II. ADVANCED COMBUSTION AND EMISSION CONTROL RESEARCH FOR HIGH-EFFICIENCY ENGINES

B. Energy Efficient Emission Controls

II.B.1 Fundamental Studies of NOx Adsorber Materials

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Objectives

- Develop a practically useful fundamental understanding of NOx adsorber technology operation.
- Focus on chemical reaction mechanisms correlated with catalyst material characterization.
- Actively participate in the CLEERS lean-NOx trap (LNT) subgroup. This latter activity now includes an additional 3-way collaboration between Oak Ridge National Laboratory (Stuart Daw and coworkers), Sandia National Laboratories-Livermore (Rich Larson), and PNNL.
- Transfer the developing fundamental understanding to industry via the CLEERS activity as well as periodic technical meetings with industry scientists and engineers.

Approach

- Utilize state-of-the-art catalyst characterization and testing facilities in the Institute for Interfacial Catalysis at PNNL, including:
  - Synchrotron temperature programmed X-ray diffraction (XRD): catalyst structural changes.
  - Transmission electron microscopy (TEM)/ energy dispersive X-ray (EDX) and scanning electron microscope (SEM) microscopies: catalyst morphological changes.
  - X-ray photoelectron spectroscopy: oxidation state and relative surface concentrations.
  - Fourier transform infrared (FTIR) and solid-state nuclear magnetic resonance (NMR) spectroscopies: catalyst reaction mechanisms.
  - Temperature programmed desorption (TPD)/ thermal gravimetric analysis (TGA): surface chemistry.
  - Lab Reactor: performance measurements, kinetics and mechanisms.
- Participate as an active member of the CLEERS subgroup on LNTs.

Accomplishments

- In prior work, the morphology of BaO/Al_2O_3 LNT materials was shown to be remarkably dynamic during NOx storage and reduction. A "monolayer" of $Ba(NO_3)_2$ forms on the alumina surface in addition to large "bulk" $Ba(NO_3)_2$ particles.
- These different morphologies were also found to display dramatically different behavior with respect to NOx removal temperature, formation of a deactivating high-temperature $BaAl_2O_4$ phase, and temperature requirements of desulfation.
- *In this past year, the effects of H_2O and CO_2 on these morphology changes were found to be profound under certain conditions.* While the effect of CO_2 is minimal (but results in $BaCO_3$ formation AFTER $Ba(NO_3)_2$ decomposition!), the presence of H_2O leads to a dramatic loss of the "monolayer" $Ba(NO_3)_2$ phase via formation of even larger particles of the "bulk" phase.
- Using a one-of-a-kind very high field NMR instrument at PNNL, the nucleation sites for Ba on the γ-alumina catalyst support material have been identified (discussed in the following).
- The chemical form and stability of barium carbonate species formed during stored NOx removal in the presence of CO_2 has been determined.
- Studies of the effects of water on the decomposition of the deactivating $BaAl_2O_4$ phase show how treatments may be devised to restore performance after deactivation.
- The relative performance of all alkaline earth oxide storage materials has been determined (discussed in the following).
- Numerous publications (nine), invited talks (six), and other presentations (11) have resulted from this project in the past year (see following list).

Future Directions

- Continue studies of CO_2 and H_2O effects on BaO morphology changes and NOx storage properties:
  - Ba-loading studies.
  - Are water-induced morphology changes reversible? If so, how?
- Detailed characterization (e.g., FTIR, TEM) of the roles (especially with respect to deactivation) and material properties of promoter species (such as ceria).

- Initial studies of interactions between multiple emission control devices (e.g., how to optimize LNT regeneration for NH_3 production if a downstream urea selective catalytic reduction catalyst system is present).

Introduction

One of the key challenges facing the catalysis community is the elimination of harmful gases emitted by internal combustion engines. In particular, the reduction of NOx from an exhaust gas mixture that contains an excess amount of oxygen is difficult. Traditional three-way catalysts do not work under lean conditions because the concentrations of the reductants (CO and hydrocarbons) are greatly reduced by their oxidation with O_2 on the noble metal components of these catalysts. Therefore, new approaches to NOx reduction have been considered in the last decade. In spite of all the efforts to develop new emission control technologies for lean NOx reduction, only limited applications have been achieved. One of the most promising technologies under consideration is the NOx adsorber catalyst (aka NOx storage/reduction [NSR] or LNT) method. This process is based on the ability of certain oxides, in particular alkaline and alkaline earth oxide materials, to store NOx under lean conditions and release it during rich (excess reductant) engine operation cycles. Since the original reports on this technology from Toyota in the mid `90s [1], the most extensively studied catalyst system continues to be based on barium oxide (BaO) supported a high surface area alumina (Al_2O_3) material [2].

Our project is aimed at developing a practically useful fundamental understanding of the operation of the LNT technology especially with respect to the optimum materials used in LNTs. As noted above in the summary Accomplishments section, we have made significant progress in a fairly wide-array of areas. For the purposes of this report, we briefly highlight progress in two areas: studies of i) the effect of Ba-loading and water on the formation and stability of $BaAl_2O_4$; and ii) the effects of water on BaO morphology and NOx uptake.

Experimental Details

Catalyst Preparation and Characterization

In a microcatalytic reactor system, LNT performance is evaluated in a fixed bed reactor operated under continuous lean-rich cycling. Rapid lean-rich switching is enabled just prior to the elevated temperature zone (furnace) where the LNT materials are contained in quartz tubing. After removing water, the effluent of the reactor can be analyzed by mass spectrometry and by a chemiluminescent NOx analyzer. For a typical baseline performance test, the sample is heated to a reaction temperature in flowing He, the feed switched to a 'lean-NOx' mixture containing oxygen and NO, as well as CO_2 and/or H_2O. After an extended period (15 minutes or more), multiple rich/lean cycles of one and four minute duration, respectively, are run and NOx removal performance is assessed after at least three of these are completed. In the LNT technology, the state of the system is constantly changing so that performance depends on when it is measured. Therefore, we obtain NOx removal efficiencies as "lean conversion (four minutes)", which measures NOx removal efficiencies for the first four minutes of the lean-period.

The BaO/Al_2O_3 LNT catalysts were prepared by the incipient wetness method, using an aqueous $Ba(NO_3)_2$ solution (Aldrich) and a γ-alumina support (200 m^2/g, Condea) to yield nominal two, eight and 20 wt% BaO-containing samples, dried at 125°C and then 'activated' via a calcination at 500°C in flowing dry air for two hours. State-of-the-art techniques such as solid-state NMR [3], XRD, XPS, TEM/EDS, FTIR, BET/pore size distribution, and temperature programmed desorption/reaction (TPD/TPRX), available at PNNL, were utilized to probe the changes in physicochemical properties of the catalyst samples. The time-resolved X-ray diffraction (TR-XRD) experiments were carried out at beam line X7B of the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory. The detailed experimental set-up and protocol have been discussed elsewhere [4,5].

Results

In prior years' reports, we have described studies that determined the cycle of morphology changes for BaO/Al_2O_3 NSR catalysts using synchrotron TPD, FTIR, TR-XRD, TEM and EDS. The results showed that large $Ba(NO_3)_2$ crystallites are formed on the alumina support material during its preparation by an incipient wetness method using an aqueous $Ba(NO_3)_2$ solution. A large fraction of the alumina surface remains Ba-free after this procedure. Upon thermal treatment, these large $Ba(NO_3)_2$ crystallites decompose to form nanosized BaO particles. In fact, we propose that a thin BaO film (monolayer) forms on the alumina support, and the BaO nanoparticles are located on top of this interfacial BaO layer. During room temperature NO_2 uptake, nanosized (<5 nm) $Ba(NO_3)_2$ particles form, and these particles are stable at room temperature. Heating the material to higher temperature (300°C) in the presence of NO_2 results in the formation of larger $Ba(NO_3)_2$ crystals (~15–30 nm). At still higher temperatures, as $Ba(NO_3)_2$ decomposes, the nano-sized BaO particles reform. These LNT material morphological changes during operation are summarized in Figure 1. We have also

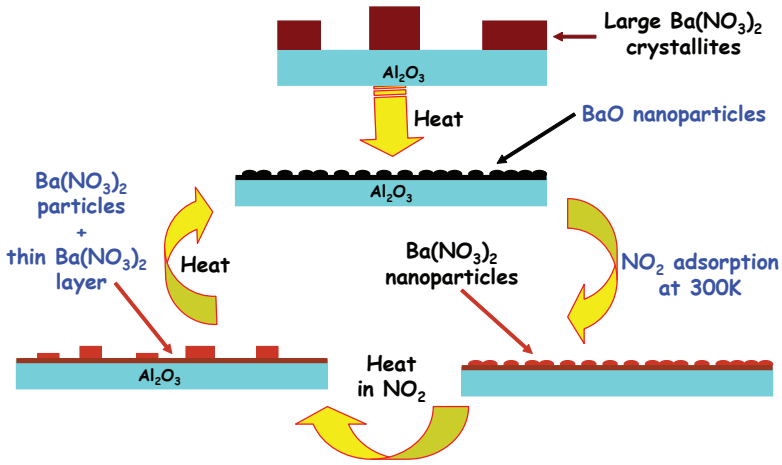

FIGURE 1. Schematics of the Cycle Of Morphology Changes Taking Place during NO_2 Uptake and Release on BaO/Al_2O_3 NOx Storage/Reduction Materials

previously described a number of important practical consequences of these cyclic morphology changes. In particular:

- From TPD experiments, the "monolayer" morphology is found to decompose at lower temperature in vacuum and in a reducing atmosphere than "bulk" nitrates [5,6];
- "Monolayer" Ba-phase is also easier to 'de-sulfate' [7];
- Formation of a high-temperature (deactivating?) $BaAl_2O_4$ phase requires BaO coverages above one monolayer [8]; and
- Morphology model at least partially explains relatively small use of Ba species (often <20%) in storing NOx during typical lean-rich cycling [9].

We have more recently studied the effects of water and/or CO_2 on these morphology changes (manuscripts in preparation).

In this year's report, we highlight two other aspects of our recent studies, the first of which is related to determining the Ba-phase morphologies on the surface of the γ-alumina support material.

Penta-Coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ-Al_2O_3: an Ultra-High Magnetic Field ^{27}Al MAS NMR Study

In a recently published paper [3], we reported the first observation of preferential anchoring of an impregnated catalytic phase onto penta-coordinated Al^{3+} sites on the surface of γ-Al_2O_3. The interaction of barium oxide with a γ-alumina support was investigated by a high resolution solid state ^{27}Al magic angle spinning (MAS) NMR at an ultra-high magnetic field of 21.1T and at sample spinning rates of up to 23 kHz. Under these experimental conditions, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, assigned to 5-coordinated Al^{3+} ions, is clearly distinguished from the two other peaks representing Al^{3+} ions in tetra-, and octahedral coordination. Figure 2 shows the high resolution solid state center band ^{27}Al MAS NMR spectrum of γ-alumina – to our knowledge, the highest resolution spectrum of this material obtained to date. The spectrum contains the well-known peaks at 0 (by definition here) and ~59 ppm, which are assigned to octa- and tetrahedral Al^{3+} ions, respectively. Interestingly, an additional clearly resolved peak at ~23 ppm with relatively low intensity was also observed when the sample was spun at 23 kHz, consistent with an assignment to penta-coordinated Al^{3+} ions [10]. Note, however, that this peak is not readily observable for typical γ-alumina samples in conventional low field (7.05T), low sample spinning rate (~5 kHz) MAS experiments [11], and is only poorly resolved at intermediate fields and spinning rates [12]. Importantly, spin-lattice ^{27}Al relaxation time measurements clearly show that the penta-coordinated Al^{3+} sites are located on the surface of the γ-alumina support.

BaO deposition onto this γ-alumina sample resulted in the loss of intensity of the 23 ppm peak. Figure 3 shows the 23 kHz center band ^{27}Al MAS NMR spectra obtained from γ-alumina samples loaded with BaO to

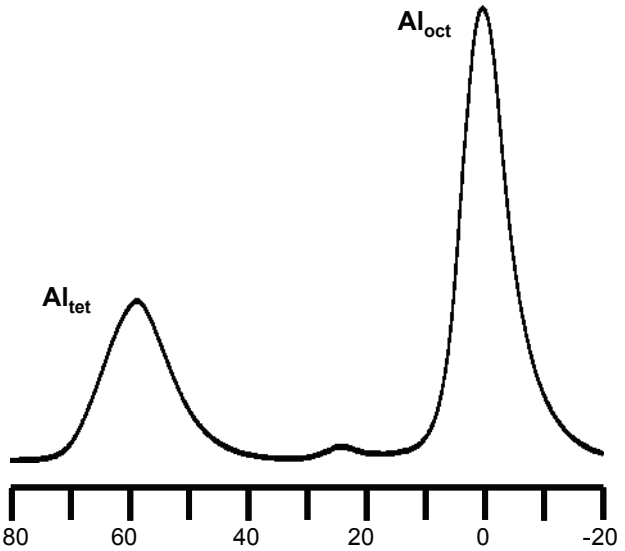

FIGURE 2. Solid State ^{27}Al MAS NMR Spectrum of γ-Alumina, Activated at 500°C for 2 hours, Collected at 21.1 T and a 23 kHz Spinning Rate

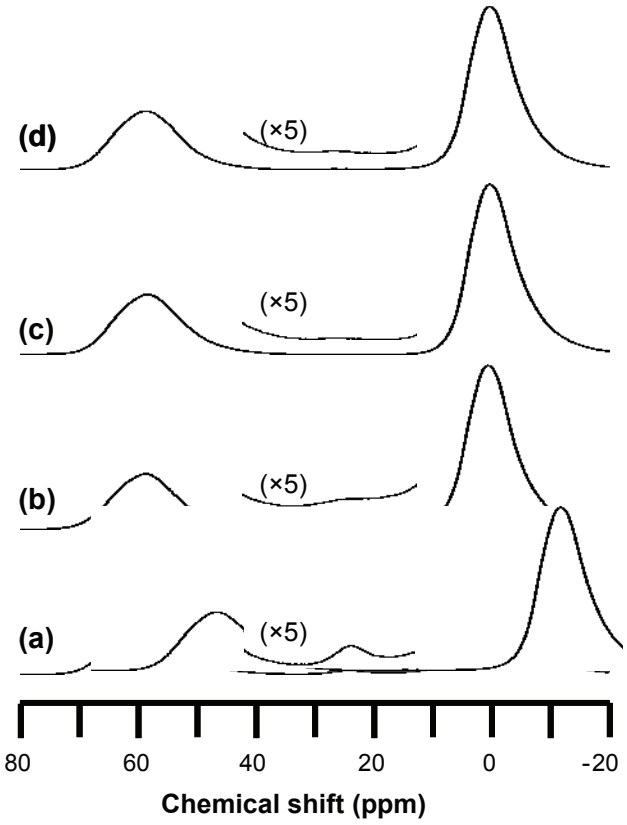

FIGURE 3. Solid State ^{27}Al MAS NMR Spectra, Collected at 21.1 T and 23 kHz Spinning Rate, as a Function of BaO loading: (a) γ-Al_2O_3; (b) 2%BaO/Al_2O_3; (c) 8%BaO/Al_2O_3; and (d) 20%BaO/Al_2O_3

varying levels via wet impregnation, and then activated at 500°C. Neither the peak positions nor the line shapes of the tetra- and the octahedral Al^{3+} ions changed as a function of barium loading. However, the intensity of the ~23 ppm peak decreased significantly for 2% BaO/Al_2O_3 relative to that of the BaO-free γ-alumina. Furthermore, there is essentially no intensity observed at 23 ppm for the eight and 20% BaO/Al_2O_3 samples. These results suggest that initially BaO preferentially occupied the penta-coordinated Al^{3+} sites during the impregnation and subsequent calcination (500°C) processes. The decrease, and eventual disappearance of the 23 ppm NMR peak upon BaO loading also strongly supports the assignment of this peak to Al^{3+} ions located on the surface of the alumina support, and not distributed homogeneously as crystalline defect sites in the bulk. Indeed, separate experiments (not shown) demonstrated that the intensity loss observed was linearly proportional to the amount of BaO deposited. Thus, the results of this study strongly suggest that, at least for BaO, these penta-coordinated Al^{3+} ions are the nucleation sites.

On the basis of the results reported here, the possibility that penta-coordinated Al^{3+} ions on the γ-Al_2O_3 surface generally serve as anchoring sites for catalytically important materials (possibly both oxides and metals) is intriguing. One of the main reasons that γ-Al_2O_3 is used so commonly as a catalyst support material is its ability to form and stabilize active centers (metal and metal oxide particles) with high dispersion. As noted above, our recent studies have shown that BaO, the active NOx storage phase in the LNT technology, initially anchors to these coordinatively unsaturated, pentahedral Al^{3+} sites. This is in excellent agreement with our previous observation that well dispersed BaO nano-particles formed upon the thermal decomposition of a $Ba(NO_3)_2$ precursor loaded onto the γ-Al_2O_3 surface [5]. However, the generality of this phenomenon is not established yet. As such, in our on-going research efforts we are studying the impregnation of other catalytically interesting metal and metal oxide particles onto γ-Al_2O_3 in order to determine whether these penta-coordinated Al^{3+} sites are the anchoring points (nucleation sites) for other catalytically active species. In particular, we are using both ultra-high field NMR and ultra-high resolution TEM, using the ACEM in the High Temperature Materials Laboratory at ORNL, to study Pt dispersion on γ-Al_2O_3. If this correlation holds for other active phase/γ-Al_2O_3 systems such as Pt/Al_2O_3, it could open up the possibility of systematically varying the number of penta-coordinated Al^{3+} sites, and thereby providing good control of dispersion of the catalytically active phase.

NOx uptake on Alkaline Earth Oxides (BaO, MgO, CaO and SrO) Supported on γ-Al_2O_3

NOx uptake experiments were performed on a series of alkaline earth oxide (AEO; *i.e.*, MgO, CaO, SrO, BaO) materials supported on γ-alumina [13]. TPD experiments were conducted on these catalysts in flowing He, revealing the presence of two kinds of nitrate species; i.e., bulk and surface nitrates. The ratio of these two types of nitrate species strongly depends on the nature of the alkaline earth oxide. For example, Figure 4 shows the results of TPD experiments conducted on each NO_2-saturated sample. Figure 4a displays the evolution of NO_2 as a function of temperature for each alkaline earth oxide. A generally systematic increase in the temperature of maximum NO_2 desorption rate can clearly be seen from the lowest temperature for MgO/γ-Al_2O_3 (~400°C), to the highest ones for SrO/ and BaO/ γ-Al_2O_3 (~440°C). (The smaller NO_2 desorption peak at low temperatures, around 120°C, has been attributed [8] to the desorption and decomposition of weakly held N_2O_3 species formed in the reaction of NO+NO_2, and adsorbed primarily on the Al_2O_3 support. This assignment has been confirmed by infrared spectroscopy.) The corresponding TPD profiles of NO evolution are shown in Figure 4b for each alkaline earth oxide. The temperature of maximum NO desorption rate for these materials fall into the very narrow range of 520-530°C. Significantly, the amount

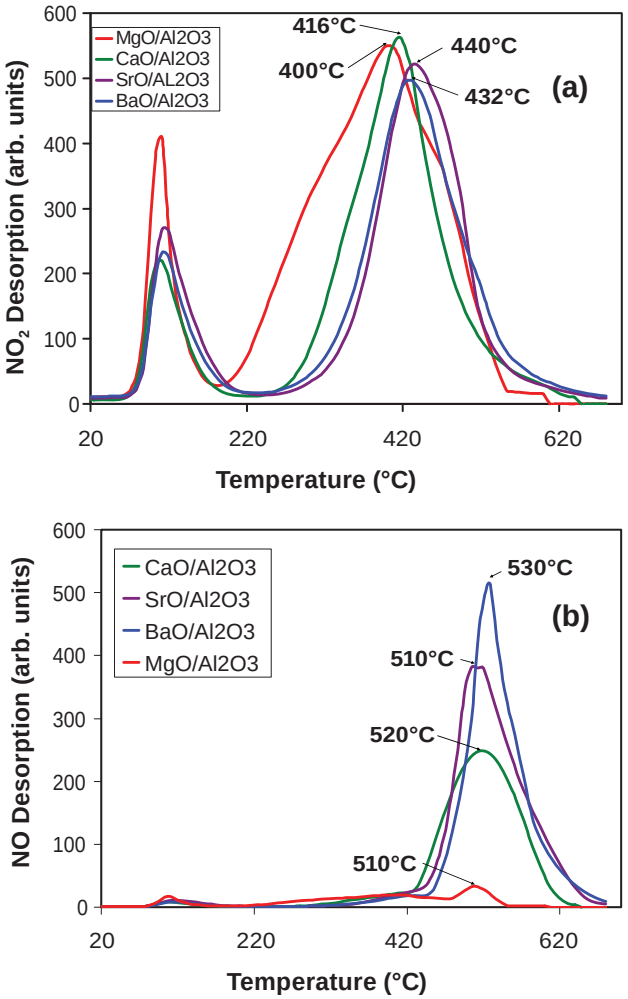

FIGURE 4. TPD Spectra from BaO-, SrO-, CaO- and MgO/γ-Al_2O_3 after NO_2 Saturation at 300 K (heating rate: 8°C/min): (a) NO_2 and (b) NO Desorption Curves

of NO released systematically decreases in the order of BaO > SrO > CaO > MgO. The amount of NO released for MgO/Al_2O_3 is very small (almost nonexistent), while that for the BaO/Al_2O_3 and SrO/Al_2O_3 systems are almost identical. Thus, the amount of bulk nitrate species increases with the basicity of the alkaline earth oxide. This conclusion was supported by the results of FTIR and ^{15}N solid-state NMR spectroscopic studies of NO_2 adsorption.

The effect of water on the NOx species formed in the exposure of the AEOs to NO_2 was also investigated. In agreement with our previous findings for the BaO/γ-Al_2O_3 system, an increase of the bulk nitrate species and the simultaneous decrease of the surface nitrate phase were observed for all of these materials. This is demonstrated in Figure 5 which shows FTIR spectra of NO_2 adsorbed on the various AEO catalysts before and after exposure to water. In the FTIR cell, the activated samples were first saturated with NO_2, the excess NOx was then evacuated and finally these NO_x/AEO/γ-Al_2O_3 samples were exposed to 1 Torr of H_2O, followed by evacuation at 300 K. The changes in the FTIR spectra can primarily be understood as decreases in the intensities of the surface nitrate-related infrared bands with corresponding increases in those due to bulk nitrates.

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FY 2007 Presentations

INVITED

1. Peden, C.H.F. "Fundamental Studies of Catalytic NOx Vehicle Emission Control." Invited Presentations made by Chuck Peden at the following locations:

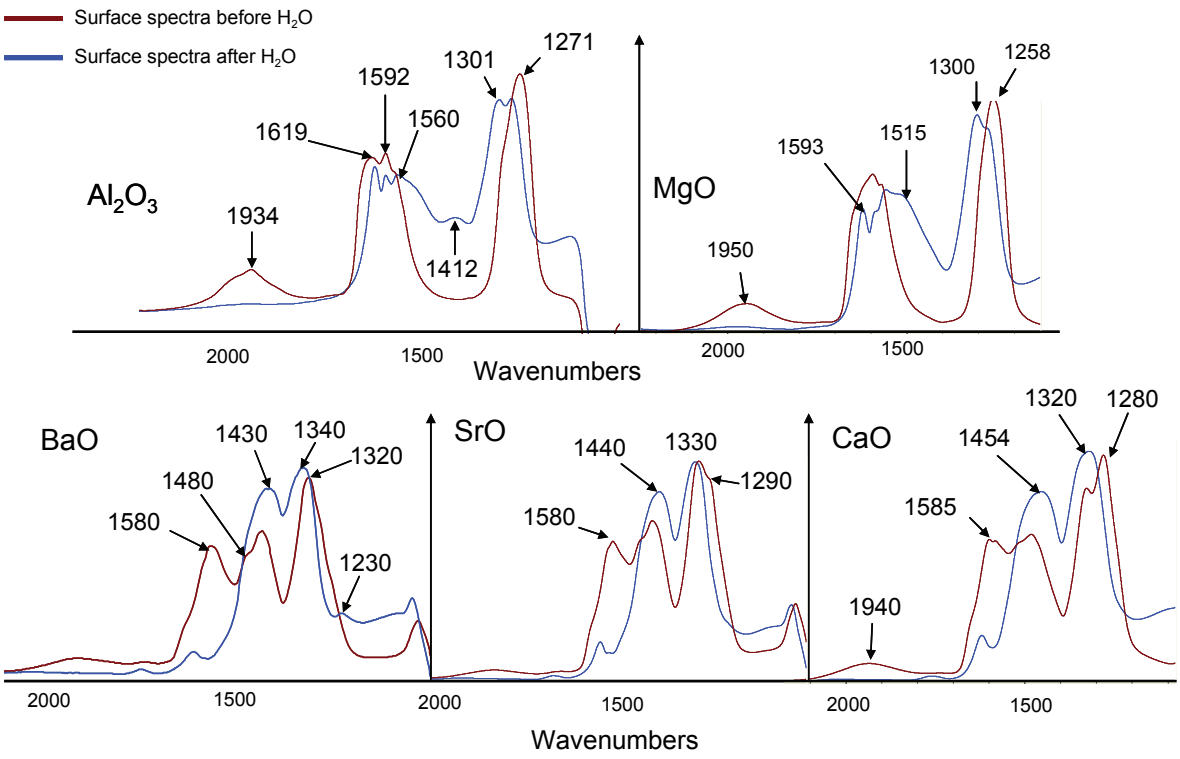

FIGURE 5. Infrared Spectra after NO_2 Adsorption and Evacuation (Brown Curves), Followed by Water Adsorption and Evacuation (Blue Curves) on BaO-, SrO-, CaO- and MgO/γ-Al_2O_3

- Dalian Institute of Chemical Physics, Dalian, China, December 11, 2007.
- Dalian University of Technology, Dalian, China, December 12, 2007.
- Tianjin University, Tianjin University, December 14, 2007.
- Texas A&M University, College Station, TX, January 29, 2007.

