Final Report of a CRADA Between Pacific Northwest National Laboratory and the General Motors Company (CRADA No. PNNL/271): "Degradation Mechanisms of Urea Selective Catalytic Reduction Technology"

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December 2011

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under Contract DE-AC05-76RL01830

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Final Report of a CRADA Between Pacific Northwest National Laboratory and the General Motors Company (*CRADA No. PNNL/271*): "Degradation Mechanisms of Urea Selective Catalytic Reduction Technology"

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Abstract

Diesel engines can offer substantially higher fuel efficiency, good driving performance characteristics, and reduced carbon dioxide (CO_2) emission compared to stoichiometric gasoline engines. Despite the increasing public demand for higher fuel economy and reduced dependency on imported oil, however, meeting the stringent emission standards with affordable methods has been a major challenge for the wide application of these fuel-efficient engines in the US market. The selective catalytic reduction of NOx by urea (urea-SCR) is one of the most promising technologies for NOx emission control for diesel engine exhausts. To ensure successful NOx emission control in the urea-SCR technology, both a diesel oxidation catalyst (DOC) and a urea-SCR catalyst with high activity and durability are critical for the emission control system. Because the use of this technology for light-duty diesel vehicle applications is new, the relative lack of experience makes it especially challenging to satisfy the durability requirements. Of particular concern is being able to realistically simulate actual field aging of the catalyst systems under laboratory conditions, which is necessary both as a rapid assessment tool for verifying improved performance and certifiability of new catalyst formulations. In addition, it is imperative to develop a good understanding of deactivation mechanisms to help develop improved catalyst materials. In this CRADA program, General Motors Company and PNNL have investigated fresh, laboratory- and vehicle-aged DOC and SCR catalysts. The studies have led to a better understanding of various aging factors that impact the long-term performance of catalysts used in the urea-SCR technology, and have improved the correlation between

laboratory and vehicle aging for reduced development time and cost. This Final Report briefly highlights many of the technical accomplishments and documents the productivity of the program in terms of peer-reviewed scientific publications (2 total), reports (3 total including this Final Report), and presentations (5 total).

Objectives

- Develop an understanding of the deactivation mechanisms of and interactions between the diesel oxidation catalyst (DOC) and the urea selective catalytic reduction (urea-SCR) catalyst used in diesel aftertreatment systems.

- Develop correlations relating the degree of performance deterioration to the catalyst aging parameters. Use this information to determine the role of the various aging factors impacting long-term performance of these catalyst systems, in order to provide information about what operating conditions should be avoided to minimize catalyst deactivation.

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

Accomplishments

- **This program included two major thrusts:**
  1. Physicochemical investigations of the degradation mechanisms for DOC catalysts.
  2. Physicochemical investigations of the degradation mechanisms for SCR catalysts.

- Specific accomplishments of the program have included:
  - Several state-of-the-art characterization tools were found to be useful for investigating degradation mechanisms of 'development' DOC and SCR catalysts. In particular, we have used:
    - TEM/XRD: to obtain structural and catalytic phase/morphology information.
    - XPS: to investigate chemical state of active catalytic phases.
  - Based on a correlation of performance measurements (GM) and characterization results (PNNL) obtained, the following are indicated as the primary reasons for deactivation:
  - DOC catalyst: sintering of active alloy metal (Pt/Pd) particles and corresponding loss in the number of active sites.
  - SCR catalyst: structure destruction of the zeolite-based catalysts and agglomeration of ion-exchanged metal species.

- The output of this program has included five public presentations and five publications (including this final report).

Introduction

Diesel engines can offer substantially higher fuel efficiency, good driving performance characteristics, and reduced carbon dioxide (CO_2) emissions compared to stoichiometric gasoline engines. For these reasons along with favorable taxation policies, diesel-powered passenger vehicles have been gaining popularity in Europe in recent years. Despite the increasing public demand for higher fuel economy and reduced dependency on imported oil, however, meeting the stringent emission standards with affordable methods has been a major challenge for the wide application of these fuel-efficient engines in the U.S. light-duty vehicle market. The selective catalytic reduction of NOx by urea (urea-SCR) is one of the most promising technologies for NOx emission control for diesel engine exhausts [1]. Compared to the competing lean NOx reduction technologies such as the NOx adsorber technology (aka lean NOx trap, LNT, and NOx storage/reduction, NSR), urea-SCR offers a number of advantages, including excellent low-temperature NOx reduction efficiency, a wide temperature window of operation, and no PGM requirement, etc. Therefore, the urea-SCR technology is being implemented by many automotive manufacturers as a primary path to meeting the emission standards for 2010 and beyond diesel vehicles. To ensure successful NOx emission control, both a diesel oxidation catalyst (DOC) and a urea-SCR catalyst with high activity and durability are critical for the emission control system. An example diesel emission control system is shown in Figure 1. Because the use of this technology for mobile applications is new, the lack of experience makes it especially challenging to satisfy the durability requirements. Of particular concern is being able to realistically simulate the actual field aging of diesel aftertreatment catalysts under laboratory conditions, which is necessary as a rapid assessment tool for verifying improved performance and certifiability of new promising catalyst formulations. In addition, it is imperative to understand deactivation mechanisms to develop improved catalyst materials.
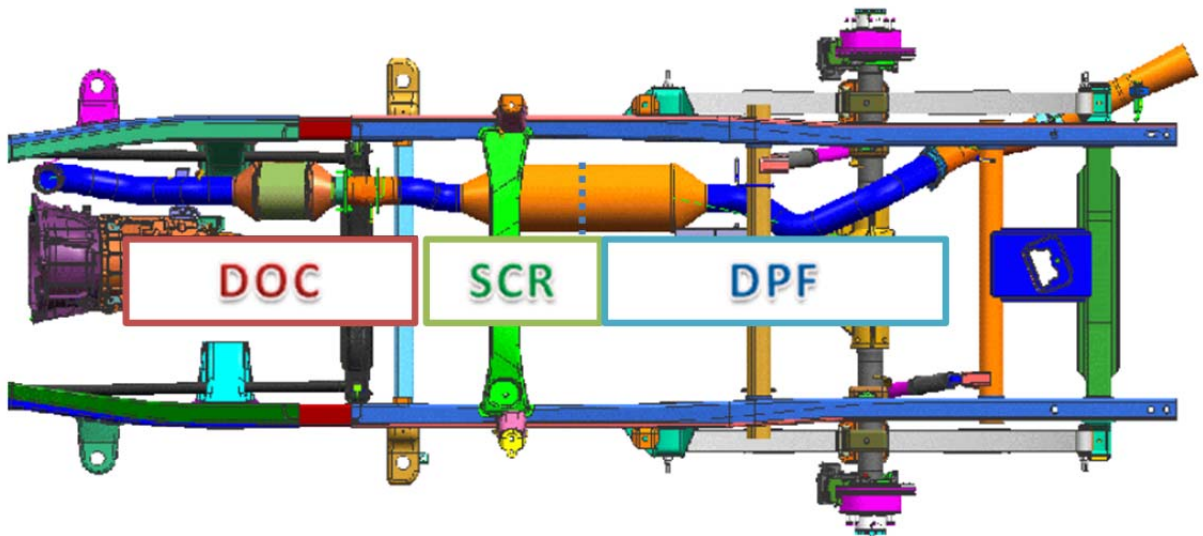

