1995
Ag	$KHCO_3$	20	CO	86	-1.73	Hara	1997
Pt	$KHCO_3$	20	CH_4	39	-1.73	Hara	1997
CoTPP	$KHCO_3$	20	CO	97	-0.76	Sonoyama	1999
Ni	$KHCO_3$	1	CO	67	-1.36	Yamamoto	2000

a) Sánchez-Sánchez, C. M., V. Montiel, D. A. Tryk, A. Aldaz, and A. Fujishima, 2001. “Electrochemical Approaches to Alleviation of the Problem of Carbon Dioxide Accumulation,” *Pure and Applied Chemistry* **73**, 1917-1927.

Comparison to Bioethanols

Some comparisons of a carbon dioxide-neutral carbon dioxide recycling to transportation fuel concept (say "solar methanol") may be made with fermentation bioethanol. Table 17 shows a comparison of the land-use requirement for bioethanol versus the solar methanol normalized to the energy content of the fuel. The bioethanol numbers are not corrected for any external energy input needed to grow the crops or convert the biomass to fuel. They include just the yield of ethanol from crops.

The 2001 results for photovoltaic systems were used for this comparison. These systems have field-tested array efficiencies of 6-8 percent, much less than the nominal efficiencies of 10-13 percent and much less than efficiencies projected for photovoltaic arrays in the future. An average daily solar radiance of 4 kWh/m^2 (middle of the United States) was used, annualized without correction for seasonal variation. The efficiency for syngas production by electrolysis was taken to be 50 percent, and the efficiency for production of methanol from syngas was taken to be 80 percent.

Table 17: Comparison of energy yield per unit of land area for bioethanol and solar-methanol.

Crop	Yield (gal/acre)[a]	Energy Yield (10^6 kWh/km^2)
Corn	300	1.9
Sugarcane	700	4.4
Switchgrass	1000	6.3
Miscanthus	1500	9.4
Energy Yield for Solar Methanol[b]		**48**

a) CLEAN Energy, "Cellulosic Ethanol: a greater alternative," www.cleanhouston.org.
b) Solar Electric Power Association. 2001. *PV Performance Data Report.* Solar Electric Power Association, Washington, D.C. Accessed October 17, 2007, at http://www.resourcesaver.com/file/toolmanager/O63F22751.pdf (undated webpage).

The land-use requirements for these two solar-derived fuels scenarios are quite different. With bioethanol, even the much discussed but not yet commercialized cellulosic ethanol from switchgrass requires nearly an order of magnitude more land area to produce the same amount of transportation fuel energy.

The current gasoline consumption in the United States is 385 million gallons per day. To replace this consumption entirely with bioethanol, as may someday be required for a sustainable transportation economy, would require 2100 million acres of switchgrass, approximately half of all the arable land area in the United States (4350 million acres). Even with current photovoltaic technology, the equivalent amount of solar methanol would require only one-eighth of that area, about 260 million acres, and the land need not be arable. If photovoltaic array efficiencies were improved by about a factor of 2 in the coming decades, there is likely enough land in the desert southwest of the United States and enough available water from the Colorado River to produce the equivalent of our total requirement for transportation fuel exploiting renewable but nonbiological processes.

REFERENCES

Lewis, S. L., and G. Crabtree. 2005. *Basic Research Needs for Solar Energy Utilization.* U.S. Department of Energy, Washington, D.C. Available at http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf.

Olah, G. A. 2005. "Beyond Oil and Gas: The Methanol Economy," An*gewandte Chemie International Edition* **44**, 2636-2639.

Sánchez-Sánchez, C. M., V. Montiel, D. A. Tryk, A. Aldaz, and A. Fujishima. 2001. "Electrochemical Approaches to Alleviation of the Problem of Carbon Dioxide Accumulation." *Pure and Applied Chemistry* **73**, 1917-1927.

Solar Electric Power Association. 2001. *PV Performance Data Report.* Solar Electric Power Association, Washington, D.C. Accessed October 17, 2007, at http://www.resourcesaver.com/file/toolmanager/O63F22751.pdf (undated webpage).

Yamamoto, T., D. A. Tryk, A. Fujishima, and H. Ohata. 2002. "Production of Syngas Plus Oxygen from CO_2 in a Gas-Diffusion Electrode-Based Electrolytic Cell," *Electrochimica Acta* **47**, 3327-3334.

FOR FURTHER READING

Fossil Feedstock Processes

General catalytic processes

Bartholomew, C. H., and R. J. Farrauto. 2006. *Fundamentals of Industrial Catalytic Processes*. Wiley: New York.

