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.
- Interact with Oak Ridge National Laboratory (ORNL) project aimed at development of 'aging' protocols (Bruce Bunting), and actively participate in the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) lean-NOx trap (LNT) subgroup. This latter activity now includes an additional 3-way collaboration between ORNL (Stuart Daw and coworkers), Sandia National Laboratory-Livermore (Rich Larson), and Pacific Northwest National Laboratory (PNNL).
- Transfer the developing fundamental understanding to industry via the CLEERS activity as well as periodic technical meetings with industry scientists and engineers.

Accomplishments

- Determined the practical significance of our previously discovered two morphological 'forms' of the storage Ba-phase – a 'monolayer' phase and a 'bulk' phase. Notably:
  - the "monolayer" morphology is found to decompose at lower temperature in vacuum and in a reducing atmosphere than "bulk" nitrates;
  - the "monolayer" Ba-phase is also easier to 'de-sulfate';
  - the formation of a high-temperature (deactivating?) $BaAl_2O_4$ phase requires BaO coverages above 1 monolayer; and
  - the morphology model at least partially explains relatively small use of Ba species (often <20%) in storing NOx during typical lean-rich cycling.
- Water was found to have a profound effect on the relative distribution of Ba-species morphologies, but may not be practically important at typical LNT operating conditions.
- Studies provided important information regarding the chemical mechanisms of processes occurring during the rich phase of LNT operation.
- We have identified possible methods for restoring the performance of LNTs deactivated by $BaAl_2O_4$ formation, via controlled water exposures.
- One new invention disclosure, and numerous publications (9), invited talks (5), and other presentations (7) have resulted from this project in the past year (see below list).

Future Directions

- BaO morphology studies
  - Effects of CO_2 and effects of both CO_2 and H_2O on morphology changes during NOx uptake and release. Temperature programmed x-ray diffraction (TP-XRD) studies to be performed at National Synchrotron Light Source (NSLS) as beamtime becomes available.
  - *In situ* transmission electron spectroscopy (TEM) studies to watch morphology changes in real time.
  - Effects of additional catalyst components (e.g., ceria as used in CLEERS Umicore material), and alternative support materials (e.g., MgO and $MgAl_2O_4$).
  - Role of Pt/BaO interface for optimum NOx storage.
- Detailed characterization (e.g., Fourier transform infrared, TEM) of alternative materials.
- Studies of CLEERS Umicore samples.
  - CLEERS performance protocol experiments.
  - Nitrogen balance experiments (mechanism(s) of reductive regeneration).

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 lean-NOx trap, 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 1 and 4 minute duration, respectively, are run and NOx removal performance is assessed after at least 3 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 (4 minutes)", which measures NOx removal efficiencies for the first 4 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 2, 8 and 20 wt% BaO-containing samples, dried at 125°C and then 'activated' via a calcination at 500°C in flowing dry air for 2 hrs. State-of-the-art techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM)/energy dispersive spectroscopy (EDS), Fourier transform infrared (FTIR), Brunauer, Emmett and Teller (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 NSLS, at Brookhaven National Laboratory. The detailed experimental set-up and protocol have been discussed elsewhere [3,4].

Nitrogen Balance Experiments

We also utilize a recently constructed experimental apparatus for conducting nitrogen balance experiments on core samples of monolith-supported LNT catalysts. *As far as we know, our studies represent the only quantitative measurement of nitrogen balance for LNT operation conducted to date* [5]. This year, we have continued studies of a degreened (16 hrs in air at 700°C in 10% H_2O at Oak Ridge National Laboratory) commercial LNT catalyst manufactured by Umicore (provided by Umicore through ORNL as part of the CLEERS activity). This Umicore catalyst contains the precious metals Pt, Pd and Rh (in descending quantities), added ceria and zirconia (for oxygen storage) and BaO for NOx storage.

In prior work, we found for the first time that the reduction of stored NOx by H_2 in a commercial LNT catalyst produces primarily N_2 with smaller quantities of N_2O. For insufficiently long rich periods, the adsorbed NOx builds up until the lean-cycle NOx storage is drastically reduced, degrading the overall performance significantly. Under these conditions, the catalyst never fully removes stored NOx, and NO and NO_2 are observed throughout the entire lean-rich cycle. During overly long rich periods, NOx is never observed but, unfortunately, NH_3 is. Compared to an optimized rich cycle length, similar amounts of N_2 are produced early in the rich period, but its production drops off significantly once the stored NOx is depleted. Thus, the appearance of ammonia is an excellent indication that nitrogen production from stored NOx is complete, and that the optimal rich period has been reached or exceeded. Importantly, the proper choice of the rich period length prevents the production of significant amounts of NH_3 altogether. In our prior studies, a small but noticeable

amount of N_2O was unavoidably produced. In this report, we will emphasize work on other elements of the project.

Results

In last year's report we 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. In this year's work, we have determined 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 [4,6];
- "Monolayer" Ba-phase is also easier to 'de-sulfate' [7];

The morphology cycle of BaO/A_2O_3 in NO_2 in NO

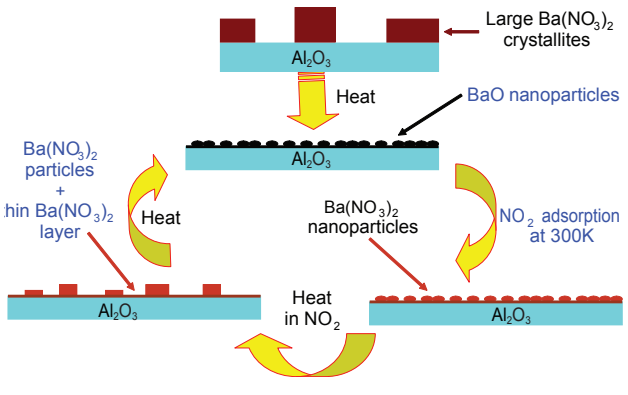

FIGURE 1. Schematics of the cycle of morphology changes taking place during NO_2 uptake and release on BaO/Al_2O_3 NO_x storage/reduction materials.

