Final Report of a CRADA Between Pacific Northwest National Laboratory and the Ford Motor Company (CRADA No. PNNL/265): "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials"

F Gao, JH Kwak, JH Lee, D Tran, CHF Peden
Pacific Northwest National Laboratory

K Howden *Department of Energy*

Y Cheng, J Lupescu, G Cavataio, C Lambert, R McCabe
Ford Motor Company

February 2012

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

**Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov**

**Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm**

This document was printed on recycled paper.
(9/2003)

Final Report of a CRADA Between Pacific Northwest National Laboratory and the Ford Motor Company (*CRADA No. PNNL/265*): "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials"

Feng Gao, Ja Hun Kwak, Jong H. Lee, Diana Tran, Chuck Peden (Primary Contact)

Institute for Integrated Catalysis

Pacific Northwest National Laboratory

P.O. Box 999, MS K8-93

Richland, WA 99354

(509) 371-6501; fax: (509)371-6498; e-mail: chuck.peden@pnnl.gov

DOE Program Manager: Ken Howden

(202) 586-3631; fax: (202)586-7409; e-mail: Ken.Howden@ee.doe.gov

CRADA Partners: Yisun Cheng, Jason Lupescu, Giovanni Cavataio, Christine Lambert, Robert McCabe (Ford Motor Company)

Objectives:

- Develop an improved understanding of the deactivation mechanisms of the urea selective catalytic reduction (urea SCR) catalyst used in diesel aftertreatment systems.

- Understand similarities and differences between actual field aging and aging under laboratory conditions, information essential in developing a rapid assessment tool for emission control technology development.

- Determine the role of the various aging factors, including poisons like sulfur and phosphorous, and unique aging due to urea exposure that can impact long-term performance of SCR catalyst systems, in order to provide information about what operating conditions or system configurations should be avoided to minimize catalyst deactivation.

- Leverage PNNL's catalyst characterization capabilities and scientific knowledge of zeolite materials to aid Ford in the further development of urea SCR catalysts and systems.

- Help fuel-efficient advanced combustion engines meet the current and future hydrocarbon (HC) emission standards with effective, inexpensive and reliable HC adsorber technologies using zeolite materials.

- Improve the understanding of interaction between engine-out HCs and HC adsorber materials during the cold-start and the catalyst warm-up periods.

Accomplishments:

- Completed studies of the differing effects of SO_2 to SO_3, including identification of the mechanism of more severe poisoning by SO_3, reinforcing that ultralow sulfur fuel is required for high NOx reduction efficiency, and implying that highly loaded Pt oxidation catalysts are not preferred upstream of the SCR catalyst. Pd can be used instead, lowering catalyst system cost. A strategy to desulfate the catalyst at filter regeneration conditions was successful.

- Characterized the nature and distribution of phosphorus deposits observed on engine-aged urea SCR catalysts and determined the impact to be less severe than sulfur.

- Performed studies aimed at an understanding of unusual hydrothermal aging of zeolite-based urea SCR catalysts observed at Ford that severely impacted the front edge of the catalyst and changed the nature of the catalyst from reduction to oxidation.

- Investigated the physicochemical properties of model zeolite materials with respect to hydrothermal aging for comparison to commercially available SCR catalyst materials. Identified a Cu aluminate phase that generated higher NOx conversion at filter regeneration conditions and could result in better SCR catalyst systems with wider temperature windows of operation.

- Evaluated the effects of physicochemical properties of model zeolite materials on the adsorption and desorption of ethanol for E10 to E85 applications.

- Six publications and thirteen public presentations.

Introduction:

Reducing NOx emissions and particulate matter (PM) are primary concerns for diesel vehicles required to meet current LEV II and future LEV III emission standards which require 90+% NOx conversion. Currently, diesel oxidation catalysts, urea SCR as the NOx reductant [1] and a Catalyzed Diesel Particulate Filter (CDPF) are being used for emission control system components by Ford Motor Company for 2010 and beyond diesel vehicles. Because the use of SCR technology for vehicle applications is new, the relative lack of experience makes it especially challenging to satisfy durability requirements. Of particular concern is being able to realistically simulate actual field aging of the catalyst systems under laboratory conditions. This is necessary both as a rapid assessment tool for verifying improved performance and

certifiability of new catalyst formulations, and to develop a good understanding of deactivation mechanisms that can be used to develop improved catalyst materials.

In addition to NOx and PM, the hydrocarbon (HC) emission standards are expected to become much more stringent during the next few years. Meanwhile, the engine-out HC emissions are expected to increase and/or be more difficult to remove. Since HC can be removed only when the catalyst becomes warm enough for its oxidation, three-way catalyst (TWC) and diesel oxidation catalyst (DOC) formulations often contain proprietary zeolite materials to hold the HC produced during the cold start period until the catalyst reaches its operating temperature (e.g., >200°C). Unfortunately, much of trapped HC tends to be released before the catalyst reaches the operating temperature. Among materials effective for trapping HC during the catalyst warm-up period, siliceous zeolites are commonly used because of their high surface area and high stability under typical operating conditions. However, there has been little research on the physical properties of these materials related to the adsorption and release of various hydrocarbon species found in the engine exhaust. For these reasons, automakers and engine manufacturers have difficulty improving their catalytic converters for meeting the stringent HC emission standards.

In this collaborative program, scientists and engineers in the Institute for Integrated Catalysis at Pacific Northwest National Laboratory and at Ford Motor Company investigated laboratory- and engine-aged SCR catalysts, containing mainly base metal zeolites. These studies led to a better understanding of various aging factors that impact the long-term performance of SCR catalysts and improve the correlation between laboratory and engine aging, saving experimental time and cost. We have also studied materials effective for the temporary storage of HC species during the cold-start period. In particular, we have examined the adsorption and desorption of various HC species produced during the combustion with different fuels (e.g., gasoline, E85, diesel) over potential HC adsorber materials, and measured the kinetic parameters that have potential use in developing system models.

Since this CRADA has now been completed, in this final report we will provide brief summaries of most of the work carried out on this CRADA over the last several years.