Figure 1. Components of a diesel exhaust emission control system, identifying locations of major catalyst components as well as a variety of sensors used in these systems.

In this CRADA program that began in January, 2009, General Motors Company and PNNL have investigated fresh, laboratory- and vehicle-aged DOC and SCR catalysts. These studies were intended to obtain a better understanding of various aging factors that impact the long-term performance of catalysts used in the urea-SCR technology, and to develop/improve the correlation between laboratory and vehicle aging in order to reduce emission control system development time and cost. Investigations of DOC catalysts have included hydrocarbon and NO oxidation, and of SCR catalysts for low temperature NOx conversion activity, ammonia storage and slip at low temperatures and ammonia oxidation at high temperatures. A timeline for the entire program is shown in Figure 2.
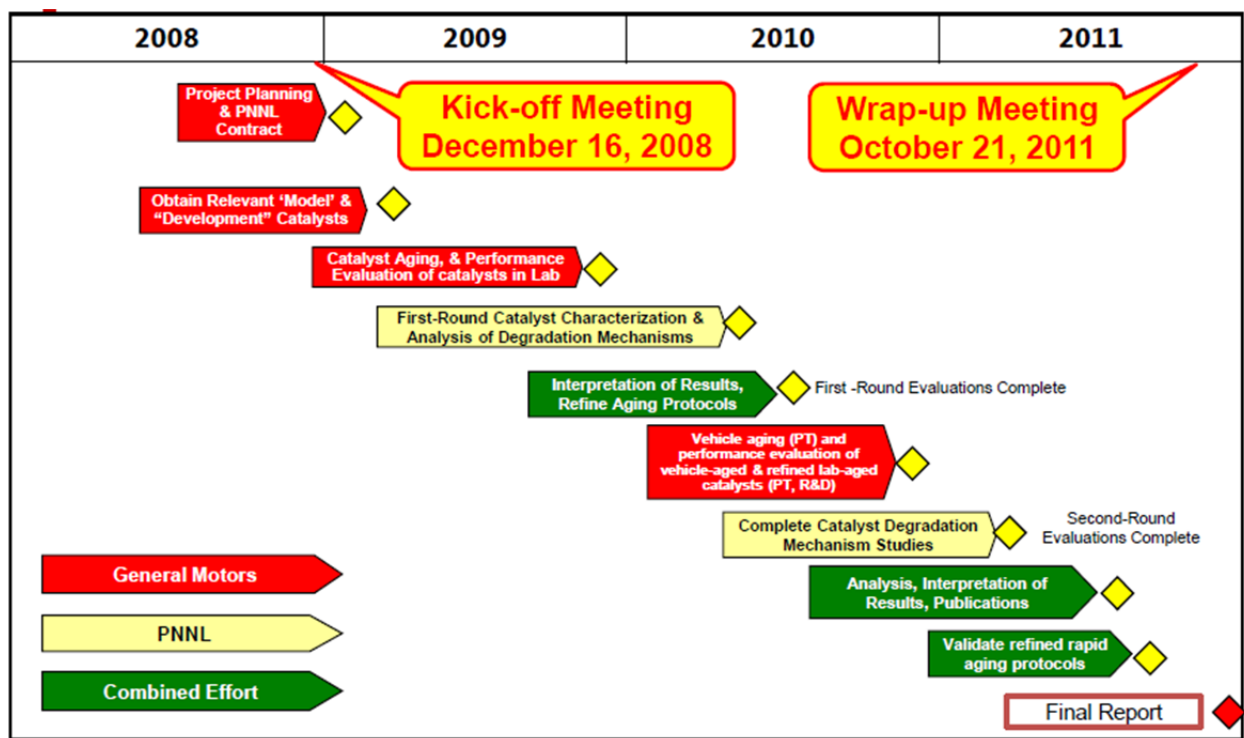

Figure 2. Timeline for this CRADA program between GM and PNNL, highlighting distribution of tasks, project milestones and meetings.

Approach

This project has focused on the characterization of catalyst materials used in the urea-SCR technology 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 has been on establishing the relevance of rapid laboratory catalyst aging protocols with the specific aging phenomena observed in realistic engine operating conditions. This information has aided in the optimal integration of GM's diesel aftertreatment systems. More importantly, the information has also aided in understanding how catalyst degradation occurs in the field, and suggested ways to improve the durability of catalyst materials.