- Formation of a high-temperature (deactivating?) $BaAl_2O_4$ phase requires BaO coverages above 1 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 also studied the effect of water on these morphology changes (manuscripts in preparation). In the following, we highlight a few of these areas of recent work.

The Effect of Ba-Loading and Water on the Formation and Stability of $BaAl_2O_4$

It is widely reported that BaO and Al_2O_3 react at high temperature (>800°C) to form an aluminate phase, $BaAl_2O_4$ (for example, see [10] and references therein). However, there is considerable disagreement about the effectiveness of the $BaAl_2O_4$ phase for NOx storage. We have studied the effect of barium loading on $BaAl_2O_4$ formation for various BaO/Al_2O_3 samples. As illustrated in Figure 2, 2 (Figure 2a) and 8 (Figure 2b) wt% BaO/Al_2O_3 samples showed essentially no detectable morphological changes upon high temperature thermal treatment, while $BaAl_2O_4$ formation occurred readily for a 20 wt% one (Figure 2c). Because the 8 wt% sample contains approximately just enough BaO to completely cover the alumina surface (*i.e.*, is ≈ 1 monolayer, ML), these results led us to the conclusion that a surface (monolayer) BaO phase is stable to high temperature thermal treatment, while a more 'bulk-like' BaO phase provides the source of Ba for $BaAl_2O_4$ formation.

Recently, Gorte and coworkers [11] reported the formation of a bulk $Ba(NO_3)_2$ phase when NO_2 is adsorbed onto both moderate (~500°C) and high temperature (≥600°C) calcined BaO/Al_2O_3 materials, the latter containing $BaAl_2O_4$ as the primary Ba-containing phase observable in XRD. These authors further claimed that BaO and $BaAl_2O_4$ appear to be equally effective as NOx storage materials, both being able to fully utilize the Ba content to form stoichiometric $Ba(NO_3)_2$ upon NO_2 exposure at room temperature. Although the reaction of $BaAl_2O_4$ with NO_2 and O_2 to form $Ba(NO_3)_2$ is exothermic, to our knowledge this was the first report that such a dramatic phase change could occur upon room temperature NO_2 adsorption. However, the authors do acknowledge possible uncharacterized effects of H_2O on their results. Considering the importance of barium phases as active sites for NOx storage, we investigated these processes in more detail [10] with specific emphasis on the effect of NO_2 adsorption and subsequent water treatment on the phase changes of $BaO(x)/Al_2O_3$ (x = 8 and 20 wt%) materials by using XRD and solid state ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR). Furthermore, we followed the changes in NOx adsorption capacity of the

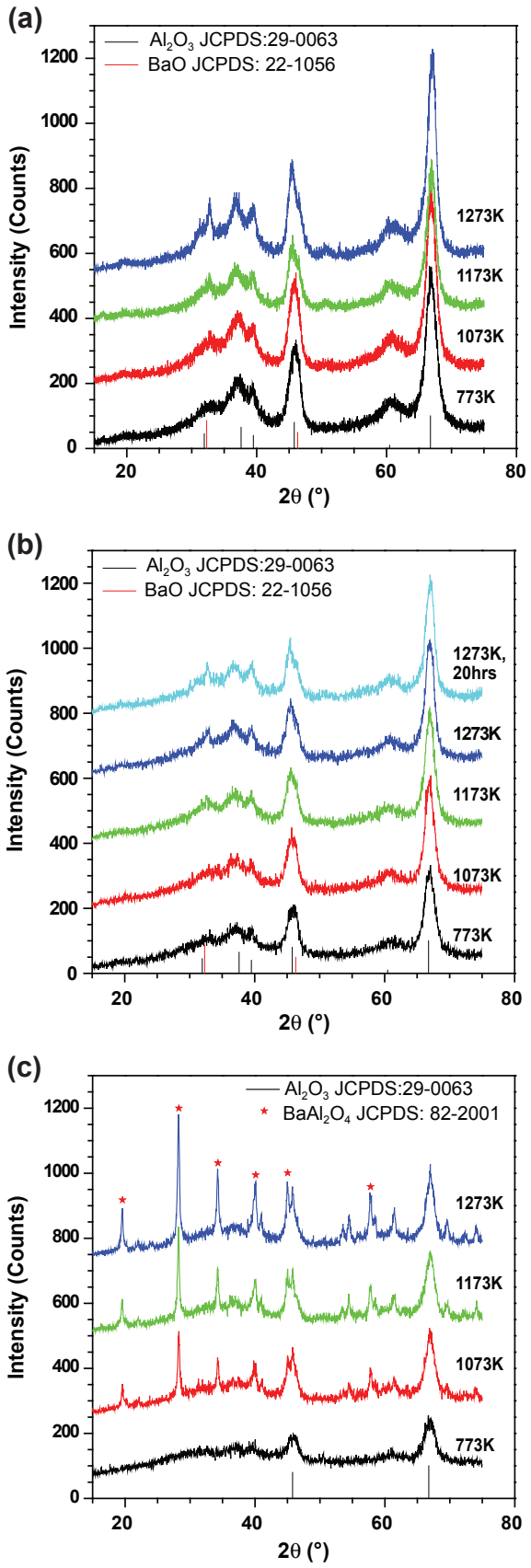

FIGURE 2. XRD spectra of 2% (A), 8% (B) and 20 wt% BaO/Al_2O_3 (C) NSR catalysts after calcination for two hours to different temperatures.

resulting materials in TPD experiments subsequent to NO_2 exposure at room temperature.