Approach:

This project focused on the characterization of catalyst materials used in the urea SCR and HC absorber technologies with special attention to changes in the materials properties under conditions of laboratory (e.g., oven and laboratory reactor) and realistic (e.g., engine dynamometer and vehicle) aging protocols. In particular, a primary area of emphasis of earlier studies on this project was establishing the relevance of rapid laboratory catalyst aging protocols with the specific aging phenomena observed in realistic engine operating conditions. This information aided in the development of optimized rapid aging protocols at Ford.

Ford provided both fresh and aged catalyst materials used in the urea SCR technology, and made experimental measurements of changes in the catalytic performance of these materials before and after the aging. PNNL has utilized state-of-the-art analytical techniques to investigate the surface and bulk properties of these catalysts as well as the changes in these properties induced by the aging process. In particular, catalyst characterization techniques such as XRD, XPS, TEM/EDS, BET/pore size distribution, and ^{27}Al solid state NMR have been utilized to probe the changes in physicochemical properties of SCR catalyst and HC absorber samples after

various pretreatments. This work has been performed on a group of model and development catalysts. Specifically, we have utilized a variety of zeolites, a class of microporous aluminosilicate materials that include a wide range of natural minerals. For SCR, Cu-exchanged beta and SSZ-13 zeolite catalysts were exposed to deactivating conditions; *e.g.*, hydrothermal aging at various temperatures. For HC absorbers, we used candidate catalytic materials that are effective for the temporary storage of HCs produced from different fuels during the cold-start period or advanced combustion processes. Various silicate and aluminosilicate materials, including novel zeolites, were evaluated with respect to hydrophobicity, surface area, pore size and connectivity for the adsorption and desorption of hydrocarbon species found in the engine exhaust. Once the potential materials are characterized, fuel component and combustion product HC species are used to probe the adsorption and desorption characteristics of different HC adsorber materials. These characterization measurements were complimented by studies at Ford that included performance testing following a variety of laboratory and realistic engine aging protocols.

Results:

Physicochemical investigations of the degradation mechanisms for SCR catalysts

NMR Studies of Hydrothermally Aged Cu/Zeolite SCR Catalysts with Urea: The effects of hydrothermal aging of Cu/zeolite urea-SCR catalysts on their reactivity and material properties was assessed by performance tests and multiple characterization techniques that included ^{27}Al NMR and XRD [2]. Three aging protocols were used that consisted of varying temperature during hydrothermal aging with or without exposure to aqueous urea solution, and the results of NOx performance tests performed after these three different treatments are shown in Figure 1. Differences in behavior were even found for samples hydrothermally aged immediately following exposure to the urea solution or if the sample was dried overnight before hydrothermal aging. The combination of urea and high temperature exposure increased the deactivation of Cu/zeolite SCR catalysts beyond that observed by hydrothermal aging alone, with an immediate high temperature exposure following wetting of the catalyst core with aqueous urea causing the most significant deterioration in performance. The impact of urea on SCR catalyst durability was also found to increase with the aging temperature. NMR analysis (Figure 2) suggests that aging with urea resulted in relatively more dealumination of the zeolite for the SCR catalysts in this study.
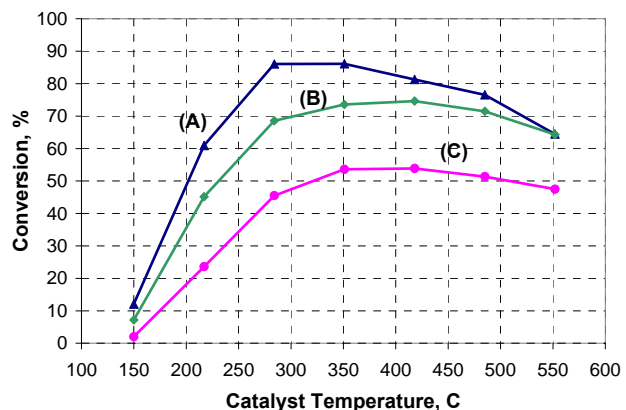
Figure 1: Steady state NOx conversions for a Cu/zeolite catalyst after aging at 860°C for 30 min: (A) hydrothermal aging only; (B) "dry urea" + hydrothermal aging; and (C) "wet urea" + hydrothermal aging.

Figure 2: Relative dealumination of a Cu/zeolite catalyst after aging at 670°C hydrothermal only, and after aging at 860°C in the three aging conditions.
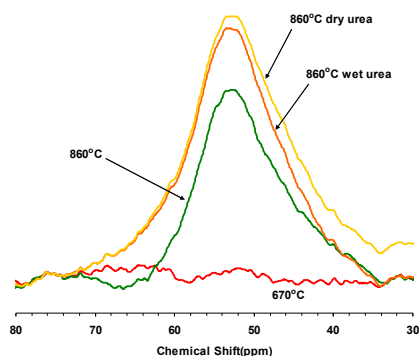
The Different Impacts of SO₂ and SO₃ on Cu/Zeolite SCR Catalysts: The different impacts of SO_2 and SO_3 on Cu/zeolite SCR catalysts were investigated by SCR performance tests and multiple characterization techniques including temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) [3]. The results indicate that a larger amount of highly dispersed $CuSO_4$ formed in the zeolite catalysts (Z-$CuSO_4$) upon SO_3 poisoning, explaining the much more significant deactivation of the Cu/zeolite catalysts that were exposed to SO_3 compared to poisoning by SO_2. Diesel oxidation catalysts containing high levels of Pt for NO oxidation, a common industry strategy to improve low temperature NOx reduction and soot oxidation, also oxidize SO_2 to SO_3. In these studies, we provided the first demonstration that active sites of Cu/zeolite SCR catalysts involved in the storage and removal of sulfur can react with SO_2 and SO_3 in very different ways. In particular, the significant differences in the extent of sulfur uptake account for the considerably different impacts of SO_2 and SO_3 poisoning on the performance of Cu/zeolite SCR catalysts. The Cu/zeolite SCR catalyst used in this study was a fully-formulated cordierite monolith with Cu/zeolite washcoat from a catalyst supplier.