Dresselhaus, M., G. Crabtree, and M. Buchanan. 2003. *Basic Research Needs for the Hydrogen Economy*. U.S. Department of Energy, Washington, D.C. Available at http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf.

Fluidized catalytic cracking

Avidan, A. A. 1993. "Origin, Development and Scope of FCC Catalysis." *Studies in Surface Science and Catalysis* (Fluid Catalytic Cracking: Science and Technology) **76**, 1-39.

Avidan, A. A., and M. Edwards. 1990. "Fluid Catalytic Cracking: Past and Future Challenges," *Reviews in Chemical Engineering* **6**(1), 1-71.

de Lasa, H., and D. Kraemer. 1992. "Novel Techniques for FCC Catalyst Selection and Kinetic Modeling," *NATO ASI Series, Series E: Applied Sciences* (Chemical Reactor Technology for Environmentally Safe Reactors and Products) **225**, 71-131.

Kissen, Y. V. 2001. "Chemical Mechanisms of Catalytic Cracking over Solid Acidic Catalysts: Alkanes and Alkenes," *Catalysis Reviews, Science and Engineering* **43**(1/2), 85-146.

Alkylation

Albright, L. F., and A. R. Goldsby. 1977. *Industrial and Laboratory Alkylations.* ACS Symposium Series American Chemical Society, Washington, D.C.

Gary, J. H., and G. E. Handwerk. 1994. *Petroleum Refining – Technology and Economics.* 3rd Ed., Marcel Dekker: New York.

Maples, R. E. 2000. *Petroleum Refinery Process Economics,* 2nd Ed., Pennwell Corp.: Tulsa, Oklahoma.

Nowak, F. M., J. F. Himes, and R. L. Mehlberg. 2003. "Advances in Hydrofluoric Acid Catalyzed Akylation," NPRA Report AM-03-18. National Petrochemical & Refiners Association, Washington, D.C. Available at: http://uop.com/objects/NPRASpr2003HFAlky.pdf.

Hydrodesulfurization

Brunet, S., D. Mey, G. Perot, C. Bouchy, and F. Diehl. 2005. "On the Hydrodesulfurization of FCC Gasoline: A Review," *Applied Catalysis, A, General* **278**(2), 143-172.

Chianelli, R. R., G. Berhault, P. Raybaud, S. Kasztelan, J. Hafner, and H. Toulhoat. 2002. "Periodic Trends in Hydrodesulfurization: In Support of the Sabatier Principle," *Applied Catalysis, A*, *General* **227**(1-2), 83-96.

Delannay, F. 1985. "High Resolution Electron Microscopy of Hydrodesulfurization Catalysts: A Review," *Applied Catalysis* **16**(2), 135-152.

Gates, B. C. 1992. *Catalytic Chemistry.* Wiley: New York.

Reforming

Hughes, T. R., R. L. Jacobson, and P. W. Tamm. 1988. "Catalytic Processes for Octane Enhancement by Increasing the Aromatics Content of Gasoline," In: *Catalysis 1987*, *Studies in Surface Science and Catalysis,* ed. J. W. Ward, **38**, 317-33, San Diego, California, Elsevier, Amsterdam.

Martino, G. 2000. "Catalysis for Oil Refining and Petrochemistry: Recent Developments and Future Trends," In: *12th International Congress on Catalysis, Studies in Surface Science and Catalysis,* ed. A. Corma, **130A,** 83-104. July 9-14, 2000, Granada, Spain. Elsevier, Amsterdam.

Sinfelt, J. H. 1981. "Catalytic Reforming of Hydrocarbons," In: *Catalysis: Science and Technology,* **1,** 257-300, eds. J. R. Anderson and M. Boudart, Springer-Verlag, Berlin.

Wei, D. H., M. D. Moser, and R. S. Haizmann. 1996. "An Update on Catalytic Reforming," *Chemtech* **26**(10), 37-41.

Hydrogen production

Armor, J. N. 2005. “Catalysis and the Hydrogen Economy,” *Catalysis Letters* **101**(3-4), 131-135.

Farrauto, R. J., Y. Liu, W. Ruettinger, O. Ilinich, L. Shore, and T. Giroux. 2007. “Precious Metal Catalysts Supported on Ceramic and Metal Monolithic Structures for the Hydrogen Economy,” *Catalysis Reviews-Science and Engineering* **49**(2), 141-196.

Fierro, J. L. G., and M. A. Pena. 2005. “Supported Metals in the Production of Hydrogen,” *Catalytic Science Series* (Supported Metals in Catalysis) **5**, 229-282.

Huber, G. W., and J. A. Dumesic. 2006. “An Overview of Aqueous-phase Catalytic Processes for Production of Hydrogen and Alkanes in a Biorefinery,” *Catalysis Today*, **111**(1-2), 119-132.