After calcination in dry air at 1000°C, the XRD and solid state ^{27}Al MAS NMR results confirm that stable surface BaO and bulk $BaAl_2O_4$ phases are formed for 8 and 20 wt% BaO/Al_2O_3, respectively. Following NO_2 adsorption on either high-temperature treated sample, we observed little if any evidence for $Ba(NO_3)_2$ formation, in contrast to the recent results of Gorte and coworkers [11]. However, when water was added to the thermally aged samples after NO_2 exposure, the formation of bulk crystalline $Ba(NO_3)_2$ particles was observed in both samples. For example, Figure 3 shows solid state ^{27}Al MAS NMR of 20% BaO/Al_2O_3 samples following various treatments, with peak assignments made on the basis of model compounds. The spectrum obtained from the 20 wt% BaO/Al_2O_3 material after calcination at 1000°C for 10 hrs (Figure 3a) shows three peaks arising from Al_2O_3 (peaks at 3 and 63 ppm) and $BaAl_2O_4$ (at 70 ppm) – note that there is an insufficient amount of Ba (20 wt%) to fully transform the alumina into $BaAl_2O_4$. When NO_2 is adsorbed at room temperature, there is no change in the ^{27}Al MAS NMR spectrum as shown in Figure 3b, consistent with our XRD results [10]. Thus, both the XRD and NMR data demonstrate that the $BaAl_2O_4$ phase is not altered significantly by room temperature NO_2 adsorption. However, when the sample is treated with water at room temperature (Figure 3c), aluminum

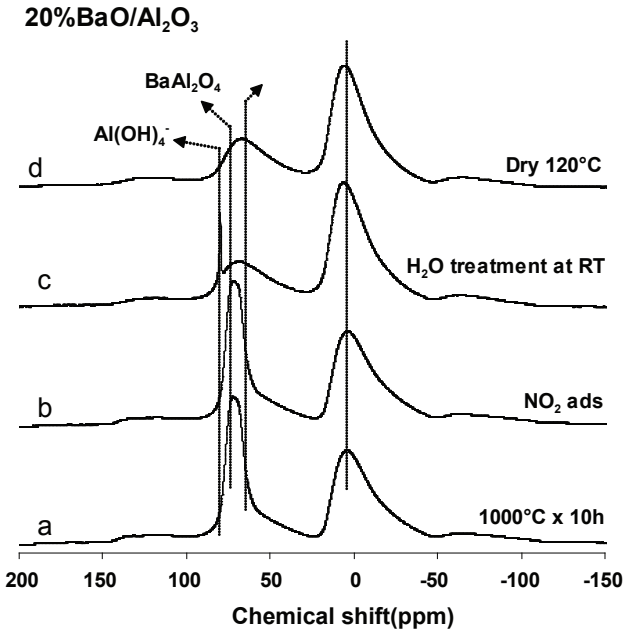

FIGURE 3. Solid state ^{27}Al MAS NMR spectra of a 20 wt% BaO/Al_2O_3 sample treated at 1000°C for 20 hrs (a) exposed to NO_2 at room temperature (b) and following a subsequent room temperature H_2O treatment (c). Spectrum (d) was obtained after an additional drying step at 120°C for sample (c).

species from $BaAl_2O_4$ completely disappear and a new peak, assigned to $Al(OH)_4^-$, develops. The $Al(OH)_4^-$ species readily converts to alumina by dehydration when the sample is dried in an oven at 120°C as shown in Figure 3d. NO_2 TPD results demonstrate a significant loss of uptake for the 20 wt% model catalysts upon thermal treatment indicating that formation of $BaAl_2O_4$ results in LNT deactivation. However, the just described phase transformations upon subsequent water treatment gave rise to the partial recovery of NOx uptake, demonstrating that such a water treatment of thermally aged catalysts can provide a potential method to regenerate LNT materials.

Effects of Water on BaO Morphology and NOx Uptake

The effects of H_2O and CO_2 on the uptake of NOx over BaO/Al_2O_3-based storage systems have been recognized and reported. However, the extent of the effects of these compounds on the NOx uptake, and the mechanisms by which these compounds influence NOx uptake are still widely debated. For this reason, we have initiated studies of the effects of water on the morphology of BaO/Al_2O_3-based NOx storage materials using FTIR, TPD, and TR-XRD techniques [12].