GM's primary task has been to develop catalyst aging protocols capable of mimicking vehicle aging. Specifically, GM has provided both fresh, laboratory- and vehicle-aged catalyst materials used in the DOC and urea-SCR technology and made experimental measurements of changes in the catalytic performance of these materials before and after the aging. GM has also correlated the catalyst characterization results obtained at PNNL (as described in the next paragraph) with the GM-obtained emissions performance data.

PNNL's role has been to identify major catalyst deactivation modes and to elucidate performance degradation mechanisms. For this, PNNL has utilized state-of-the-art analytical techniques to investigate the surface and bulk properties of the GM-provided catalysts as well as the changes in these properties induced by the aging process. In particular, catalyst characterization techniques such as x-ray diffraction (XRD), transmission electron microscopy (TEM) / energy dispersive X-ray (EDX) spectroscopy, BET/pore size distribution, and ^{27}Al solid state NMR have been utilized to probe the changes in physicochemical properties of DOC and SCR catalyst samples under deactivating conditions; *e.g.*, hydrothermal aging at various temperatures.

Additional experimental details can be found in our two recent publications [2,3].

By developing a good understanding of performance degradation mechanisms during the catalyst aging, PNNL and GM have provided a framework for developing robust DOC and urea-SCR catalyst systems, and a better definition of the optimal operational window for current materials.

Results

Physicochemical investigations of the degradation mechanisms for DOC catalysts

Currently precious metal-based diesel oxidation catalysts (DOC) containing platinum (Pt) and palladium (Pd) are most commonly used for the oxidation of hydrocarbons and NO in diesel exhaust. In this program, we have investigated mechanisms of DOC deactivation due to actual vehicle operation by correlating its catalytic activity measurements with a variety of characterization techniques including x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS). The vehicle-aged catalyst was obtained from a General Motors 2010 Silverado pick-up truck with a Duramax 6.6 L light-duty diesel engine. The vehicle had accumulated approximately 135,000 miles via the General Motors Standard Road Cycle and was equipped with a complete exhaust emissions aftertreatment system that included a DOC (49 g/ft^3 PGM at the mass ratio of 7:1 Pt-Pd on 400 cpsi cordierite) followed by the urea-SCR catalysts (two separate bricks) and a diesel particulate filter (DPF). For these experiments, an additional brick of the DOC was obtained from BASF Corporation. Multiple core samples were taken from the untreated brick and were hydrothermally aged in a laboratory oven at various temperatures and for various lengths of time in flowing air that contained 10% H_2O. The performance of the vehicle-aged sample was compared to the laboratory hydrothermally-aged samples. In addition, materials characterization of several model catalyst samples with varying Pt/Pd ratios was performed, in part, to understand the sensitivity of deactivation to this Pt/Pd ratio observed in prior GM studies [4]. Besides the hydrothermal sintering of the Pt-Pd precious metal, the deterioration of hydrocarbon and NO oxidation performance of the vehicle-aged sample were also caused by surface poisoning. The role of these various aging factors in determining long-term performance in mobile applications was determined.

The NO and C_3H_6 oxidation activity of a variety of laboratory hydrothermally-aged samples are shown in Figure 3. It is clear that both the aging temperature and time strongly influence the performance of the DOC catalyst, although the NO oxidation activity appears to be more significantly impacted by the hydrothermal aging. Since Pt has been reported to be exclusively active for NO oxidation [5,6] while both Pt and Pd are active for hydrocarbon oxidation [7], this result suggests that the deactivation of Pt particles may be more sensitive to the aging temperature.

In order to establish the relationship of the rapid laboratory catalyst aging protocols to the specific deactivation phenomena observed after extended exposure to realistic engine operating conditions, Figure 3 also plots the NO and C_3H_6 oxidation activity (solid black line) of a core sample from the vehicle-aged part extracted from the middle of the full size brick. The activity of this sample is much closer to that of the sample aged at 700°C for 24 hours, especially for hydrocarbon oxidation. Note, however, that the oxidation activity of the vehicle-aged DOC varied along its axis from inlet to outlet (data not shown here [2]). In particular, the inlet sample appeared to have been most severely deactivated, with a HC light-off temperature nearly 10°C higher and much lower NO oxidation performance than for samples from the rest of the DOC. These observations suggest that the front portion of DOC is most susceptible to deactivation, and that the real-world vehicle operation may also yield deactivation that follows a different mechanism. Carbon soot, sulfur, and P-, Ca- and Zn-contaminants from engine oil were all found to accumulate on the front section of the vehicle-aged sample. Of these, the soot was certainly responsible for at least some of the deactivation of this inlet section. Indeed, removal of the soot by oxidation restored the NO oxidation activity of the inlet section sample to be even greater than a similarly treated sample from the end section [2].
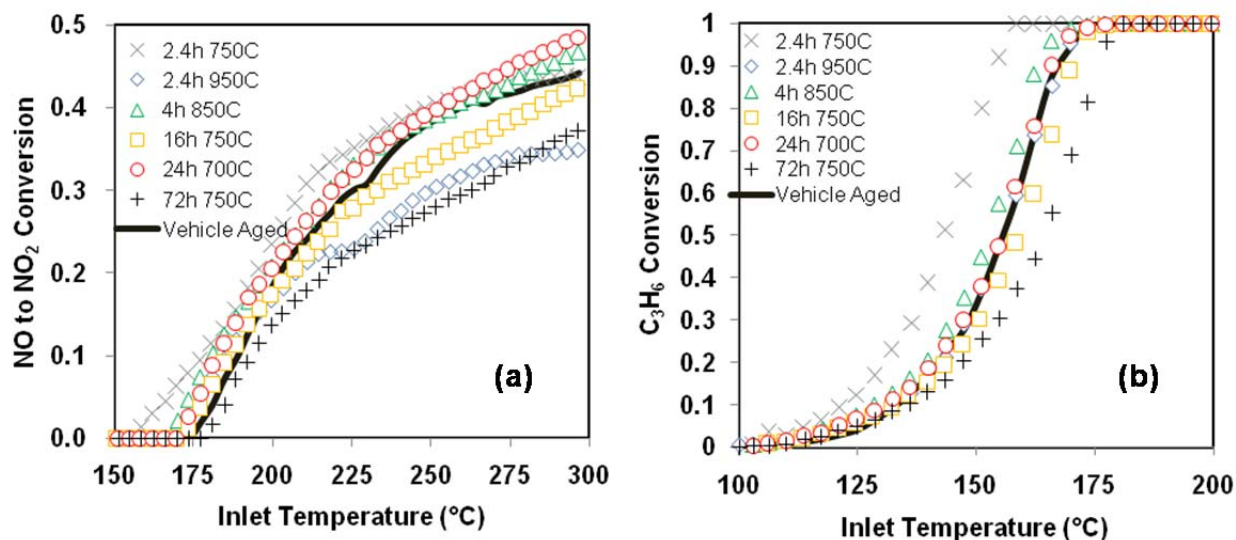