Mundschau, M. V., X. Xie, C. R. Evenson, and A. F. Sammells. 2006. “Dense Inorganic Membranes for Production of Hydrogen from Methane and Coal with Carbon Dioxide Sequestration,” *Catalysis Today* **118**(1-2), 12-23.

Sigfusson, T. 2007. “Pathways to Hydrogen as an Energy Carrier,” *Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences* **365**(1853), 1025-1042.

Coal liquefaction

Bellemare, B. 2006. *Coal-to-Liquids Economic Drivers.* UtiliPoint International, Inc.: Albuquerque, New Mexico.

Burke, F. P. 1995. “The Role of Recycle Oil in Direct Coal Liquefaction Process Development,” *Fuel and Energy Abstracts* **36**(6), 415-415(1).

Burke, F. P., S. D. Brandes, D. C. McCoy, R. A. Winschel, D. Gray, and G. Tomlinson. 2001. *Summary Report of the DOE Direct Liquefaction Process Development Campaign of the Late Twentieth Century: Topical Report.* DOE/PC 93054-94, CONSOL Energy Inc: South Park, Pennsylvania. Available at http://www.osti.gov/energycitations/servlets/purl/794281-khohbO/native/.

Fry, W. R. 2001. *Energy Research at DOE: Was It Worth It? Energy Efficiency and Fossil Energy Research 1978-2000.* National Academies Press: Washington, D.C., pp. 164-166.

Given, P. H., ed. 1996. “Coal Science,” *Advances in Chemistry Series 55*. American Chemical Society: Washington, D.C.

Gorbaty, M. L., J. W. Larsen, and I. Wender. 1983. *Coal Science, Vol. 2.* Academic Press: New York.

International Energy Agency Coal Industry Advisory Board. 2006. “Workshop Report: Coal-to-Liquids – An Alternative Oil Supply?” International Energy Agency: Paris.

Lowry, H. H. 1945. *The Chemistry of Coal Utilization, Vol.1 and Vol. 2,* John Wiley & Sons: New York. Supplementary Volume; John Wiley & Sons: New York, 1963. Ellott, M. A. 2nd Supplementary Volume, Wiley-Interscience: New York, 1981.

May V. B., C. L. Koralek, S. S. Patel, and C. L. Parker. 1968. *Application of Modern Coal Technologies to Military Facilities. Volume II. Evaluation of the Applicability and Cost of Current and Emerging Coal Technologies for the Utilization of Coal as a Primary Energy Source.* CERL-E130-Vol. 2, ADA055995, Hittman Associates Inc. Columbia, Maryland.

Miller, C. L. 2007. "Coal Conversion – Pathway to Alternate Fuels," *EIA Energy Outlook Modeling and Data Conference*, Washington, D.C. Available at: http://www.eia.doe.gov/oiaf/aeo/conf/pdf/miller.pdf.

Neuworth, M. B., and D. Gray. 1985. *Fundamental Aspects of Primary Coal Liquefaction.* SAND-85-7211, Mitre Corporation: McLean, Virginia.

Pelofsky, A. H. 1979. "Coal Conversion Technology." *ACS Symposium Series 110,* American Chemical Society: Washington, D.C.

Speight, J. G., ed. 1990. *Fuel Science and Technology Handbook.* Marcel Dekker: New York. Second Edition, 1998.

Spinks, A., J. M. Thomas, and J. Gibson. 1981. *New Coal Chemistry.* The Royal Society: London.

Sun, Q., R. A. Bajura, J. J. Fletcher, Y. Zhang, and X. Ren. 2004."Coal to Clean Fuel – The Shenhua Investment in Direct Coal Liquefaction," *Twenty-First International Pittsburgh Coal Conference,* September 13-17, 2004, Osaka, Japan. Pittsburgh Coal Conference: Pittsburgh, Pennsylvania.

Whitehurst, D. D. 1966. "Coal Liquefaction Fundamentals." *ACS Symposium Series* **139**, American Chemical Society: Washington, D.C.

Gasification

Goyal, A., and A. Rehmat 1992. "Fuel Evaluation for a Fluidized-bed Gasification Process (U-GAS)," *American Chemical Society Symposium Series (Clean Energy from Waste and Coal)* **515**, 58-71.

Matsumura, Y., T. Minowa, B. Potic, S. R. A. Kersten, W. Prins, W. P. M. Swaaij, B. V. D. Beld, D. C. Elliott, G. G. Neuenschwander, A. Kruse, and M. J. Antal. 2005. "Evaluation of a Constant Volume Sampling Setup for Residential Biomass Fired Appliances—Influence of Dilution Conditions on Particulate and PAH Emissions," *Biomass Bioenergy* **29**, 269-292.