2. Peden, C.H.F; Ozensoy, E.; Yi, C.-W.; Szanyi, J. "Model Studies of BaO/Al2O3 NOx Storage Materials." Invited Presentation made by Chuck Peden at the 233rd American Chemical Society National Meeting, Chicago, IL on April 3, 2007.

3. Disselkamp, R.; Kim, D.-H.; Kwak, J.-H.; Szanyi, J.; Tonkyn, R.; Wang, X.; Peden, C.; Howden, K. "Fundamental Studies of NOx Adsorber Materials." Invited Presentation made by Chuck Peden at the 2007 Advanced Combustion Engine Peer Review Meeting, Washington, D.C. on June 18, 2007.

CONTRIBUTED

4. Kim D, J Kwak, J Szanyi, Y Chin, X Wang, JC Hanson, and CHF Peden. "The Various Roles of Water in the Pt-BaO/Al_2O_3 Lean NOx Trap Catalyst System." Presented by Do Heui Kim at the 2006 American Institute of Chemical Engineers (AIChE) Annual Meeting, San Fransisco, CA on November 13, 2006.

5. Peden CHF, D Kim, J Kwak, X Wang, T Szailer, WS Epling, JC Hanson, and J Szanyi. "LNT Morphology Changes with Lean/Rich Cycling." Presented by Chuck Peden at the 2006 American Institute of Chemical Engineers (AIChE) Annual Meeting, San Francisco, CA on November 14, 2006.

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7. Peden CHF. "Fundamental Studies of NOx Adsorber Materials at PNNL." Presented by Chuck Peden at the 10th DOE CLEERS Workshop, Dearborn, MI on May 2, 2007.

8. Kwak J, D Kim, J Szanyi, and CHF Peden. "Solid State ^{27}Al NMR Study of BaO/Al_2O_3 Catalysts: $BaAl_2O_4$ Formation and Decomposition." Presented by Ja Hun Kwak at the 20th North American Meeting of the Catalysis Society, Houston, TX on June 18, 2007.

9. Verrier C, J Kwak, D Kim, CHF Peden, and J Szanyi. "NOx Storage over Alkaline Earth Oxides Supported on γ-Al_2O_3." Presented by Christelle Verrier at the 20th North American Meeting of the Catalysis Society, Houston, TX on June 18, 2007.

10. Szanyi J, J Kwak, D Kim, J Hanson, and CHF Peden. "The Effect of Water on the Adsorbed NOx species over BaO/Al_2O_3 NOx Storage Materials: A Combined FTIR and *In-Situ* Time-Resolved XRD study." Presented by Janos

Szanyi at 20th North American Meeting of the Catalysis Society, Houston, TX on June 21, 2007.

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1. Kwak J, D Kim, T Szailer, CHF Peden, and J Szanyi. 2006. "NOx Uptake Mechanism on $Pt/BaO/Al_2O_3$ Catalysts." *Catalysis Letters* **111**(3-4):119-126.

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3. Kim D, J Kwak, J Szanyi, SD Burton, and CHF Peden. 2007. "Water-induced Bulk $Ba(NO_3)_2$ Formation From NO_2 Exposed Thermally Aged BaO/Al_2O_3." *Applied Catalysis. B, Environmental* **72**(3-4):233-239.

4. Kwak J, J Hu, D Kim, J Szanyi, and CHF Peden. 2007. "Penta-coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ-Al_2O_3: an Ultra-high Magnetic Field ^{27}Al MAS NMR Study." *Journal of Catalysis* **251**(2):189-194.

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8. Verrier C, J Kwak, D Kim, CHF Peden, and J Szanyi. 2007. "NOx uptake on alkaline earth oxides (BaO, MgO, CaO and SrO) supported on γ-Al_2O_3." *Catalysis Today*, in press.

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II.B.2 Mechanisms of Sulfur Poisoning of NOx Adsorber Materials

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CRADA Partners:
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- Hai-Ying Chen, Howard Hess - Johnson Matthey, Wayne, PA

Objectives

- Develop and apply characterization tools to probe the chemical and physical properties of NOx adsorber catalyst materials for studies of deactivation due to sulfur poisoning and/or thermal aging. Utilize this information to develop mechanistic models that account for NOx adsorber performance degradation.
- Develop protocols and tools for failure analysis of field-aged materials.
- Provide input on new catalyst formulations; verify improved performance through materials characterizations, and laboratory and engine testing.

Accomplishments

Three major thrusts this year:

- Strong metal-support interactions (SMSIs) in Pt-BaO/Al_2O_3, and their effects on NOx storage. We observed:
  - A decrease in Pt accessibility for H_2 chemisorption with increasing reduction temperature without a corresponding change in Pt particle size, implying that BaO covers at least part of the Pt surface during reduction.
  - An increase in NOx storage capacity up to a reduction temperature of 500°C, strongly suggests that there is a promotional effect of this SMSI-like (Pt-BaO) interaction on NOx storage.
- Sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated NOx trap catalysts.
  - Based on prior work, water promotes sulfur removal from deactivated lean-NOx trap (LNT) materials, although it can have a negative effect on Pt sintering, at least partially offsetting the benefits of desulfation on regenerating NOx storage activity.
  - We developed an approach that consists of two separate processes of high temperature reduction with H_2 followed by a low temperature hydrolysis step. As a result, Pt sintering is significantly inhibited and optimized NOx storage performance is achieved.
- The roles of Pt and BaO in the sulfation of Pt/BaO/Al_2O_3 LNT materials.
  - In last year's annual report, we described S X-ray absorption near-edge spectroscopy (XANES) and Pt X-ray absorption fine structure (XAFS) studies of the effect of initial barium morphology on the desulfation behavior of Pt-BaO/Al_2O_3 catalysts. In this last year, the same techniques were applied to elucidate the sulfation mechanism, and the roles of each catalyst component in the sulfation process for model LNT materials.
  - The results indicate that barium species have an ability to make sulfate species even without gaseous oxygen and Pt. In addition, even if aluminum sites are available, barium is preferentially sulfated to make barium sulfate.
  - We also find that Pt-O plays a crucial role in making sulfate until its pre-existing levels are consumed. If gaseous oxygen is present in the environment, such species can reform and continue to react with SO_2 to make additional sulfate species.

Four public presentations and four manuscripts have been cleared for release by the Cooperative Research and Development Agreement (CRADA) partners. One of the manuscripts has appeared in the National Synchrotron Light Source activity report as a highlight article.

Future Directions

- Further refine function-specific measures of 'aging':
  - More detailed studies to verify that techniques such as NO_2 temperature programmed desorption (TPD) and H_2 temperature programmed reaction (TPRX) are providing information content suggested by studies to date.

  - Some effort still to identify new approach to unravel some key unknowns (*e.g.*, role of precious metal/storage material 'contact').
- Validate most-suitable function-specific measures on samples incrementally 'aged' under realistic conditions.
- Apply developed techniques to the commercial fresh and "aged" samples in the monolith form:
  - Determine optimized regeneration conditions by using program-developed reaction protocol.
  - X-ray photoelectron spectroscopy (XPS), S XANES, time resolved (TR)-X-ray diffraction (XRD) studies to follow the changes of sulfur species with sulfation/desulfation.
  - Use technique capable of spatially resolving sulfur distributions, including scanning electron microscope energy dispersive (X-ray) spectroscopy and XPS, to follow changes in these distributions with sulfation/desulfation.
- Continue to improve mechanistic understanding of sulfur removal processes:
  - Investigate the role of Pt during desulfation.
  - Identify important desulfation intermediates.
  - Investigate the effects of sulfur concentration on Pt accessibility and barium phase changes.

Introduction

The NOx adsorber (also known as a LNT) technology is based upon the concept of storing NOx as nitrates over storage components, typically barium species, during a lean-burn operation cycle and then reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst [1]. This technology has been recognized as one of the most promising approaches for meeting stringent NOx emission standards for diesel vehicles within the Environmental Protection Agency's 2007/2010 mandated limits. However, problems arising from either or both thermal and SO_2 deactivation must be addressed to meet durability standards. Therefore, an understanding of these processes will be crucial for the development of the LNT technology.

This project is focused on the identification and the understanding of the important degradation mechanism(s) of the catalyst materials used in LNTs. 'Simple' and 'Enhanced Model' $Pt/BaO/Al_2O_3$ samples were investigated. In particular, the changes in physicochemical properties related to the reaction performances of these LNT materials, due to the effects of high temperature operation and sulfur poisoning, are the current focus of the work. By comparing results obtained on 'Simple Model' $Pt/BaO/Al_2O_3$ with 'Enhanced Model' materials, we try to understand the role of various additives on the deactivation processes. We now move on to the real commercial sample which is being used in a Dodge Ram truck with a Cummins diesel emission control system. However, the results about the 'commercial sample' will not be covered in this report. We further note here that while program progress for the entire year is summarized above in the "Accomplishments" section, we present in the following more detail about results obtained in this last year in three specific areas: i) SMSI in $Pt\text{-}BaO/Al_2O_3$ and their effects on NOx storage, ii) sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated NOx trap catalysts, iii) the roles of Pt and BaO in the sulfation of $Pt/BaO/Al_2O_3$ LNT materials.

Approach

In a microcatalytic reactor system, LNT performance is evaluated in a fixed bed reactor operated under continuous lean-rich cycling. Rapid lean-rich switching is enabled just prior to the elevated temperature zone (furnace) where the LNT materials are contained in quartz tubing. After removing water, the effluent of the reactor can be analyzed by mass spectrometry and by a chemiluminescent NOx analyzer. For a typical baseline performance test, the sample is heated to a reaction temperature in flowing He, the feed switched to a 'lean-NOx' mixture containing oxygen and NO, as well as CO_2 and/or H_2O. After an extended period (15 minutes or more), multiple rich/lean cycles of 1 and 4 minute duration, respectively, are run and NOx removal performance is assessed after at least three of these are completed. In the LNT technology, the state of the system is constantly changing so that performance depends on when it is measured. Therefore, we obtain NOx removal efficiencies as "Lean conversion (30 minutes)", which measures NOx removal efficiencies for the first 30 minutes of the lean-period. In addition, material treatments such as SO_2 aging, and post mortem catalyst characterizations were conducted in the same test stand without exposing the catalyst sample to air. We have established a reaction protocol, which evaluates the performance of samples after various thermal aging and sulfation condition. In this way, we could identify optimum de-sulfation treatments to rejuvenate catalyst activities.

State-of-the-art catalyst characterization techniques such as XRD, XPS, transmission electron microscopy (TEM)/EDS, Brunauer, Emmett and Teller pore size distribution, and TPD/TPRX were utilized to probe the changes in physicochemical properties of the catalyst samples under deactivating conditions; *e.g.*, thermal aging and SO_2 treatment. Specifically, H_2 TPRX, Sulfur K-edge XANES and TR-XRD methods were used extensively to quantify the levels, speciation and phase

of sulfur on the model adsorber material (Al_2O_3, Pt/Al_2O_3, BaO/Al_2O_3 and Pt-BaO/Al_2O_3) as a function of desulfation process.

Results

SMSIs in Pt-BaO/Al_2O_3 and Their Effects on NOx Storage

H/Pt values determined from H_2 chemisorption measurements is a common way to measure the number and accessibility of active sites for many supported Pt catalysts. Figure 1 shows the H/Pt curve obtained as a function of reduction temperature for a Pt-BaO/Al_2O_3 catalyst. It shows that the H/Pt ratio decreases uniformly as a function of reduction temperature. Estimating Pt particle sizes based on this ratio, the results suggest that Pt particle sizes uniformly increased with increases in the reduction temperature, with an estimated Pt particle size of about 26 nm for the case of the sample after reduction at 800°C. However, the particle size from TEM images obtained from these samples is ~5-10 nm, suggesting that the actual Pt particle sizes were much smaller than those determined from the H_2 chemisorption method. Such an apparent discrepancy in the results from these two techniques strongly supports the existence of SMSI in the samples reduced at high temperature, especially above 500°C. In other words, the decrease in the H/Pt ratio actually arises from an encapsulation of Pt by a migrating BaO_x layer. We measured NOx uptakes of the Pt/Ba-Al_2O_3 catalysts after they were reduced at different temperatures. As shown in Figure 1, the results clearly show an increase in the NOx uptake up to a reduction temperature of 500°C, followed by a gradual decrease with further increases in the reduction temperatures. The decrease in NOx uptake after 500°C is attributed to a thermal aging effect.

Sequential High Temperature Reduction, Low Temperature Hydrolysis for the Regeneration of Sulfated NOx Trap Catalysts

Water is known to promote desulfation of LNT catalysts; however, it has also been shown to have a negative effect on catalytic performance via the promotion of Pt sintering. In addition, our group [2] has previously demonstrated that the NOx uptake efficiency is adversely affected by the growth of platinum particles arising from thermal aging. Hence, Pt sintering is detrimental to the performance of these LNT catalysts. Even more important is the irreversible nature of this deactivation process since the sintered Pt particles can not be re-dispersed. To explore ways to prevent such sintering, we designed a desulfation process in which H_2 and H_2O are separately introduced in two sequential steps as shown in Figure 2: desulfation with H_2 only at high temperatures (up to 800°C), followed by H_2O treatment at lower temperatures (maximum of 300°C). The first step transforms the sulfate species into sulfides and even desorbs some of the sulfur as H_2S, while minimizing the Pt sintering. In the second step, the thus formed BaS reacts with H_2O in a hydrolysis reaction to form BaO and additional H_2S. The second process is regarded as a key factor for promoting irreversible Pt sintering behavior. By using this sequential desulfation process, we can significantly decrease the levels of Pt sintering as shown in the TEM pictures of Figure 3, while the amount of sulfur removed from the sample is less than

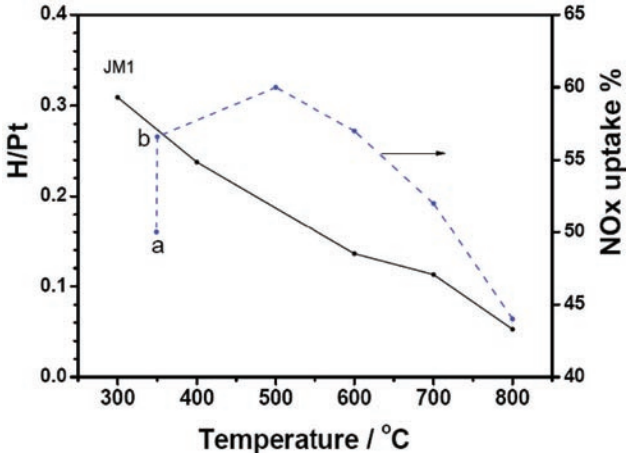

FIGURE 1. Comparison of a H/Pt curve with NOx Uptake as a Function of Reduction Temperature for a Pt-BaO/Al_2O_3 Sample

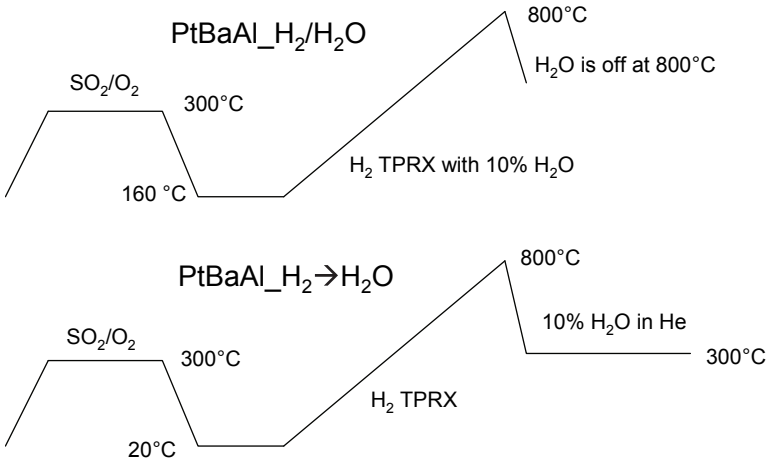

FIGURE 2. Two Regeneration Protocol Steps used to Desulfate Sulfated Pt-BaO(20)/Al_2O_3 Samples

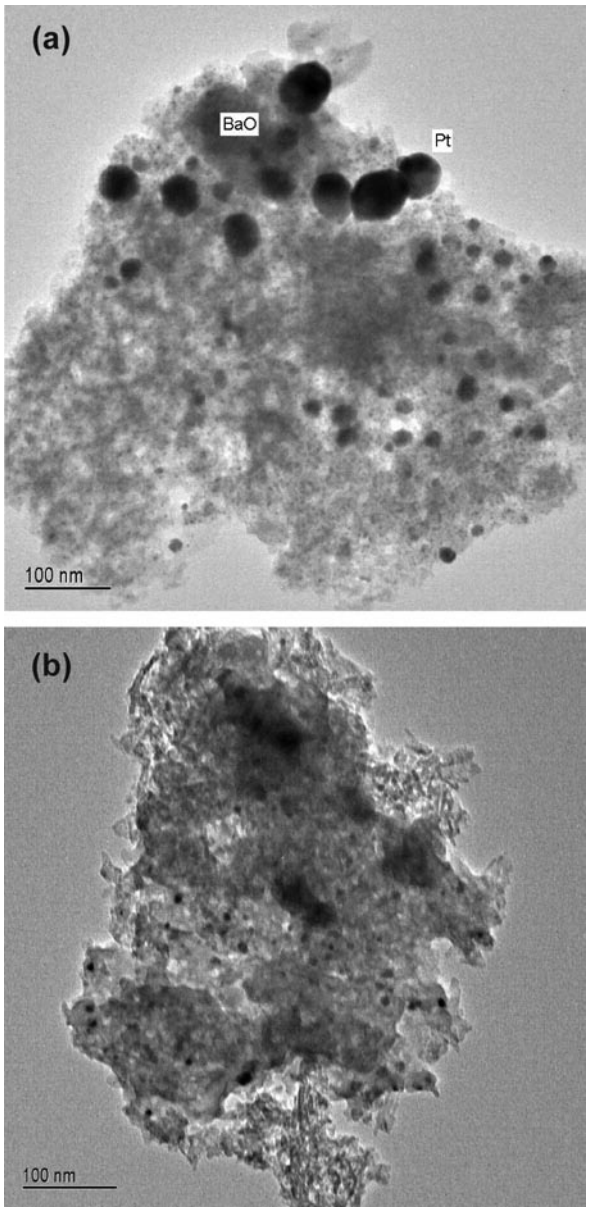

FIGURE 3. TEM Images of Samples of PtBaAl_H_2→H_2O (a) and PtBaAl_H_2/H_2O (b)

cooperative desulfation with H_2 and H_2O. The NOx uptake results showed similar NOx uptake performance for catalysts desulfated cooperatively with H_2 and H_2O or sequentially. Although the amount of H_2S desorbed during the cooperative desulfation process is larger than that of sequential one under the experimental conditions presented here, a modification of the two-step desulfation protocol may offer a means to improve the desulfation efficiency while maintaining the lack of Pt particle size growth. This can be achieved by optimizing the experimental conditions, in particular H_2O concentration and hydrolysis temperature.

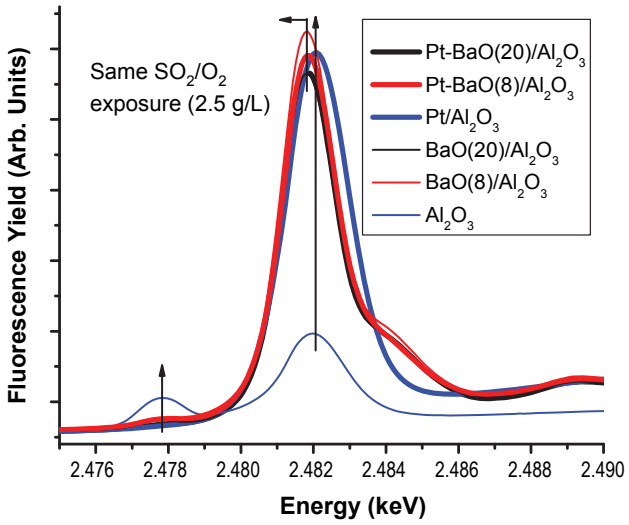

FIGURE 4. Sulfur K-edge XANES Spectra of Al_2O_3, Pt/Al_2O_3, BaO(8 or 20)/Al_2O_3 and Pt-BaO(8 or 20)/Al_2O_3, each Sample Having Been Given an Equivalent Sulfation Exposure of 2.5 g/L

The Roles of Pt and BaO in the Sulfation of Pt/BaO/Al_2O_3 LNT Materials

The roles of barium oxide and platinum during the sulfation of Pt-BaO/Al_2O_3 LNT catalysts were investigated by S K-edge XANES and Pt L_{III} XAFS. All of the samples studied (Al_2O_3, BaO/Al_2O_3, Pt/Al_2O_3 and Pt-BaO/Al_2O_3) were pre-sulfated prior to the X-ray absorption measurements.

Figure 4 compares the S XANES spectra obtained for Al_2O_3, BaO(8 or 20)/Al_2O_3 samples, in the presence and absence of Pt, after the same SO_2/O_2 sulfation processes. For the case of the Al_2O_3 support itself, two peaks are observed near 2,478 eV and 2,482 eV, which can be assigned to aluminum sulfites (SO_3^{2-}) and aluminum sulfates (SO_4^{2-}), respectively. The intensity of the white line at 2,482 eV for sulfated Al_2O_3 is much smaller than in samples containing Pt or BaO, implying that all SO_2 dosed was not fully adsorbed on Al_2O_3. The greater intensity for the Pt- and Ba-containing samples is consistent with the results of SO_2 breakthrough measurements indicating that all dosed SO_2 was adsorbed by Pt/Al_2O_3 and Pt-BaO(8 or 20)/Al_2O_3 up to sulfation levels of 2.5 g/L. Thus, both Pt and barium oxide play a critical role in promoting sulfation for the catalysts supported on alumina.

The 8 wt% and 20 wt% BaO on Al_2O_3 materials are estimated to correspond to 0.26 and 0.75 monolayer coverages of BaO on the alumina surface [3]. Therefore, significant areas of the alumina surface would still be available for SO_2 to adsorb to form aluminum sulfates. Despite this, the essentially identical peak shapes of the primary S XANES feature for the barium loaded samples, clearly showing that SO_2 preferentially

favors the formation of barium sulfates as long as barium remains available for this reaction. It can be summarized that barium oxide itself has the ability to directly form barium sulfate even in the absence of Pt and gas phase oxygen. In the platinum-containing samples, the presence of Pt-O species plays an important role in the formation of sulfate species. However, when oxygen is absent from the gas phase, the sulfation route that involves Pt-O is eliminated after the initially present Pt-O species are completely consumed.

Conclusions

PNNL and its CRADA partners from Cummins Inc. and Johnson Matthey are carrying out a project to study the mechanisms of deactivation of the materials proposed for use in LNTs arising from thermal aging and SO_2 poisoning. Results demonstrate that a strong metal support interaction between Pt and BaO was observed and resulted in a decrease in hydrogen uptake during chemisorption even though Pt particle sizes were not changing. By using a sequential desulfation process, *i.e.*, high temperature desulfation and low temperature hydrolysis, we can significantly decrease levels of Pt sintering. The NOx uptake results showed similar performance for catalysts desulfated cooperatively with H_2 and H_2O or sequentially. Combination of S XANES and Pt XAFS experiments allow us to elucidate sulfation mechanisms, and the roles in the sulfation processes of each component in the LNT catalyst. Overall, these studies are providing valuable information for overcoming critical durability issues in LNT catalysts.

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7. Do Heui Kim, Ja Hun Kwak, Xianqin Wang, Janos Szanyi, and Charles H.F. Peden, "The Roles of Pt and BaO in the Sulfation of $Pt/BaO/Al_2O_3$ Lean NOx Trap Materials: Sulfur K-Edge XANES and Pt L_{III} XAFS Studies", Journal of Physical Chemistry C, (2008) in press.