The results of this multi-spectroscopy study reveal that, in the presence of water, surface Ba-nitrates convert to bulk nitrates, and water facilitates the formation of large $Ba(NO_3)_2$ particles. For example, Figure 4 shows a series of FTIR spectra obtained during step-wise H_2O exposure to NO_2-saturated 8 wt% BaO/Al_2O_3 samples demonstrating dramatic changes in the spectra upon water exposure. Specifically, the intensities of the infrared bands characteristic of surface nitrates (1294 and 1582 cm^{-1}) gradually decreased with increasing amounts of H_2O introduced, while those of the bulk nitrates (1325 and 1434 cm^{-1}) increased. After the 7th H_2O dose, the intensities of peaks due to surface Ba-nitrate species almost completely diminished, while those of the bulk Ba-nitrates reached their maxima. This process is completely reversible; *i.e.*, after the removal of water from the storage material, a significant fraction of the bulk nitrates re-convert to surface nitrates (Figure 5 summarizes the just-described morphology changes). The amount of NOx taken up by the storage material is, however, essentially unaffected by the presence of water, regardless of whether the water was dosed prior to or after NO_2 exposure. Based on the results of this study, we are now able to explain most of the observations reported in the literature on the effect of water on NOx uptake on similar storage materials.

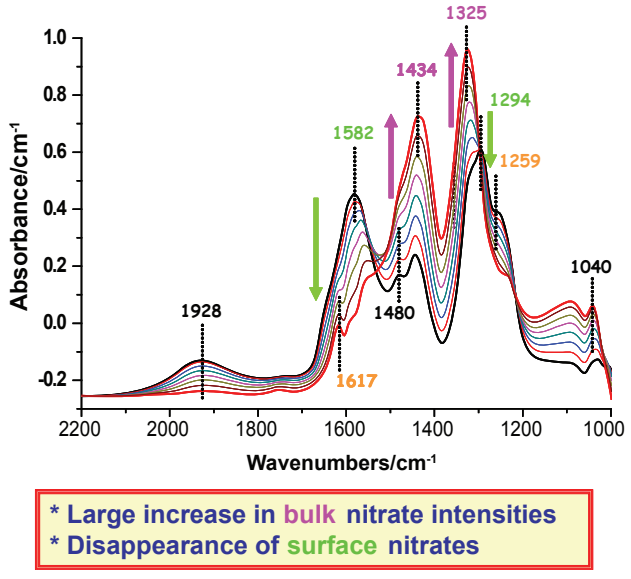

FIGURE 4. Infrared spectra collected during the step-wise H_2O adsorption at 300 K on NO_2/8 wt% BaO/Al_2O_3 (each H_2O dose was 1 Torr).

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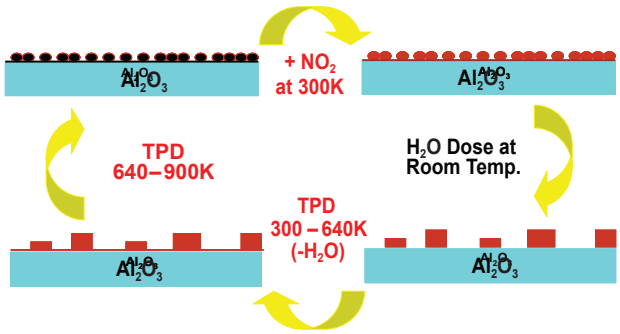

FIGURE 5. Schematics of changes in the cycle of morphology changes as a result of water exposure.

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FY 2006 Presentations

Invited

1. C.H.F. Peden (invited presenter), C.M. Wang, J.H. Kwak, D.H. Kim, J. Szanyi, R. Sharma, and S. Thevuthasan, "In-Situ TEM Study of Morphological Evolution of Emission Control Catalysts During Operation", presentation at the NSF Workshop on "Dynamic in-situ electron microscopy as a tool to meet the challenges of the nanoworld", Tempe, AZ, January, 2006.

2. C.H.F. Peden (invited presenter), J. Szanyi, D.H. Kim, J.H. Kwak, "The Adsorption and Reaction of NOx (NO and NO_2) on BaO/Al_2O_3 Storage/Reduction Materials", presentation at Ford Research Laboratories Seminar, Detroit, MI, March, 2006.

3. C.H.F. Peden (invited presenter), J. Szanyi, D.H. Kim, J.H. Kwak, "The Adsorption and Reaction of NOx (NO and NO_2) on BaO/Al_2O_3 Storage/Reduction Materials", presentation at Topsøe Company, Copenhagen, Denmark on April, 2006.

4. J. Szanyi (invited presenter), D.H. Kim, J.H. Kwak, J.C. Hanson, and C.H.F. Peden, "In-Situ Synchrotron Studies of BaO/Al_2O_3 NOx Storage/Reduction Materials for Vehicle Emission Control", presentation at the 2006 National Synchrotron Light Source (NSLS) Annual Meeting, Upton, NY, May, 2006.

5. C.H.F. Peden (invited presenter), "Fundamental Studies of Catalytic NOx Vehicle Emission Control", Presentation at the University of California, Santa Barbara, CA, August, 2006.

Contributed

6. D.H. Kim, J.H. Kwak, J. Szanyi, T. Szailer, J.C. Hanson, and C.H.F. Peden, "Understanding of NOx storage/release mechanism over Pt-BaO/Al_2O_3 lean NOx trap catalysts", presentation at the AIChE Annual Meeting, Cincinnati, OH, November, 2005.

7. C.M. Wang, J.H. Kwak, D.H. Kim, J. Szanyi, R. Sharma, S. Thevuthasan, and C.H.F. Peden, "In-Situ TEM Study of Morphological Evolution of $Ba(NO_3)_2$ Supported on α-$Al_2O_3(0001)$", presentation at the MRS Fall Meeting, Boston, MA, November, 2005.

