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PNNL-36671

Conversion of Syngas to Light Olefins and Oxygenates using Multi-Functional Catalysts

September 2024

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U.S. DEPARTMENT OF ENERGY

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Abstract

This report describes our effort in developing catalysts for the conversion of syngas to light olefins and oxygenates. We have developed a series of metal/zeolite catalysts and tested their activity towards the conversion of syngas to light olefins. Light olefins produced in our case mostly comprised of C_2/C_3. A series of Mult metallic catalyst also synthesized and their performance was evaluated for the conversion of syngas to the production of oxygenates. In case of oxygenates, our specific focus was to maximize the selectivity of C_{2+} oxygenates which is a precursor for fuel or can be used as high value chemicals. In this direction, we have identified several Rh based catalysts that are specifically shows superior activity towards oxygenates formation.

Acknowledgments

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1.0 Introduction

Light olefins—generally referring to ethylene, propylene and butylene—are not only basic building blocks for chemical industry, but also precursors for production of sustainable aviation fuel (SAF). With the depleting of fossil fuels, the direct synthesis of light olefins from syngas (a mixture of H_2 and CO) has wide attentions, because syngas can be obtained from multiple sources including coal, natural gas and sustainable biomass. Fischer-Tropsch process (FTP) is a classic process for the syngas-to-hydrocarbon transformation since 1925.[1-6] However, the "Fischer–Tropsch to olefins" (FTO) technology is still challenged by the product selectivity to light olefins, because the hydrocarbon products typically follow the so-called Anderson–Schulz–Flory (ASF) distribution, which is basically a statistic distribution of the polymerization of CH_x (x = 1,2, or 3) monomers on an unconfined catalyst surface, with a maximum C_2–C_4 hydrocarbon fraction of about ~58%.[1, 4, 5] Therefore, development of catalyst that allows to break the ASF distribution is critical to improve the selectivity of light olefins. Researchers have put many efforts and made some progress in modifying the conventional Co- and Fe- FTP catalysts to increase the light olefin selectivity, but still suffers from generation of undesired products, mainly due to the trade-off between the over-hydrogenation (forming CH_4) and overgrowth of carbon chain (forming C_{5+} hydrocarbons). For instance, Zhong et al.[7] synthesized a cobalt carbide nanoprism catalyst for FTO and achieved an improved C_2-C_4 olefin selectivity of 60.8% and a low CH_4 selectivity of 5%, but the selectivity to C_{5+} hydrocarbon was as high as 31.4%. In contrast, Galvis et al. [8] reported a carbon nanofiber (CNF)-supported Fe nanoparticle catalyst which showed a C_2-C_4 olefin selectivity of 61% but meanwhile a CH_4 selectivity of 22%. Despite research activities, it is critical to develop a catalyst system that produces light olefins with higher selectivity.

Thermochemical conversion of syngas to oxygenates is also represents an appealing route for because of their broad range of application. In this project we specifically targeted for the production of higher alcohols which are typically contain two or more carbon atoms. These classes of compounds are widely employed as the feedstocks for and intermediates for the synthesis of commodity and specialty chemicals and consequently have high value in the chemical and polymer industry.[8,9] In addition to the chemical value, mixed alcohols also represent an attractive feedstock for the sustainable aviation fuel. Pathways utilizing C_{4+} alcohol as feedstock for the preparation of SAF has recently been demonstrated.[10] Currently higher alcohols such as ethanol and isobutanol are produced via either sugar fermentation or hydration of petroleum derived alkene. While the former suffers from high energy demand, low carbon yield of the latter process requires an energy efficient technology that converts either CO2 or syngas (CO and H2 mixture) to produces higher alcohols or oxygenates.

Catalyst Characterization

The composition of the catalyst was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin Elmer Optima 7300DV instrument. Before ICP measurements, the bimetallic catalysts were digested in concentrated nitric acid in a sealed vessel using CEM MARS 6 microwave digestion unit. The crystal structure of the catalysts was studied using a benchtop Rigaku MiniFlex 600 X-ray diffractometer equipped with a Cu K_α X-ray source (wavelength of 1.54 Å). To obtain X-ray diffraction (XRD) patterns, the was placed on a glass sample holder and diffraction patterns were collected over the scattering angle range of 5° to 80°, with a scan rate of 0.1° min^{-1} and a step size of 0.01°. Microscopic characterization of the catalysts were performed using JEOL TEM instrument.