Meyer, E. G. 2003. "Syngas, Chemicals, and Clean Fuels from Coal by Coal Refining," *Proceedings of the 20th Annual International Pittsburgh Coal Conference,* September 15-19, 2003, Pittsburgh, Pennsylvania. Pittsburgh Coal Conference: Pittsburgh, Pennsylvania. pp. 2080-2083.

Salge, J. R., B. J. Dreyer, P. J. Dauenhauer, and L. D. Schmidt. 2006. "Pattern Formation and Shape Changes in Self-Oscillating Polymer Gels," *Science* **314**, 801-804.

Wen, W. Y. 1980. "Mechanism of Alkali Metal Catalysis in the Gasification of Coal, Char, or Graphite," *Catalysis Reviews – Science and Engineering* **22**(1), 1-28.

Fischer-Tropsch

ChemSystems. 2005. *PERP 03/04S4 – Developments in Syngas Technology.* Nexant: White Plains, New York.

De Kerk, A. 2007. "Environmentally Friendly Refining: Fischer-Tropsch versus Crude Oil," *Green Chemistry* **9**, 560-565.

Eisenberg, B., R. A. Fiato, T. G. Kaufmann, and R. F. Bauman. 1999. "The Evolution of Advanced Gas-to-Liquids Technology," *Chemtech* **29**(10), 32-37.

Elliott, M. A. 1981. *Chemistry of Coal Utilization, Second Supplementary Volume*. Wiley: New York.

Geerlings, J. J. C., J. H. Wilson, G. J. Kramer, H. P. C. E. Kuipers, A. Hoek, and H. M. Huisman. 1999. "Fischer-Tropsch Technology – From Active Site to Commercial Process." *Applied Catalysis A: General* **186**(1-2), 27-40.

Hildebrandt, D., and D. Glasser. 2007. *An Introduction to a Novel Fischer-Tropsch Technology*. Centre of Materials and Process Synthesis: Johannesburg, South Africa.

Iglesia, E. 1997. "Design, Synthesis, and Use of Cobalt-based Fischer-Tropsch Synthesis Catalysts," *Applied Catalysis, A: General* **161**(1-2), 59-78.

Iglesia, E., S. C. Reyes, R. J. Madon, and S. L. Soled. 1993. "Selectivity Control and Catalyst Design in the Fischer-Tropsch Synthesis: Sites, Pellets, and Reactors," *Advances in Catalysis* **39**, 221-302.

Khodakov, A. Y., W. Chu, and P. Fongarland. 2007. "Advances in the Development of Novel Cobalt Fischer-Tropsch Catalysts for Synthesis of Long-chain Hydrocarbons and Clean Fuels," *Chemical Reviews* **107**, 1692-1744.

Leconte, M. 1994. "An Approach to the Mechanisms of C-C Bond Formation and Cleavage on Metal Surfaces Using Model Elementary Reaction Steps of Organometallic Chemistry," *Journal of Molecular Catalysis* **86**(1-3), 205-220.

Maitlis, P. M. 2004. "Fischer-Tropsch, Organometallics, and Other Friends," *Journal of Organometallic Chemistry* **689**(24), 4366-4374.

Maitlis, P. M., R. Quyoum, H. C. Long, and M. L. Turner. 1999. "Towards a Chemical Understanding of the Fischer-Tropsch Reaction: Alkene Formation," *Applied Catalysis, A: General* **186**(1-2), 363-374.

Robinson, K. K., and D. F. Tatterson. 2007. "Special Report: Fischer-Tropsch Oil-from-Coal Promising as Transport Fuel," *Oil & Gas Journal* **105**(8), 20-31.

Schulz, H. 2003. "Major and Minor Reactions in Fischer-Tropsch Synthesis on Cobalt Catalysts," *Topics in Catalysis* **26**(1-4), 73-85.

Van Bibber, L., E. Shuster, J. Haslbeck, M. Rutkowski, S. Olson, and S. Kramer. 2007. *Baseline Technical and Economic Assessment of a Commercial Scale Fischer-Tropsch Liquids Facility.* Final Report for Subtask 41817.401.01.08.001; National Energy Technology Laboratory, Pittsburgh, Pennsylvania.

Biological Feedstock Processes

General

Agrawal, R., R. S. Navneet, F. H. Ribeiro, and W. N. Delgass. 2007. “Sustainable Fuel for the Transportation Sector,” *Proceedings of the National Academy of Science USA* **104**(12) 4828-4833.