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II.B.3 Characterizing Lean-NOx Trap Regeneration and Desulfation

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Objectives

- Establish relationships between exhaust species and various lean-NOx trap (LNT) regeneration strategies.
- Characterize effectiveness of in-cylinder regeneration strategies.
- Develop stronger link between bench and full-scale system evaluations.
- Provide data through Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) to improve models. Use models to guide engine research.

Accomplishments

- Analyzed model and commercial LNT catalysts on a full-scale engine system with in-cylinder regeneration techniques.
- Measured NH_3 emissions from LNTs and determined the effect of ceria on NH_3 control.
- Interacted with the CLEERS modeling community by presenting results in a CLEERS teleconference and the CLEERS workshop and by uploading data to the CLEERS web site database.

Future Directions

- Conduct experiments to analyze the potential benefit of NH_3 emissions from LNT catalysts for downstream selective catalytic reduction.
- Evaluate lower precious metal LNT catalysts to study possibilities for cost reduction (a key limitation to introduction of the technology).
- Examine LNT catalysts for lean gasoline engine applications.

Introduction

As part of the Department of Energy's strategy to reduce imported petroleum and enhance energy security, the Office of FreedomCAR and Vehicle Technologies has been researching enabling technologies for more efficient diesel engines. NOx emissions from diesel engines are very problematic and the U.S. Environmental Protection Agency (EPA) emissions regulations require ~90% reduction in NOx from light- and heavy-duty diesel engines in the 2004-2010 timeframe. One active research and development focus for lean-burn NOx control is in the area of LNT catalysts. LNT catalysts adsorb NOx very efficiently in the form of a nitrate during lean operation, but must be regenerated periodically by way of a momentary exposure to a fuel-rich environment. This rich excursion causes the NOx to desorb and then be converted by nobel metal catalysts to harmless N_2. The momentary fuel-rich environment in the exhaust occurs 2-4 seconds for every 30-90 seconds of normal lean operation (depending on operating conditions). The rich exhaust can be created by injecting excess fuel into the cylinder or exhaust, throttling the intake air, increasing the amount of exhaust gas recirculation (EGR), or through some combination of these strategies. The controls methodology for LNTs is very complex, and there is limited understanding of the how all of the competing factors can be optimized.

While LNTs are effective at adsorbing NOx, they also have a high affinity for sulfur. As such, sulfur from the fuel and possibly engine lubricant (as SO_2) can adsorb to NOx adsorbent sites (as sulfates). Similar to NOx regeneration, sulfur removal (desulfation) also requires rich operation, but for several minutes, at much higher temperatures. Desulfation intervals are much longer, on the order of hundreds or thousands of miles, but the conditions are more difficult to achieve and are potentially harmful to the catalyst function. Nonetheless, desulfation must be accomplished periodically to maintain effective NOx performance. There is much to be learned with regard to balancing all the factors in managing LNT NOx control performance, durability, and sulfur tolerance.

The objective of this project is to understand the complex chemistry that occurs during the regeneration processes for LNTs through experiments conducted on a full size engine-LNT catalyst system. Different strategies for introducing the excess fuel for regeneration can produce a wide variety of hydrocarbon and other species. Specific regeneration strategies were developed for this project by operating the engine with net rich air-to-fuel ratios; such "in-cylinder" techniques utilize throttling to reduce air flow and extra fuel injection

pulses during the combustion event to increase fueling. A primary focus of this work is to examine the effectiveness of various regeneration strategies in light of the species formed and the LNT formulation since the combined chemistry of the exhaust produced by the regeneration strategy and the chemistry of the LNT catalyst dictate performance.

Approach

A 1.7-L Mercedes Benz common rail engine and motoring dynamometer have been dedicated to this activity. The engine is equipped with an electronic engine control system that provides full-bypass of the original engine controller. The controller is capable of monitoring and controlling all the electronically controlled parameters associated with the engine (i.e., fuel injection timing/duration/number of injections, fuel rail pressure, turbo wastegate, electronic throttle, and electronic EGR). The experimental setup allows for full exhaust species characterization throughout the catalyst system. This includes the measurement of key reductants such as H_2, CO, and hydrocarbons as well as NOx and potential nitrogen-based byproducts like NH_3 at five locations within the LNT system. A full set of analyzers is applied to sample the various species; analysis techniques include: chemiluminescence for NOx, Fourier transform infrared spectroscopy for NH_3, magnetic sector mass spectrometry for H_2, non-dispersive infrared analysis for CO, and flame ionization detector analysis for hydrocarbons.

In the study presented here, three different LNT formulations were analyzed with in-cylinder regeneration strategies. The LNT formulations included a commercial LNT made by Umicore and two model LNTs that are of a more generic formulation. The active NOx adsorbing component for all of the LNTs was Ba, but the LNTs differed in Ba and CeO_2 (ceria) loadings. Ceria is an oxygen storage component commonly used in automotive catalysis. Table 1 contains a table that summarized the LNTs studied. Highlights from the study will be presented here; a detailed manuscript on the study has been submitted for the upcoming 2008 SAE Congress conference [1].

TABLE 1. LNT Formulations Studied

	Umicore	Low Ba	Med Ba
BaO	29 g/l	~11 g/l	~27 g/l
Al_2O_3	160 g/l	~137 g/l	~137 g/l
CeO_2	98 g/l	—	—

Results

The NOx conversion of all three LNTs was compared under different operating conditions. The lean-rich operating parameters were varied while the engine load and speed were held constant at 50 ft-lb and 1,500 rpm, respectively. LNT performance was characterized for 20-second and 60-second lean-rich periods each having a three second rich regeneration phase. Two types of in-cylinder regeneration techniques were used. The first technique referred to as the delayed and extended main (DEM) technique is initiated by slightly delaying the main injection pulse and extending its duration to enrich the air and fuel mixture; DEM results in high H_2 and CO reductants with lower amounts of hydrocarbons. The second technique referred to as the Post 80º (P80) technique is initiated by adding another fuel injection at 80º past top dead center in the combustion cycle; P80 generates relatively lower amounts of H_2 and CO and relatively higher amounts of hydrocarbons in comparison to the DEM technique. Specific details on the DEM and P80 regeneration strategies can be found in previous publications [2]. Figure 1 shows the NOx conversion for all three LNTs for the four different combinations of lean-rich period and regeneration strategy. Higher NOx conversions were obtained for the 20-second lean-rich periods as expected since less NOx is trapped by the catalysts per frequency of regeneration. Another trend consistent to all catalysts is that the DEM strategy leads to higher NOx conversion than the P80 strategy for all cases; this trend has been observed previously as is likely due to the greater concentration of the efficient CO and H_2 reductants for the DEM strategy [2]. Overall, the Umicore LNT gave the highest NOx conversion. The Medium Ba LNT was close to the Umicore LNT in performance, but the Low Ba LNT gave significantly poorer NOx conversion. So, NOx performance was

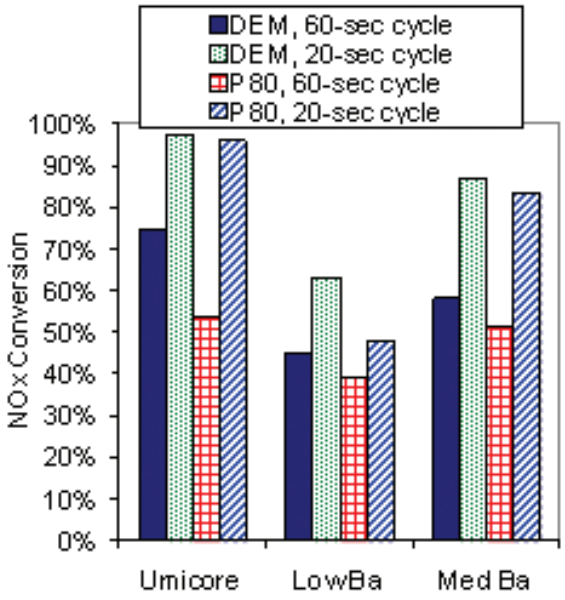

FIGURE 1. NOx Conversion for all Three LNTs for the Parameters Studied

closely associated with Ba load with higher Ba loadings giving greater NOx trapping capacity and improved NOx conversion performance.

In addition to the exhaust measurements made downstream of the LNT which resulted in the data shown in Table 1, exhaust measurements were made from points internal to the LNT to better understand the differences in chemistry occurring for the different LNT formulations. Figure 2 shows the cycle average NOx concentration for all three LNTs for the DEM 60-second cycle; exhaust samples were collected at engine-out (EO), at the LNT inlet (or AI, adsorber inlet), at the ¼ bed position of the LNT, at the ½ bed position of the LNT, at the ¾ bed position of the LNT, and at the tailpipe (TP) position. While the Medium Ba and Umicore LNTs have similar NOx levels at the TP position, the profile of NOx for these LNTs differs significantly. The Medium Ba LNT reduces NOx more effectively in the upstream half of the LNT, but the Umicore LNT reduces NOx more effectively in the downstream half of the LNT. These results indicate that the ceria content of the Umicore LNT may reduce regeneration effectiveness in the upstream half of the LNT since ceria consumes reductants as it is reduced. These internal chemical differences in the way the LNTs perform are important to understand in developing models for the LNTs and in optimizing performance for engine catalyst systems.

One important model parameter is the molar efficiency of the Ba storage component in the LNT. Every mole of Ba on the LNT is not capable of storing NOx; instead, the percentage of Ba moles that are active in storing NOx (the "molar efficiency") is dependent on the dispersion of the Ba material on the high surface area catalyst support material. The molar efficiencies for the Low and Medium Ba LNTs are shown in Figure 3. The lower Ba loading leads to higher Ba dispersion and higher molar efficiencies for NOx storage relative to the Medium Ba LNT case as expected. However, interestingly a similar trend in the molar efficiency as a function of catalyst position occurs. Thus, models that are effective in modeling one Ba load may also be effective in modeling other Ba loads since the mechanisms for NOx storage along the length of the LNT appear to be consistent for different Ba loads.

Internal NH_3 levels were also found to be quite different for the LNT formulations. Figure 4 shows cycle average NH_3 at different catalyst locations for the three LNT formulations for the DEM 60-second cycle. Although the Low Ba LNT gave the lowest NOx reduction efficiency, it had the highest N_2 selectivity and produced negligible amounts of NH_3. In contrast, the

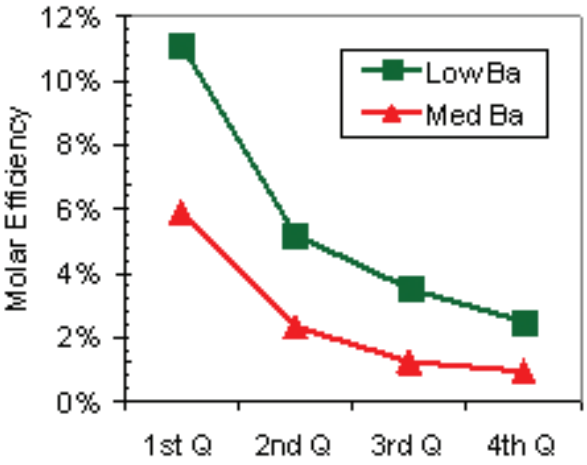

FIGURE 3. Molar Efficiency of the Ba Storage Component of the LNT for the Low and Medium Ba LNTs

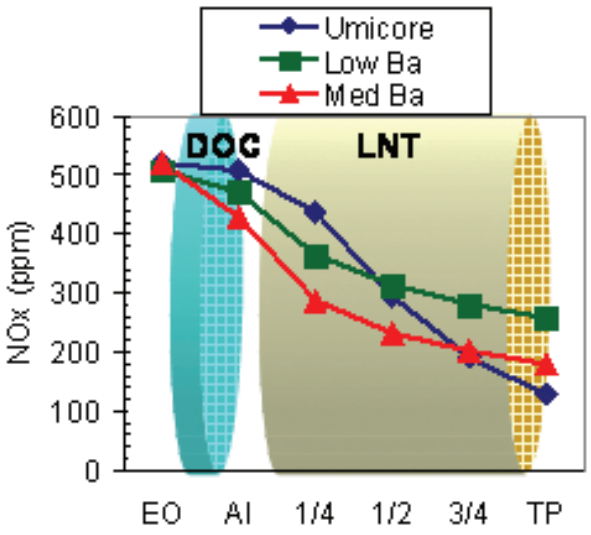

FIGURE 2. Cycle Average NOx Concentration vs. Position in the LNT System for the DEM 60-Second Cycle Condition

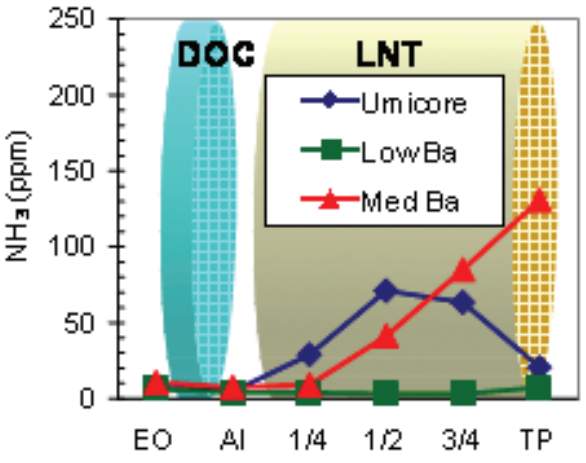

FIGURE 4. Cycle Average NH_3 Concentration vs. Position in the LNT System for the DEM 60-Second Cycle Condition

Medium Ba LNT produced a high amount of NH_3 which is consistent with bench reactor studies that have shown higher NH_3 production with higher Ba loadings [3]. Interestingly, the Umicore LNT produced NH_3 internally in the LNT but consumed the NH_3 in the downstream half of the LNT resulting in relatively low NH_3 emissions at the tailpipe. The downstream consumption of NH_3 is likely due the ceria content of the Umicore LNT. Understanding these NH_3 emissions are important since NH_3 can either (1) be an undesired emission if it exits the tailpipe or (2) be a useful reductant in hybrid systems were an LNT catalyst is combined with a selective catalytic reduction catalyst that reduces NOx with NH_3 catalytically.

Conclusions

- NOx conversion and NOx trapping increased with increasing Ba load.
- Reductant utilization is affected by LNT formulation.
  - The addition of ceria (Umicore LNT) alters the reductant utilization of the LNT and thereby alters the NOx storage as function of LNT position.
- Molar NOx trapping efficiency of the Ba storage component was greater for the Low Ba LNT as compared with the Medium Ba LNT, but trends of NOx sorption through the two LNTs were similar.
- N_2 selectivity decreased (NH_3 emissions increased) with Ba load for the Low vs. Medium Ba model LNTs.
- Although NH_3 was created in the commercial Umicore LNT, tailpipe NH_3 emissions were controlled at a lower level than the equivalent Ba loaded Medium Ba model LNT. The effect of ceria on NH_3 oxidation is the likely mechanism for the NH_3 control.

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II.B.4 Development of Chemical Kinetics Models for Lean NOx Traps

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Objectives

- Identify a set of elementary (microkinetic) surface reactions that can account for the observed behavior of a lean NOx trap (LNT) during both the storage and regeneration phases of operation.
- Optimize the kinetic parameters associated with these reactions by matching model predictions with laboratory reactor data.
- Use the validated reaction mechanism to suggest improvements in the usage of existing LNT materials and to help in the development of a new generation of catalysts.

Accomplishments

- Completed construction and optimization of a thermodynamically consistent reaction mechanism for the precious metal sites on a benchmark LNT catalyst.
- Assembled tentative mechanisms for the NOx storage and oxygen storage sites on the catalyst and formulated the corresponding thermodynamic constraints.
- Using the combined reaction mechanism together with a Chemkin-based transient plug flow code and the Sandia APPSPACK optimization software, carried out a preliminary evaluation of the storage parameters by fitting simulations of full LNT cycles to experimental data from Oak Ridge National Laboratory (ORNL).

Future Directions

- Complete parameter optimization for the combined storage/regeneration mechanism, re-evaluating kinetic constants for the precious metal sites if necessary.
- Introduce reactions needed to describe sulfur poisoning and desulfation.
- Use the validated reaction mechanisms to investigate coupling between an LNT and other devices in the aftertreatment train.

Introduction

The increasingly strict constraints being placed on emissions from diesel and other lean-burn engines require the development of a new generation of aftertreatment technologies. LNTs represent one option for achieving the stated targets with regard to NOx emissions. In an LNT, NOx produced during normal lean engine operation is trapped and stored via adsorption on high-capacity catalytic sites, and periodically this stored NOx is released and reduced to harmless N_2 on precious metal sites by imposing rich conditions for a short time. While this qualitative description is widely accepted, a detailed quantitative understanding of the underlying chemistry is not yet available. Such knowledge is needed in order to use the LNT concept to best advantage, so it is the principal goal of this project to develop an elementary reaction mechanism that describes both phases of LNT operation.

Clearly, a comprehensive kinetics model with the ability to simulate an entire LNT cycle must account for the chemistry occurring on all kinds of catalytic sites: the metal oxide sites used to store NOx, additional oxide sites used (sometimes) for oxygen storage, and the precious metal sites involved primarily in the reduction of released NOx. While it is tempting to associate each of these kinds of sites with a particular phase of LNT operation, it must be remembered that the desorption of NOx from the storage sites is an integral part of the regeneration process, while oxidation of NO on the precious metal sites is thought to be a key part of the storage phase. Nevertheless, it is possible to design experiments that isolate a particular subset of the chemistry, and this has been used to facilitate model development in this project, as described below. The ultimate goal is to obtain a mechanism that can simulate LNT operation over a range of input NOx (NO and/or NO_2) compositions, a range of reductant (H_2 and/or CO) compositions, and a suitably wide range of temperatures.

Approach

The basic approach to mechanism development adopted here is to assemble a candidate set of elementary reactions, often with poorly known kinetic parameters, and then to optimize the parameters by fitting the results of reactor simulations to bench-scale experimental data provided by our collaborators at ORNL. This process requires two principal pieces of supporting software: a reactor code to simulate flow through a single monolith channel using the proposed reaction mechanism (expressed in Chemkin format), and an optimization code to carry out the fitting process on a massively parallel machine. For the former we have used either a steady-state or a transient Chemkin-based plug flow code, as appropriate, and for the latter we have adopted the Sandia APPSPACK code [1], which is ideally suited to this application.

As suggested above, we have found it helpful to split the mechanism development process into two parts. The first relies on a set of steady flow temperature ramp experiments conducted at ORNL. These were carried out with a variety of NOx/reductant and other related input mixtures, the aim being to minimize the possibility of NOx storage and thus to isolate the chemistry on the precious metal sites [2]. These experiments have been simulated with the steady-state Chemkin plug flow code and used to develop a submechanism for these metal sites alone. The second part of the process relies on a set of full cycle experiments using the same catalyst. The analysis in this case involves a complete mechanism with all three kinds of catalytic sites, together with a fully transient plug flow reactor code. At first the precious metal submechanism is fixed, and the storage submechanisms are optimized to provide the best overall fit to the cycle data. Then, if needed, all of the kinetic parameters can be allowed to vary as the complete mechanism is fit to both the cycle data and the temperature ramp data simultaneously.

A significant issue that must be addressed in all of the parameter estimation processes is that not all of the parameters can be varied independently if thermodynamic consistency is to be maintained. Thus, a number of well-defined relationships among the various parameters are enforced; this reduces the size of the optimization problem, but it greatly increases the programming complexity. In addition, all of the activation energies, whether varied independently or computed from thermodynamic constraints, are required for physical reasons to be non-negative. Fortunately, the resulting inequality constraints are easily handled by APPSPACK.

Results

The development of a submechanism for the precious metal sites on our benchmark LNT catalyst has been completed. While a great deal of the work involved in meeting this objective was carried out in FY 2006, a number of issues remained to be addressed this year. Foremost among these was the need to account for a puzzling experimental fact, namely that oxidation of NH_3 produces very significant amounts of N_2O, while reduction of N_2O (by either H_2 or CO) produces no measurable NH_3. Generally, an attempt to reconcile the mechanism with one of these observations tends to destroy its ability to match the other. Our solution to this was to introduce a third-order reaction that allows N_2O to be formed directly from surface fragments that would otherwise form the very stable N_2. While not a perfect solution, either on conceptual grounds or in terms of fitting the data, it seems at this point to be the best option available.

The submechanism ultimately adopted involves 10 gas-phase species, 13 surface species, and 28 surface reactions (all reversible). Thus, it is slightly larger than the preliminary version described last year. Among the reactions are 11 adsorptions, seven surface decompositions, and seven atom transfers. In addition, there are again two alternate pathways for hydrogen production from CO, namely the water-gas shift reaction and a two-step process involving an isocyanate intermediate. This submechanism is quite successful in reproducing the results of all 21 of the steady-state temperature ramp experiments conducted at ORNL. One of the more interesting cases is shown in Figures 1 and 2. These plots show, respectively, the experimental and simulated outlet gas concentrations for the case in which 200 ppm of NH_3 was fed to the reactor along with a large excess of O_2. Unlike the rest of the experiments, this one certainly did not involve reducing conditions,

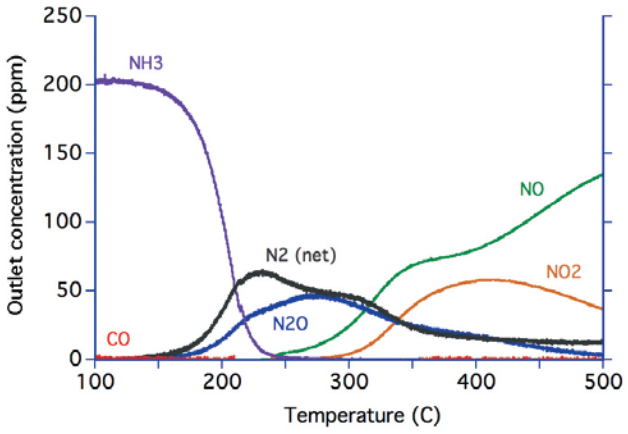

FIGURE 1. Experimental Outlet Concentrations for a Steady Flow Temperature Ramp Experiment with a Feed Stream Containing 200 ppm NH_3 and 10% O_2

so the assumption of no NOx storage can be questioned. However, this may not be a serious issue at steady-state, and the simulation results show that the model is quite capable of reproducing the data even for this unusual case. It remains to be seen whether the inclusion of storage reactions in the mechanism will have a significant effect on the simulated behavior.

Close examination of the computed results for the steady flow temperature ramps shows that the model admits multiple steady-state solutions for some of the cases over limited ranges of temperature. Specifically, multiplicity is found for all of the cases involving reduction of NO or NO_2 by CO. Not surprisingly, it can be shown that this phenomenon is due to the presence of the isocyanate pathway for water splitting by CO. Similar behavior is observed when a fully transient, rather than steady-state, plug flow code is used to simulate the pseudo-steady temperature ramps. An example of this is given in Figure 3, which shows results

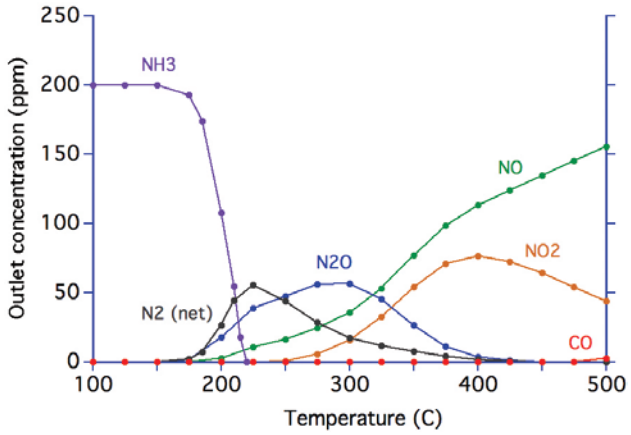

FIGURE 2. Simulated Outlet Concentrations for a Steady Flow Temperature Ramp Experiment with a Feed Stream Containing 200 ppm NH_3 and 10% O_2

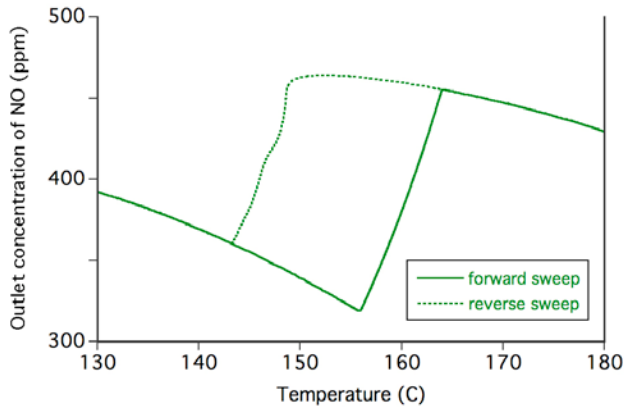

FIGURE 3. Fully Transient Simulations of Steady Flow Temperature Ramps for a Feed Stream Containing 500 ppm NO and 1250 ppm CO

for a feed stream containing NO and CO in a 1:2.5 ratio. The temperature is ramped both upward and downward through the given temperature range, and the previously observed steady-state multiplicity is manifested here as a pronounced hysteresis. While it is not clear that the catalyst would actually exhibit this behavior in practice, the possibility does exist, and certainly the capability of the model to produce unusual results of this kind should be kept in mind.