The NOx activities for Cu/zeolite samples before and after sulfur poisoning by SO_2 or SO_3 at 200°C, 300°C, and 400°C are shown in Figure 3. Also shown in this figure are results for a freshly degreened catalyst (T1). The NOx activity of SO_2-poisoned Cu/zeolite SCR catalysts decreased to a relatively small extent after being exposed to 40 ppm SO_2 for 1.5 hours regardless of the aging temperatures. The lower SO_2 aging temperature resulted in higher NOx activity decreases: the NOx activities performed at 178°C decreased by 33%; by 21% for the sample aged at 300°C, and only by 8% for the sample aged at 400°C. In contrast, the NOx activities of CatA Cu/zeolite catalysts after sulfur poisoning by SO_3 at 200, 300, and 400°C were significantly decreased for all samples after being exposed to 40 ppm SO_3 for 1.5 hours regardless of the exposure temperatures, with NOx activities of all samples being extremely low at T <250°C. The sample aged with SO_3 at lower temperature had better NOx activity between 250°C and 340°C. Notably at a 340°C test temperature, the NOx activity of the sample aged at 200°C was close to 100%, while the NOx activity of sample aged at 400°C showed only 70% conversion.

In order to obtain the information on the oxidation state and amount of sulfur species, we applied XPS for the Cu/zeolite catalyst samples treated at 200°C with SO_2 and SO_3. For the 27 mm (1 inch) long monolith samples, five points were analyzed separated by a distance of 6 mm, allowing us to determine the spatial distribution along the monolith z-axis. Spectra of both samples contain a single peak at 169 eV, indicating that only sulfates (SO_4^{2-}) are formed by the

interaction with either SO_2 or SO_3. However, there was a drastic difference in the amount of sulfate species between the samples treated with SO_2 or SO_3. As shown in Figure 4, the sample treated with SO_3 clearly had larger amounts of sulfur, especially up to 13 mm from the inlet, followed by a significant decrease thereafter. We suggest that sulfate saturates the catalyst from the inlet, gradually moving toward the outlet. In contrast, the sample treated with SO_2 had considerably smaller amount of sulfur in the inlet and along the monolith. The summed amounts of sulfur along the monolith indicates that the sample treated with SO_3 contained at least five times larger concentrations than the one treated with SO_2, which points to the relative ease of sulfate formation by reaction with SO_3. XPS results on the samples after the desulfation (deSOx) showed essentially no sulfur remained on the surface of the catalyst (not shown). This result implies that all sulfates are desorbed as a result of thermal desorption during the deSOx, as evidenced also by the full recovery of the activity after deSOx (not shown). The results reinforce that ultralow sulfur diesel fuel is required for modern Cu/zeolite SCR systems, and Pt upstream of the SCR catalyst is not preferred. Pd is a good alternative for diesel oxidation catalysts that do not oxidize SO_2 to SO_3.
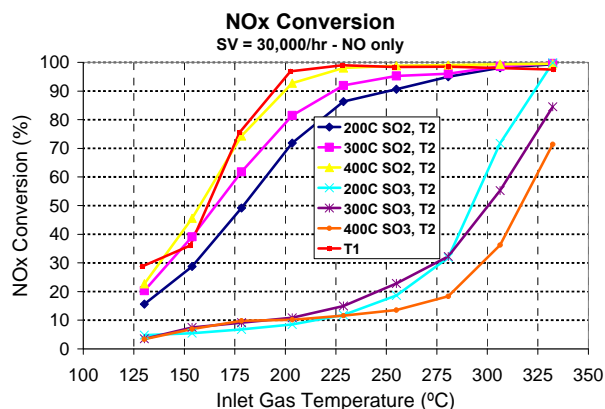
Figure 3: Steady-state NOx conversions for Cu/zeolite SCR catalysts before and after SO_2 and SO_3 aging at 200°C, 300°C, and 400°C. Also shown are results for a freshly degreened catalyst (T1).
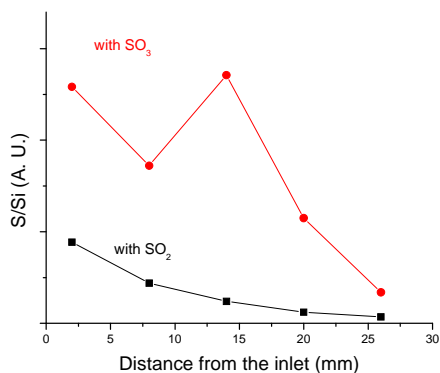
Figure 4: Distribution of sulfur, plotted as normalized S/Si ratios, as a function of distance from the inlet of the monolith-type Cu/zeolite catalyst.

Non-uniform Aging on Super Duty Diesel Truck Aged Cu/Zeolite Urea SCR Catalysts: Previous studies have shown that deactivation of engine aged SCR catalysts is not uniform, with the inlet section of the catalyst brick deactivating the most and becoming more oxidizing in nature. To better understand this non uniform aging phenomena, a set of Cu/zeolite SCR catalysts aged for 50K miles on a Super Duty diesel truck were investigated with postmortem analyses emphasizing studies of the inlet section [4,5]. The analyses included catalyst activity evaluation and catalyst characterization, such as BET surface area, TPR, XRF, XPS and TEM. The results suggest that the inlet section of the brick experienced all the aging factors in the most severe way, and that this section deactivates in a more complicated manner than the rest of the brick which mainly deteriorated due to hydrothermal aging. This is demonstrated in Figure 5 which shows a comparison of steady state SCR NOx conversion of cores taken from the middle of the brick, labeled as "M", from the 1st, 2nd, 3rd, and 5th inch of inlet gas direction. Changes of Cu state and high levels of C, P and Zn impurities in very front

region might explain the more severe deactivation of the inlet section of the SCR catalyst. For example, Figure 6 shows the levels of these three impurities as a function of distance from the front of the catalyst monolith obtained by XPS.
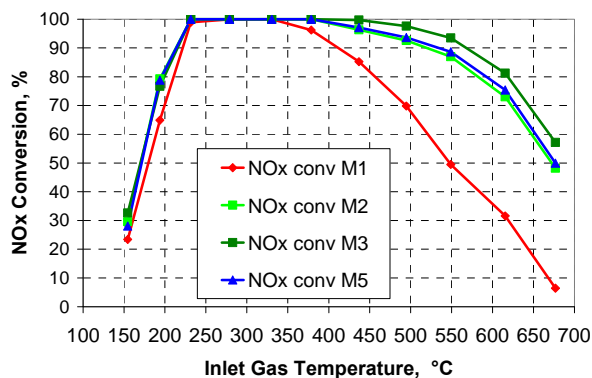
Figure 5: Steady state NOx conversions of engine aged Cu/CHA SCR catalysts.
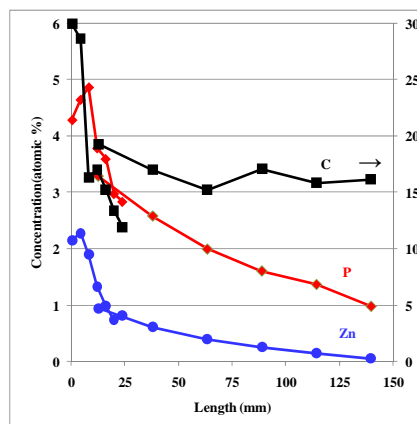

Figure 6: XPS intensities of carbon (C), phosphorus (P), and zinc (Zn) as a function of distance from the front of a vehicle aged (50K miles) Cu/zeolite SCR catalyst.