European Chemical News (undated). *PHYLLIS: ECN Database on Composition of Biomass and Waste.* Available at http://www.ecn.nl/phyllis.

Huber, G. W., S. Iborra, and A. Corma. 2006. “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering,” *Chemical Reviews* **106**, 4044-4098.

Kotz, J. C., and K. F. Purcell. 1991. *Chemistry and Chemical Reactivity 2nd Ed*. Sauders College Publishing: Philadelphia.

Maier, D. E., J. L. Briggs, and R. W. Gann. 1997. *1996 Indiana Soybean Composition Data.* Grain Quality Task Force #31. Purdue University Cooperative Extension Service, West Lafayette, Indiana. Available at http://www.ces.purdue.edu/extmedia/GQ/GQ-31.html.

Marker, T. L. 2005. *Opportunities for Biorenewables in Oil Refineries: Final Technical Report.* UOP: Des Plaines, Illinois. Available at http://www.osti.gov/bridge/servlets/purl/861458-Wv5uum/.

Miller, D. J., and J. E. Jackson. 2004. *NSF Workshop Report on Catalysis for Biorenewables Conversion.* National Science Foundation, Arlington, Virginia. Available at http://www.nsf.gov/eng/cbet/workshops/catalysis_for_biofuels_workshop_2004.pdf.

Noller, C. R. 1966. *Textbook of Organic Chemistry 3rd Ed.* WB Saunders Company: Philadelphia, Pennsylvania.

Soares, T. T., D. A. Simonetti, and J. A. Dumesic. 2006. “Glycerol as a Source for Fuels and Chemicals by Low-Temperature Catalytic Processing,” *Angewandte Chemie International Edition* **45**, 3982-3985.

U.S. Department of Energy (DOE). 2006. *Breaking the Biological Barriers to Cellulosic Ethanol,* DOE/SC-0095. U.S. Department of Energy Office of Science and Office of Energy Efficiency and Renewable Energy, Washington, D.C. Available at http://genomicsgtl.energy.gov/biofuels/2005workshop/b2blowres63006.pdf.

Pyrolysis

Bridgwater, A.V., and G. V. C. Peacocke. 2000. "Fast Pyrolysis Processes for Biomass," *Renewable and Sustainable Energy Reviews* **4**, 1-73.

Bridgwater, A. V., D. Meier, and D. Radlein. 1999. "An Overview of Fast Pyrolysis of Biomass," *Organic Geochemistry* **30**, 1479-1493.

Elliott, D. C. 2007. "Historical Developments in Hydroprocessing Bio-oils," *Energy & Fuels,* **21**, 1792-1815. Available at http://pubs.acs.org/cgi-bin/abstract.cgi/enfuem/2007/21/i03/abs/ef070044u.html.

Elliott, D. C., D. Beckman, A. V. Bridgwater, J. P. Diebold, S. B. Gevert, and Y. Solantausta. 1991. "Developments in Direct Thermochemical Liquefaction of Biomass: 1983-1990," *Energy & Fuels* **5**(3), 399-410.

Elliott, D. C., and R. R. Maggi. 1996. "Workshop Report: Catalytic Processes." *Developments in Thermochemical Biomass Conversion, Vol. 2,* ed. A. V. Bridgwater and D. G. B. Boocock, Blackie Academic & Professional: London, 1626-1630.

Fort, D. A., R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna, and R. D. Rogers. 2007. "Can Ionic Liquids Dissolve Wood? Processing and Analysis of Lignocellulosic Materials with 1-n-Butyl-3methylimidazolium Chloride," *Green Chemistry* **9**, 63-69.

Furimsky, E. 2000. "Catalytic Hydrodeoxygenation," *Applied Catalysis A: General* **199**, 147-190.

Maggi, R., and B. Delmon. 1994. "Comparison between 'Slow' and 'Flash' Pyrolysis Oils from Biomass," *Fuel* **73**(5), 671-677.

Maggi, R. R., and D. C. Elliott. 1996. "Upgrading Overview." *Developments in Thermochemical Biomass Conversion, Vol. 1,* ed. A. V. Bridgwater and D. G. B. Boocock, Blackie Academic & Professional: London, 575-588.

Carbohydrate and ethanol production

Bothast, R. J., and M. A. Schlicher. 2005. "Biotechnological Processes for Conversion of Corn into Ethanol," *Applied Microbiology and Biotechnology* **67**, 19-25.

Gray, K. A., L. Zhao, and M. Emptage. 2006. "Bioethanol," *Current Opinion in Chemical Biology* **10**(2), 141-146.

Hahn-Hagerdal B., M. Galbe, M. F. Gorwa-Grauslund, G. Liden, and G. Zacchi. 2006. "Bioethanol – The Fuel of Tomorrow from the Residues of Today," *Trends in Biotechnology* **24**(12), 549-556.