We have also made significant progress in constructing a complete mechanism involving all three of the catalytic surface phases of the LNT. As noted above, this involves adding to the so-called regeneration submechanism a set of reactions describing storage of both NOx and oxygen, each on its own type of site. The submechanism for the baria (NOx storage) phase involves five kinds of surface species, namely empty sites and adsorbed oxygen atoms, carbonates, nitrites, and nitrates. The first step in the proposed reaction scheme is the dissociative adsorption of oxygen. Reaction of gas-phase CO_2, NO, and NO_2 with the oxygenated sites yields surface carbonates, nitrites, and nitrates, respectively. Nitrites and nitrates can also be formed via displacement of carbonates by NO and NO_2, and nitrites can be oxidized to nitrates via reactions with adsorbed oxygen, carbonates, or gas-phase NO_2. Additional nitrite-forming reactions include direct adsorption of NO_2 on bare sites and spillover from adjacent precious metal sites. By contrast, the submechanism for the ceria (oxygen storage) phase is much simpler, consisting currently of just a single adsorption step.

As noted above, the kinetic parameters for the storage phases are evaluated by fitting transient plug flow simulations that use the complete mechanism to experimental data for complete LNT cycles. In the first round of optimization calculations, the parameters for the precious metal phase are held fixed. Because the surface site densities for all three phases are not known with any accuracy, they are also treated as adjustable parameters. However, they are first mathematically decoupled from the reaction rate terms (as opposed to the capacity terms) in the conservation equations, in much the same way that the activation energies are decoupled from the rate constants. This greatly facilitates the optimization process.

At this point, the model has been fitted simultaneously to data at three temperatures, namely 200°C, 300°C, and 400°C. The experimental [3] and simulated results at 400°C are shown in Figures 4 and 5, respectively. Given the relative crudeness of the storage models and the use of independently derived regeneration constants, the agreement is fairly encouraging. In particular, the slip of NO through the catalyst at the beginning of the regeneration period is reproduced nicely, although the subsequent production of NH_3 is somewhat overpredicted. It should be noted that, among other things, washcoat diffusional resistance

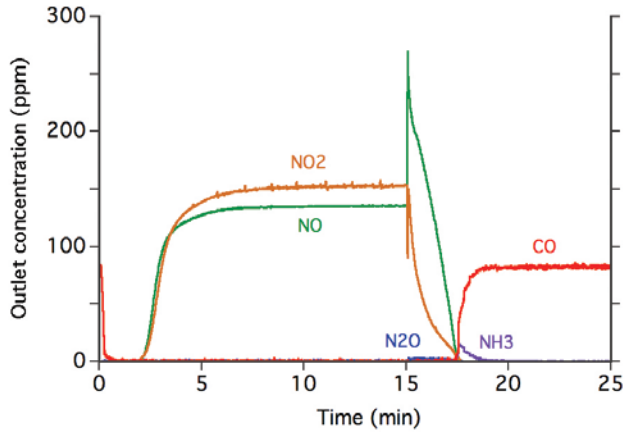

FIGURE 4. Experimental Outlet Concentrations for a Benchmark Long Storage/Regeneration Cycle at 400°C [3]

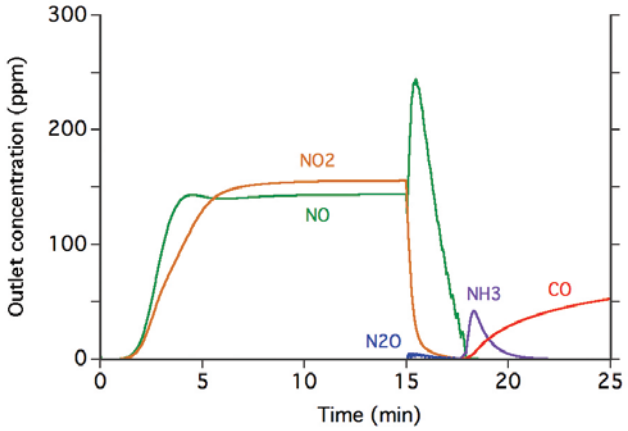

FIGURE 5. Simulated Outlet Concentrations for a Benchmark Long Storage/Regeneration Cycle at 400°C

has not yet been included in the model, so excellent agreement is not to be expected. The incorporation of such phenomena is to be considered in the near future.

Conclusions

- The steady-state behavior of an LNT under reducing conditions can be simulated quite well with an elementary reaction mechanism involving only the precious metal sites of the catalyst.
- Under certain conditions, simulations of LNT regeneration can exhibit multiple steady-state solutions and associated complex transient behavior.
- A reasonably successful storage/regeneration mechanism that incorporates the previously developed precious metal mechanism can be constructed, but further adjustment of the rate parameters will be beneficial.

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II.B.5 Advanced Engine/Aftertreatment System Research and Development

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Ken Howden

Objectives

- Study effects of typical engine variation on a series of fully-formulated lean-NOx trap (LNT) catalysts in bench reactors; variants include temperature, space velocity, lean-rich cycle time and reductant.
- Identify factors limiting NOx conversion during low-temperature operation with CO and hydrocarbon (HC) reductants.

Accomplishments

- Evaluated engine-aged LNT samples in ORNL bench reactor.
- Determined reductant reactivity is the key parameter limiting low-temperature performance of the catalysts studied.
- Established trends in NOx conversion and product selectivity with temperature, space velocity, lean-rich cycle time, and reductant species.
- Provided input for calibration of operating strategies.

Future Directions

Refocus efforts on impacts of NH_3 storage on selective catalytic reduction catalyst performance, particularly at low temperatures and for aged catalysts.

Introduction

Both heavy- and light-duty emissions standards call for significant reductions in NOx emissions by 2009-2010. The LNT catalyst is a promising technology to help meet these stringent new NOx standards, but there are open issues that must be resolved prior to commercialization. Widening the operating temperature range of LNTs is one issue that must be resolved, particularly at the low-temperature end for heavy-duty applications. Another critical area where development is needed is sulfur poisoning and removal. The catalytic components degrade after a series of high-temperature desulfurizations. This degradation has a particularly significant impact on low-temperature operation. Prior work in this CRADA project has used engine experiments with full-scale LNT systems to quantify the activity of various hydrocarbon reductants and to study desulfurization strategies. Efforts during this year shifted to bench-scale experiments and focused on low-temperature LNT operation to better understand the fundamental limitations of the chemistry.

A second focus of the CRADA was to involve use of a unique camless engine prototype with infinitely variable valve timing. Limited resources and revised technical focus precluded activity with the camless engine.

Approach

Efforts during this year focused on developing a better understanding of the factors that limit the low-temperature performance of LNT catalysts. We relied on flow reactor experiments to enable better control over operating conditions than could be achieved in engine operation. Core samples (one inch diameter by three inches long) were cut from engine-aged LNTs and installed in a bench-scale flow reactor at ORNL. The experiments were designed to examine the effects of temperature, space velocity, lean/rich cycle duration, and reductant speciation on overall NOx conversion, reductant conversion, and product selectivity. The catalysts were held at constant temperature and exposed to a simulated exhaust gas stream that cycled rapidly between lean and rich conditions, as is typical for LNT operation. Measurements were performed once the catalyst had achieved pseudo-steady-state cycling (cycle-to-cycle variations in the catalyst effluent were negligible).

Results

Figure 1 illustrates that LNT performance is a strong function of temperature for the conditions used in this study. NOx conversion decreases rapidly below 250°C, with a particularly steep decline between 225 and 200°C. In this and all subsequent plots, space velocity is abbreviated SV, and SV1 < SV2 < SV3 < SV4. Space

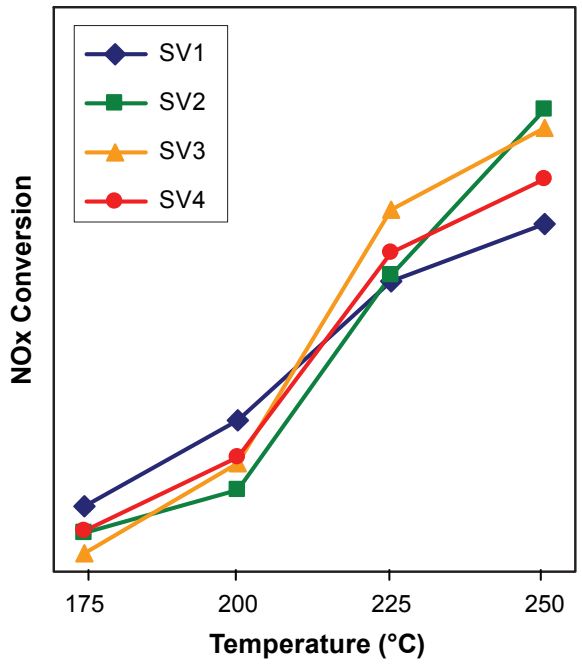

FIGURE 1. NOx Conversion as a Function of Temperature and Space Velocity for a Fully Formulated LNT with CO Reductant

velocity had a much smaller impact on overall NOx conversion than temperature, and the plot does not reveal any clear trends in NOx conversion with changes in space velocity.

Looking at the NOx breakthrough profiles (such as those for SV2 shown in Figure 2) yields additional insight regarding the factors limiting performance. Research on the NOx storage process has determined that oxidation of the NO in the exhaust stream to NO_2 is required to achieve high storage efficiencies. Low NO oxidation activity is often cited as a reason why LNT performance drops off at low temperatures [1]. However, looking at Figure 2, NO_2 can be observed at the catalyst outlet even at the lowest temperature. Thus, NO oxidation activity is not limiting the low-temperature LNT performance.

The flat breakthrough profile at 175°C indicates that essentially zero NOx is stored during the lean phase of the cycle. However, NOx storage capacity increases as temperature decreases, and NO_2 readily stores on LNT catalysts at temperatures as low as 25°C. The observed lack of NOx uptake when there should be significant storage capacity available implies that the catalyst has been saturated with NOx. Thus, the reduced NOx conversion at low temperatures is due to the inability of the reductant species (in this case CO) to regenerate the catalyst during the rich phase of the operating cycle.

The CO conversion trends illustrated in Figure 3 are consistent with limited reductant activity at low temperatures. The CO conversion is relatively high

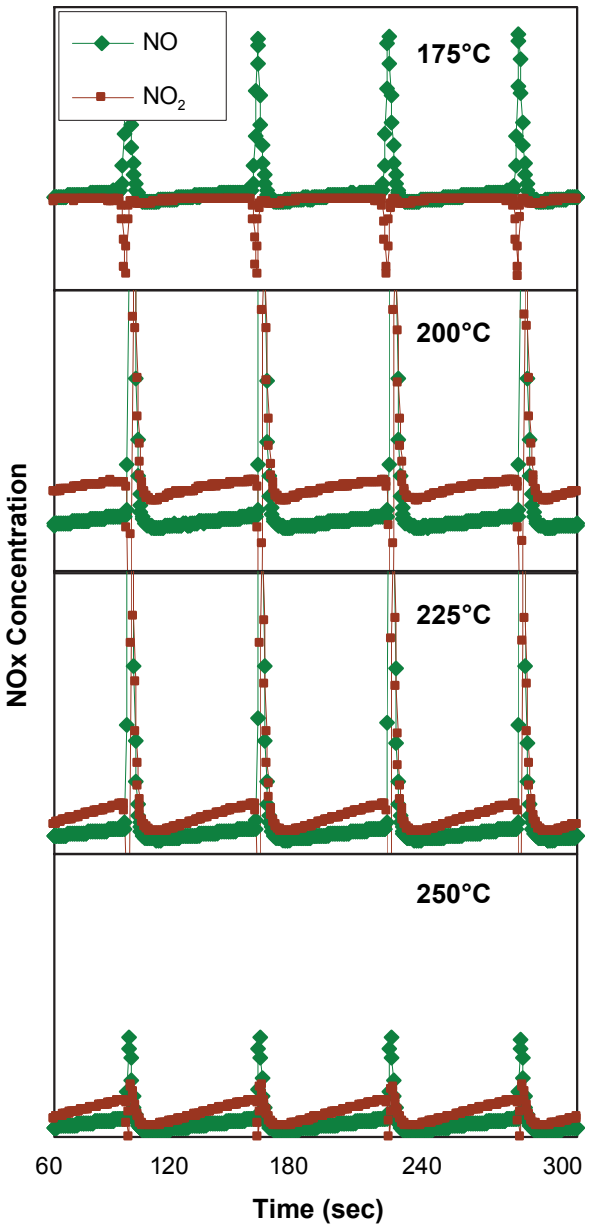

FIGURE 2. Catalyst Outlet NOx Concentrations During Pseudo-Steady-State Cycling at SV2

at 250°C, but drops substantially as the temperature is reduced. Unlike the NOx conversion results, there is a discernable trend with space velocity: lower space velocities lead to higher CO conversion. Interestingly, the CO conversion is higher than what would be expected from the amount of NOx reduced by the catalyst.

Product selectivity during the regeneration phase of the LNT operating cycle was also examined. Figure 4 shows the yield of each of the major nitrogen-atom-containing products for the cases shown in Figures 1 and 3. All cases showed a lack of selectivity to N_2.

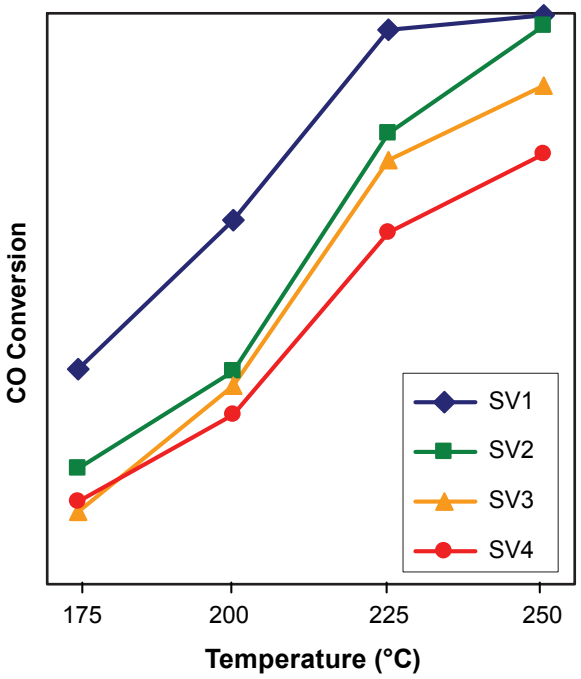

FIGURE 3. CO Conversion as a Function of Temperature and Space Velocity for a Fully Formulated LNT

This is consistent with regeneration product speciation experiments we have conducted previously that showed low temperatures tend to generate a mixture of N_2, N_2O, and NH_3. Formation of NH_3 increased at higher space velocities, while N_2O showed the opposite trend. A possible explanation for these trends can be found in the relative ratios of reductant delivered to NOx stored on the catalyst surface. Since the catalyst was approaching saturation for many of the operating conditions, the amount of NOx stored on the surface was the same regardless of space velocity. However, a higher space velocity results in a larger dose of reductant during the regeneration. The increased reductant will result in a higher ratio of reductant to stored NOx, which has been shown to generate more NH_3 [2]. Alternatively, the increased outlet concentration of NH_3 at higher space velocities could indicate that NH_3 is an intermediate in the regeneration reactions.

Experiments were also performed with propene (C_3H_6) rather than CO as the reductant. Figure 5 shows the NOx conversions at SV1 and SV2 for both C_3H_6 and CO. The performance with C_3H_6 is significantly lower than that achieved with CO for all but the lowest temperature. Considering our previous conclusion that reductant reactivity is limiting the performance for these conditions, it is not surprising that the less reactive C_3H_6 generates lower performance than CO. The corresponding hydrocarbon conversion for the C_3H_6 cases is shown in Figure 6. As expected, the C_3H_6 conversion is lower than the CO conversions shown

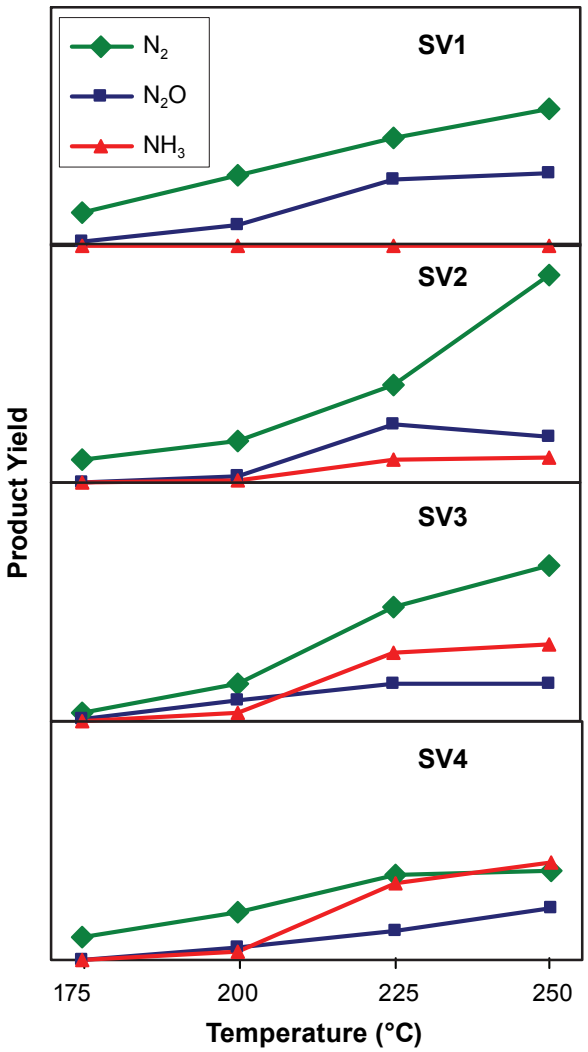

FIGURE 4. Product Yield as a Function of Temperature and Space Velocity for a Fully Formulated LNT with CO Reductant

in Figure 3, confirming the lower reactivity of the C_3H_6 reductant.

Improving the performance of these catalysts at low temperature will require increasing the activity of the reductant. Increasing the amount of H_2 in the reductant mixture could accomplish this goal. Strategies for increasing the H_2 concentration include altering the catalyst formulation to increase the water-gas shift and/or HC reforming activity, incorporating an upstream reformer catalyst, or changing engine operation to alter the exhaust chemistry.

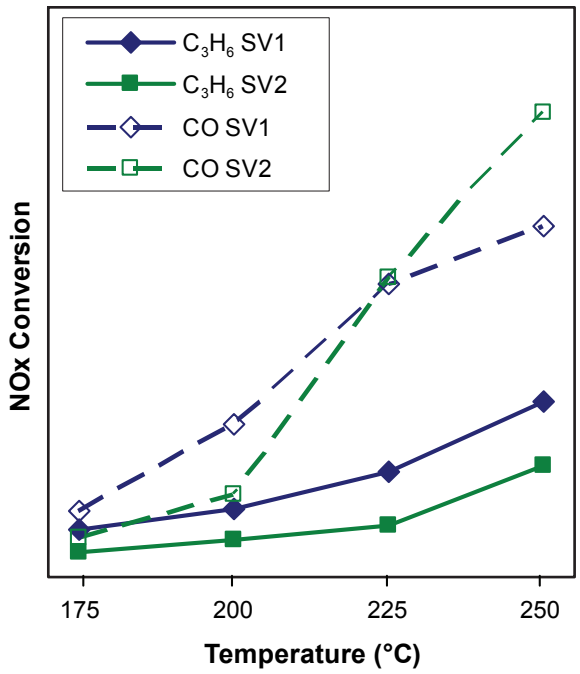

FIGURE 5. NOx Conversion as a Function of Temperature and Space Velocity for a Fully Formulated LNT with C_3H_6 reductant

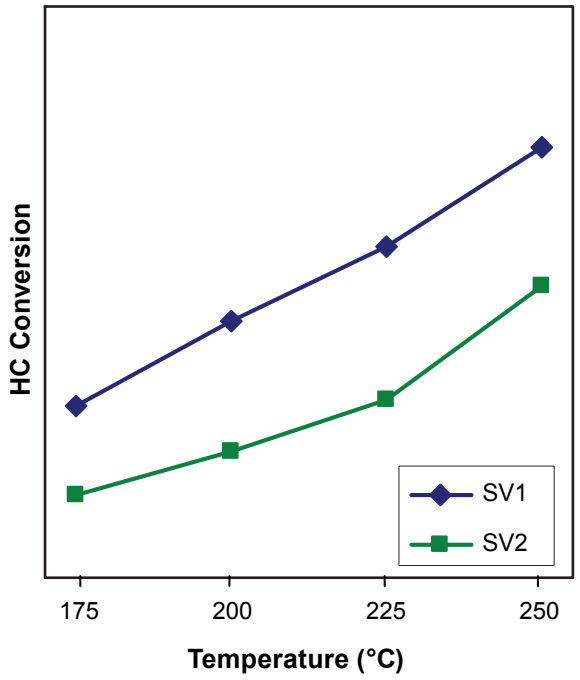

FIGURE 6. Hydrocarbon Conversion as a Function of Temperature and Space Velocity for a Fully Formulated LNT with C_3H_6 Reductant

Conclusions

A series of engine-aged LNT samples have been evaluated in ORNL bench reactors. The focus of the effort was to measure the low-temperature NOx conversion and product selectivity while using either CO or HC reductants. Specific conclusions include:

- LNT performance with CO reductant drops off rapidly below 250°C.
- The drop in performance at low temperatures is due to low reactivity of the reductant species and the associated inability to completely regenerate the catalyst.
- Outlet NH_3 concentrations increase at higher space velocities; N_2O formation shows the opposite trend.
- Propene is even less effective than CO at regenerating the LNT at low temperatures.

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II.B.6 Fundamental Sulfation/Desulfation Studies of Lean NOx Traps, DOE Pre-Competitive Catalyst Research

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Objectives

- Provide a better understanding of the fundamental deactivation mechanisms that result during regeneration and desulfation of lean-NOx traps (LNTs).
  - Investigate ways to limit the impact of these mechanisms.
  - Guide models and help design desulfurization strategies that minimize fuel economy losses, sulfur inhibition of NOx activity, and the effects of thermal aging.

Approach

- Conduct pre-competitive LNT research.
  - Allows open dissemination of results and data.
- Study deactivation mechanism fundamentally.
- Evaluate deactivation from sulfur poisoning and de-sulfurization.
  - Use 15 ppm SO_2 to rapidly introduce sulfur.
  - Desulfurize under controlled temperature ramps with realistic exhaust constituents.
- Employ multiple analytical techniques to monitor activity and morphology effects.
  - Investigate surface species reactivity using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).
  - Monitor activity over typical operating range, 200-400°C.
  - Investigate morphological effects.

Accomplishments

- Presented recent efforts at the 20th North American Meeting (NAM), 2007 AIChE National Meeting, and DOE Advanced Combustion Engine (ACE) Merit Review.
- Submitted paper to Catalysis Today.
- Completed full sulfation study on model catalysts.
  - Study indicates temperature of sulfur exposure affects storage process but not desulfurization.
  - Presented at 20th NAM of the North American Catalysis Society and 2007 AIChE National Meeting.
- Completed full sulfation study on commercial LNT. Analysis in progress.
  - Abstract submitted for 2008 International Congress on Catalysis.

Future Directions

- Investigate fast desulfation to potentially drive off weakly bound sulfates before they convert to strongly bound sulfates.
- Determine sulfation/desulfation behavior of mixed model catalysts.
  - Investigate which phases preferentially adsorb/desorb sulfur first.
- Investigate effects of doping storage phase with other alkali/alkaline components to affect sulfate stability.

Introduction

Under future vehicle regulations, the efficiency of a diesel engine system will be correlated to the efficiency of the emissions aftertreatment system since a fuel penalty is sustained to achieve the emissions requirements. Computational modeling is an effective way to improve the efficiency of the emissions control systems, and basing the model on fundamental chemistry is critical for it to be transportable and broadly useful to industry; parametric-based models will not fill the need.

The complex heterogeneous nature of production catalyst washcoats critically obscures research of fundamental mechanisms. Model catalyst materials represent a subset of production materials, but allow isolation of individual fundamental processes. These processes include detailed mechanisms for desorption and poisoning, the existence and role of intermediate species, and NOx reduction details. Hence, this project has primarily employed model catalyst materials for experimental investigation of fundamental catalyst phenomena.

Approach

The emphasis of this project is to improve detailed understanding of mechanisms limiting catalyst performance. We work with catalyst-industry representatives to identify and investigate pre-competitive catalyst performance issues of broad relevance across the catalysis industry. Specific objectives are to improve the fundamental understanding of adsorption, reduction, and poisoning processes and their influence on catalyst morphology. The objectives of this project are consistent with those of the Diesel Cross-Cut Team regarding details of sulfur poisoning and catalyst morphology effects.

Having developed a base knowledge of the model catalysts, we have begun investigations on a commercial catalyst this year. A commercially available Umicore gasoline direct injection LNT catalyst, designated as the sample catalyst by the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) LNT focus group, has been implemented in sulfation studies in the microreactor and DRIFTS reactor. The information gained here will be used to complement efforts under the CLEERS kinetics efforts and Cummins Cooperative Research and Development Agreement.