8. C.H.F. Peden, J. Szanyi, D.H. Kim, J.H. Kwak, "The Adsorption and Reaction of NOx (NO and NO_2) on BaO/Al_2O_3 Storage/Reduction Materials", presentation at at PacifiChem 2005, Honolulu, HI, December, 2005.

9. J. Szanyi, C.H.F. Peden, D.H. Kim, J.H. Kwak, X. Wang, W.S. Epling, and J.C. Hanson, "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", presentation at the 2nd International Congress on Operando Spectroscopy, Toledo, Spain, April, 2006.

10. R.S. Disselkamp, D.H. Kim, J.H. Kwak, C.H.F. Peden, J. Szanyi, R.G. Tonkyn, and X. Wang, "Recent Results from PNNL Studies of NOx Adsorber Materials", presentation at the 9th CLEERS Workshop, Dearborn, MI, May, 2006.

11. R.G. Tonkyn, R.S. Disselkamp, and C.H.F. Peden, "Mechanistic Studies of the Reduction of Stored NOx on BaO/Al_2O_3-Based Lean-NOx Traps", presentation at the 9th CLEERS Workshop, Dearborn, MI, May, 2006.

12. C.H.F. Peden, J. Szanyi, D.H. Kim, J.H. Kwak, X. Wang, W.S. Epling, and J.C. Hanson, "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", presentation at the 232nd National Meeting of the American Chemical Society, San Francisco, CA, September, 2006.

FY 2006 Publications

1. Szailer, T.; Kwak, J.H.; Kim, D.H.; Szanyi, J.; Wang, C.; Peden, C.H.F. "Effects of Ba Loading and Calcination Temperature on $BaAl_2O_4$ Formation for Ba/Al_2O_3 Storage and Reduction Catalysts." Catal. Today **114(1)** (2006) 86-93.

2. Tonkyn, R.G.; Disselkamp, R.S.; Peden, C.H.F. "Nitrogen Release from a NOx Storage and Reduction Catalyst." Catal. Today **114(1)** (2006) 94-101.

3. Disselkamp, R.S.; Tonkyn, R.G.; Chin, Y.-H.; Peden, C.H.F. "A Multiple-Site Kinetic Model to Simulate $O_2 + 2\ NO \leftrightarrow 2\ NO_2$ Oxidation-Reduction Chemistry on Pt(100) Catalysts." J. Catal. **238(1)** (2006) 1-5.

4. Szailer, T.; Kwak, J.H.; Kim, D.H.; Hanson, J.; Peden, C.H.F.; Szanyi, J. "Reduction of Stored NO_x on Pt/Al_2O_3 and $Pt/BaO/Al_2O_3$ Catalysts with H_2 and CO." J. Catal. **239(1)** (2006) 51-64.

5. Wang, C.M.; Kwak, J.H.; Kim, D.H.; Szanyi, J.; Sharma, R.; Thevuthasan, S.; Peden, C.H.F. "In-Situ TEM Study of Morphological Evolution of $Ba(NO_3)_2$ Supported on α-$Al_2O_3(0001)$." J. Phys. Chem. B **110** (2006) 11878-11883.

6. Disselkamp, R.S.; Kim, D.-H.; Kwak, J.H.; Szanyi, J.; Szailer, T.; Tonkyn, R.G.; Peden, C.H.F.; Howden, K. "Fundamental Studies of NOx Adsorber Materials." Combustion and Emission Control for Advanced CIDI Engines, FY2005 Progress Report (2006) 141-150.

7. Kim, D.H.; Szanyi, J.; Kwak, J.H.; Szailer, T.; Hanson, J.C.; Wang, C.; Peden, C.H.F. "Sulfur K-edge XANES and TR-XRD Studies of Pt-BaO/Al_2O_3 lean NO_x Trap Catalysts: Effects of Barium Loading on Desulfation." National Synchrotron Light Source Annual Activity Report (2006) in press.

8. Kim, D.H.; Kwak, J.H.; Szanyi, J.; Peden, C.H.F. "Water-induced Bulk $Ba(NO_3)_2$ Formation From NO_2 Exposed Thermally Aged BaO/Al_2O_3." Appl. Catal. B, in press.

9. Kwak, J.H.; Kim, D.H.; Szanyi, J.; Szailer, T.; Peden, C.H.F. "NO_x Uptake Mechanism on $Pt/BaO/Al_2O_3$ Catalysts." Catal. Lett., in press.

Special Recognitions & Awards/Patents Filed/ Patents Issued

1. Ja Hun Kwak, Do Heui Kim, Xianqin Wang, Janos Szanyi, and Charles H.F. Peden, "New Desulfurization Process for Suppression of Pt Sintering of Sulfated Lean NOx Traps." PNNL Invention Disclosure #15330-E, filed in August, 2006.