Himmel, M. E., S. Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady, and T. D. Foust. 2007. "Biomass Recalcitrance: Engineering Plants and Enzymes for Biofuels Production," *Science* **315**(5813), 804-807.

Lynd, L. R., P. J. Weimer, W. H. van Zyl, and I. S. Pretorius. 2002. "Microbial Cellulose Utilization: Fundamentals and Biotechnology," *Microbiology and Molecular Biology Reviews* **66**, 506-577.

Lynd, L. R., W. H. van Zyl, J. E. McBride, and M. Laser. 2005. "Consolidated Bioprocessing of Cellulosic Biomass: An Update," *Current Opinion in Chemical Biology* **16**(5), 577-83.

U.S. Department of Energy. 2006. *Breaking the Biological Barriers to Cellulosic Ethanol,* DOE/SC-0095. U.S. Department of Energy Office of Science and Office of Energy Efficiency and Renewable Energy, Washington, D.C. Available at http://genomicsgtl.energy.gov/biofuels/2005workshop/b2blowres63006.pdf.

van Maris, A. J., D. A. Abbott, E. Bellissimi, J. van den Brink, M. Kuyper, M. A. Luttik, H. W. Wisselink, W. A. Scheffers, J. P. van Dijken, and J. T. Pronk. 2006. "Alcoholic Fermentation of Carbon Sources in Biomass Hydrolysates by *Saccharomyces cerevisiae*: Current Status," *Antonie Van Leeuwenhoek* **90**(4), 391-418.

Wheals, A. E., L. C. Basso, D. M. Alves, and H. V. Amorim. 1999. "Fuel Ethanol after 25 Years," *Trends in Biotechnology* **17**(12), 482-487.

Carbon Dioxide Recycle

BASF. 2007. "Ag – Biotech Factsheet." Available at http://www.corporate.basf.com.

Citizens League for Environmental Action Now. 2006. "CLEAN ENERGY – Cellulosic Ethanol: A Greener Alternative." Available at http://www.cleanhouston.org.

Davis, G. 2001. "Evolving Sources or Revolutionary Technology— Exploring Alternative Energy Paths to 2050," *Proceedings of the Oil and Money Conference*, London, pp. 1-11.

Gottesfeld, S. 2002. "New Fuel Cells for Portable Power Sources – Introduction" *Electrochemistry* **70**, 913-913.

Hashimoto, K., H. Habazaki, M. Yamasaik, S. Merguro, T. Sasaki, H. Katagiri, T. Matsui, K. Fujimura, K. Izumiya, N. Kumagai, and E. Akiyama. 2001. "Atom Probe Studies of Microstructural Evolution in Nd–Fe–B-based Nanocomposite Magnets," *Materials Science and Engineering A* **304-306**, 88-96.

Hoffert, M. I., K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter, M. E. Schlesinger, S. H. Schneider, R. G. Watts, T. M. L. Wigley, and D. J. Wuebbles. 1998. "Energy Implications of Future Stabilization of Atmospheric CO_2 Content," *Nature* **395**, 881-884.

Kazmerski, L. L., and K. Broussard. 2004. *Solar Photovoltaic Hydrogen: The Technologies and Their Place in Our Roadmaps and Energy Economics*, NREL/CP-520-36401. National Renewable Energy Laboratory, Golden, Colorado.

Olah, G. A., and S. Prakash. 1999. "Recycling of Carbon Dioxide into Methyl Alcohol and Related Oxygenates for Hydrocarbons." U.S. Patent 5,928,806 (July 27).

Solar Electric Power Association. 2001. *PV Performance Data Report*. Solar Electric Power Association: Washington, D.C.

U.S. Department of Energy. 2003. *Hydrogen, Fuel Cells and Infrastructure Technologies Program, Multiyear Research, Development and Demonstration Plan.* U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Washington D.C.

Yamamoto, T., D. A. Tryk, A. Fujishima, and H. Ohata. 2002. "Production of Syngas Plus Oxygen from CO_2 in a Gas-Diffusion Electrode-Based Electrolytic Cell," *Electrochimica Acta* **47**, 3327-3334.