Unusual Performance Behavior for Cu-zeolite SCR catalysts After Mild Hydrothermal Aging: The hydrothermal stability of Cu/beta NH_3 SCR catalysts, with respect to their interesting ability to maintain and even enhance high-temperature performance for the "standard" SCR reaction after modest (900°C, 2 hours) hydrothermal aging, was studied [6]. Characterization of the fresh and aged catalysts was performed with an aim to identify possible catalytic phases responsible for the enhanced high temperature performance. Two model catalysts, suggested by these characterization data as possible mimics of the catalytic phase formed during hydrothermal aging of Cu/beta, were prepared and tested for their performance in the "standard" SCR and NH_3 oxidation reactions. The similarity in their reactivity compared to the 2-hour hydrothermally-aged Cu/beta catalyst suggests possible routes for preparing multi-component catalysts that may have wider temperature windows for optimum performance than those provided by current Cu/zeolite catalysts. As perhaps the most promising zeolite-based SCR catalyst prior to the discovery of the newest generation of CHA zeolite-based materials, the catalyst chosen for this study was Cu ion-exhanged beta zeolite. The beta zeolite (CP-814C, $Si/Al_2 = 38$) was obtained from Zeolyst International Co., and Cu/beta catalysts were prepared by aqueous ion-exchange using a $Cu(NO_3)_2$ precursor. These Cu-exchanged/beta (Cu/beta) catalysts were calcined in an oven at 500°C for 2 hours prior to testing and characterization.

As part of studies carried out a couple of years ago at Ford on the comparative hydrothermal stability of several pre-commercial Cu/zeolite catalysts [7], some very interesting SCR performance behaviour was observed after hydrothermal aging at very high (900°C) temperatures. In particular, this study described Ford's first observations of an SCR Cu-zeolite formulation (referred to as a "best in class 2007 SCR formulation" in this SAE International paper) that is able to maintain stable NOx performance at 200°C after exposure to such severe hydrothermal aging conditions. Not discussed in this paper, however, was the maintenance of unusual high-temperature SCR performance for an older generation catalyst ("best in class 2006 formulation"), even though this latter catalyst's low-temperature activity was reduced significantly due to the high-temperature aging (see Figure 7 in reference [7]). Here, we briefly

describe our collaborative studies aimed at understanding the properties of zeolite-based catalysts after hydrothermal aging, especially with respect to shedding light on the nature of the material giving rise to this interesting, and potentially useful high temperature SCR performance.
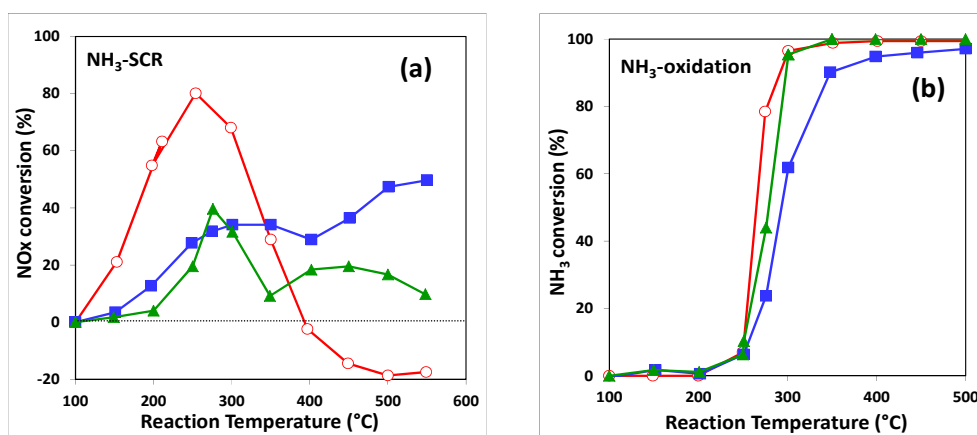

Figure 7: (a) NO conversion to N_2 during the "standard" SCR reaction, and (b) NH_3 conversions during the NH_3 oxidation reaction (no NOx present) over a Cu-beta zeolite catalyst as a function of temperature after various thermal aging treatments at 900°C: 1 hour in dry air (open red circles); 2 hours in air with 10% H_2O (solid blue squares); and 10 hours in air with 10% H_2O (solid dark green triangles). Gas composition for SCR reaction: 350 ppm NO, 350 ppm NH_3, 14% O_2, 2% H_2O in balance N_2. Gas composition for the NH_3 oxidation reaction: 350 ppm NH_3, 14% O_2, 2% H_2O in balance N_2.

Figure 7 shows results for the temperature dependence of the "standard" SCR (Figure 7a) and NH_3 (Figure 7b) oxidation reactions over the Cu/beta catalyst after various hydrothermal treatments. These treatments, separately performed on fresh catalyst samples, included calcination at 900°C for one hour in the absence of H_2O (red curves), 900°C hydrothermal (H_2O present) treatment for 2 hours (blue curves), and hydrothermal treatment at 900°C for 10 hours (green curves). Following a 900°C calcination without H_2O present, the Cu/beta catalyst still displays good performance for the "standard" SCR reaction at lower temperatures (Figure 7a, red curve), although its higher (>300°C) temperature activity is significantly degraded. In fact, negative NOx conversions observed at temperatures above 400°C indicate little, if any, SCR activity for this catalyst aged by calcination, while non-selective NH_3 oxidation by O_2 (light-off just below 300°C, red curve in Figure 7b) is responsible for the formation of NOx.