Results

A sulfation study on a model LNT, $Pt/K/Al_2O_3$, shows the impact of sulfur on NOx stored during the lean phase (6.5 minutes with 300 ppm NO, 10% O_2, 5% CO_2 and 5% H_2O), unconverted NOx released during the rich phase (1 minute 0.56% CO, 0.34% H_2, 5% CO_2 and 5% H_2O), and overall NOx conversion. The NOx stored during the lean phase is the difference between the blank reactor NOx profile and the experimental NOx profile during the lean phase portion only. The unconverted NOx released is calculated from the NOx detected during the rich phase. Figure 1a shows that the NOx conversion during the first four hours of sulfation with 15 ppm SO_2 is not significantly impacted at any of the temperatures. After four hours, conversion decreases steadily, with the rate of deactivation increasing significantly with increasing temperature. Comparison to Figure 1b shows that the loss in conversion is directly related to the lean phase NOx storage at each temperature.

While the deactivation is generally linear and correlated to lean-phase storage for all temperatures, the impact of sulfation on the NOx profiles has a significant temperature variation. Figure 2a shows the complete lean and rich NOx profiles during sulfation at 300°C, and Figure 2b magnifies this profile at the lean to rich transition for the first three hours. It is clear in Figure 2b that the first portion of the NOx profile that is impacted is the NOx "puff" (or the unconverted

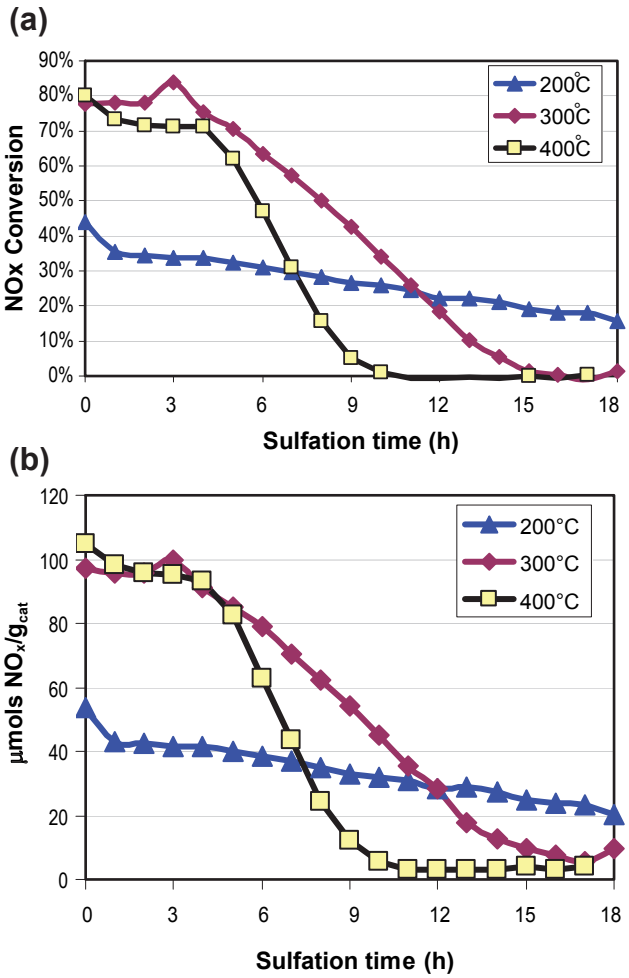

FIGURE 1. Model LNT ($Pt/K/Al_2O_3$): (a) NOx conversion and (b) lean phase NOx storage as a function of sulfation time at 200, 300 and 400°C.

NOx release during rich phase transition) directly after the switch from lean to rich. Based on a hypothesis proposed by several researchers [1-3], this observation suggests that the sulfur is initially poisoning storage sites in close proximity to the Pt and does not migrate away from these sites. Figure 3 shows the similar profiles for sulfation at 400°C. Here it is clear that the lean-phase storage is moderately decreasing during the first three hours while the NOx puff remains relatively constant. Working from the same hypothesis, it suggests that the sites near Pt are remaining free of sulfur; however, since the same processes that happen at 300°C will likely occur at 400°C, it suggests that sulfur is first adsorbing near Pt, but then is migrating away from the sites proximal to Pt.

At 200°C, it is difficult to study the sulfation route with this hypothesis since the release of NOx during the transition is significantly slow to not allow

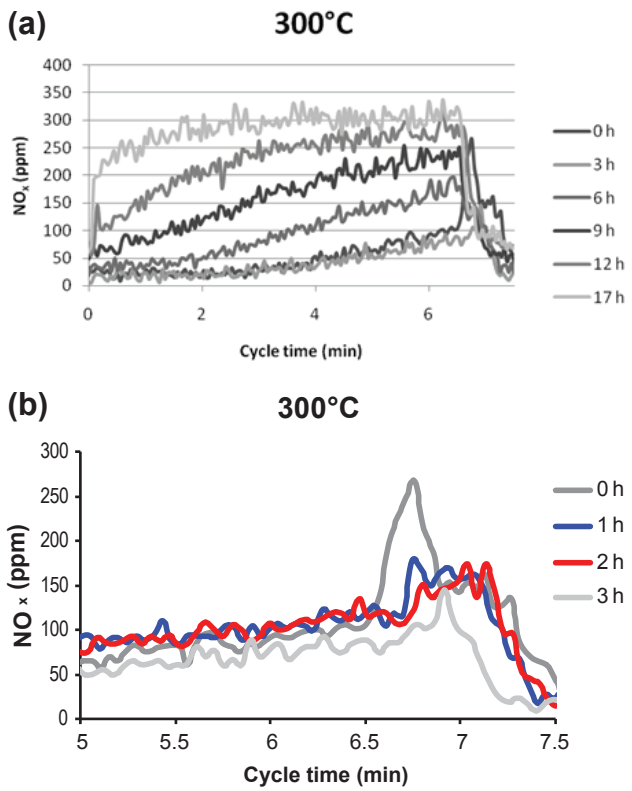

FIGURE 2. Model LNT ($Pt/K/Al_2O_3$): (a) Complete lean-rich NOx profiles at 300°C during sulfation. (b) Profiles during lean to rich transition shows the profiles experience reduction in the NOx puff first followed by decrease in lean phase storage.

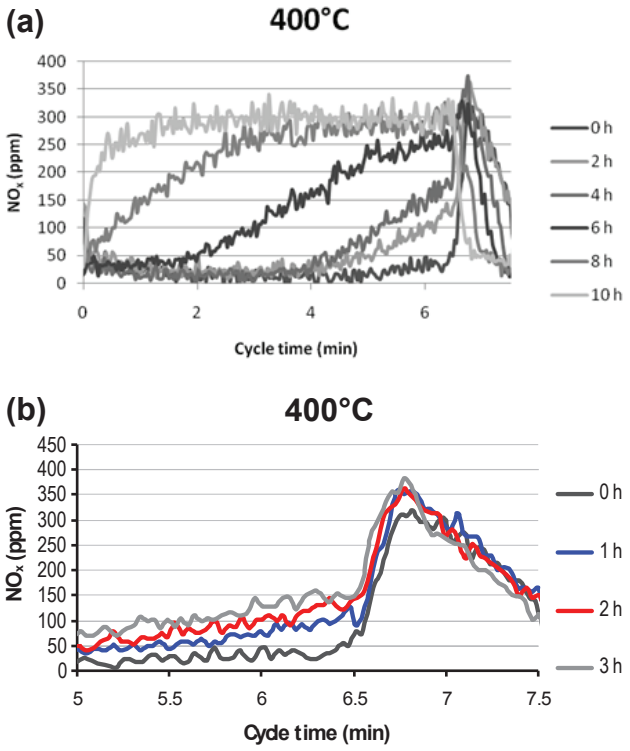

FIGURE 3. Model LNT ($Pt/K/Al_2O_3$): (a) Complete lean-rich NOx profiles at 400°C during sulfation. (b) Profiles during lean to rich transition shows the profiles experience reduction in NOx storage first followed by decrease in NOx puff.

a significant puff (Figure 4a). However, in performing the post sulfation performance sequence, i.e. evaluate performance while decreasing in temperature from 400°C to 300°C to 200°C, an interesting change was observed. Figure 4b shows the NOx profile at the end of sulfation at 200°C and compares it to the profile after heating to 400°C. There is a dramatic impact on the amount of NOx released during the lean to rich transition. To understand this impact it is necessary to draw on some results that were obtained using DRIFTS. We studied the same materials in the DRIFTS reactor and, following sulfation at each of the three temperatures, we heated the catalyst to 500°C while switching between lean and rich conditions. This similar approach showed that, even without the addition of SO_2 in the gas stream, the mild thermal treatment resulted in a loss of NOx capacity on the catalyst at 200°C. This effect is illustrated in Figure 4c, which shows the amount of NOx stored on the catalysts at the end of the lean phase for each sulfation temperature studied. The decrease in stored NOx is apparent at 200°C after heating to 500°C. This effect was minimal, or not observed, in the catalysts sulfated at 300 and 400°C. This observation shows that there must be sulfur stored on a non-potassium based site, i.e. alumina, and upon mild heating the sulfur is released and readsorbed on the potassium sites. To explain the increase in NOx released, it can be surmised that the desulfated alumina is then active for NOx storage. This low temperature NOx storage capacity of alumina has been reported in the past by many groups including our own [4-5]. Following the arguments that we have presented to this point it would follow that the sites being poisoned by sulfur and thus desulfated would be an alumina site proximal to Pt. This would then explain the observations for the profile with a large release of NOx at 200°C. The large release of NOx is observed in this case, rather than on the fresh catalyst, because 200°C is near the maximum temperature at which nitrates are stable on alumina. Therefore, the large release is observed here is analogous to the larger release that K displays at 400°C.

De-sulfurization was performed using a temperature programmed reaction (TPR) procedure with the rich conditions described above flowing continuously. This resulted in sulfur removal in the form of both SO_2 and H_2S for each sulfation temperature. The general shapes of the TPR curves are similar for each condition. The starting sulfation temperatures for each sulfur form as

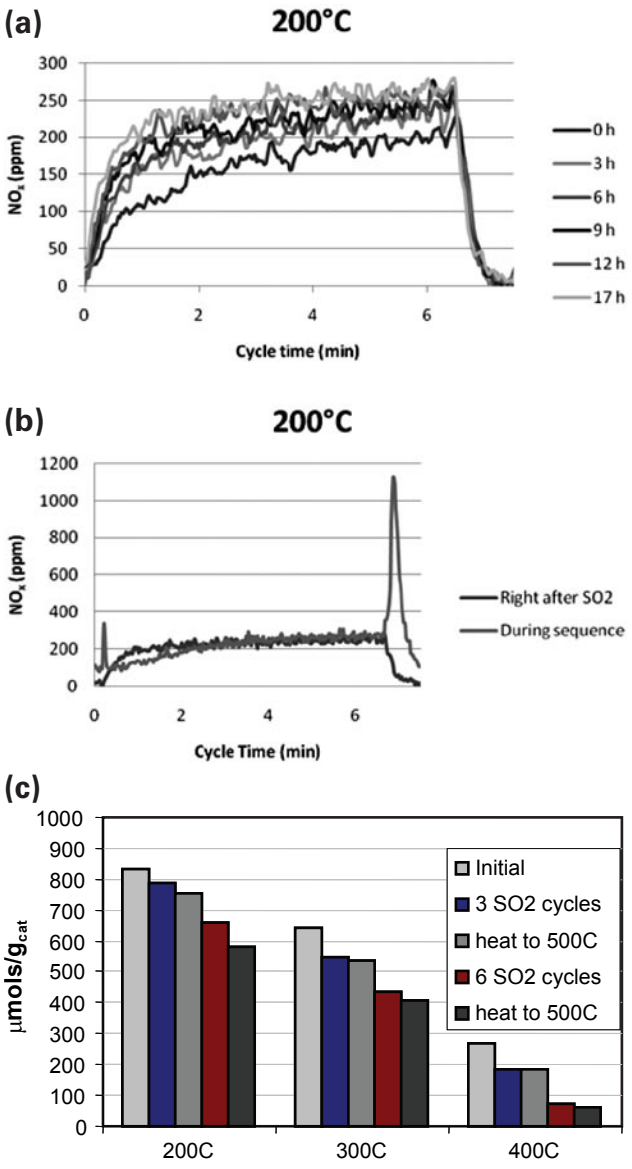

FIGURE 4. Model LNT ($Pt/K/Al_2O_3$): (a) Complete lean-rich NOx profiles at 200°C during sulfation. (b) NOx profiles at 200°C at the end of sulfation and after heating to 400°C then cooling to 200°C. (c) Quantified DRIFT spectra results showing that heating a sulfated catalyst from 200°C to 500°C in the absence of sulfur results in lost storage capacity; results not observed at 300 and 400°C.

well as the temperature of maximum release are listed in Table 1. This tabular comparison illustrates the similarities regardless of sulfation temperature. Further desulfated performance measurements also did not show a significant trend with respect to NOx conversion.

TABLE 1. Temperatures associated with the beginning of desulfation and the maximum sulfur release for sulfation temperatures of 200, 300, and 400°C on a model LNT ($Pt/K/Al_2O_3$).

T_S	200°C	300°C	400°C
De-S Start T			
H_2S	460°C	460°C	450°C
SO_2	460°C	400°C	470°C
De-S max T			
H_2S	690 + 750°C	750°C	735°C
SO_2	780°C	780°C	770°C

Additional efforts this year were focused on applying these techniques to Umicore's commercial catalyst. Figure 5 shows the progression of desulfation in the commercial catalyst is very similar to the general progression observed in the model $Pt/K/Al_2O_3$ LNT; specifically, the loss in activity is closely related to the amount of NOx stored during lean-phase operation (Figure 5b). Further analysis on this effort will be presented in the coming year.

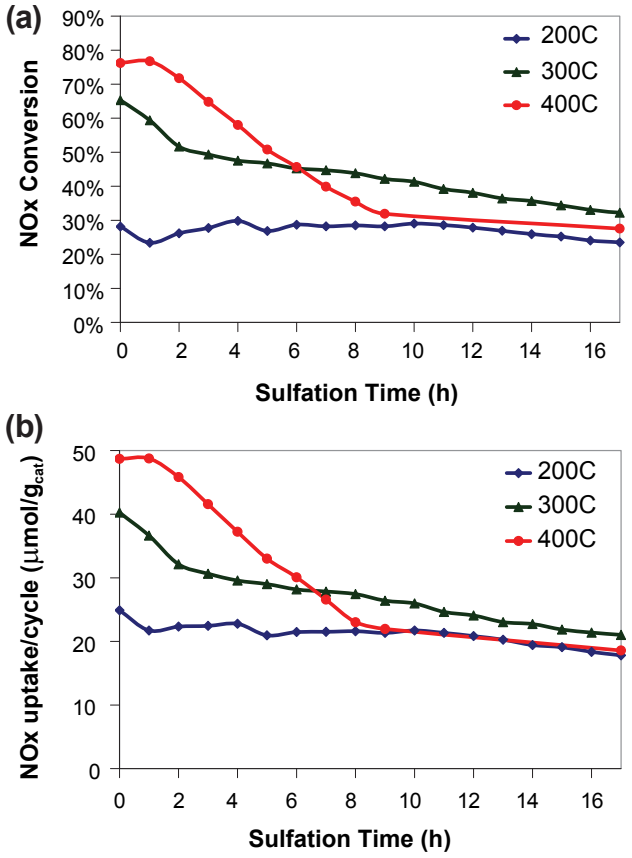

FIGURE 5. Commercial LNT (Umicore): (a) NOx conversion and (b) lean phase NOx storage as a function of sulfation time at 200, 300 and 400°C.

Conclusions

- Sulfation rate differs with temperature.
  - Rate of impact increases at higher temperatures.
  - NOx conversion closely linked to lean phase storage capacity.
- Sulfation routes are temperature dependent. Model catalyst results suggest:
  - Sulfur stored at 200°C migrates upon heating to 400°C.
  - At 300°C, SO_2 adsorbs near Pt before either diffusing to non-proximal sites or simply adsorbing on other sites.
  - At 400°C, if SO_2 adsorbs near Pt it quickly migrates to non-proximal sites.
- Sulfation temperature does not significantly impact de-sulfurization.
  - De-sulfurization temperature and form of sulfur release similar.
  - Sulfation temperature has minimal impact on recovery of NOx conversion activity.

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2. T.J. Toops, J.A. Pihl, "Sulfation and Desulfation Studies of Model Lean NOx Traps", 20th North American Catalysis Society Meeting, Houston, TX, June 2007.

3. T.J. Toops and J.A. Pihl, "Sulfation of Model K-based Lean NOx Trap while Cycling Between Lean and Rich Conditions", submitted to Catalysis Today, August 2007.

II.B.7 NOx Control and Measurement Technology for Heavy-Duty Diesel Engines

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Objectives

- Improve diesel engine-catalyst system efficiency through detailed characterization of chemistry and degradation mechanisms.
- Work with industrial partner to develop full-scale engine-catalyst systems to meet efficiency and emissions goals.

Accomplishments

- Demonstrated real-time on-engine measurements of oil dilution by fuel using a diagnostic developed under this cooperative research and development agreement (CRADA), and showed that results trend with more conventional but slower-feedback off-line measurements.
- Characterized impact of sulfation on the spatial nature of various lean-NOx (LNT) catalyst reactions, and used results to develop a conceptual model of LNT sulfation which explains integral catalyst performance.

Future Directions

- Quantify engine-system nonuniformities and mitigation strategies.
- Quantify selected LNT sulfation effects.
- Investigate selected nitrogen-selectivity issues related to LNT regeneration and hybrid catalyst systems.
- Develop and improve analytical techniques as necessary.

Introduction

Diesel engine technology has advanced significantly over the last decade. Modern diesels utilize advanced injector technology to enable multiple injections of fuel per combustion cycle. Precise control of injection timing allows optimization of efficiency and emissions. One application where the control of fuel injection offers a great advantage is the operation of the diesel engine in net-fuel-rich modes to regenerate LNT catalysts. The regeneration is necessary for catalyst operation which reduces engine-out NOx to regulated levels. During engine operation for catalyst management, extra fuel is injected into the cylinder, often in conjunction with throttling or higher exhaust gas recirculation rates to generate rich exhaust. The reductants present in the rich exhaust regenerate the catalyst, and specific parameters of the engine rich mode are adjusted to control both the overall magnitude and chemistry of the exhaust reductant mixture. However, extra fuel injection into the cylinder can lead to other issues of concern such as torque control, noise and vibration control, and oil dilution. CRADA work has addressed the potential problem of oil dilution that can occur when advanced in-cylinder fuel injection techniques are employed on a diesel engine. In some cases oil dilution can occur at levels that may impact engine durability.

The conventional method for quantifying oil dilution is based on gas chromatography (ASTM D 3524-04), and involves extractive sampling and off-line analysis. Using this methodology, a development engineer would design and run an engine test matrix, collect oil samples and send them out for analysis. The results from each measurement operation point would be received days later, correlated with the real-time performance data collected during the matrix run, and a new matrix designed. Thus, oil dilution analysis represents a significant delay in engine control development. Diagnostics that provide real-time on-engine assessment of oil dilution would significantly streamline the engine control development process. The CRADA has developed such a diagnostic, and evaluated it on a running engine and in parallel with conventional gas chromatographic (GC) methods.

Approach

Laser-induced fluorescence (LIF) spectroscopy is used to rapidly measure the fuel dilution of oil *in situ* on an operating engine. A fluorescent dye, commercially available and suitable for use in diesel fuel and oil systems, is added to the engine fuel. The LIF spectra

are monitored to detect the growth of the dye signal relative to the background oil fluorescence; fuel mass concentration is quantified based on a known sample set. The diagnostic is based on fiber optic probes for excitation light delivery and fluorescence collection; this allows flexibility of sampling location in the engine oil system, and could even be implemented in the cylinder-wall oil film where oil dilution is highest. A low cost 532-nm laser diode is used for excitation. Spectrally resolved fluorescence detection is effected via small fiber-coupled spectrometers. The diagnostic is portable.

The conventional approach for quantifying oil dilution requires off-line, and often off-site, analysis, and thus the oil-dilution data comes in at a significantly slower rate (days) compared to the other performance data. This forces a slow and iterative development process using conventional oil dilution diagnostics. The oil dilution diagnostic developed in the CRADA significantly shortens the engine-development time, by providing on-engine measurement and real-time feedback of the instantaneous oil dilution. This allows real-time tuning of the engine system to optimize the network of performance criteria; e.g., power, exhaust composition, durability, etc.

Results

The oil-dilution diagnostic has been demonstrated on a Mercedes 1.7-liter engine operated on a dynamometer. The timing of a late cycle fuel injection event was varied, as is typical of engine-managed reductant generation for catalyst management; such late-cycle injection often leads to oil dilution. In addition to real-time monitoring of oil dilution via the LIF-based diagnostic, oil samples were collected and analyzed using a modified ASTM method.

Figure 1 shows oil-dilution variations with and without (shaded region) post injection, and for various post-injection timings. The timing of the additional fuel injection for rich combustion operation was varied while holding the minimum air-to-fuel ratio during the rich event constant. The main injection pulse was kept constant, while the additional fuel was added at starting crank angles of 15º, 30º 45º, 60º, 75º, and 90º past top dead center. Results of the conventional GC analysis are also shown. It is apparent from both the LIF and GC methods that oil dilution increases with post injection. The LIF technique has greater precision and sensitivity than the GC technique which allows detection of smaller rates of dilution. Although the LIF- and GC-based dilution trends are similar, the magnitude of reported oil dilution differs by a factor of seven. The most likely explanation for the discrepancy is that the LIF technique is based on the dye which does not evaporate from the oil like fuel components. The LIF technique is most useful in applications where evaporation is of less significance; i.e., as a tool to measure dilution rates so that engineers can rapidly obtain feedback for controls development. Observations from this engine work leads to guidance for engineers to minimize fuel dilution during LNT regeneration strategy development, and is outlined in SAE paper 2007-01-4108 which describes the diagnostic and engine application [1].

Conclusions

- The LIF-based diagnostic provides fast feedback (ca. five min) of oil dilution significantly streamlining engine system development.
- The LIF-based oil-dilution diagnostic accurately trends with conventional off-line ASTM methodology.

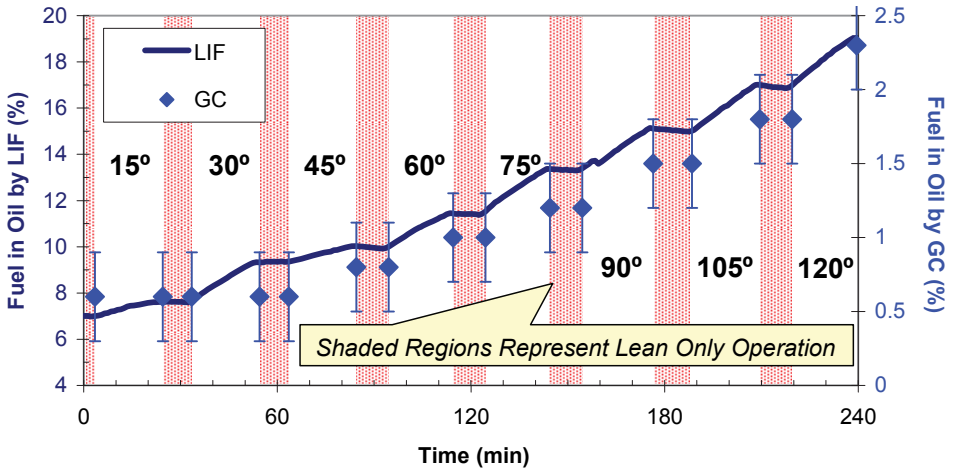

FIGURE 1. Comparison of LIF- and GC-based fuel in oil measurements. The shaded regions represent lean-only operation. Lean-rich cycling caused fuel dilution to occur during periods between the shaded regions.

- Optical probes for the oil-dilution diagnostic provide flexibility of sampling point within the engine system.
- A conceptual model of LNT sulfation effects which explains integral catalyst performance was developed based on detailed intra-LNT measurements.
- LNT sulfation produces a sulfated zone at the catalyst front where NOx storage and regeneration (NSR) reactions are inactive but oxygen storage capacity (OSC) reactions remain active but degraded.
- Sulfation impacts LNT NSR reactions in a plug-like manner and displaces the NSR zone down the catalyst axis.
- Sulfation has a more gradual impact on OSC reactions.
- As sulfation progresses, the NSR zone is continuously displaced down the catalyst axis, in turn shortening the OSC-only zone in the back of the catalyst downstream of the NSR zone; thus, the capacity to oxidize reductants such as hydrogen and ammonia slipping from the NSR region decreases with increasing sulfation, and reductant slip out of the catalyst can be expected.