APPENDIX 2

WORKSHOP PROGRAM

APPENDIX 2 • WORKSHOP PROGRAM

Sunday, August 5, 2007 • EVENING

Pre-meeting: panel co-leads and workshop organizers only

6:00 pm – 6:15 pm	Welcome & purpose of meeting	
6:15 pm – 6:30 pm	Overview of agenda	Doug Ray
6:30 pm – 7:00 pm	Discussion of breakout sessions	Alex Bell
7:00 pm – 8:00 pm	Working dinner: Workshop report & additional discussion	Kathryn Lang

Registration

5:00 pm – 6:00 pm	Early Registration

Monday, August 6, 2007 • MORNING

7:30 am – 8:30 am	Registration and continental breakfast

Plenary Opening Session

8:30 am – 8:40 am	Introductory remarks	Pat Dehmer, Director, OBES
8:40 am – 8:50 am	Introduction to the workshop	Bruce Gates
8:50 am – 9:15 am	Strategic Research in Fossil Energy-NETL's Perspectives	Anthony Cugini, Director, Office of R&D, NETL
9:15 am – 9:40 am	Catalysis Research for Efficient and Renewable Energy	Brian Valentine, Industrial Technologies Pgm., EERE
9:40 am – 10:25 am	Transforming the Chemical Industry Through Feedstock Diversification	William Banholzer, VP and CTO, Dow Chemical Co.
10:25 am – 10:50 am	Break	
10:50 am – 11:35 am	Bio-Derived Feedstocks and Other Energy Sources Technology and Research Challenges	Harvey Blanch, Prof., U. California-Berkeley
11:35 am – 12:20 pm	Catalysis by Design	Rutger van Santen, Prof., Eindhoven Univ. of Technology
12:20 pm – 1:30 pm	Working lunch – Charge to breakout sessions	

Workshop Breakout Sessions

1:30 pm – 6:00 pm	Individual session agendas will be provided at the meeting
6:00 pm – 7:30 pm	Working dinner – to be held in individual breakout rooms
7:30 pm – 9:00 pm	Prioritize 3-5 one-sentence proposed research directions

Tuesday, August 7, 2007 • MORNING

7:30 am – 8:00 am	Continental breakfast

Breakout Sessions

8:00 am – 10:00 am	Discussions continue
10:00 am – 10:30 am	Break

Plenary Midpoint Session

10:30 am – 12:30 pm	Presentations of draft proposed research directions	Four 30-min. blocks of time (for presentations and discussion)
12:30 pm – 1:45 pm	Working lunch	

Breakout Sessions

1:45 pm – 6:00 pm	Discussions continue
6:00 pm – 7:00 pm	Reception

Wednesday, August 8, 2007 • MORNING

7:30 am – 8:00 am	Continental breakfast

Breakout Sessions

8:00 am – 10:15 am	Panel report drafting
10:15 am – 10:45 am	Break

Plenary Closing Session

10:45 am – 12:15 pm	Panel 1 – Panel 4, Summaries of Panel Reports	
12:15 pm – 1:30 pm	Lunch	
1:30 pm – 3:00 pm	Priority Research Directions (10 minutes each)	Alex Bell, Session Chair
3:00 pm – 3:30 pm	Crosscutting Themes	
3:30 pm – 3:45 pm	4-Column Chart	
3:45 pm – 4:00 pm	Final closing remarks	Doug Ray, Session Chair
4:00 pm	Close of workshop, Panelists excused	
5:00 pm – 7:00 pm	Working dinner for writing groups	

Thursday, August 9, 2007 • MORNING

Writing groups and workshop organizers only

7:30 am – 8:00 am	Continental breakfast

Final Writing of Panel Reports

8:00 am – 10:00 am	Selected writers, panel co-leads, and workshop co-chairs complete writing and integration of panel reports, proposed research directions, crosscutting research directions, and technology assessment[1] into final workshop report
10:00 am – 10:15 am	Break
10:15 am – 12:30 pm	Continue with tasks
12:30 am – 1:30 pm	Working Lunch
1:30 am – 3:00 pm	Finish tasks
3:00 pm	Writers Excused

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1) The pre-read technology assessment, which describes the present state and expected development of technology for catalytic processing chemical energy feedstocks, is available at http://brncatalysis.labworks.org/pdf/BRNCatalysisFactReport_v8_1.pdf