Significantly different "standard" SCR performance data were obtained following a 2-hour hydrothermal (H_2O present) aging treatment (Figure 7a, blue curve with square symbols). In this case, while lower (< 350°C) temperature performance is significantly degraded, NOx conversions above 400°C are maintained and even perhaps enhanced. Also interesting to note is the fact that the light-off temperature for NH_3 oxidation by O_2 has increased (Figure 7b, blue curve). Further increasing the hydrothermal aging time to 10 hours results in a loss of SCR performance for the Cu/beta catalyst at all temperatures (Figure 7a, green curve). The distinct "standard" SCR and NH_3 oxidation activity of the hydrothermally-aged Cu/beta catalysts, particularly after a relatively short aging time of 2 hours, suggests that a new catalytic phase may have formed during the moderately severe treatment. In order to identify the nature of this potential new phase, we characterized the fresh and aged catalysts with XRD, TEM and ^{27}Al NMR spectroscopy.

Figure 8 shows the XRD patterns obtained for the fresh (Figure 8a) and hydrothermally-aged Cu/beta catalysts. In all of these diffraction patterns, only peaks arising from the beta zeolite are evident. Following calcination of the Cu/beta catalyst at 900 °C for 1 hour, the diffraction pattern obtained (not shown) is essentially identical to that for the fresh catalyst shown in Figure 8a. After a very short (1 hour) hydrothermal aging treatment, XRD features associated with Cu/beta are still evident (Figure 8b), although the peaks are somewhat smaller and broader indicating that there has been some loss of the zeolite structure as a result of this treatment. However, increasing the 900 °C hydrothermal treatment time to 2 hours results in a nearly complete loss of zeolite structure (Figure 8c). The small beta zeolite peaks still remaining after 2 hours treatment are essentially fully absent in the diffraction pattern obtained from the sample hydrothermally aged for 10 hours (Figure 8d). For both hydrothermally-aged samples, a broad feature centered at ~22° 2θ indicates the formation of amorphous material.

Strong peaks in the ^{27}Al NMR spectra of alumino-silicate zeolites at ~50-60 ppm (using the signal due to aluminum in an aqueous solution of $Al(NO_3)_3$ as a 0 ppm reference) are due to tetrahedrally-coordinated Al atoms that substitutionally occupy Si lattice sites within the zeolite. For fresh Cu-beta zeolite, the peak associated with tetrahedral zeolite-lattice Al appears at ~55 ppm as illustrated in Figure 9 (black curve). Calcination at 900°C results in little, if any, change in the ^{27}Al NMR spectrum (Figure 9, red curve), consistent with both XRD and TEM data (not shown). In contrast, hydrothermal aging at 900°C for 2 hours results in a dramatic decrease in the size of the peak associated with tetrahedrally-coordinated Al (Figure 9, blue curve). This feature is essentially absent from the Cu/beta catalyst that was hydrothermally aged for 10 hours (Figure 9, green curve). Note, however, that no new features appear in the spectra for the hydrothermally-aged samples. A possible explanation for this loss of signal in the ^{27}Al NMR spectra for these aged catalysts is a strong interaction between paramagnetic Cu and the Al species that are newly formed as a result of hydrothermal dealumination. Such a strong interaction would render the ^{27}Al NMR signal 'invisible'.
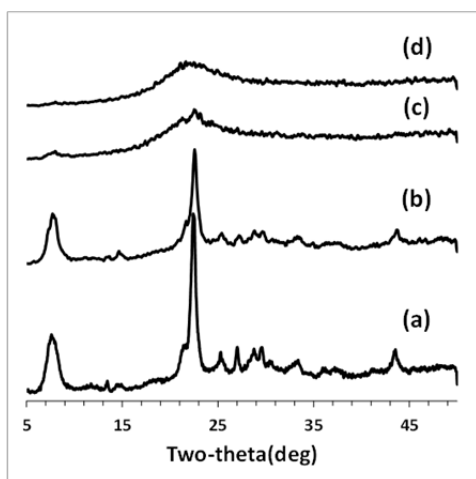

Figure 8: XRD patterns of a fresh Cu/beta catalyst (a), and after hydrothermal aging at 900°C for (b) 1, (c) 2, and (d) 10 hours in dry air that contained 2% H_2O separately added, at a total gas flow rate during of 500 SCCM.
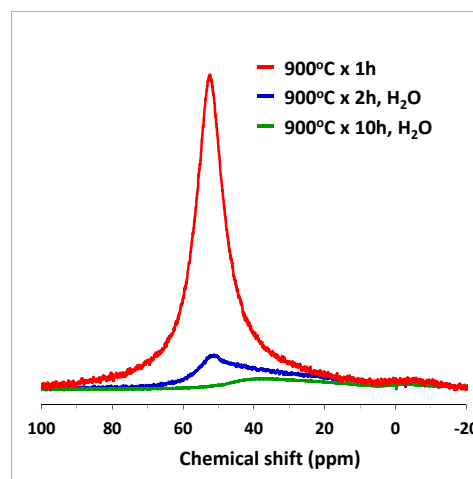

Figure 9: ^{27}Al solid state NMR spectra of the Cu/beta samples aged at 900°C in dry air for 1 hour (red curve), and in dry air that contained 2% H_2O separately added for 2 (blue curve) and 10 (green curve) hours.

The characterization results obtained in these studies were used to suggest possible model catalyst mimics of the catalytic phase formed upon hydrothermal aging that is responsible for its enhanced high temperature performance for the "standard" SCR reaction shown in Figure 7. In fact, the reactivity of the model catalysts (not shown here) were remarkably similar to those of the hydrothermally-aged Cu/beta catalyst suggesting the possibility that multi-component catalysts can be prepared with wider temperature windows than currently available with Cu/zeolite catalysts alone. A specific catalyst structure able to achieve both good high- and low-temperature NOx reduction performance is not proposed here since it will depend on the locations of other emission control components (i.e., diesel oxidation catalyst, diesel particulate filter, etc.). However, the results presented here suggest that an SCR catalyst system consisting of both Cu-zeolite and Cu-alumina materials will provide for a desirably wider temperature window for optimum SCR performance [6].