Figure 3. Conversion as a function of temperature for: (a) NO oxidation; and (b) C_3H_6 oxidation over samples that were laboratory aged for 2.4 hours at 750 °C (×), 2.4 hours at 950 °C (◇), 4 hours at 850 °C (Δ), 16 hours at 750 °C (□), 24 hours at 700 °C (○), 72 hours at 750 °C (+), and vehicle aged (—). All activity measurements were made at GHSV of 30,000 h^{-1} in a gas mixture that contained 200 ppm of NO, 1050 ppm of C_3H_6, and 8% of O_2 in a balance of N_2.

The behavior just described can be understood to result from a greater degree of precious metal sintering towards the rear of the monolith catalyst which, in turn, is due to the fact that the DOC is also used to generate exotherms (by post-injecting and converting raw diesel fuel) used to combust accumulated soot on the downstream DPF (see Figure 1). To demonstrate the change in precious metal sintering as a function of position in the monolith catalyst, Figure 4 shows the x-ray diffraction (XRD) patterns obtained from the vehicle aged part, with samples C1 thru C6 representing samples obtained from the inlet to outlet sections of the monolith, respectively. The XRD fine scan of the Pt region in Figure 4 indicates the formation of Pt-Pd crystallites. The crystallite size, obtained from the Sherrer equation, was found to grow significantly from the inlet toward the outlet (from 11 to 42 nm) as a result of PGM sintering. These changes in particle size were also evident in TEM micrographs obtained from several of these samples [2].
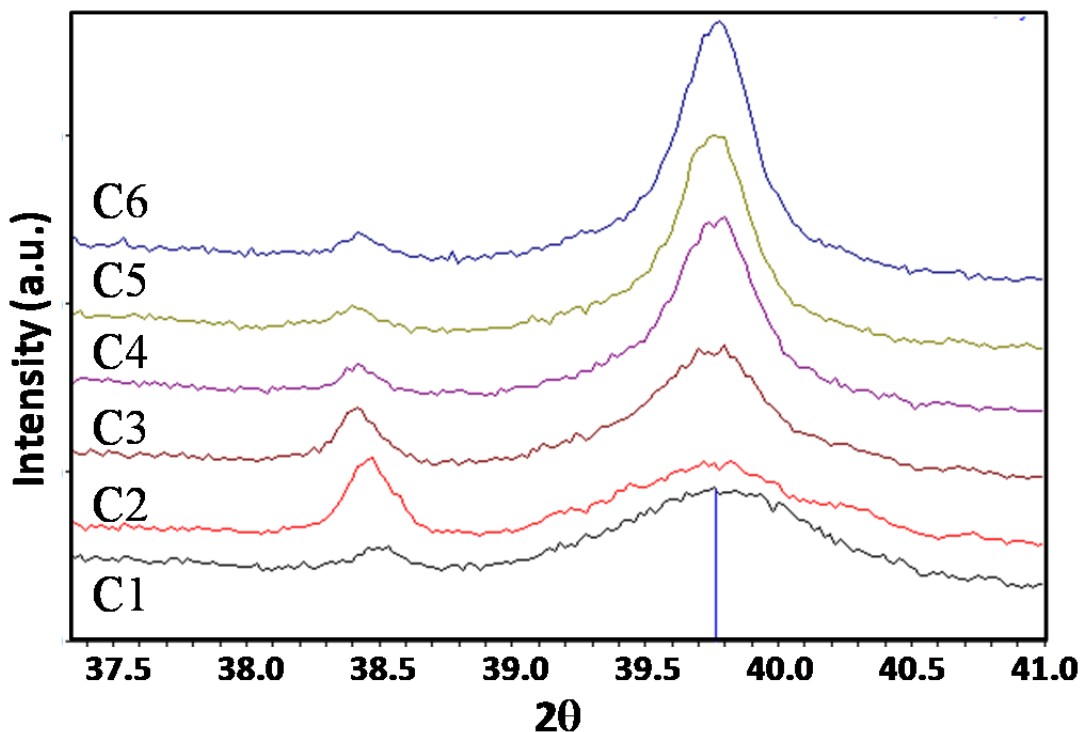

Figure 4. X-ray diffraction patterns for monolith core samples extracted from the 135,000 mile vehicle-aged DOC catalyst brick. These samples are labeled C1 to C6, representing cores obtained from the inlet to the outlet section of the monolith brick, respectively.