APPENDIX 3

WORKSHOP PARTICIPANTS

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Name	Company
Alexis Bell	University of California, Berkeley
Bruce Gates	University of California, Davis
Douglas Ray	Pacific Northwest National Laboratory
R. A. (Rutger) van Santen	Eindhoven University of Technology
William Banholzer	The Dow Chemical Company
Anthony V. Cugini	U.S. Department of Energy National Energy Technology Laboratory
Brian Valentine	U.S. Department of Energy
Harvey W. Blanch	University of California, Berkeley
Jingguang G. Chen	University of Delaware
Bruce Garrett	Pacific Northwest National Laboratory
Victor S.-Y. Lin	Iowa State University
T. Don Tilley	University of California, Berkeley
Mark Barteau	University of Delaware
Daniel G. Nocera	Massachusetts Institute of Technology
R. Tom Baker	Los Alamos National Laboratory
Charles T. Campbell	University of Washington
Raymond J. Gorte	University of Pennsylvania
Clark R. Landis	University of Wisconsin–Madison
Suljo Linic	University of Michigan
Simon R. Bare	UOP, LLC
Christopher (Kit) Cummins	Massachusetts Institute of Technology
Cynthia Friend	Harvard University
Karen I. Goldberg	University of Washington
Charles T. Kresge	The Dow Chemical Company
Tobin Marks	Northwestern University
Ayusman Sen	Pennsylvania State University
Jeff Siirola	Eastman Chemical Company
Levi Thompson	University of Michigan
J. Mike White	University of Texas at Austin
Peter T. Wolczanski	Cornell University
Marvin Johnson	Retired, Phillips Petroleum Company
Johannes Lercher	Technische Universität München
W. Nicholas Delgass	Purdue University
Michael T. Klein	Rutgers, The State University of New Jersey

Name	Company
Chuck Peden	Pacific Northwest National Laboratory
Daniel E. Resasco	University of Oklahoma
Dean M. Roddick	University of Wyoming
Eric Altman	Yale Universtiy
Paul T. Barger	UOP, LLC
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Donald Cronauer	Argonne National Laboratory
Maria Flytzani Stephanopoulos	Tufts University School of Engineering
Benjamin Gracey	BP Group Technology
William D. Green	Massachusetts Institute of Technology
James F. Haw	University of Southern California
Harold H. Kung	Northwestern University
Christopher L. Marshall	Argonne National Laboratory
Carl Mesters	RDS–Shell Global Solutions
Lanny Schmidt	University of Minnesota
William F. Schneider	University of Notre Dame
John M. Vohs	University of Pennsylvania
George W. Huber	University of Massachusetts at Amherst
Harvey W. Blanch	University of California, Berkeley
David A. Dixon	University of Alabama
Christopher W. Jones	Georgia Institute of Technology
Alexander Katz	University of California, Berkeley
Blake Simmons	Sandia National Laboratories
Phil Britt	Oak Ridge National Laboratory
Burtron Davis	University of Kentucky Center for Applied Energy Research
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Douglas Elliot	Pacific Northwest National Laboratory
Matthew Francis	University of California, Berkeley
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Leo E. Manzer	Catalytic Insights, LLC
Greg Stephanopoulos	Massachusetts Institute of Technology
Yong Wang	Pacific Northwest National Laboratory
Mike Henderson	Pacific Northwest National Laboratory
Peter C. Stair	Northwestern University
Anne M. Gaffney	ABB Lummus Global
Carl Koval	University of Colorado at Boulder

Name	Company
Clifford Kubiak	University of California, San Diego
Matthew Neurock	University of Virginia
Perla Balbuena	Texas A&M University
R. Morris Bullock	Pacific Northwest National Laboratory
Richard Eisenberg	University of Rochester
Heinz Frei	Lawrence Berkeley National Laboratory
Etsuko Fujita	Brookhaven National Laboratory
Michael R. Hoffmann	California Institute of Technology
Prashant V. Kamat	University of Notre Dame
Carol Korzeniewski	University of Texas
Nenad Markovic	Argonne National Laboratory
Anders Nilsson	Stanford Synchrotron Radiation Laboratory
Kenneth Poeppelmeier	Northwestern University
Philip N. Ross, Jr.	Lawrence Berkeley National Laboratory
Jim Boncella	Los Alamos National Laboratory
Stefan Czernick	National Renewable Energy Laboratory
Dan Ginosar	Idaho National Laboratory
John Gordon	Los Alamos National Laboratory
Mark Gordon	Ames Laboratory
Jeff Greeley	Argonne National Laboratory
Alex Harris	Brookhaven National Laboratory
Wayne Hess	Pacific Northwest National Laboratory
Mitch Jacobi	Chemical & Engineering News
Tina Masciangioli	National Research Council, National Academy of Sciences
Emilio Mendez	Brookhaven National Laboratory
Jim Miller	Sandia National Laboratories
Steve Overbury	Oak Ridge National Laboratory
Lucia Petkovic	Idaho National Laboratory
Marek Pruski	Ames Laboratory
John Regalbuto	National Science Foundation
Bill Rhodes	Savannah River National Laboratory
Chuck Turick	Savannah River National Laboratory
John Turner	National Renewable Energy Laboratory
Jud Virden	Pacific Northwest National Laboratory
Robert Wilson	SRI
Randy Winans	Argonne National Laboratory
Kyung Woo	ExxonMobil