Deactivation of Cu/Zeolite SCR Catalysts Caused by Phosphorous: A specific role for phosphorus in the loss of SCR performance of Cu/zeolite was investigated by reactivity tests and catalyst characterization measurements as a function of aging conditions with and without phosphorus [8]. While these studies were not completed during the CRADA, they did demonstrate a possible concern if significant quantities of this species accumulated on the SCR catalyst as a result of the breakdown of engine lubricants. In particular, addition of small amounts of phosphorus species to the gas mixture used during laboratory aging resulted in a small but significant drop in NOx reduction performance at both low and high temperatures for a state-of-the-art Cu/zeolite catalyst as illustrated in Figure 10. The loss of high temperature activity can be rationalized by enhanced rates of non-selective ammonia oxidation with P aging as illustrated in Figure 11. To determine possible changes in the Cu/zeolite catalyst, we characterized these materials after various aging treatments with and without P with a number of methods.
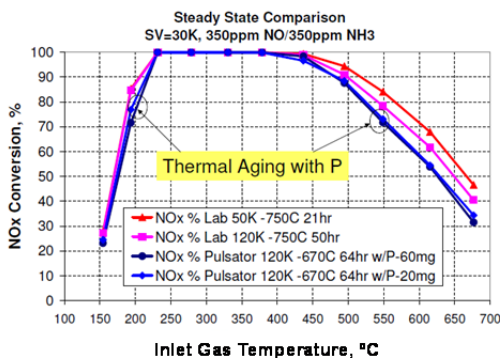

*Figure 10:* Steady state NOx conversions of lab-aged Cu/CHA SCR catalysts with and without P.
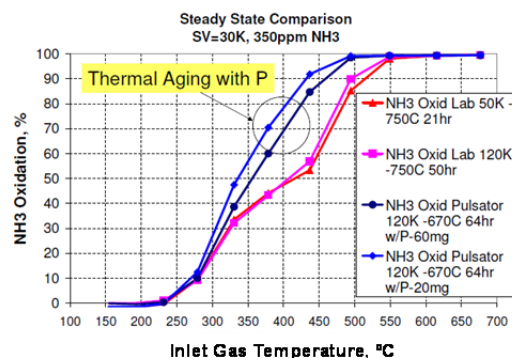
Figure 11: Steady state NH$_3$ oxidation rates of lab-aged Cu/CHA SCR catalysts with and without P.

Essentially no differences in surface area were observed for the Cu/zeolite catalysts as a function of the various lab-aging treatments. Using NH$_3$ TPD to characterize ammonia storage properties of the variously treated catalysts, a small but consistently observed drop in ammonia adsorption capacity was observed for the catalysts aged in the presence of P. Cu(2p) XPS results (not shown) reveal no changes in the state of Cu even though P species are readily detected on the P-aged catalysts as shown in Figure 12. ^{31}P NMR studies have tentatively identified two types of phosphorus species that are present as a function of impurity P levels. This is

demonstrated in ^{31}P NMR spectra shown Figure 13 for samples that were aged in low (black curve) and high (red curve) P levels. At low levels, the P species appears to be in the form of a monomeric phosphate-like species while the spectrum obtained for the sample with higher P levels is consistent with the presence of a bulk-like phosphate species. The overall impact was much less severe than sulfur.
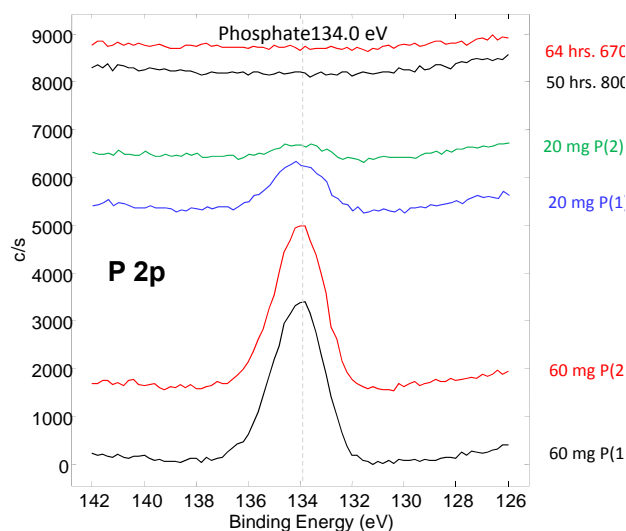
Figure 12: XPS spectra in the P(2P) region of a state-of-the-art Cu/zeolite after laboratory aging with various levels (0-60 mg) of P in the feed. Data was taken at 2 locations ("1" and "2") for the P-aged samples.
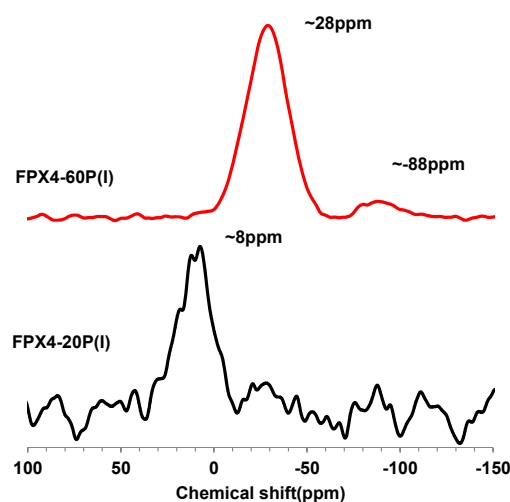
Figure 13: ^{31}P solid state NMR spectra of a state-of-the-art Cu/zeolite after laboratory aging with various levels of P in the feed: low (black curve) and high (red curve) P loading.

## *Physicochemical investigations of HC absorber materials*

For the last two years of this CRADA, HC adsorbers were investigated with a focus on understanding the effects of various physicochemical properties of zeolite materials [9]. In particular, three model zeolite materials were obtained to probe the effects of different pore size and connectivity: beta (large pore, 3-D pore connectivity); ZSM-5 (medium pore, 3-D pore connectivity); and ZSM-12 (large pore, 1-D pore structure). The effects of hydrothermal aging on their physicochemical properties were then examined using various analytical techniques, including XRD and NH_3-TPD. Studies of performance as a function of laboratory aging conditions were carried out at Ford using complex, realistic mixtures of hydrocarbons of various types [10]. For example, Figure 14 shows an example of experiments carried out at Ford that utilize complex hydrocarbon mixtures and a variety of zeolite materials to determine optimized hydrocarbon trap materials for specific applications [9]. In particular, the results shown here were obtained with a hydrocarbon mixture that also contained high concentrations of ethanol and acetaldehyde as expected in the exhausts of E85 fueled vehicles.