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

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CRADA Partners:
- Randy Stafford, John Stang, Alex Yezerets, Neal Currier - Cummins Inc.
- Hai-Ying Chen, Howard Hess, Andy Walker - Johnson Matthey

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

- Mechanisms of thermal aging as a function of gas composition (reducing or oxidizing).
  - As noted by others, we find that thermal deactivation is very sensitive to the atmosphere (*i.e.*, oxidizing or reducing). Additional studies aimed at understanding these differences were initiated this year.
  - Samples treated with H_2, which results in the smaller Pt particles, show much higher activity than ones treated under oxidizing conditions, again supporting the correlation between Pt particle size and NOx storage activity.
- Robust methods for Pt particle size measurement in aged catalysts.
  - Based on prior work, the issue of Pt sintering as a primary cause of lean-NOx trap (LNT) performance degradation was clearly established. Thus, it has become a primary concern to establish 'routine' methods to determine Pt particle size in aged parts from the field in order to clearly establish their mode of failure.
  - Low Pt accessibility after H_2 reduction, as determined by H_2 chemisorption methods, does not correlate with NOx uptake activity. Rather, it is likely evidence of the strong Pt-Ba interactions that reduce the effectiveness of the H_2 chemisorption method for determining Pt particle size.
- The chemical mechanisms of the sulfur removal processes.
  - In previous year's work, we have identified conditions for effective removal of sulfur while also minimizing thermal degradation. This year, we have initiated studies of the sulfur removal mechanisms in order to provide guidance for further optimization of the required periodic sulfur removal processes.
  - As noted by others, CO_2 and H_2O significantly enhance the reductive removal of sulfur species and reduce the formation of a 'refractory' BaS phase. Experiments aimed at determining the chemical mechanisms of these effects have been initiated.
  - When H_2O is present in the desulfation step, the evolution of sulfur containing species is enhanced, regardless of the nature of the reductant.
  - The initial barium morphology differences play a crucial role in determining the extent of desulfation and the temperature at which it occurs, therefore, it was found that the removal of sulfur is significantly easier at lower barium loading.
- Three public presentations and two manuscripts have been cleared for release by CRADA partners. One of the manuscripts has appeared (in the Journal of Physical Chemistry B, 110 (2006) 10441.), and the other has been accepted for publication and will appear soon in the journal, Industrial & Engineering Chemistry Research.

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.
- Continue development of LNT thermal history diagnostics techniques
  - Establish reference treatment conditions that can be applied to aged parts with minimal additional changes.
  - More detailed studies to investigate the Pt-Ba interaction.
- Apply to real-life engine "aged" samples.
- Continue to improve mechanistic understanding of sulfur removal processes.
  - Identify important desulfation intermediates.
  - Effects of sulfur concentration on Pt accessibility and barium phase changes.

Introduction

The NOx adsorber (also known as lean-NOx trap – 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 (EPA'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 are being 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 further note here that while program progress for the entire year is summarized above in the "Accomplishments" section, we present below more detail about results obtained in this last year in three specific areas: i) the effect of barium loading on the desulfation process; ii) the design of a reaction protocol to specifically investigate desulfation behavior; and iii) the effect of water on desulfation processes.

Approach

In a microcatalytic reactor system (Figure 1), 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 testing, 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 (4 minutes)", which measures NOx removal efficiencies for the first 4 minutes of the lean-period.

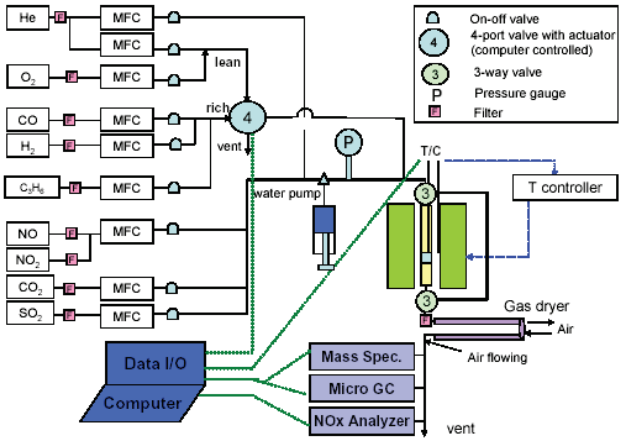

FIGURE 1. Schematic of the Microreactor Constructed for this Project's Studies

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 are able to identify optimum de-sulfation treatments to rejuvenate catalyst activities (a new manuscript describing this protocol is currently undergoing review by the CRADA partners).

State-of-the-art catalyst characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM)/energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET)/pore size distribution, and temperature programmed desorption/reaction (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 (temperature programmed reaction), sulfur K-edge XANES (X-ray absorption near edge spectroscopy) and TR-XRD (time-resolved X-ray diffraction) methods were used extensively to quantify the levels, speciation and phase of sulfur on the adsorber material as a function of desulfation process.

Results

Effect of Barium Loading on the Desulfation of Pt-BaO/Al_2O_3

We have previously shown that NOx adsorption/desorption chemistry is strongly dependent on the loading of barium on the basis of Fourier Transform Infrared Spectroscopy (FTIR) and NO_2 TPD experiments [2]. With reference to these results, we addressed an important question about how the sulfation and desulfation chemistry varies as a function of barium content in the LNT formulation. For this, we performed a multi-technique study, using H_2 temperature programmed reaction, synchrotron time resolved X-ray diffraction, sulfur K-edge X-ray absorption near-edge spectroscopy (XANES), and transmission electron microscopy (TEM).