Catalytic activity test

All the catalytic experiments were performed using a flow reactor. Experiments were performed using syngas as the feedstocks where CO:H_2 ratio was maintained as 2:1. The experiments were carried out at different temperature ranging from 100-400 ºC and at different pressure such as 10-35 bar. Prior to the reaction the catalyst was pelletized and sieved. The catalysts were loaded in the reactor and reduced under H_2 to obtain the metallic phase. The products were analyzed by micro-GC, GC-FID and GC-MS.

2.0 Results and Discussion

All the novel catalysts were synthesized and characterized by using microscopy and spectroscopy techniques prior to their testing. All the catalysts are typically synthesized using wet chemistry approach such as co-precipitation technique.

We have synthesized a series of zeolite supported Fe and Co catalyst and tested their performance for the synthesis of light olefin production. The details of this study has recently been submitted for provisional patent application and the corresponding US Provisional Application Serial No. 63/686,306.

In addition to our study towards light olefin production, we have also synthesized a library of acidic and basic metal oxide and mixed metal oxide catalyst and used these as the support materials for Rh catalyst and tested their effect towards the conversion of syngas to oxygenates, specifically to higher alcohols. Figure 1 shows activity results of some of the supported Rh catalysts and corresponding support materials.

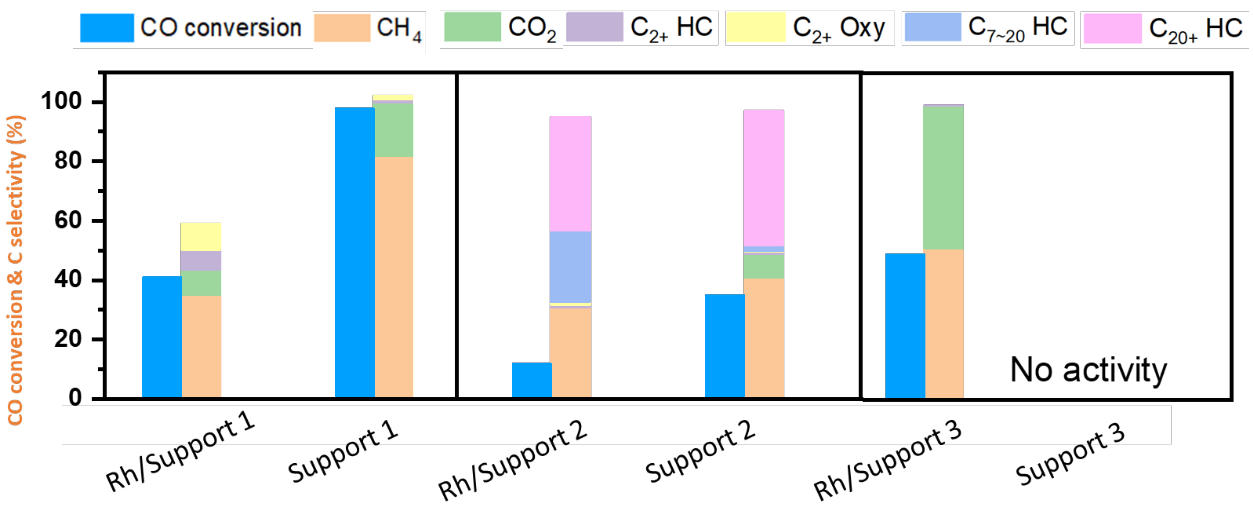

Figure 1. Activity comparison different supported Rh catalyst. All the supported catalyst are basic metal oxide or mixed metal oxide. Support 1 and 2 represents mixed metal oxide and support 3 represents metal oxide.