At PNNL, detailed catalyst characterization was performed in addition to model studies of performance with gas mixtures containing a single hydrocarbon type. Considering the challenges associated with renewable fuels (e.g., E85), the adsorption and desorption of ethanol was examined in detail. As an example of the mechanistic studies performed, Figure 15 shows temperature-programmed desorption data obtained after exposure of a beta zeolite material to

ethanol. Both unreacted ethanol (EtOH) and a reaction product, ethylene (C_2H_4), were observed in the TPD data. Weakly adsorbed ethanol was found to desorb at <200°C, whereas chemisorbed ethanol was dehydrated to ethylene which desorbed at higher temperatures (i.e., >200°C). Interestingly, the presence of water was found to primarily affect the weakly adsorbed ethanol. As also shown in Figure 15, the amount of desorbed ethanol and ethylene from the zeolite depends on the order of water and ethanol exposure, with a post-dose of water leading to the removal of a significant fraction of the adsorbed hydrocarbon species (EtOH and C_2H_4) [9].
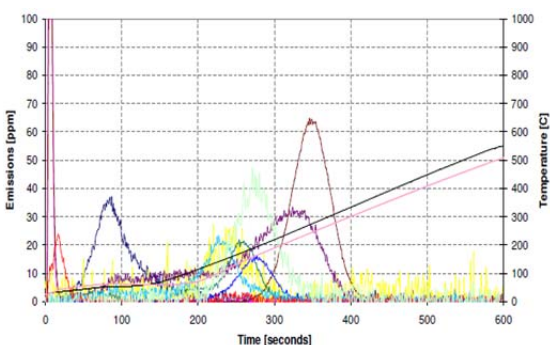
Figure 14: Adsorption/desorption experiment carried out at Ford aimed at determining an optimum zeolite for exhausts of E85 fueled vehicles. A complex hydrocarbon mixture [10], that also included ethanol and acetaldehyde, was used as a realistic model of hydrocarbon exhaust emissions from these vehicles. Among the various desorbing species, ethanol (purple curve) and ethylene (brown curve with peak near 350 seconds) are useful for comparing with model studies.
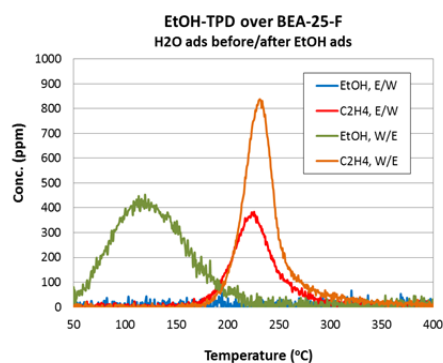
Figure 15: Temperature-programmed desorption (TPD) data obtained after exposure of a beta-zeolite material to ethanol at room temperature. Ethanol exposures were performed before (E/W) and after (W/E) a separate water exposure to probe the relative stability of these two species.

Following the hydrothermal treatment at 800°C for 60 hours, it was found that the surface area, number of acid sites and acidic strength were all reduced significantly, although the zeolite frameworks were found to remain largely intact. Interestingly, the loss of acid sites was more pronounced among samples of high Si/Al ratios. Following this hydrothermal treatment, significant loss of ethanol adsorption was observed because of the reduced surface area and acidity.

Conclusions:

PNNL and its CRADA partners from Ford carried out a program to study the properties and mechanisms of deactivation of SCR and HC-absorber materials arising from thermal aging. Because the catalytically active sites certainly include isolated and very small (even mono-atomic) ion-exchanged metals in the zeolite cages, we pursued a molecular-level understanding of the deactivation mechanisms related to the activity degradation by using a number of state-of-the-art catalyst characterization techniques. This understanding led to improved aging protocols for SCR catalysts and new SCR catalyst system designs. The effects of hydrothermal aging on physicochemical properties of model zeolite hydrocarbon trap materials were also examined. In

particular, the adsorption and desorption of ethanol on model zeolite materials were investigated with respect to physicochemical properties.

References:

1. S. Brandenberger, O. Krocher, A. Tissler, R. Althoff, Catal. Rev.-Sci. Eng. **50** (2008) 492-531.

2. Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, C.H.F. Peden, *Catalysis Today* **136** (2008) 34-39.

3. Y. Cheng, C.K. Lambert, D.H. Kim, J.H. Kwak, S.J. Cho, C.H.F. Peden, *Catalysis Today* **151** (2010) 266-270.

4. Y. Cheng, H. Jen, M. Jagner, C.K. Lambert, J.H. Kwak, D.H. Kim, C.H.F. Peden, Oral presentation made by Yisun Cheng at the *2010 DEER Conference* (September, 2010).

5. Y. Cheng, M. Jagner, H. Jen, C.K. Lambert, J.H. Kwak, D.H. Kim, C.H.F. Peden, Oral presentation made by Yisun Cheng at the *22nd Meeting of the North American Catalysis Society* (June, 2011).

6. C.H.F. Peden, J.H. Kwak, S.D. Burton, R.G. Tonkyn, D.H. Kim, J.H. Lee, H.W. Jen, G. Cavataio, Y. Cheng, C.K. Lambert, *Catalysis Today* **184** (2012) 245-251.

7. G. Cavataio, H.W. Jen, J.R. Warner, J.W. Girard, J.Y. Kim, C.K. Lambert, SAE 2008-01-1025.

8. Y. Cheng, D. Dobson, C.K. Lambert, J.H. Kwak, C.H.F. Peden, unpublished results.

9. J.H. Kwak, J.H. Lee, C.H.F. Peden, D.N. Tran, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, presentation made by Chuck Peden at the *DOE Combustion and Emission Control Review* (May, 2012).

10. J.A. Lupescu, T.B. Chanko, J.F. Richert, A.A. Mauti, SAE 2009-01-1068.

Publications (6 total):

1. F. Gao, J.H. Kwak, J.H. Lee, D.N. Tran, C.H.F. Peden, K. Howden, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials", in *Advanced Combustion Engine Research and Development: FY2012 Annual Progress Report*, in press.