Our previous work [2] has clearly shown that two kinds of barium nitrate species (surface and bulk barium nitrates) are formed upon NOx uptake, and the relative distribution of these nitrate species depends on the barium loading. In particular, an 8 wt% BaO/Al_2O_3 sample will contain primarily surface nitrates, while a significant quantity of both surface and bulk nitrates were present for a 20 wt% BaO/Al_2O_3 sample following NOx adsorption. As H_2 TPRX results demonstrate in Figure 2, sulfated Pt-BaO(8)/Al_2O_3, consisting of predominantly of surface BaO/$BaCO_3$ species, displays

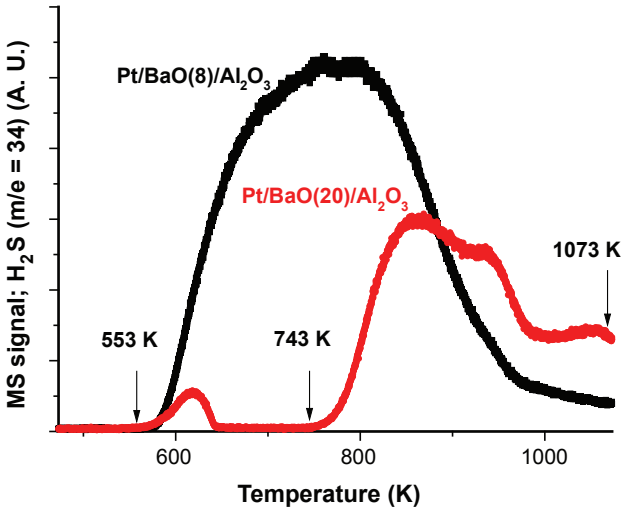

FIGURE 2. H_2 TPRX Spectra for 5 g/L Pt-BaO(8)/Al_2O_3 and 5 g/L Pt-BaO(20)/Al_2O_3 Samples

more facile desulfation by H_2 at lower temperature than sulfated Pt-BaO(20)/Al_2O_3, a material containing primarily bulk BaO/$BaCO_3$ species. Furthermore, after desulfation the amount of residual sulfur species on the former material is much less than on the latter as evidenced by S K-edge XANES and TEM/EDX results. After high temperature desulfation for both samples, residual sulfur exists in a reduced form, primarily as fairly large BaS particles. This suggests that the initial morphology differences between these two samples plays a critical role in determining the extent of desulfation and the temperature at which it occurs, potentially providing important information for the development of more sulfur resistant LNT catalyst systems.

A Reaction Protocol to Investigate Desulfation Behavior for Lightly Sulfated Samples

In the previous year, we demonstrated that a newly developed reaction protocol provided a useful tool to optimize desulfation conditions for deactivated LNT catalysts. Because actual LNT catalysts will experience frequent regenerations, we modified the reaction protocol to determine how repeated regenerations will affect the recovery of NOx performance. In other words, how easily are sulfur species removed for the case of successive sulfations and regenerations? NO_x uptake was measured in the presence of SO_2 for 2 hrs, followed by regeneration at 600°C in the absence of SO_2. These two steps were repeated six times until the total amount of sulfur deposited onto the materials was 4 g/L. For comparison purposes, the reaction was performed without SO_2 to identify the effects of thermal deactivation during these successive treatments at 600°C (not shown). In this latter case,

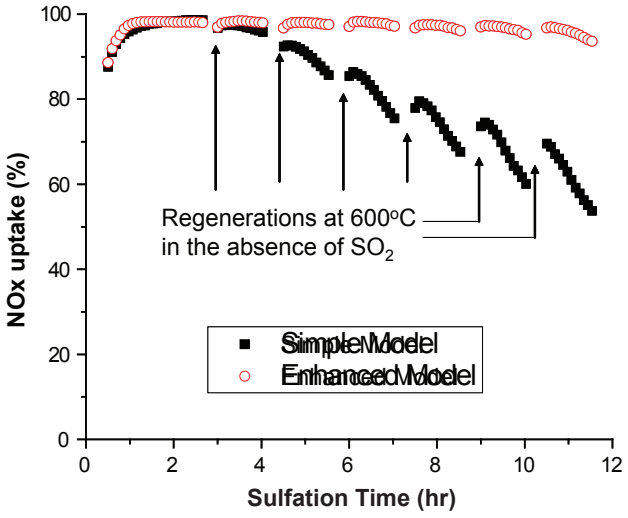

FIGURE 3. Change of NOx uptake with time during repeated sulfation and regeneration over simple model and enhanced model samples.

the NO_x uptake for 4 min was not changed for either sample; therefore, we can exclude the effects of thermal deactivation on performance during these successive sulfation and regeneration processes at 600°C. Figure 3 shows the change of NOx uptake as a function of sulfur exposure. The break in the sets of data points indicates the regenerations at 600°C in the absence of SO_2. For the case of the simple model sample, sulfur appears to deposit on the sample, even after successive regeneration treatments at 600°C, resulting in deactivation. Although there is a slight increase after each of the regeneration processes, the NOx uptake decreases rapidly. On the other hand, the enhanced model sample shows only a slight decrease in NOx uptake performance after multiple regenerations. Up to the sulfation level of 1 g/L, the NOx uptakes of the two samples are essentially identical. However, after several successive sulfation followed by regeneration, the differences becomes larger, demonstrating that the enhanced model sample has a much more significant ability to remove the low amounts of sulfur.