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1. Jae-Soon Choi, William P. Partridge and C. Stuart Daw (2007). "Sulfur impact on NOx storage, oxygen storage and ammonia breakthrough during cyclic lean/rich operation of a commercial lean NOx trap," Applied Catalysis B: Environmental 77, 145–156; doi:10.1016/j.apcatb.2007.07.025.

2. Bill Partridge, Jae-Soon Choi, Stuart Daw "Distributed Impact of Sulfation on LNT Catalyst Reactions," 10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation, University of Michigan, Dearborn, Michigan, May 2nd, 2007.

3. Jae-Soon Choi, Bill Partridge, Stuart Daw, "Assessing a Commercial Lean NOx Trap Performance via Spatiotemporal Species Profile Measurements: Sulfation & Its Impacts," North American Catalysis Society, 20th North American Meeting, Houston, Texas, June 22, 2007.

4. Jim Parks, Bill Partridge, and Shawn Whitacre, Rapid In Situ Measurement of Fuel Dilution of Oil in a Diesel Engine Using Laser-Induced Fluorescence Spectroscopy, presented at the SAE Powertrain and Fluid Systems Conference in Chicago, IL on October 29–31, 2007.

5. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, C. Stuart Daw, "Sulfur Effects on Spatiotemporal Distribution of Reactions in a Commercial Lean NOx Trap," AIChE National Meeting, Salt Lake City, Utah, November 7, 2007.

Special Recognitions & Awards/Patents Issued

1. The unique value of this CRADA to Cummins' development program, and specifically to the successes related to the 2007 Dodge heavy duty pickup launch, was emphasized in a letter from Dr. John C. Wall, Cummins Vice President and Chief Technical Officer: "The knowledge and tools developed in our CRADA were critical to the R&D efforts that culminated in the release of the aftertreatment technology that meets the 2010 environmental standards in 2007."

2. Patent No. US7,211,793 B2; Date of Patent May 1, 2007; Neal W. Currier and Aleksey Yezerets, Cummins Inc., Mass spectrometry system and method.

II.B.8 Efficient Emissions Control for Multi-Mode Lean DI Engines

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Objectives

- Assess the relative merits of meeting emission regulations via catalytic aftertreatment or advanced combustion for engines capable of operating in multiple combustion modes ("multi-mode" engines).
- Determine the fuel efficiency of combinations of catalytic aftertreatment and advanced combustion modes.
- Characterize exhaust chemistry from advanced combustion and the resulting evolution of chemistry in catalysts for emissions control.

Accomplishments

Compared emissions and fuel efficiency for lean-NOx trap (LNT) catalysis with three combustion modes: no exhaust gas recirculation (EGR), production level EGR, and high efficiency clean combustion (HECC).

Future Directions

- Continue engine-based study to assess combination of LNT catalysis for HECC and traditional modes.
- Examine ability of catalysts to control increased carbon monoxide (CO) and hydrocarbon emissions from advanced combustion modes.

Introduction

New combustion regimes are being investigated as a means to increase the efficiency of, and to reduce the emissions from, diesel engines. The reduction of emissions during combustion is beneficial to the fuel efficiency of the system as a whole (engine plus emissions control system or "aftertreatment"). Specifically, lower engine-out NOx emissions can remove some burden from post-combustion emissions controls, and can thereby reduce the fuel penalty associated with NOx reduction. Although new combustion techniques have been developed that offer advantages for both engine fuel efficiency and emissions, often the techniques are not attainable over the entire range of load and speed required. Thus, engines seeking to implement the new combustion techniques often operate in a "multi-mode" fashion where, at certain loads, the engine is operated with advanced combustion techniques and, at other loads, the engine is operated with more traditional combustion. While modern control systems enable switching between the multiple modes of operation, the optimization of the system for fuel efficiency and emissions becomes more complex. One particular challenge is optimizing the size, cost, and complexity of the emissions control system. This project is aimed at understanding the complex issues of efficiency and emissions management for multi-mode engines with advanced emission control systems. Characterization of combustion exhaust chemistry and catalytic control are conducted to assist industry in the design of multi-mode engine and emission control systems.

Approach

This research has been conducted at ORNL in conjunction with ongoing engine studies. Two related projects at ORNL ("Measurement and Characterization of LNTs," and "Exploring Advanced Combustion Regimes for Efficiency and Emissions" in the Advanced Combustion Engines Program) are being leveraged with this activity. Experiments were performed on a Mercedes-Benz 4-cylinder, 1.7-liter diesel engine that has been significantly upgraded with advanced technologies (variable geometry turbocharger, high-throughput EGR, multi-injection control, etc.) to enable advanced combustion studies. The engine is operated on an engine dynamometer in ORNL's facility. All experiments were conducted at steady-state load and speed conditions which were chosen and weighted for estimating Federal Test Procedure (FTP) drive cycle emissions based on industry input.

LTC is a relatively new combustion mode that enables an order of magnitude reduction in NOx and particulate matter (PM) emissions through high levels of EGR. HECC is a new evolution of LTC that achieves extremely low NOx and PM emissions while maintaining low brake specific fuel consumption; HECC has comparable fuel efficiency to traditional modes [1]. HECC achieves good efficiency and emissions by coupling high levels of EGR with advanced injection timing. Although NOx and PM emissions are reduced in HECC, CO and hydrocarbon emissions increase. Formaldehyde emissions increase as well;

formaldehyde is classified as a mobile source air toxic by the Environmental Protection Agency. Thus, while the emissions control system does not need to reduce NOx and PM significantly during HECC, higher CO and hydrocarbon emission control is needed.

In FY 2006, experiments were conducted in an attempt to reduce NOx via hydrocarbon selective catalytic reduction (HC-SCR). This approach uses excess hydrocarbons emitted during HECC to control the smaller NOx emissions. Despite encouraging results with this approach on a bench-scale flow reactor with simulated exhaust, the results did not translate well to engine experiments, and the HC-SCR was not deemed efficient enough for practical use. This year (FY 2007) efforts shifted to LNT catalysis and focused on comparing fuel efficiencies of the combined engine and emissions control system for three combustion modes: no EGR, production-level EGR, and HECC. The LNT used for the study was provided by a member of the Manufacturers of Emission Control Association and has been used in other studies at ORNL.

Results

The engine was operated at 2.6 bar and 1,500 rpm which is point #2 of the engine set points shown in Figure 1; these load-speed points are representative of operation in the transient FTP driving cycle. With no exhaust emission control, engine-out NOx was reduced by the addition of EGR and by HECC. Figure 2 shows the reduction in NOx obtained by the production level EGR (17%) and HECC; results are shown relative to the 0% EGR case. As shown by Figure 2, HECC offers dramatic NOx reduction (96%) as compared with the significant but modest levels of NOx reduction obtained by traditional EGR levels (23%).

The effect of adding LNT emission control is shown in Figure 3; here the LNT was regenerated every 60 seconds with a 3-second duration of enrichment of exhaust at an air-to-fuel ratio of 13.5. For the 0% and 17% EGR cases, the LNT increased the NOx reduction efficiency significantly but not to desired levels. At the low exhaust temperatures associated with this load point, regeneration of the LNT is difficult and limits the performance in comparison to higher temperatures where >90% NOx reduction efficiencies can be achieved. HECC operation already reduced NOx by 96% relative to 0% EGR at the engine-out position, and the NOx reduction efficiency was actually reduced by the LNT to

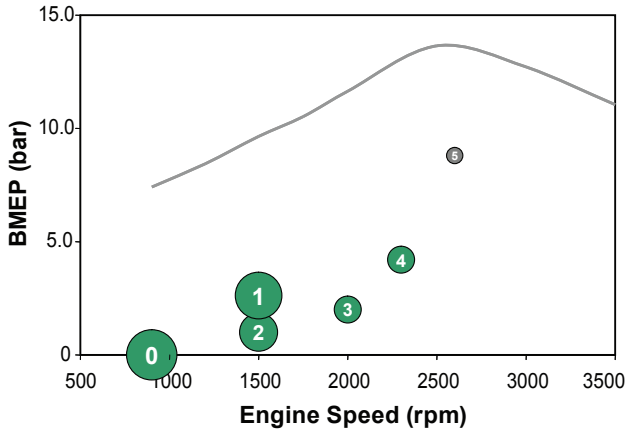

FIGURE 1. Steady-State Points for FTP Simulation on the Engine Load vs. Speed Map

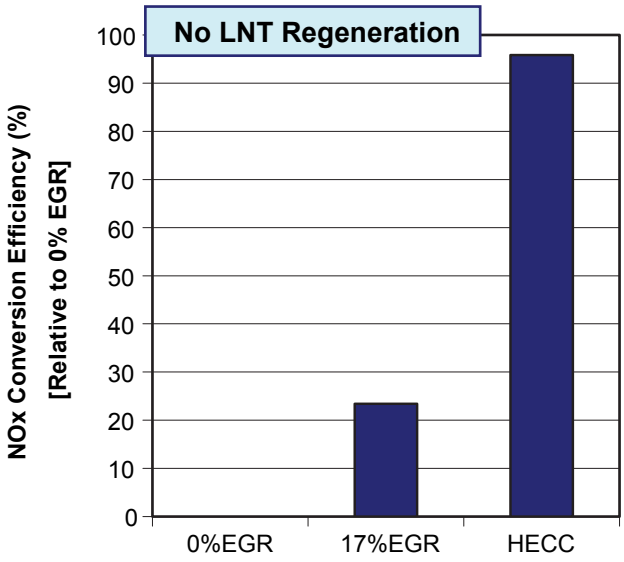

FIGURE 2. NOx Conversion Efficiency for Production EGR (17%) and HECC Relative to No EGR

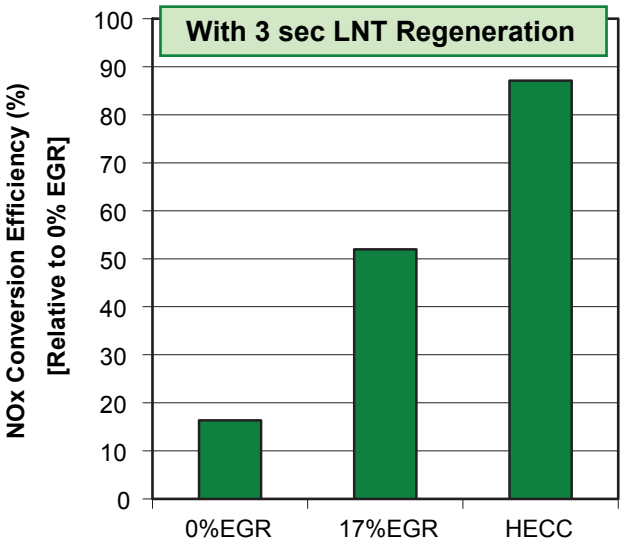

FIGURE 3. NOx Conversion Efficiency with LNT Emission Control at 3-Second Duration Regeneration for No EGR, Production EGR (17%) and HECC Relative to No EGR with No LNT Regeneration

87%. The increase in tailpipe NOx emissions was due to emissions of stored NOx on the LNT that occurred during the regeneration event. The reductants in the regeneration event create an exothermic reaction on the catalyst surfaces which can result in some NOx release.

The duration of the LNT regeneration enrichment was reduced to 1 second for the HECC case to further examine the effect of regeneration on NOx emissions during HECC operation; Figure 4 shows the result as compared with no regeneration and the 3 second duration regeneration. The 1 second duration did result in lower NOx emissions and gave 98% NOx reduction as compared to the 0% EGR base case. Thus, a correct amount of regeneration can enable the LNT to further reduce NOx emissions from the already extremely low NOx emissions of HECC operation. Here "correct amount" refers to the amount of reductant delivery to the LNT during regeneration. Larger amounts of reductant (produced during the 3-second duration regeneration) may reduce some stored NOx but can lead to NOx emission from the resulting exothermal desorption of NOx. Smaller amounts of reductant (the 1 second duration case) allow for NOx reduction and LNT regeneration while reducing the exotherm responsible for NOx desorption.

Overall, the advanced HECC mode is more fuel efficient at attaining NOx reduction at this load point. Fuel consumption for HECC is comparable to the 0% EGR case. However, adding LNT regeneration to the 0% and 17% EGR cases with a 3-second duration every 60 seconds entails a fuel penalty of 1%, and the resulting NOx reduction efficiency is much less than obtained with HECC. Thus, at low loads where LNT performance is limited by exhaust temperatures, HECC is favorable to traditional combustion coupled with LNT emission control. Results for higher loads may differ since HECC becomes more difficult but LNT regeneration becomes more efficient; future studies will investigate higher load points.

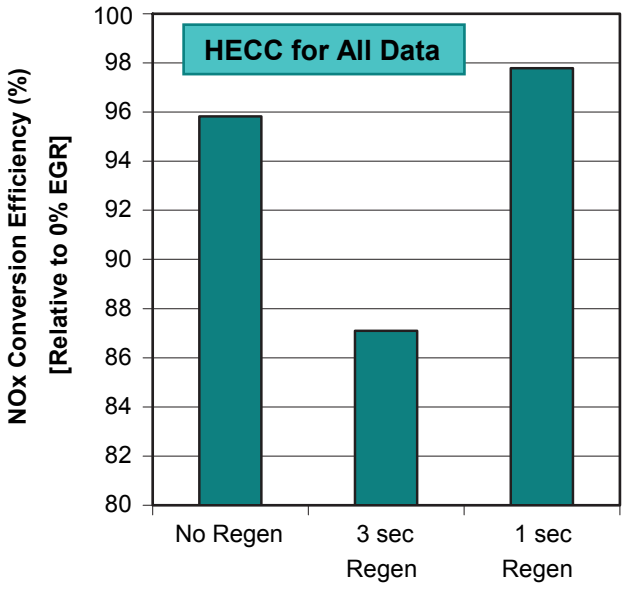

FIGURE 4. NOx Conversion Efficiency for HECC with No LNT Regeneration, 3-Second Duration Regeneration, and 1 Second Duration Regeneration (All Relative to No EGR with No LNT Regeneration)

Conclusions

- At the low load point studied (2.6 bar):
  - HECC enables a 96% reduction in NOx emissions as compared with traditional combustion with 0% EGR.
  - Low exhaust temperatures limited LNT performance by reducing regeneration efficiency.
  - Optimal combined NOx emissions and fuel efficiency are greater for HECC alone than for combined traditional combustion and LNT emission controls.
- Future studies will address higher load points where HECC becomes more difficult to control but LNT regeneration becomes more efficient.

References

1. C. Scott Sluder and Robert M. Wagner, "An Estimate of Diesel High-Efficiency Clean Combustion Impacts on FTP-75 Aftertreatment Requirements", *SAE Technical Paper Series* 2006-01-3311 (2006).

FY 2007 Publications/Presentations

1. Matt Swartz, Shean Huff, James Parks, and Brian West, "Intra-Catalyst Reductant Chemistry and NOx Conversion of Diesel Lean NOx Traps at Various Stages of Sulfur Loading", *SAE Technical Paper Series* 2006-01-3423 (2006).

2. Josh A. Pihl, James E. Parks II, C. Stuart Daw, and Thatcher W. Root, "Product Selectivity During Regeneration of Lean NOx Trap Catalysts", *SAE Technical Paper Series* 2006-01-3441 (2006) (*Selected for SAE 2006 Transactions*).

3. Jim Parks, Shean Huff, Matt Swartz, and Brian West, "Comparison of LNT Catalyst Performance with In-Cylinder Regeneration Techniques", *Presentation at the 10th DOE Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop* in Dearborn, MI on May 1–3, 2007.

4. Jim Parks, Shean Huff, Mike Kass, and Brian West, "Lean NOx Trap Formulation Effect on Performance with In-Cylinder Regeneration Strategies", *Poster Presentation at the 13th Diesel Engine-Efficiency and Emissions Research (DEER) Conference* in Detroit, MI on August 13–16, 2007.

5. Jim Parks, Shean Huff, Mike Kass, and John Storey, "Characterization of In-Cylinder Techniques for Thermal Management of Diesel Aftertreatment", *SAE Technical Paper Series* 2007-01-3997 (2007).

6. Jim Parks, Brian West, Matt Swartz, and Shean Huff, "Characterization of Lean NOx Trap Catalysts with In-Cylinder Regeneration Strategies", *submitted for the 2008 SAE Congress conference (under review)*.

II.B.9 Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS): Administrative Support

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Objectives

Coordinate the CLEERS activity for the Diesel Cross-Cut Team to accomplish the following:

- Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and associated emissions controls.
- Promote development of performance models for emissions control components such as exhaust manifolds, catalytic reactors, and sensors.
- Provide consistent framework for sharing information about emissions control technologies.
- Help identify emissions control R&D needs and priorities.

Accomplishments

- Continued co-leading the CLEERS Planning Committee and facilitation of the Selective Catalytic Reduction (SCR), Lean-NOx Trap (LNT), and Diesel Particulate Filter (DPF) Focus Group teleconferences with strong domestic and international participation.
- Continued co-leading the LNT Focus Group and refinement of the standard LNT materials protocol.
- Identified key R&D priorities from CLEERS community, including coordination of R&D priorities survey with response from 14 DOE Diesel Cross-Cut Team companies and their partners in January, 2007.
- Provided regular update reports to the DOE Diesel Cross-Cut Team.
- Organized the 10th CLEERS workshop at University of Michigan, Dearborn on May 1-3, 2007.
- Maintained website functionalities, security, and data to facilitate web meetings and serve Focus Group interactions.

Future Directions

- Continue co-leading CLEERS planning committee.
- Continue co-leading the LNT Focus Group and support the DPF and SCR Focus Groups as needed.
- Continue providing standard reference LNT materials and data for Focus Group evaluation.
- Continue assisting in refinement of CLEERS technical priorities, especially in regard to the balance between LNT and urea-SCR R&D and synergies between these two technology areas.
- Organize the 11th CLEERS workshop in the spring of 2008.
- Continue maintenance and expansion of CLEERS web site.
- Continue providing regular update reports to the DOE Diesel Cross-Cut team.

Introduction

Improved catalytic emissions controls will be essential for utilizing high efficiency lean-burn engines without jeopardizing the attainment of much stricter U.S. Environmental Protection Agency emission standards scheduled to take effect in 2010. Simulation and modeling are recognized by the DOE Diesel Cross-Cut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity was initiated to promote improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. Specific activities supported under CLEERS include:

- Public workshops on emissions control topics;
- Collaborative interactions among Cross-Cut Team members, emissions control suppliers, universities, and national labs under organized topical focus groups;
- Development of experimental data, analytical procedures, and computational tools for understanding performance and durability of catalytic materials;
- Establishment of consistent frameworks for sharing information about emissions control technologies;

- Recommendations to DOE and the DOE Cross-Cut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is involved in two separate DOE-funded tasks supporting CLEERS:

- Overall administrative support; and
- Joint development of benchmark LNT kinetics with Sandia National Laboratories and Pacific Northwest National Laboratory.

Approach

In the administrative task, ORNL coordinates the CLEERS Planning Committee, the CLEERS Focus groups, CLEERS public workshops, and the CLEERS website (http://www. cleers.org). The specific activities involved include:

- Coordination of the CLEERS Planning Committee and the LNT Focus Group;
- Organization of the annual CLEERS public workshops;
- Maintenance of the CLEERS web site;
- Preparation and presentation of status reports to the Cross-Cut Team; and
- Response to requests and inquiries about CLEERS from the public.

Results

The 10th CLEERS workshop was held May 1–3, 2007 at the Dearborn campus of the University of Michigan. As with previous workshops, there were more than 100 registrants from emissions controls suppliers, universities (both foreign and domestic), software vendors, and consultants. The three traditional emissions control technology areas (LNTs, DPFs, and SCR) were highlighted as well as topics related to systems integration and component interactions. The technical program and presentations are available on the website (http://www. cleers.org) under the 10th workshop heading. Key observations coming from the workshop include:

- Integration of LNTs with NH_3-SCR continues to be a promising possibility.
- Kinetic mechanisms for LNT simulation continue to improve.
- Reliable public-domain kinetics for NH_3 storage and hydrocarbon poisoning are still lacking for urea-SCR modeling and simulation.
- Publicly available DPF soot oxidation kinetics continue to be inadequate for low-temperature combustion modes and with unconventional fuels (e.g., biodiesel).
- Integrated system performance (including combinations of diesel oxidation catalysts, SCR, LNTs, and DPFs) continues to increase in priority.

The LNT, SCR, and DPF Focus Groups have continued regular phone/web meetings throughout the year under the new single monthly meeting format adopted last year. So far this new format has worked well. R&D priorities identified by the CLEERS members were updated in an anonymous poll conducted in January 2007 by New West Technologies. Questionnaires developed by the CLEER Planning Committee were sent to 22 organizations (including heavy-duty and light-duty diesel and gasoline original equipment manufacturers, Tier 1 emissions control suppliers, and energy companies) and 64% responded. The results were summarized in a public presentation at the 2007 Diesel Engine Emissions Reduction (DEER) meeting (see Daw et al, 2007) and discussed at length with the Diesel Cross-Cut Team. Highlights from the poll include:

- Diesel respondents recommended that CLEERS-related R&D resources be allocated as: 31% SCR, 29% DPF, 25% integrated systems (IS), and 15% LNT.
- Lean gasoline respondents recommended that CLEERS-related R&D resources be allocated as: 60% LNT, 20% DPF, 16% IS, and 4% SCR.
- For both SCR and LNT technology areas, the top issues/concerns centered on poisoning, thermal aging, and development of improved kinetic mechanisms.

The above results are also summarized in Figure 1. Preliminary analyses of the poll results have been made by the CLEERS Planning Committee and focus group

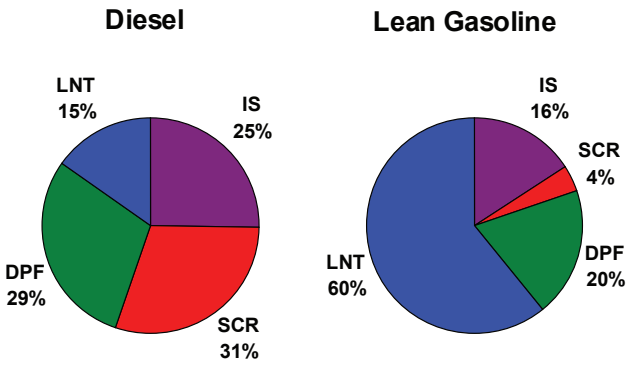

FIGURE 1. Summary of results from the 2007 anonymous poll of DOE Diesel Cross-Cut companies and their partners regarding emissions control R&D resource allocation preferences. Responses were separately averaged for diesel and gasoline responders according to technology area.

leaders to determine where there might be gaps in the current CLEERS-related research activities both in DOE and in industry. This analysis is expected to continue on the basis of a new poll planned for 2008.

Conclusions

CLEERS is playing an increasing role in coordinating emissions control R&D among the Cross-Cut Team members and their partners. The success of CLEERS is most noticeable in the broad industry, national lab, and university participation in the public workshops; the strong domestic and international participation in the monthly focus meetings; the heavy interest in the R&D priority survey among CLEERS community; and the large number of visits to the CLEERS web site.

FY 2007 Publications/Presentations

1. http://www.cleers.org

2. Stuart Daw, Michael Laughlin, and Richard Blint, "Aftertreatment Research Prioritization: A CLEERS Industrial Survey", Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007.

II.B.10 Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS): Joint Development of Benchmark Kinetics

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Key ORNL personnel involved in this activity are Stuart Daw, Kalyana Chakravarthy, Todd Toops, Jae-Soon Choi, Jim Parks, Josh Pihl, and Vitaly Prikhodko.

Objectives

Coordinate ORNL's collaboration with the Pacific Northwest National Laboratory (PNNL) and Sandia National Laboratories (SNL) in the development of kinetics information needed for aftertreatment component simulation through the following:

- Provide benchmark laboratory measurements of NOx reduction chemistry and reaction rates.
- Correlate laboratory measurements of lean-NOx trap (LNT) and selective catalytic reduction (SCR) materials with test-stand/vehicle studies in the NTRC facility.
- Develop and validate global chemistry and (low-order) models for LNT and SCR kinetics.

Accomplishments

- Continued refinement and validation of the LNT material characterization protocol in conjunction with the LNT Focus Group, SNL, and PNNL and collaborating suppliers.
- Initiated benchmarking of Umicore commercial reference LNT material for sulfation and desulfation characteristics.
- Continued in-depth study of the global kinetics of LNT regeneration, with specific emphasis on formation of byproduct N_2O and NH_3, effective fuel penalty, and potential coupling of LNT with SCR.
- Continued diffuse-reflectance infrared spectroscopy (DRIFTS) measurements of the fundamental mechanisms involved in S poisoning and desulfation of LNTs.

Future Directions

- Continue expansion of the ORNL bench-flow and micro-reactor capabilities.
- Continue development and demonstration of methods for utilizing LNT protocol data to generate global reaction kinetics and simulate device-scale performance.
- Continue characterization of Umicore LNT reference catalyst over a range of conditions relevant to both diesel and lean gasoline engine exhaust and transmit results to the LNT Focus Group as they become available.
- Update and post revised LNT kinetic models with input from SNL, literature, and ORNL experimental data as these become available.
- Continue identification of synergies between LNT NH_3 generation kinetics and NH_3-SCR as a potential alternative to urea-SCR NOx control.
- Coordinate bench reactor studies of the impact of sulfation and desulfation on LNT durability and kinetics.