2. C.H.F. Peden, J.H. Kwak, S.D. Burton, R.G. Tonkyn, D.H. Kim, J.H. Lee, H.W. Jen, G. Cavataio, Y. Cheng, and C.K. Lambert, "Possible Origin of Improved High Temperature Performance of Hydrothermally-Aged Cu/Beta Zeolite Catalysts", *Catalysis Today* **184** (2012) 245-251.

3. J.H. Kwak, J.H. Lee, D.H. Kim, S. Li, D.N. Tran, C.H.F. Peden, K. Howden, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials", in *Advanced Combustion Engine Research and Development: FY2011 Annual Progress Report*, 231-237.

4. Y. Cheng, C.K. Lambert, D.H. Kim, J.H. Kwak, S.J. Cho, C.H.F. Peden, "The Different Impacts of SO_2 and SO_3 on Cu/Zeolite SCR Catalysts." *Catalysis Today* **151** (2010) 266-270.
5. Y. Cheng, C. Montreuil, G. Cavataio, and C. Lambert, "The Effects of SO_2 and SO_3 Poisoning on Cu/Zeolite SCR Catalysts", SAE 2009-01-0898.
6. Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, and C.H.F. Peden, "NMR Studies of Cu/zeolite SCR Catalysts Hydrothermally Aged with Urea." *Catalysis Today* **136** (2008) 34-39.

Presentations (13 total):

1. F. Gao, J.H. Kwak, J.H. Lee, C.H.F. Peden, D.N. Tran, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Washington DC, May, 2013.
2. J.H. Kwak, J.H. Lee, C.H.F. Peden, D.N. Tran, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Washington DC, May, 2012.
3. Y. Cheng, M. Jagner, H.W. Jen, C.K. Lambert, J.H. Kwak, D.H. Kim, and C.H.F. Peden, "Characterizations of Engine Aged Cu/CHA Urea SCR Catalysts", presentation at the 22nd National Meeting of the North American Catalysis Society, Detroit, MI, June 2011.
4. C.H.F. Peden, J.H. Kwak, R.G. Tonkyn, D.H. Kim, J. Szanyi, D.N. Tran, J.H. Lee, "Excellent Activity and Selectivity of Cu-SSZ-13 in the Selective Catalytic Reduction of NOx with NH_3," presentation at the 22nd North American Catalysis Society Meeting, Detroit, MI, June 2011.
5. J.H. Kwak, D.H. Kim, J.H. Lee, C.H.F. Peden, D.N. Tran, Y. Cheng, J. Lupescu, G. Cavataio, C. Lambert, R. McCabe, "Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Washington DC, May, 2011.
6. Y. Cheng, H.W. Jen, M. Jagner, C.K. Lambert, J.H. Kwak, D.H. Kim and C.H.F. Peden, "Non-uniform Aging on Super Duty Diesel Truck Aged Urea Cu/Zeolite SCR Catalysts", presentation at the 2010 DEER Conference, Detroit, MI, September 2010.
7. Y. Cheng, C. Lambert, J.H. Kwak, D.H. Kim, and C.H.F. Peden, "Investigation of Sulfur Deactivation on Cu/Zeolite SCR Catalysts in Diesel Application", presented at the 2009 Diesel Engine Efficiency and Emissions Reduction (DEER) Conference, Dearborn, MI, August 2009.
8. Y. Cheng, C. Lambert, D.H. Kim, J.H. Kwak, and C.H.F. Peden, "The Different Impacts of SO_2 and SO_3 on Cu/Zeolite SCR Catalysts", presentation at the 21st North American Catalysis Society Meeting, San Francisco, CA. June, 2009.
9. J.H. Kwak, C.H.F. Peden, Y. Cheng, and C. Lambert, "Deactivation Mechanisms of Base Metal/ZeoliteUrea Selective Catalytic Reduction Materials", presentation at the DOE Combustion and Emission Control Review, Washington, DC, May 2009.

10. Y. Cheng, C. Montreuil, G. Cavataio, C. Lambert, and D. Dobson, "Investigation of the Sensitivity of Base Metal/Zeolite SCR to SO_3 Deactivation", presentation at the SAE Light-Duty Diesel Emission Control Symposium, Ypsilanti, MI, November, 2008.
11. Y. Cheng, C. Lambert, J.H. Kwak, and C.H.F. Peden, "Understanding the Deactivation Mechanisms of Cu/Zeolite SCR Catalysts in Diesel Applications", presented at the 2008 Diesel Engine Efficiency and Emissions Reduction (DEER) Conference, Dearborn, MI, August 2008.
12. J.H. Kwak, C.H.F. Peden, Y. Cheng, H. Hoard, and C. Lambert, "Deactivation Mechanisms of Base Metal/ZeoliteUrea Selective Catalytic Reduction Materials", presentation at the DOE Combustion and Emission Control Review, Washington, DC, February 2008.
13. Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, and C.H.F. Peden. 2007, "The Impact of Urea on Hydrothermally Aged Cu/Zeolite SCR Catalysts, "presented at the 20th North American Meeting of the Catalysis Society, Houston, TX, June 2007.

Acronyms:

ACS: American Chemical Society
BET: Branauer-Emmet-Teller particle surface area and pore-size measurement method
CARB: California Air Resources Board
CDPF: catalyzed diesel particulate filter
CRADA: cooperative research and development agreement
DOC: diesel oxidation catalyst
DPF: diesel particulate filter
E85: gasoline fuel blend containing 85% ethanol
EDX: energy dispersive x-ray spectroscopy
EPA: Environmental Protection Agency
HC: hydrocarbons
HCCI: homogeneous charge compression ignition
LEV: low emission vehicle
NMR: nuclear magnetic resonance
NOx: nitrogen oxides (NO and NO_2)
ORNL: Oak Ridge National Laboratory
PCCI: premixed charge compression ignition
PGM: platinum group metal
PNNL: Pacific Northwest National Laboratory
SAE: Society of Automotive Engineers
SCR: selective catalytic reduction
SEM: scanning electron microscopy
STEM: scanning transmission electron microscopy
SULEV: super ultralow emission vehicle
TEM: transmission electron microscopy
TPD/TPRX: temperature programmed desorption/temperature programmed reaction
TWC: three-way catalyst
XPS: x-ray photoelectron spectroscopy
XRD: x-ray diffraction