GM has previously reported on the sensitivity of DOC aging to the Pt/Pd ratio. Figure 5 [4] plots the C_3H_6 oxidation light-off temperature as a function of this ratio, where both degreened (at 750°C for 2.4 hours) and laboratory aged (at 750°C for 72 hours) catalysts are compared. Several things are of note in this figure. First, while Pd is a relatively poor C_3H_6 oxidation catalyst as evidenced by its high light-off temperature of ~230°C, adding Pd to Pt lowers the light-off temperature of the pure Pt DOC. Of equal significance is the fact that Pd addition enhances the stability of the Pt DOC to hydrothermal aging. This can be seen by the small increases in light-off temperature with aging for the mixed Pt-Pd catalysts relative to the Pt-alone DOC. In this collaborative CRADA project, we estimated the surface compositions of degreened and aged bimetallic Pt-Pd catalysts with XPS as shown in Figure 6. For the

degreened catalyst (Figure 6a), the XPS data show the expected drop in Pt and growth in Pd surface concentrations with increasing Pd content (Pt/Pd molar ratios falling from 10 to 2). However, the results shown in Figure 6b indicate that hydrothermal aging of these catalysts results in a surface enrichment in the Pd content for all three Pt/Pd ratios studied.
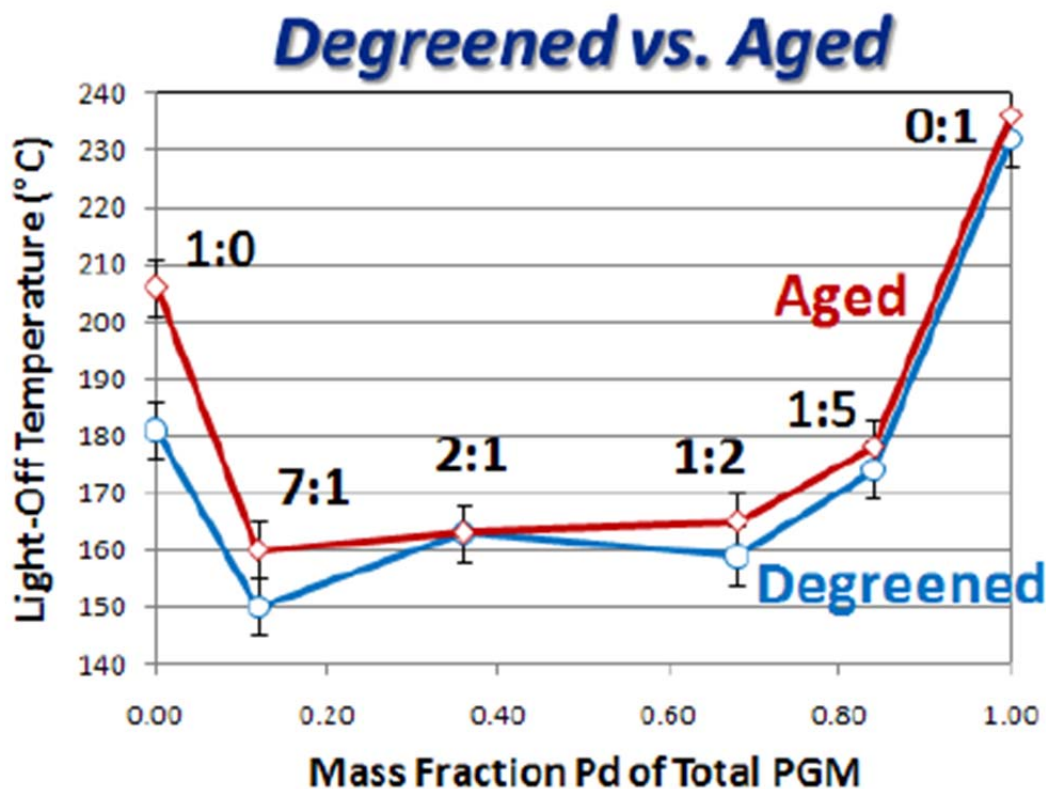

Figure 5. C_3H_6 oxidation light-off temperatures for degreened (2.4 hours at 750 °C, blue curve) and hydrothermally aged (72 hours at 750 °C, red curve) Pt-Pd DOC catalysts as a function of the mass fraction of Pd [4].

The enhanced stability with Pd addition to a Pt DOC was also observed in comparing this same set of catalysts for NO oxidation activity. However, because Pd is not very active for NO oxidation, overall activity was reduced with Pd addition. Still, these results suggest that the overall performance of the DOC for its multiple functions can be tuned by optimally adjusting the Pt/Pd ratio. Additional investigations using more analytical techniques will be needed to understand the relationship between the Pt/Pd ratio and sintering/deactivation behavior, results that will potentially provide strategies to utilize PGM amounts in effective ways.

Physicochemical investigations of the degradation mechanisms for SCR catalysts

Multiple catalytic functions (NOx conversion, NO and NH_3 oxidation, NH_3 storage) of a commercial Cu-zeolite urea-SCR catalyst were assessed in a laboratory fixed-bed flow reactor system after differing degrees of hydrothermal aging [3]. Catalysts were characterized by using XRD, ^{27}Al solid state NMR spectroscopy, and TEM/EDX spectroscopy to develop an understanding of the degradation mechanisms during catalyst aging. Correlation of these reactivity and characterization data has allowed us to obtain the universal curve to predict the