As shown in Figure 1, syngas conversion activity depending strongly on the nature (composition) of metal oxide or mixed metal oxide used as support. Support 1 consists of Ni based mixed metal oxide and shows very high conversion of CO however, most of the products obtained herein are consists of methane (~80% methane selectivity). The results were attributed to the high methanation of activity of the Ni catalyst. When Rh (typical loading ≤ 0.2 wt%) was loaded, the effect was evident because overall CO conversion reduced and both C2+ hydrocarbons and oxygenates were produced. Thus, presence of Rh generates active sites for C-C coupling reaction either between adsorbed CH_x fragments or adsorbed CH_x and CO species. When Zn based mixed metal oxide catalyst was tested, a very different activity was noted compared to Ni based support. Although methane was observed as one of the products, its selectivity reduced significantly (~40% methane selectivity). However, in this case large polymeric products was obtained. In this case, presence of Rh reduced the overall conversion of CO but produced C7-C20 products along with large polymeric compounds. Although oxygenated products were noted with Rh based catalyst, the selectivity was very low in this case. In contrast to mixed metal oxide when only base metal oxide was used as support, it didn't show any activity towards syngas conversion. However, promotion of Rh provided active sites for CO conversion however, in this case only methane and CO_2 were noted as the product. CO_2 generated in this reaction could be attributed to water gas shift reaction.

We also synthesized and tested different Rh based catalysts prepared on acidic support. It is evident that when Rh catalysts are prepared on acidic support selectivity to oxygenates were improved significantly. In these cases oxygenates were obtained as the major products as opposed to hydrocarbons as noted when basic support was used. While the exact mechanistic pathways required further investigation, we propose synergistic interaction between Rh sites and acid sites stabilizes the intermediates for the oxygenates. The fraction represented by yellow denotes the alcohol products. Among the different alcohols methanol and ethanol was obtained as the major products with nearly equal selectivity. We also noted propanol, butanol and pentanol. Among the different catalysts tested herein Rh-3 catalysts shows ~80% selectivity towards alcohol formation. The activity of Rh based catalysts was strongly dependent on the support materials as some of the catalyst did not show any activity (Rh-4) or methane as the sole product (Rh-5)

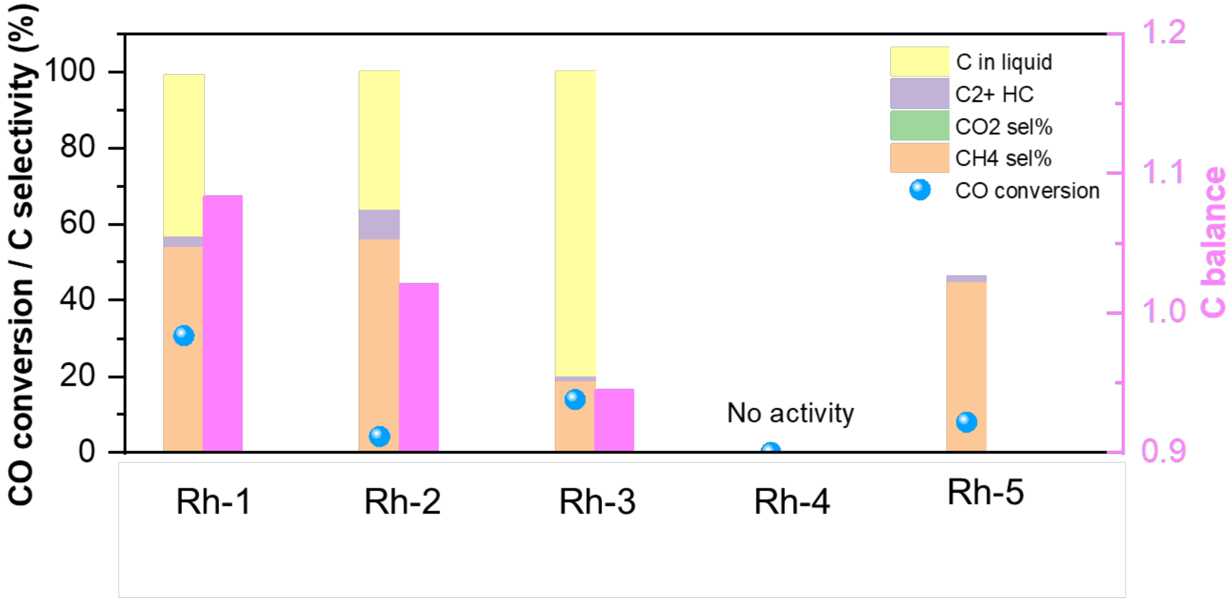

Figure 2. Performance evaluation of different Rh catalyst supported on acidic support