Introduction

Improved catalytic emissions controls will be essential for utilizing high efficiency lean-burn engines without jeopardizing the attainment of much stricter U.S. Environmental Protection Agency emission standards scheduled to take effect in 2010. Simulation and modeling are recognized by the DOE Diesel Cross-Cut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity was initiated to promote improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. Specific activities supported under CLEERS include:

- public workshops on emissions control topics;
- collaborative interactions among Cross-Cut Team members, emissions control suppliers, universities, and national labs under organized topical focus groups;
- development of experimental data, analytical procedures, and computational tools for understanding performance and durability of catalytic materials;

- establishment of consistent frameworks for sharing information about emissions control technologies; and
- recommendations to DOE and the DOE Cross-Cut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is involved in two separate DOE-funded tasks supporting CLEERS:

- overall administrative support; and
- joint development of benchmark LNT kinetics with SNL and PNNL.

Approach

In the benchmark kinetics task, ORNL is collaborating with SNL and PNNL to produce kinetics information for predicting the performance of LNTs as individual devices and integrated with catalyzed particulate filters and ammonia-based SCR. The results of this work are discussed with the LNT, DPF, and SCR Focus groups prior to publication to provide technical review and guidance to the labs. Specific activities involved include:

- Regular direct interactions among ORNL, PNNL, and SNL;
- Experimental measurements of LNT chemistry and reaction rates using laboratory reactors and prototype devices installed on engine test stands and vehicles;
- Analysis and reconciliation of experimental data from different sources with predictions from computer simulations; and
- Publications in journals and presentations in public meetings and on the website.

Results

Studies of LNT kinetics have continued at a high pace as evidenced by the large number of publications and presentations. The reader is encouraged to consult the publications listed at the end of this report for additional details. Briefly, the focus has been on NOx reduction reactions, sulfur capture, and desulfation. The Umicore reference catalyst is of considerable interest because it is specifically intended for lean gasoline applications and because it is the only commercial LNT catalyst available to the CLEERS community with no restrictions on information about its formulation.

A complete set of reaction rate parameters for reducing conditions has been submitted to Catalysis Today for publication (see Larson et al., 2007). These thermodynamically consistent kinetics accurately predict ORNL observations of steady-state conversions of CO, H_2, NO, NO_2, and NH_3 for the Umicore catalyst over a wide range of species concentrations between 200 and 400°C. One interesting aspect of these kinetics is that they appear to predict the possibility of multiple steady-states. The next step is to link these kinetics to previously developed mechanisms for NOx capture in order to simulate the details of complete lean-rich cycles.

Studies of sulfation and desulfation kinetics have utilized the ORNL bench-flow reactor with its associated spatially resolved capillary inlet mass spectrometry (SpaciMS) capability (see Figure 1) and the DRIFTS micro-reactor. It has been found that sulfation proceeds in a sharp front beginning at the leading edge of the monolith and progressing downstream with time. Upstream of the front ceria continues to capture and release NOx, but Ba loses all NOx functionality. The oxygen storage capacity of the ceria is also degraded upstream of the front. Downstream of the sulfation front, NOx capture and release appear to proceed normally. This combined scenario is depicted schematically in Figure 2. One interesting impact of sulfation is to significantly increase NH_3 at the monolith exit.

Conclusions

Closely linked laboratory experiments and modeling have improved understanding of LNT kinetics. This understanding is leading to better simulation of NOx emissions controls in lean exhaust systems and identification of opportunities for reducing the fuel penalty and S poisoning currently limiting full implementation of LNT technology.

FY 2007 Publications/Presentations

1. W. P. Partridge, J.-S. Choi, "Intra-reactor measurements of transient species distributions", Presentation at the Instrumentation, Systems, and Automation Society 2006 Technical Conference, Houston, Texas, October 17–19, 2006.

2. J.A. Pihl, J.E. Parks II, T.J. Toops, C.S. Daw, T.W. Root, "Product Selectivity During Regeneration of Lean NOx Trap Catalysts," SAE 2006-01-3441.

3. R.S. Larson, K. Chakravarthy, J.A. Pihl, C.S. Daw, "Modeling of chemistry in lean NOx traps under reducing conditions," SAE 2006-01-3446.

4. V.Y. Prikhodko, "Effect of Length on the Performance of Lean NOx Traps," M.S. Thesis, University of Tennessee, Knoxville, Tennessee, May 2007.

5. V.Y. Prikhodko, J.-S. Choi, C.S. Daw, K. Nguyen, "Bench Studies of LNT Length Effects," Presentation at the 10th CLEERS Workshop, Dearborn, Michigan, May 1–3, 2007, http://www.cleers.org.

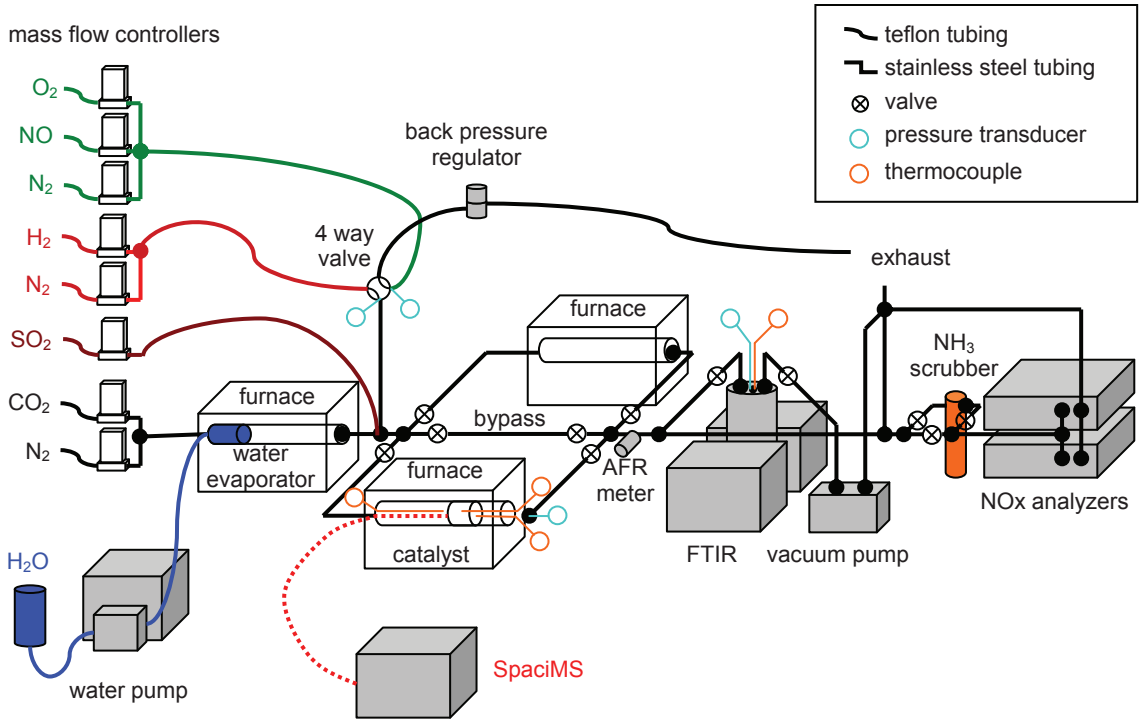

FIGURE 1. Schematic layout of the ORNL bench reactor used for sulfation and desulfation experiments. A SpaciMS capillary is installed for intra-monolith speciation.

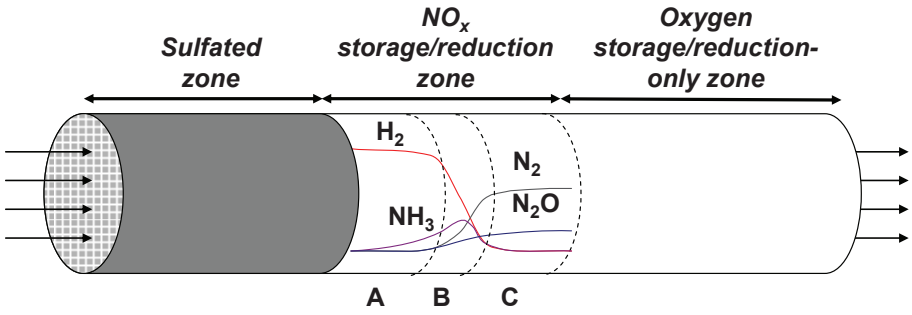

FIGURE 2. Conceptual diagram of the internal reactions occurring inside a partially sulfated LNT monolith. In the sulfated zone NOx capture and release have become deactivated, but some degree of oxygen storage and release is still present. Beyond the sulfation front, NOx capture, release and reduction still occur.

6. J.A. Pihl, C.S. Daw, T.J. Toops, "DRIFTS Investigation of Lean NOx Trap Regeneration," Presentation at the 10th CLEERS Workshop, Dearborn, MI, May 1–3, 2007, http://www.cleers.org.

7. W.P. Partridge, J.-S. Choi, C.S. Daw, "Distributed impact of sulfation on LNT catalyst reactions", Presentation at the 10th DOE Cross-Cut Workshop on Lean Emissions Reduction Simulation, Dearborn, Michigan, May 1-3, 2007, http://www.cleers.org.

8. B.G. Bunting, T.J. Toops, K. Nguyen, H. Kim, "Rapid Thermal Aging of Lean NOx Traps", Presentation at the 10th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, Michigan, May 1–3, 2007, http://www.cleers.org.

9. J. Pihl, "CLEERS Coordination & Development of Catalyst Process Kinetic Data," Presentation at the FreedomCAR Combustion & Fuels Merit Review, June 18, 2007.

10. J.A. Pihl, R.S. Larson, V.K. Chakravarthy, C.S. Daw, "Micro-kinetic modeling of Lean NOx Trap regeneration chemistry," Presentation at the 20th North American Meeting of the North American Catalysis Society, Houston, TX, June 21, 2007.

11. T.J. Toops, J.A. Pihl, "Sulfation and Desulfation Studies of Model Lean NOx Traps," Presentation at the 20th North American Meeting of the North American Catalysis Society, Houston, TX, June 21, 2007.

12. T.J. Toops, B.G. Bunting, K. Nguyen, H. Kim, A.Gopinath, "Effect of Thermal Aging on Catalyst Morphology and Performance of Lean NOx Traps", Presentation at the 20th North American Catalysis Society Meeting, Houston, TX, June 17–22, 2007.

13. J.-S Choi, W.P. Partridge, C.S. Daw, "Assessing a commercial lean NOx trap performance via spatiotemporal species profile measurements", Presentation at the 20th North American Meeting of the North American Catalysis Society, Houston, Texas, June 17–22, 2007.

14. B.G. Bunting, T.J. Toops, A. Foster, N. Ottinger, K. Nguyen "Rapid Aging/Poisoning Protocols for Diesel Aftertreatment Devices: NOx Abatement Catalysts", Presentation at the Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007.

15. J.-S. Choi, W.P. Partridge, C.S. Daw, "Sulfur impact on NOx storage, oxygen storage and ammonia breakthrough during cyclic lean/rich operation of a commercial lean NOx trap", Applied Catalysis B: Environmental 77 (2007) 145.

16. Y. Ji, T.J. Toops, M. Crocker, "Effect of Ceria on the Storage and Regeneration Behavior of a Model Lean NOx Trap Catalyst", Catalysis Letters 119 (2007) 257.

17. T.J. Toops, B.G. Bunting, K. Nguyen, A. Gopinath, "Effect of Engine-Based Thermal Aging on Surface Morphology and Performance of Lean NOx Traps", Catalysis Today 123 (2007) 285.

18. J.-S. Choi, W.P. Partridge, J.A. Pihl, C.S. Daw, "Sulfur Effects on Spatiotemporal Distribution of Reactions in a Commercial Lean Nox Trap," Presentation at the AIChE National Meeting, Salt Lake City, UT, November 7, 2007.

19. T.J. Toops, J.A. Pihl, "Fundamental Investigations of Sulfation and Desulfation in Lean Nox Trap Catalysts," Presentation at the AIChE National Meeting, Salt Lake City, UT, November 7, 2007.

20. K. Nguyen, H. Kim, B.G. Bunting, T.J. Toops, C.S. Yoon, "Rapid Aging of Lean NOx Traps by High-Temperature Thermal Cycling", SAE-07-PFL-227 (2007).

21. R.S. Larson, J.A. Pihl, V.K. Chakravarthy, T.J. Toops, C.S. Daw, "Microkinetic Modeling of Lean NOx Trap Chemistry under Reducing Conditions," Catalysis Today (in press 2007).

22. T.J. Toops, J.A. Pihl, "Sulfation of K-based Lean NOx Trap while Cycling Between Lean and Rich Conditions: I. Microreactor Study," Catalysis Today (in press 2007).

23. Y. Ji, J.-S. Choi, T.J. Toops, M. Crocker, M. Naseric, "Influence of Ceria on the NOx Storage/Reduction Behavior of Lean NOx Trap Catalysts", Catalysis Today (in press 2007).

24. J.-S. Choi, W.P. Partridge, J.A. Pihl, C.S. Daw, "Sulfur and temperature effects on the spatial distribution of reactions inside a lean NOx trap and resulting changes in global performance," Catalysis Today (in press 2007).

II.B.11 Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Diesel Particulate Filter (DPF) Modeling

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DOE Technology Development Manager:
Ken Howden

Objectives

- Develop improved modeling capabilities for diesel particulate filtration:
  - Create improved models of the local properties of the soot filter, e.g. cake permeability, density, and morphology.
  - Develop improved sub-grid representations of the local soot oxidation reactions in diesel soot filters, e.g. oxidation mechanisms, detailed kinetics, and global rates.
- Coordinate and lead the CLEERS DPF sub-team activities:
  - Provide project updates to the industry sub-team, solicit feedback, and adjust work scope accordingly.
  - Lead technical discussions, invite distinguished speakers, and maintain an open dialogue on DPF modeling issues.

Accomplishments

- Added catalytic chemistry to micro-scale DPF models.
- Performed a number of simulation studies including:
  - Effect of particle size on soot deposit location, morphology, and properties.
  - Effect of platinum loading on total oxidation rate in a given pore geometry.
  - Effect of catalyst placement within the DPF wall on overall soot oxidation rate, NOx recycle, and final NO/NO_2 ratios.
- Carried out side-by-side loading and regeneration experiments with individual uncatalyzed and platinum-catalyzed DPF channels.
- Developed techniques for loading individual filter walls with aerosolized salt particles for fundamental filtration studies.
- Participated in monthly CLEERS teleconferences and coordinated the calls focused on DPF technology.

Future Directions

Activities carried out during FY 2007 conclude the original scope of work for this multi-year project. Now that sub-grid simulation tools have been developed which meet the original project requirements, follow-on research will focus on application of these tools and further development in targeted areas. Future activities will include:

- Research into the design and optimization of 4-way devices which address soot, hydrocarbons, CO, and NOx in a single unit.
- Exploration of issues surrounding nano-particulate emissions, including nano-particle detection, identification by size and composition, and prediction of nano-particle formation and behavior in after-treatment systems.
- Filtration and regeneration experiments and simulations to improve prediction of global reaction rates during active and passive regeneration and estimation of device state from sensor data.
- Study of catalyst washcoat placement, morphology, and composition; and effects on back-pressure and species transport during filter regeneration.

Introduction

The inherent fuel efficiency of diesel engines makes them an important part of any global strategy for near-term reduction of greenhouse gas emissions from vehicles. Emissions standards for new vehicles in the U.S., Asia, and Europe require filtration of potentially dangerous soot particles from the exhaust produced by currently available diesel engines. Removal of NOx from diesel exhaust will also be an important consideration as U.S. emission standards are tightened further. In addition to the increased production costs associated with the application of these combined after-treatment technologies, fuel efficiency penalties arise due to increased back-pressure and energy required for system regeneration. Optimization of these systems will require fundamental understanding of all governing mechanisms.

The way in which soot particles interact with substrate microstructures during filtration determines

removal efficiency and back-pressure. Overall back-pressure can also be minimized by prompt and efficient oxidation of soot trapped in the filter, which involves pore-scale transport of heat and active gaseous species such as NO_2. The project described in this report seeks to elucidate pore-scale mechanisms involved in DPF operation in order to promote more effective and reliable DPF devices with a minimum negative impact on fuel economy.

Approach

A computer model has been developed to predict the nature and location of soot deposits within porous filter substrates by simulating the flight and deposition of individual soot particles. The lattice-Boltzmann method is used to solve for the flow field of exhaust through the substrate microstructure as soot deposits form. Figure 1 depicts simulated soot deposits in a small section of a cordierite filter wall (exhaust flows downward through wall along the y axis). Simulations of various DPF substrates, including cordierite and silicon carbide, show how the substrate microstructures affect filtration performance. The micro-scale model also includes the transport of active gaseous species and chemical reactions associated with soot combustion and catalytic oxidation of NO to NO_2. Studies were conducted to examine the effect of substrate microstructure and catalyst location on net rates of soot oxidation.

Experimental methods have been developed to observe the loading and regeneration of external surfaces of individual channels cut from full DPF monoliths. Catalyzed and uncatayzed channels were loaded and regenerated side-by-side and monitored using visible and infrared cameras. Techniques have also been developed to measure fundamental parameters, such as filter wall permeability and channel flow resistance, which are necessary for accurate modeling of DPF performance at the device scale. Individual filter walls were loaded with aerosolized salt particles having a controlled size distribution. Unlike soot, many salts are easily distinguished from filter substrates using techniques such as energy dispersive X-ray spectroscopy (EDS). This may allow experimental characterization of aerosol penetration into filter walls, which has been difficult up to this point.

FIGURE 1. Predicted Soot Deposits in a Cordierite Filter Wall

Results

PNNL participates in CLEERS teleconferences, which occur at intervals of approximately one month, and coordinates the teleconferences which focus on DPF and selective catalytic reduction technology. Participants include original equipment manufacturers, universities, and other national laboratories. Representation by industry and academia has been consistently good, and presentations by various special speakers have sparked helpful and informative discussions on a variety of topics. One benefit of hosting the monthly meeting has been the opportunity to receive continual feedback on the direction of specific CLEERS research activities at PNNL.

Previously developed tools for simulation of DPF performance were applied in various ways over the course of FY 2007 to improve understanding of important phenomena. One example is a study of the effect of particle size on filtration behavior. Figure 2 illustrates the differences in soot deposit consistency and location which can arise as a result of varying particle sizes. Figure 3 shows the predicted relationship between particle size and initial filtration efficiency for a cordierite DPF substrate similar to Corning's Duratrap RC. Large particles are more readily removed from the exhaust by the mechanisms of interception and inertia,

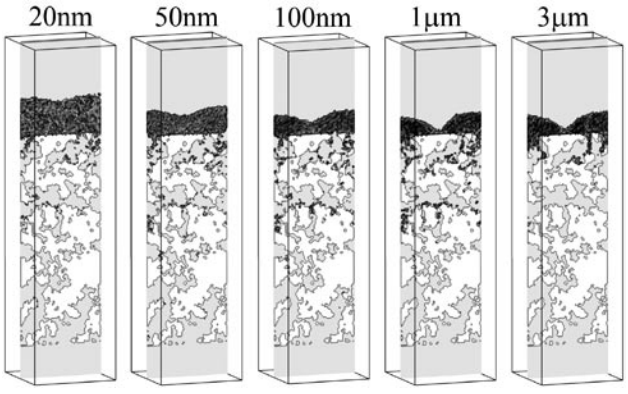

FIGURE 2. Effects of Particle Size on Deposit Location and Structure

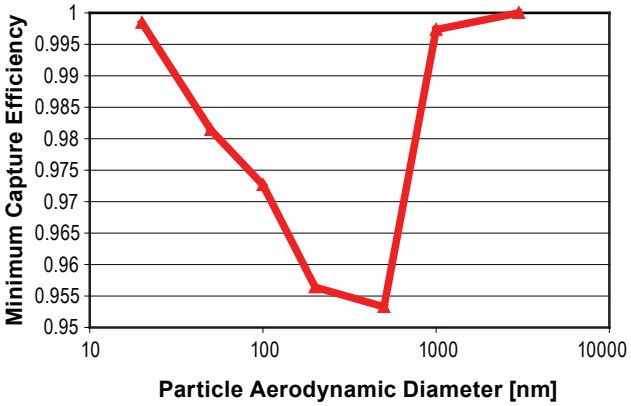

FIGURE 3. Relationship Between Particle Size and Initial Filtration Efficiency

while smaller particles are more readily removed by diffusion. This leads to a minimum efficiency at some intermediate particle size [1]. Predicted minimum removal efficiency for particle diameters lying between 100 nm and 1 µm agrees with experimental data for other types of aerosol filters [1] and other DPF substrates in particular [2].

A key addition to the micro-scale filtration model in FY 2007 was the inclusion of catalytic chemistry for conversion between NO and NO_2, which exist together in some ratio in engine-out exhaust. Soot can be oxidized by O_2 at high temperatures, but the reaction rate drops off rapidly as the temperature decreases. At moderate operating temperatures, the rate of oxidation by NO_2 (resulting in its conversion to NO) is many times faster than by O_2. Placing an oxidation catalyst upstream of the DPF can shift the NOx ratio toward NO_2 while also consuming hydrocarbons and carbon monoxide. Placing similar catalysts within the DPF itself, however, raises the possibility of a given molecule of NOx being used more than once for soot oxidation. How many times the average molecule can be 'recycled' and how this process might be affected by the substrate microstructure are key questions for DPF optimization.

To address these questions, the kinetic model for NOx oxidation presented by Mulla and associates [3] was implemented in the micro-scale simulation program. Soot oxidation kinetics were calculated using the model presented by Messerer and associates [4]. A number of catalyzed soot oxidation simulations were performed both with simple, idealized geometries and with pore geometries corresponding actual DPF substrates. One study examined the effect of catalyst placement on soot oxidation and NOx recycle. In flow-through catalytic devices (such as 3-way catalytic converters used with gasoline engines) most of the precious metal catalyst is typically placed on a base-metal washcoat layer on the substrate wall surface. This has also been the method employed in many catalyzed DPF prototypes. Advanced coating techniques may allow arbitrary placement of various catalysts within the porous substrate microstructure.

Figure 4 shows NO_2 concentration fields resulting from the placement of the same amount of platinum (equivalent to 120 g/ft^3 loading) either evenly throughout the filter wall (Figure 4a) or concentrated in the quarter of wall thickness closer to the upstream face (Figure 4b). It can be seen that the NO_2 concentration in the second case peaks within the porous wall, rather than at the down-stream face. This results in higher average NO_2 concentrations where more of the soot is located and overall soot oxidation rates roughly 30% higher than the case where platinum was distributed evenly throughout the wall. Placing the same amount of platinum in the top eighth of the substrate wall resulted in an overall oxidation rate approximately 39% higher than the uniformly distributed case. These results suggest that concentrating precious metal oxidation catalysts near the loaded surface results in higher soot oxidation rates. This is because the porous filter wall acts to some degree as a barrier to diffusion of active gaseous species generated downstream back to the loaded wall surface. This effect could actually be an advantage for multi-function catalytic systems designed to treat particulates, hydrocarbons, CO, and NOx in a single device, which may involve different catalyst systems on the upstream and downstream faces of a filter wall. In the case where Pt was distributed throughout the wall, the total soot oxidation rate was

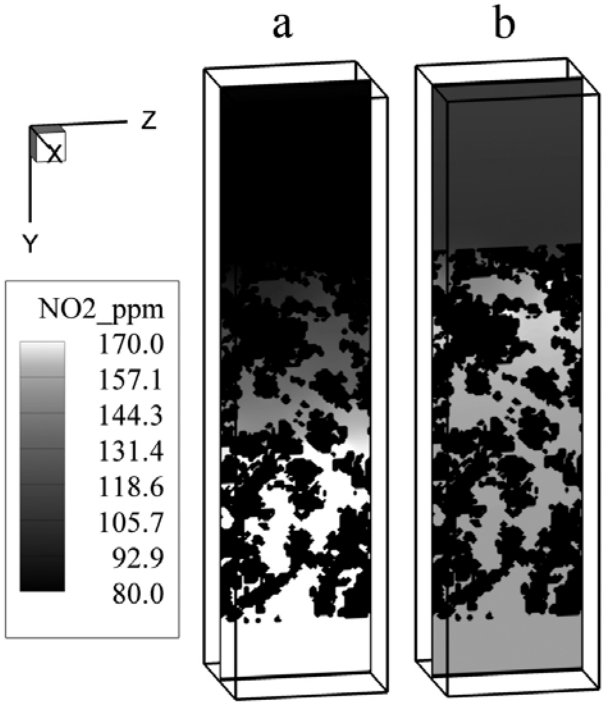

FIGURE 4. Effect of Catalyst Placement on NO_2 Concentration Profiles

nevertheless almost double that in an un-catalyzed wall under the same conditions. Soot oxidation rates were also enhanced at critical pore throats deep within the substrate. Since thick base-metal washcoats at the upstream filter wall surface tend to significantly increase the overall filter back-pressure, it is possible that advanced coating systems making use of more substrate surface area could still prove advantageous in some cases.