degree of catalyst performance deterioration as a function of time at each aging temperature. Selected laboratory aging conditions compare well with the 135,000 mile vehicle-aged catalyst for both performance and characterization criteria. The zeolite-based urea-SCR catalyst for this study was supplied by BASF Corporation. The catalyst is a Cu exchanged chabazite containing 2.8% copper expressed as copper metal, with a nominal silica to alumina molar ratio of 35:1. The exchanged zeolite was coated on a cordierite ceramic honeycomb monolith substrate, and samples for this study were ~7.6 cm long by ~1.9 cm diameter cores from the monolith. A total of 33 samples, laboratory aged at varying temperatures for varying lengths of time, were used in these studies. A variety of experimental characterization techniques were applied to a significant number of these catalyst samples. Reactivity was measured with a simulated exhaust gas feedstream consisting of 10% O_2, 5% H_2O, 8% CO_2, 200 ppm NOx, and 200 ppm NH_3 in a N_2 background at a GHSV of 30,000 hr^{-1}.
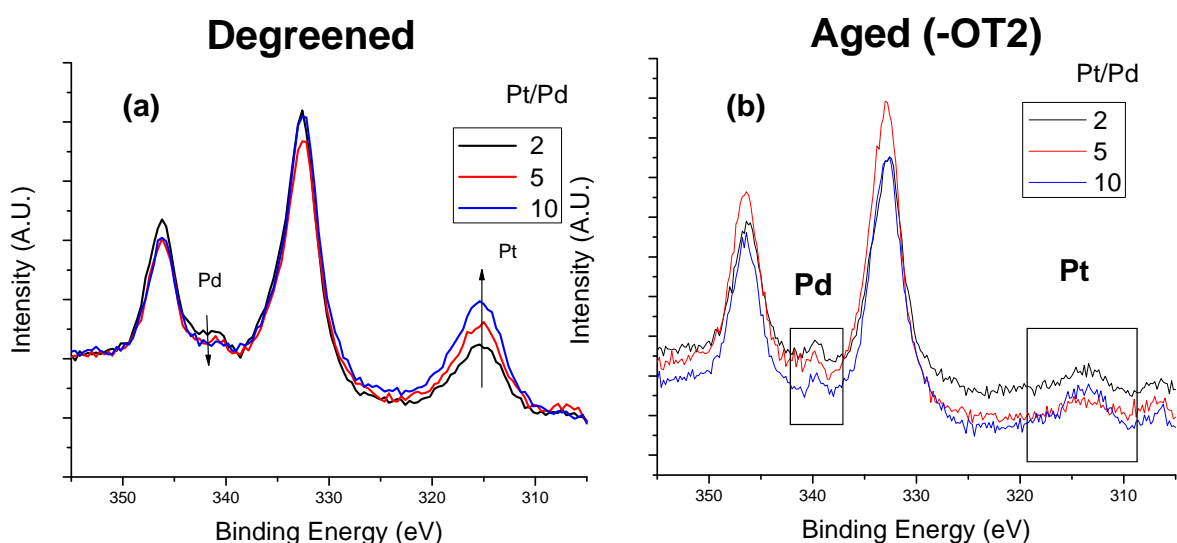

Figure 6. XPS spectra obtained from (a) degreened and (b) hydrothermally aged (24 hours at 700 °C) DOC catalysts with Pt/Pd molar ratios of 2 (black curves), 5 (red curves) and 10 (blue curves).

An example of the SCR performance data obtained in these studies is shown in Figure 7. The results presented here were for the "standard" SCR reaction (where NOx = NO) obtained for the Cu-zeolite catalyst laboratory aged for various lengths of time at 800 °C. The five aging times at 800 °C represent 5 of the 33 samples studied here. Similar data were obtained for the other 28 samples which were aged at different temperatures for varying lengths. Of course, the extent of deactivation observed at other temperatures as a function of time will be quite different than what is shown for the 800 °C samples shown in Figure 7. To make practical use of the entire set of data, we assumed that a maximum NOx conversion efficiency around 70% between 300 – 400°C is necessary to classify an SCR catalyst as "Borderline Failure". Aging conditions that led to samples with greater than 70% NOx conversion were then be considered "No Failure" while those conditions that resulted in less than 70% NOx conversion are be considered "Definite Failure". Figure 8 summarizes the impact of various combinations of aging times and temperatures, plotted based on the NOx conversion measurements for all 33 samples.
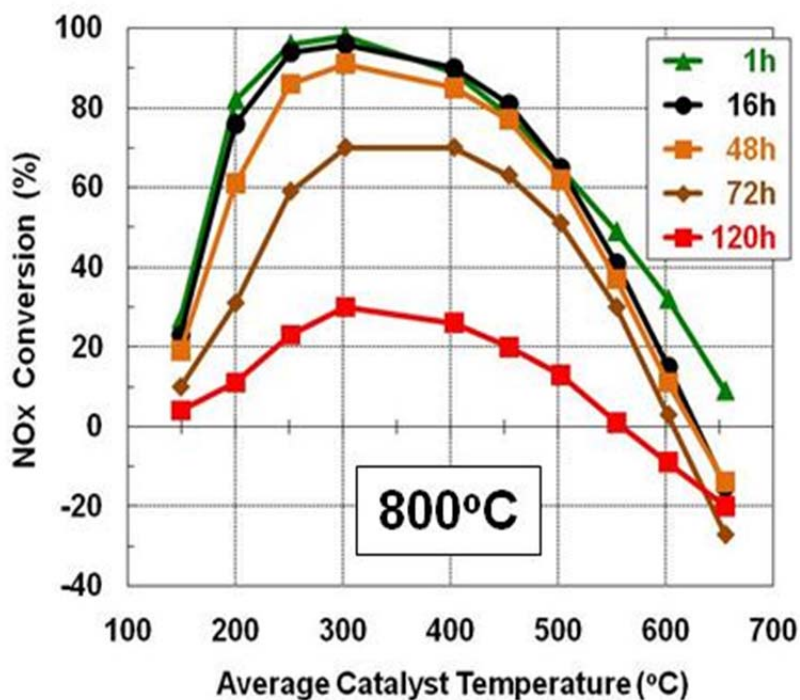
Figure 7. NOₓ conversion results for the "standard" (NOx = NO) SCR reaction. The catalyst samples were hydrothermally aged for various times at 800°C.
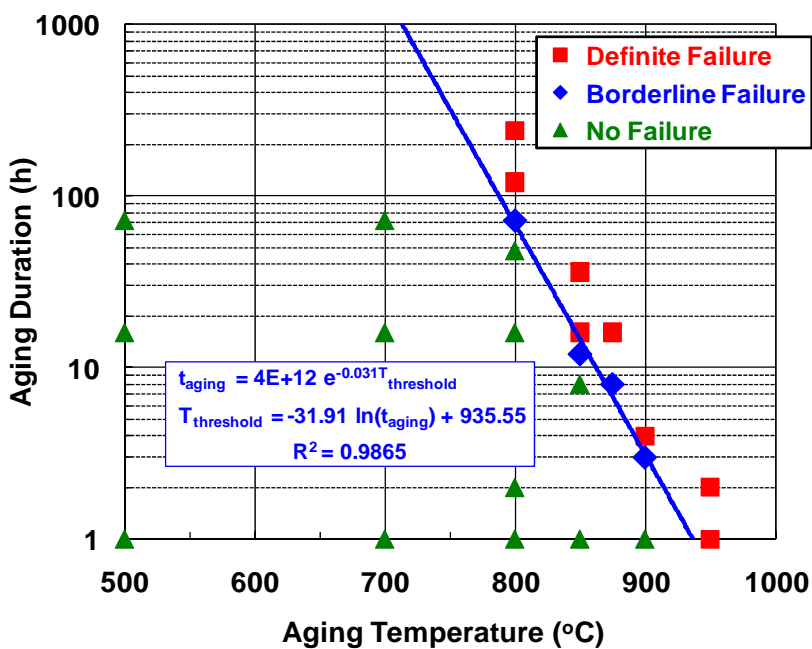