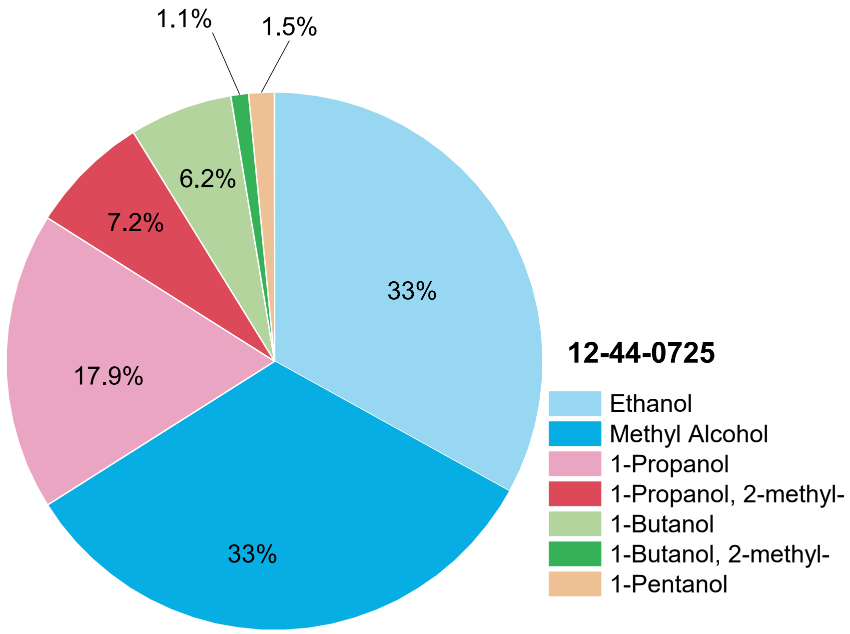

Figure 3. Detailed product distribution of the alcohol products obtained in case of Rh-3 catalysts.

Figure 3 shows the detailed distribution of alcohols products that are obtained in this case. Methanol and ethanol was obtained as major product with their corresponding selectivity ~33%. Selectivity to 1-propanol and C_4 alcohol was ~18% and 14% respectively. Small amount of C5 alcohol was also observed. While Rh-3 catalyst show very high selectivity to alcohols, conversion is ~20%. Further studies are directed to detail characterization of the catalysts and understand the underlying reaction mechanism. These studies will be key in developing further improve the CO conversion of the catalyst as well to increase the selectivity of C_{2+} alcohols. It is important to note here that we have highlighted Rh based catalysts for the oxygenates formation as it shows superior activity. We also investigated different metal combination (mostly 3d, 4d and 5d transition metals) however, their activity towards C_{2+} alcohols or oxygenates were very low.

3.0 Conclusion

In conclusion, we have prepared a novel metal/zeolite catalysts and evaluate the performance of these catalysts towards syngas conversion to light olefins which are mostly comprised of C2/C3. We have also synthesized and evaluated a library of catalysts for the syngas conversion to oxygenates, specifically to higher alcohols. Rh based catalysts show superior activity compared to other metal catalysts. When Rh based catalysts were synthesized on basic metal oxide or mixed metal oxide support materials corresponding activity was significantly influenced by the support materials. Most of the cases hydrocarbons were obtained as major projects. On the other hand, when Rh catalysts were synthesized on acidic support oxygenates were obtained as major products. While the exact reaction pathways are still unknown, we speculate that synergistic interaction between Rh and acid sites stabilizes the key intermediates for the formation of oxygenates. Using the optimized Rh catalyst we achieved ~80% selectivity of C1-C5 alcohols and ~50% selectivity to C2-C5 alcohols. Further studies will be directed to improve the CO conversion and enhance the selectivity to C2-C5 alcohols.

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