A number of experiments have been carried out to support modeling efforts and help provide fundamental understanding of filtration and regeneration mechanisms. Individual channels cut from Pt catalyzed and un-catalyzed DPFs were loaded on their exterior surfaces and regenerated side-by-side in the same exhaust stream. Observations with an infra-red camera showed slightly higher surface temperatures in the catalyzed sample, possibly indicating somewhat higher oxidation rates. The catalyst washcoat led to higher overall back-pressures under all conditions tested. However, at several engine loads, the differential pressure across the loaded catalyzed sample showed a marked downward trend, while that for the uncatalyzed sample held steady. This suggests a significant enhancement in the soot oxidation rate.

Individual filter walls were also cut from several types of DPF monoliths and mounted in a plastic manifold which allowed measurement of flow resistance at various gas velocities. The filter walls were then loaded with aerosolized salt particles. The salt particles are nearly spherical, lacking the complex, fractal structure which complicates fundamental filtration studies using soot particles. The size distribution of the salt particles may be manipulated to conduct parametric studies. Unlike soot, some salts are easily distinguished from filter substrates using EDS. Figure 5 shows an electron micrograph of a fractured filter wall which

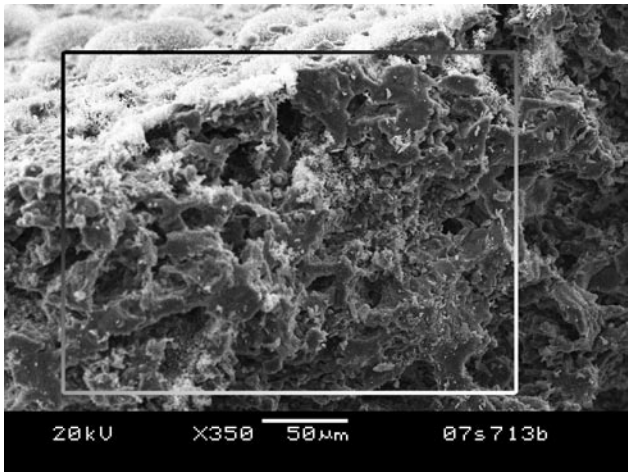

FIGURE 5. SEM Image of a Fractured Filter Wall Loaded with Ammonium Sulfate Particles

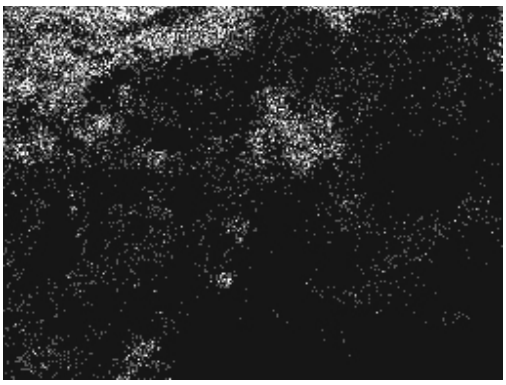

FIGURE 6. EDS Map of Sulfur in the Loaded Wall Cross-Section

has been loaded with ammonium sulfate particles. The loaded surface of the wall is visible in the upper left-hand corner. Figure 6 shows a corresponding EDS map of sulfur in the filter wall cross-section. This technique may allow quantitative measurement of aerosol penetration into the filter wall, which can then be directly compared to model predictions.

Conclusions

- Simulations demonstrate that particle size can have a dramatic effect on backpressure, filter efficiency, and the location and morphology of deposits.
- NOx oxidation catalysts have the greatest impact on soot oxidation when they are located close to the upstream filter wall face, where the majority of the soot is deposited.
- NOx oxidation catalysts distributed through the thickness of a DPF wall do, however, still enhance the overall regeneration rate, particularly increasing soot oxidation rates in critical pore throats deep within the substrate.
- Experiments demonstrate that Pt catalyzed substrates enhance the overall filter regeneration rate, but with only small observable increases in the soot surface temperature.
- Experiments with aerosolized salt particles hold promise for studying fundamental filtration mechanics, particularly the extent of particulate penetration into the filter wall.

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2. Miyairi, Y., et al., *Diesel Particulate Filter (DPF) Trapping Efficiency Improvement Under No-Soot-Layer Conditions Obtained Through Pore Size Distribution Optimization.* SAE, 2006. **2006-01-1528**.

3. Mulla, S.S., et al., *Reaction of NO and O-2 to NO2 on Pt: Kinetics and catalyst deactivation.* Journal Of Catalysis, 2006. **241**(2): p. 389-399.

4. Messerer, A., R. Niessner, and U. Poschl, *Comprehensive kinetic characterization of the oxidation and gasification of model and real diesel soot by nitrogen oxides and oxygen under engine exhaust conditions: Measurement, Langmuir-Hinshelwood, and Arrhenius parameters.* Carbon, 2006. **44**(2): p. 307-324.

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1. Dillon, H.E., M.L. Stewart, G.D. Maupin, T.R. Gallant, C. Li, F. Mao, A. Pyzik and R. Ramanathan. 2007. *Optimizing the Advanced Ceramic Material for Diesel Particulate Filter Applications*. SAE WORLD CONGRESS, Detroit, MI. SAE 2007. **2007-01-1124**.

2. Dillon, H.E., G.D. Maupin, N.T. Saenz, S. Carlson and T.R. Gallant. 2007. *Visualization Techniques for Single Channel DPF Systems*. SAE WORLD CONGRESS, Detroit, MI. SAE 2007. **2007-01-1126**.

3. Male, J. 2007. *Path to 4-way Diesel Emissions Systems*. 10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation, May 1st-3rd, 2007, Dearborn, MI.

4. Saenz, N., H.E. Dillon, S. Carlson and G.D. Maupin. *Advanced Metallographic Techniques Applied to Diesel Particulate Filters.* Microscopy Today, September 2007. **15**(5): p. 44.

5. Stewart, M.L. 2007. *Micro-Scale Simulations of Diesel Soot Oxidation*. 10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation, May 1st–3rd, 2007, Dearborn, MI.

6. Stewart, M.L. 2007. *Micro-scale Simulation of Soot Filtration with ACM DPFs*. Dow Automotive Technical Center, May 3rd, 2007, Auburn Hills, MI.

Special Recognitions & Awards/Patents Issued

1. First Place Winner of the "DuBose-Crouse Award for Unique, Unusual and New Techniques in Microscopy"; 40th Annual IMS/ASM 2007 International Meeting, Fort Lauderdale, FL: Saenz, N., H.E. Dillon, S. Carlson and G.D. Maupin. *Advanced Meatallographic Techniques Applied to Diesel Particulate Filters.*

II.B.12 Innovative Emission Control Renewal

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Objectives

Develop a robust particulate matter (PM) regeneration technique that that allows low engine exhaust temperature regeneration while minimizing:

- Impact on engine operation
- Power consumption
- Incremental cost

Accomplishments

- An external heating technology has been developed that initiates low temperature diesel particulate filter (DPF) regeneration.
- This technology reduces the fuel required for an engine-initiated DPF regeneration as much as tenfold.
- A regeneration architecture and strategy has been developed.

Future Directions

This project was completed in 2007. Continued internal development is being considered. The issues which need further work are:

- Long-term system durability studies are needed.
- Further refinements of the external heater design are needed to optimize the system efficiency.
- Evaluation of DPF materials used with the external heating technology are needed to ensure DPF durability.

Introduction

Diesel and some lean-burn engines generate particulates that exceed regulated standards. However, the lean combustion cycles of these engines also increase overall fuel efficiency. Technologies such as particulate filters are aimed at enabling the use of lean-burn engines, while also ensuring that particulate emissions remain within acceptable limits. The volume of engine-out particulates is sufficiently large that these filters need periodic cleaning (regeneration) to maintain filtration efficiency and keep the device backpressure to a minimum. The commonly used approaches to initiate trap regeneration requires either engine exhaust temperatures of approximately 600+ °C or fuel injection into a diesel oxidation catalyst to reach soot oxidation temperature within the DPF. Both approaches carry a substantial fuel economy penalty for their use. The goal of this project was to develop a low-temperature, robust PM filter regeneration technology that minimizes impacts on fuel consumption and engine operation.

Approach

This project evaluated external heating technologies that could be used to initiate trap regeneration at low engine exhaust temperatures. Two of these technologies were evaluated at both laboratory and engine scales. Both were effective in initiating DPF regeneration. One was selected for additional development based on the lower overall energy consumption. Additional development included:

- Construction of full scale devices.
- Installation of the devices in vehicles for chassis dynamometer testing.
- Determination/evaluation of regeneration conditions with a minimum of added external energy.
- Development of a driving cycle regeneration strategy.

These tasks were all completed within this project.

Results

The externally heated DPF was installed on a fully instrumented vehicle with a complete aftertreatment system. The external heating and the vehicle operation were varied, refined and tested to:

- Develop a fuel efficient DPF regeneration technique.
- Develop a control strategy designed to maintain efficient regeneration under “real world” driving.

- Refine the external heater designs to minimize loads on vehicle.
- Integrate the heater to reduce thermal stress forces within the particulate filter.
- Develop a DPF regeneration strategy to minimize the impact on other exhaust aftertreatment devices.

This approach was successful in developing a low-temperature, externally heated regeneration technology that has a very low fuel economy penalty.

Figure 1 contains a plot of the rapid progress of the DPF regeneration enabled by the use of an external heat source.

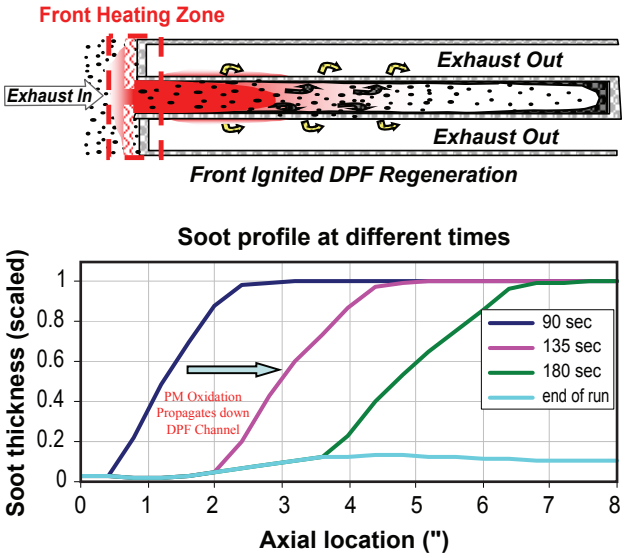

FIGURE 1. Rapid Progress of the DPF Regeneration Enabled by the Use of an External Heat Source

Conclusions

The project team developed a regeneration technique using the downselected external heating technology that provides effective filter regeneration (soot removal) with as much as a tenfold reduction in fuel consumption as compared to existing regeneration techniques currently in use on production vehicles. Major benefits of this technology also include:

- Low tailpipe temperature during the regeneration cycle.
- The ability to complete regeneration cycles in city and under other low-speed driving conditions.
- Regeneration times that are significantly lower than existing technologies. This fact provides the secondary benefit that regeneration has minimal impacts on other important exhaust aftertreatment technologies.

This project has developed a very promising technique for the regeneration of DPFs. The successful deployment of this technology has the potential to reduce the fuel consumed during regeneration cycles as much as tenfold over the prevailing existing approach. Additional work is underway that seeks to optimize the efficiency of the heating system used. Research aimed at expanding the operating range of the developed technique is also ongoing. Finally, research aimed at ensuring the reliability of DPF materials used in the application of this technique has also been initiated.

Special Recognitions & Awards/Patents Issued

The project has submitted over 40 invention disclosures related to this project. Numerous patent applications are in process.

II.B.13 Discovery of New NOx Reduction Catalysts for CIDI Engines Using Combinatorial Techniques

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Subcontractors:
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Accelrys, Inc, San Diego, CA

Objectives

- Develop new NOx selective catalytic reduction (SCR) catalysts that can operate in the lean exhaust of diesel or lean gasoline engines. These catalysts can:
  - Utilize the onboard fuel as the reductant (hydrocarbon selective catalytic reduction, HC-SCR).
  - Have oxides of nitrogen (NOx) conversion activities in excess of 80%.
  - Span the operating range (e.g.; temperature and flow rate) for these lean engines.
  - Have sufficient durability and resistance to poisoning to meet the 120,000-mile standard.

Accomplishments

- Tested over 8,000 materials for NOx reduction potential since the initiation of the project and testing of materials with simulated diesel fuel is the standard.
- Detailed engine testing has evaluated conversions over the Heavy-Duty Federal Test Procedure (HDFTP), Highway Fuel Economy Test (HWFET) and US06 test cycles, sulfur poisoning and fuel effects on coking.
- Phosphorus poisoning studies have been completed.
- Specific formulations for lean gasoline applications have been developed.

Future Directions

Project was completed at the end of the 2007 calendar year.

Introduction

This GM project was initiated 8/16/02. Its goal is to develop new NOx reduction catalysts for lean combustion systems such as both light- and heavy-duty diesels and for stratified charge gasoline engines. These new catalysts are needed to enable these engines to meet the Tier II NOx standards for the North American markets that are being phased in over the time period between 2007 and 2010.

Approach

HC-SCR is the technology that is the focus of development of the new catalytic materials. The approach is to use high throughput technology to develop the new materials (BASF), informatics to mine the data arising from the fast throughput experimentation (Accelrys and GM), classic reactor evaluation to determine the suitability of the new materials for automotive applications (GM) and engine dynamometer testing of full size catalysts.

Results

To date at BASF, over 8,000 new materials have been evaluated on the discovery system since the initiation of the project. Coatings and loadings from materials downselected from the discovery approach have been evaluated on the GM reactor for the effects of poisoning (sulfur and phosphorus poisoning), propensity to coke, thermal aging and potential control strategies. Additionally a wide range of engine dynamometer studies were completed to evaluate the potential of several of these catalysts for production applications.

This technology has been evaluated on the heavy-duty (greater than 18,000 pounds GVW) dynamometer certification cycles which include the HDFTP and the supplementary emissions test (SET). The aftertreatment configuration for this system is a diesel oxidation catalyst (DOC), followed by a fuel injector and then the HC-SCR catalyst. The heavy-duty certification requires NOx/CO/PM/NMHC = 0.2/15.5/0.01/0.14 (g/hp-hr). This is the only certification procedure for vehicles with gross vehicle weight greater than 14,000 pounds

and the engine exhaust is typically hotter for engine dynamometer certification than the chassis certifications. This work demonstrates some issues that will arise for the application of this technology to production drivetrains. The low volatility of diesel fuel makes it difficult to start dosing at temperatures much lower than 300ºC; consequently those initial portions of the test cycles before the exhaust temperature has reached 300ºC and idle conditions will not have reductant supplied to the HC-SCR catalyst. No rapid heat-up strategy was employed for this sequence of tests resulting in NOx conversions for the HDFTP of approximately 60%. For this particular engine, NOx conversions of 60% are not sufficient to reach the 2010 NOx emission standard. It is apparent from the HDFTP test cycles that much of the NOx emissions are arising from the early portions of the test before fuel dosing can be initiated. And so depending on the engine characteristics, a rapid heat-up strategy will most likely have to be employed to reach the emission standards. The SET certification test showed overall NOx conversions of about 65%. Idle (see Figure 1) had low conversions (on the order of 20%) because the exhaust gas temperatures were too low to dose. Four points of the SET test had NOx conversions in excess of 90%, five other points had conversions of 75% to 90% and the remaining three points were 45, 49 and 57% (A75, B100 and C100). Tuning of the engine operating conditions can increase the conversions at those SET points with low conversions. These results give indications of how this technology would perform on the emission standards for a 2010 heavy-duty diesel production application.

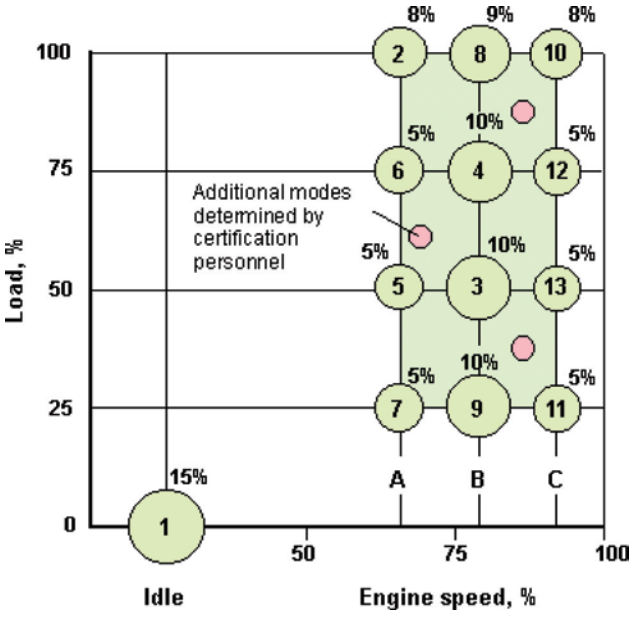

FIGURE 1. Description of the Steady-State Dynamometer Points for the SET Test for Heavy-Duty Diesel Certification

The durability requirement for 2010 production catalysts is 120,000 miles (light-duty) or 450,000 miles (heavy-duty). No long-term engine durability studies were included in this project; however, studies of poisoning and aging for the downselected catalysts were included. All catalysts were hydrothermally degreened at 650ºC for 16 hours before use. Phosphorous, sulfur and carbon are the common poisoning materials. Microprobe analysis of washcoat from an engine-tested full size catalyst piece shows accumulation of phosphorus on the top of the washcoat (Figures 2 and 3). This is a common finding and does not indicate excessive phosphorous poisoning. In addition, a systematic phosphorous loading and activity study was undertaken to provide a quantitative measure of phosphorous poisoning. This lab study also indicated that the catalyst was not especially sensitive to phosphorus poisoning. From this work and activity studies we conclude that phosphorous poisoning is not a major activity loss mechanism for these catalytic materials. Sulfur is found to cause a slow deactivation of the catalyst; however, the catalyst can be regenerated from that deactivation. The sulfur regeneration conditions are much less demanding than the common diesel particulate filter regeneration conditions. Hydrocarbon deactivation of these catalysts can be appreciable depending on temperature and exhaust gas composition. Figure 4 shows examples of very long exposure of the catalyst system to various hydrocarbons in diesel exhaust as a function temperature and exhaust. These exposure times are well in excess of any steady-state engine condition that is likely to be encountered. As can be seen, m-xylene is not a good reductant under most conditions. Long chain alkanes are typically good reductants, but do tend to slowly poison the catalyst surface at temperatures below 350ºC. At temperatures above 400ºC, most of the alkanes do not poison and typically regenerate. Ethanol appears to be a good reductant even at low temperature. In all cases the catalyst is easily regenerable from deactivation from these hydrocarbons.

Conclusions

The encouraging conversion results on the dyno test stand to a large degree have moved this project from new materials discovery for diesel NOx reduction into a product development phase. Much of the discovery work during the latter portions of FY 2006 was used to develop additives to address issues that could arise in applying this technology. Some of the discovery work has been applied to discovering active catalytic materials for lean gasoline NOx reduction.

Evaluation of the effects of sulfur poisoning, coking, phosphorous poisoning and thermal aging at this point do not seem to be a durability barrier for the use of these materials in automotive applications.

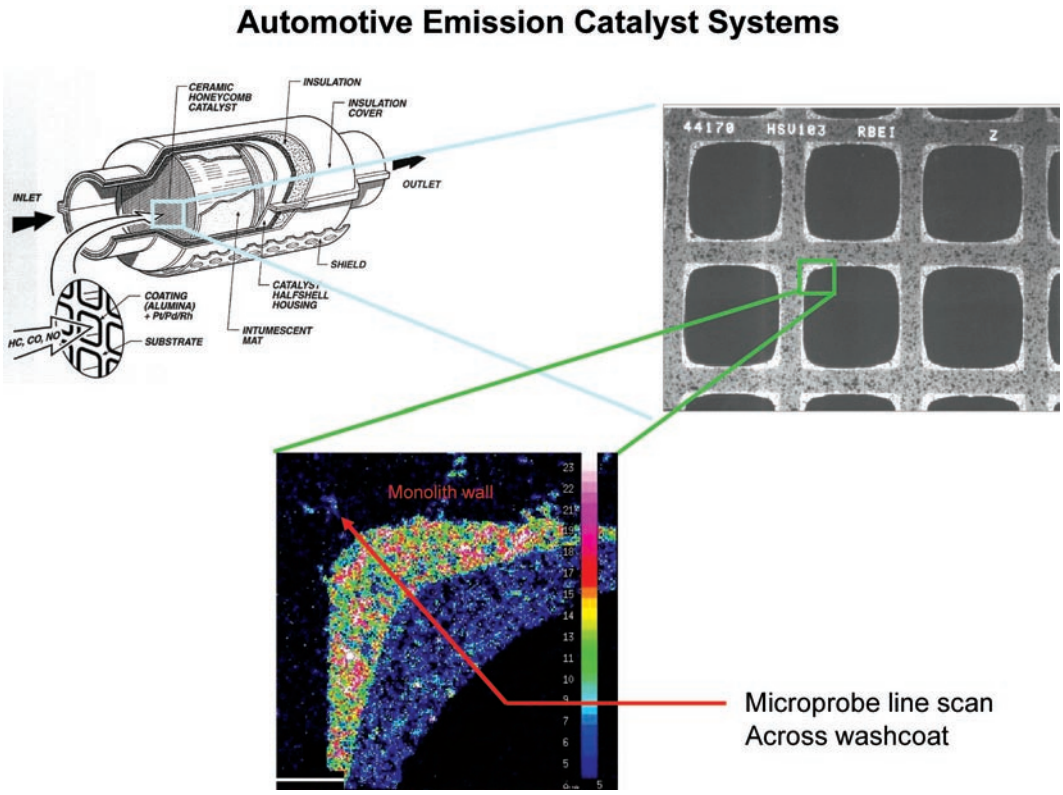

FIGURE 2. Schematic of the Monolith Area where Three Scans Across the Washcoat of an Engine-Tested Catalyst were Analyzed Using Electron Microprobe

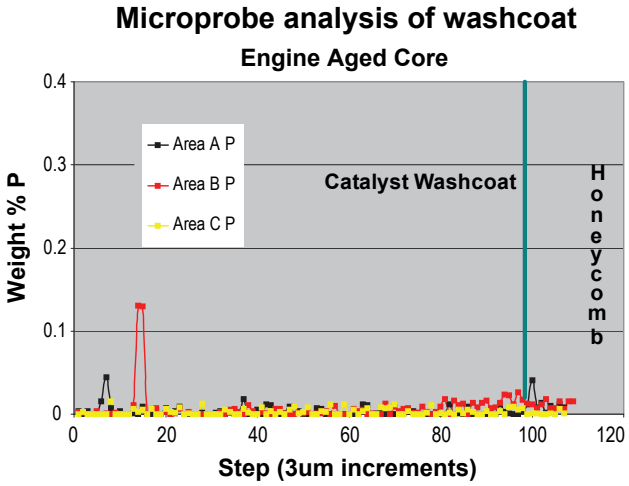

FIGURE 3. Materials Profiles of Phosphorous (P) as a Function of Linear Position for Scans Described in Figure 2

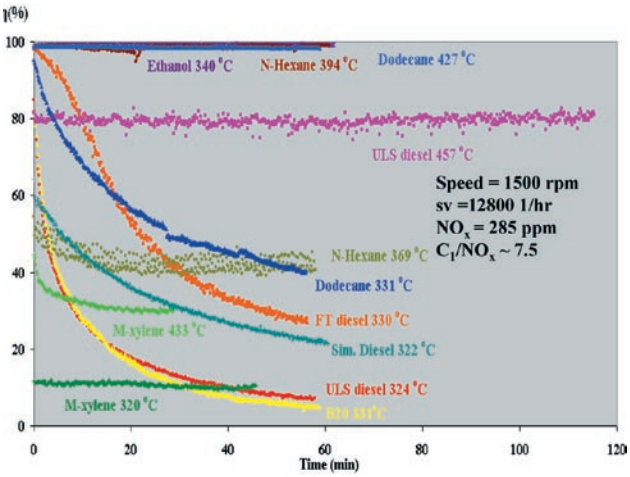

FIGURE 4. Description of NOx conversion (ή) as a function of time using a series of vaporized reductants. ULS indicates ultra-low sulfur fuel, B20 is a standard biodiesel fuel, FT indicates Fischer-Tropsch diesel fuel, and sim-diesel is the model mixture (67 vol.% n-dodecane, 33 vol.% m-xylene) used at GM.

This project is planned to complete in calendar 2007 so that refinements in the active catalytic materials will assist in developing the feasibility analysis planned for the end of the project.

FY 2007 Presentations

1. CLEERS workshop, May 1–3, 2007, Dearborn, MI.
2. DOE Peer review, June 18–19, 2007, Washington, DC.
3. Fall ACS meeting, August 19–23, 2007, Boston, MA.