Figure 8. NOx conversion performance of the commercial Cu-zeolite catalyst studied here showing the impact of various combinations of aging time and temperature.

To verify the classifications of failure just described, we next performed characterization of the physicochemical changes of the samples as a function of the thermal aging conditions. For this, we highlight here XRD data for one series of the samples aged at 850°C, which demonstrated particularly drastic changes in activity with aging time (see Figure 8), with the results shown in Figure 9. The chabazite crystalline structure, as distinguished by the many peaks between 10° and 70°, was maintained after aging at 850°C for up to 8 hours. The intensity of the zeolite peaks for the sample aged for 12 hours decreased significantly; however, the zeolite structure is still retained, as revealed by the peak at $2\theta = 21°$, although the intensity is only 10% of the catalyst aged for 8 hours. Hydrothermal treatment of the sample for 16 hours gave rise to the complete collapse of the chabazite zeolite structure, meaning that only amorphous morphology exists in the sample. According to Figure 8, the activity of the sample aged at 850°C for 8 hours is designated as "No Failure", while the ones aged for 12 hours and 16 hours are "Borderline Failure" and "Definite Failure", respectively. In addition to the good correlation between XRD and activity of the samples aged at 850°C, a similar correlation was also obtained for the samples aged at 800°C and 900°C. Furthermore, the XRD results as a function of aging time and temperature were consistent with ^{27}Al solid state NMR spectroscopy and TEM data [3]. Finally for these aged catalysts, we characterized changes in chemical properties relevant for urea SCR, including NO/NH_3 oxidation reactivity and NH_3 storage capacity, by utilizing a four step protocol developed by Yezerets and coworkers at Cummins [8] (results from these studies are not shown here but are described in our recent publication [3]).
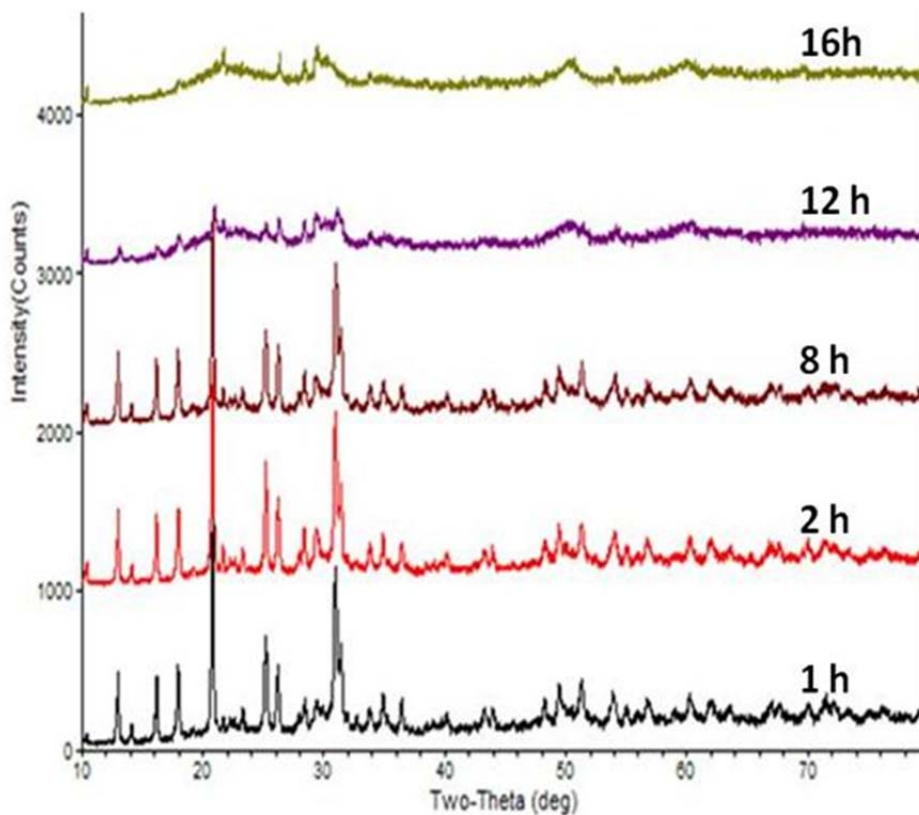

Figure 9. XRD patterns of the Cu-zeolite samples aged at 850°C for various times.

In order to understand the relationship between laboratory and vehicle aging and to establish the relevance of rapid laboratory catalyst aging protocols with the specific aging phenomena observed after extended exposure to realistic engine operating conditions, NOx performance measurements were made on series of cored samples from the vehicle aged catalyst. As shown in Figure 10, the sample that was laboratory aged at 800°C for 16 hours provided an excellent match to the behaviour of the vehicle aged catalyst for NOx conversion performance. Similarly good matches between the vehicle- and 800°C for 16 hours laboratory-aged catalysts were obtained in comparisons of catalyst characterization results, and in measurements of NO oxidation to NO_2, and NH_3 oxidation/NH_3 oxidation to NOx [3]. In this way, the relevance of this particular laboratory aging condition for mimicking vehicle aging was established.
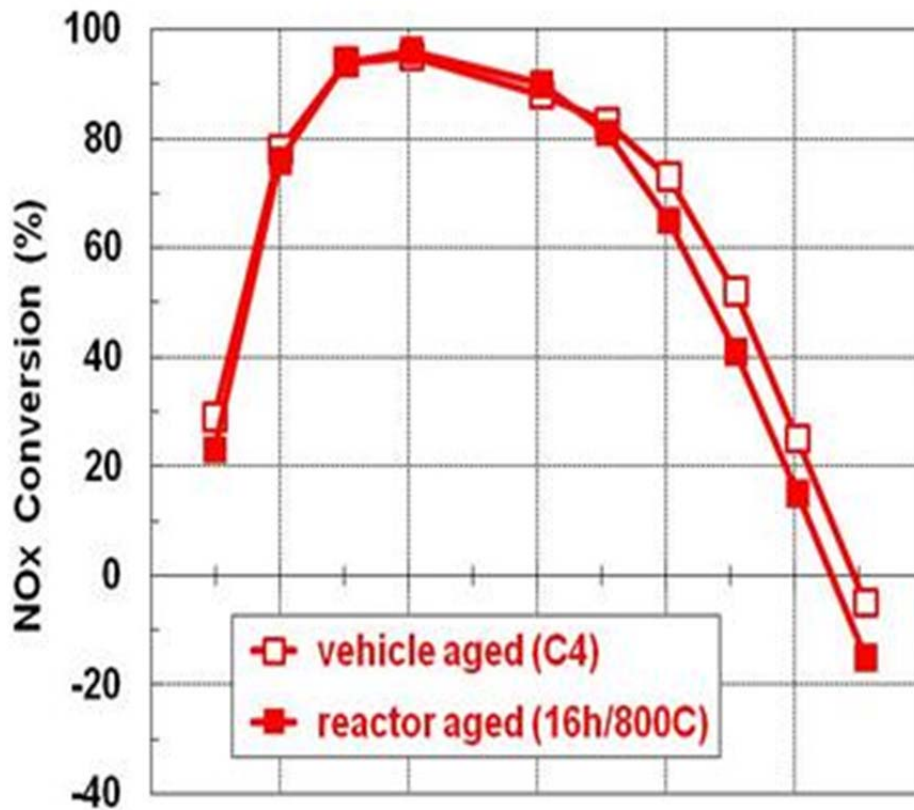

Figure 10. NO_x conversion results over a middle core of the 135,000 mile vehicle aged SCR catalyst and the reactor-aged SCR catalyst (800°C for 16 hours).

Conclusions

PNNL scientists and engineers and their colleagues from PNNL's CRADA partner at the GM Company have carried out a program to study the mechanisms of deactivation of SCR and DOC materials arising from thermal aging. Results demonstrate that the growth and alloying of PGM in the DOC catalyst are the primary materials changes and, thus, likely causes of deactivation in this emissions system component. For the case of the urea SCR catalyst, both the

collapse of the zeolite structure and the growth of particles of the active metal are observed for heavily aged samples which certainly represent important causes of activity loss. Because the SCR catalytically active sites include isolated and very small (even mono-atomic) ion-exchanged metals in the zeolite cages, we have 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.

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1. D.H. Kim, C.H.F. Peden, C.H. Kim, S.J. Schmieg, and S.H. Oh, "Degradation Mechanisms of Urea Selective Catalytic Reduction Technology", presentation at the DOE Combustion and Emission Control Review, Washington DC, May, 2009.
2. D.H. Kim, C.H.F. Peden, K. Howden, S.H. Oh, C.H. Kim, and S.J. Schmieg, "Degradation Mechanisms of Urea Selective Catalytic Reduction Technology", in *Advanced Combustion Engine Research and Development: 2009 Annual Progress Report*, pg 210-214.
3. D.H. Kim, C.H.F. Peden, C.H. Kim, S.J. Schmieg, and S.H. Oh, "Degradation Mechanisms of Urea Selective Catalytic Reduction Technology", presentation at the DOE Combustion and Emission Control Review, Washington DC, June, 2010.
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Acronyms

BET: Branauer-Emmet-Teller particle surface area and pore-size measurement method.
CRADA: cooperative research and development agreement
DOC: diesel oxidation catalyst
DPF: diesel particulate filter
EDX: energy dispersive x-ray spectroscopy
EPA: Environmental Protection Agency
GHSV: gas hourly space velocity
GM: General Motors
NOx: nitrogen oxides (NO and NO_2)
PGM: platinum group metal
PNNL: Pacific Northwest National Laboratory
SEM: scanning electron microscopy
SCR: selective catalytic reduction
TEM: transmission electron microscopy
TPD/TPRX: temperature programmed desorption/temperature programmed reaction
XPS: x-ray photoelectron spectroscopy
XRD: x-ray diffraction