Role of H_2O in the Desulfation Process

We have recently been studying the effects of H_2O during desulfation processes as a function of the reductant (*i.e.*, H_2, CO or hydrocarbons-HCs) used. Regardless of the nature of the reductant, the presence of H_2O has a dramatic effect on the evolution of the sulfur containing species during, and also results in the higher desulfation activity. For example, Figure 4 shows the compositional change in the evolving gases during the desulfation steps of the enhanced model sample using CO as the reductant, either in the absence or presence of H_2O. For the H_2O-free case, only COS was formed, via reaction between CO and sulfates. On the other

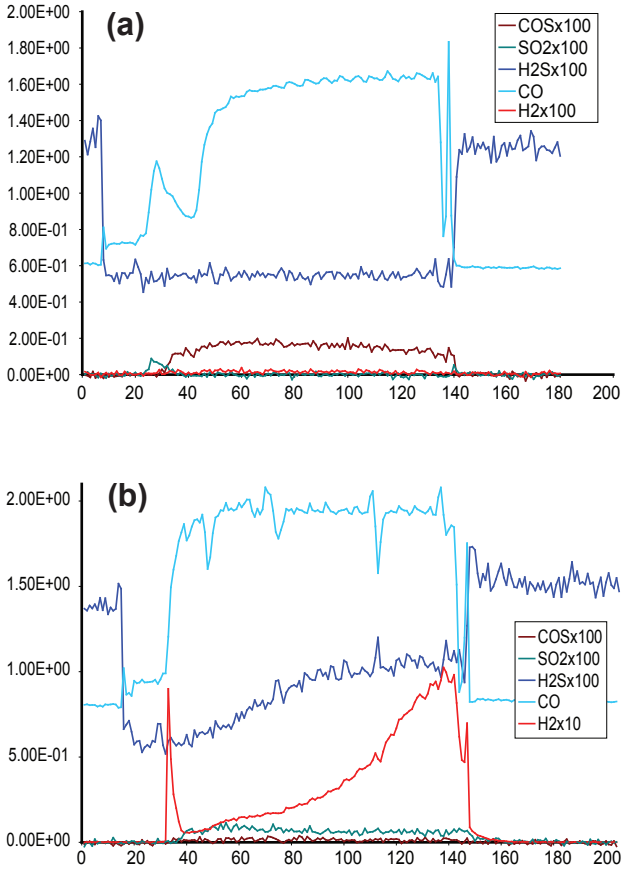

FIGURE 4. Change of composition of the gas phase with time during regeneration of the enhanced model sample at 600°C with CO, in the absence (a) or presence (b) of H_2O.

hand when H_2O is present, H_2 is generated from the water-gas-shift reaction (WGS) between CO and H_2O. The formed hydrogen is more actively involved in the desulfation process than CO, resulting in the formation of H_2S and SO_2, as in the case when hydrogen was present in the reductant stream. Although not shown, C_3H_6 also generates hydrogen via, in this case, the steam reforming (SR) reaction with water. Therefore, it can be summarized that water is an essential component for desulfation processeses, by facilitating the formation of hydrogen via the WGS and SR reactions, and also by reacting with BaS (as described above), thereby decomposing this otherwise refractory sulfur compound that would otherwise reduce the performance of LNTs for NOx storage and reduction.

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 complete

desulfation of the barium species in Pt-BaO(20)/Al_2O_3 is difficult due to the relative inaccessibility of sulfate species in the interior region of the particulate Ba phase. Therefore, it was found that the lower barium loadings provide for more optimum conditions for the removal of sulfur and, correspondingly, reduced deactivating effects. Use of a modified reaction protocol enables us to compare the relative performance of various LNT samples after regeneration processes for light sulfated conditions. The reaction protocol is easily modified to also give information about the regeneration characteristics of the samples. H_2O promotes desulfation process by generating the hydrogen arising from the WGS or SR reaction when CO or C_3H_6, respectively, are used as reductants.

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1. D.H. Kim, J. Szanyi, J.H. Kwak, T. Szailer, J.C. Hanson, C.M. Wang, C.H.F. Peden, "Effect of Barium Loading on the De-sulfation of Pt-BaO/Al_2O_3 Studied by H_2 TPRX, TEM, Sulfur K-edge XANES and *In-situ* TR-XRD." Journal of Physical Chemistry B **110** (2006) 10441-10448.

2. D.H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, W.S. Epling, N. Currier, H.Y. Chen, H. Hess, and D. Lafyatis, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2005 Annual Progress Report*, pp. 151-157.

3. D.H. Kim, Y.-H. Chin, G.G. Muntean, A. Yezerets, N. Currier, W.S. Epling, H. Chen, H. Hess, C.H.F. Peden, "Relationship of Pt Particle Size with the NOx Storage Performance over Thermally Aged Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts." Industrial and Engineering Chemical Research, in press.

4. D. H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, B. Epling, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Argonne, IL, May 2006.

5. D.H. Kim, J.H. Kwak, J. Szanyi, T. Szailer, J.C. Hanson, C.H.F. Peden, "Effect of Barium loading on the NOx storage and Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", presentation at the 2006 *Diesel Engine Emissions Reduction Conference, Detroit, MI, August 2006*.

6. D.H. Kim, J.H. Kwak, J. Szanyi, T. Szailer, J.C. Hanson, C.H.F. Peden, "Effect of Barium loading on the NOx storage and Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", presentation at the 2006 Pacific Coast Catalysis Society Meeting, Seattle, WA, September 2006.

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

- Improved data quality and experimental method.
- Investigated mitigation of fuel penalty with LTC-based regeneration.
- Studied sulfur effects:
  - Characterized intra-catalyst reductant utilization.
  - Determined effect of sulfur on unregulated species.
  - Determined impact of sulfur on regeneration strategy performance.
- Examined additional LNT formulations:
  - Two model catalyst formulations.
  - Umicore gasoline direct injection (GDI) catalyst (CLEERS focus group).
- Presented progress at DEER 2006.
- Collaborated with CLEERS:
  - Presented at CLEERS workshop.
  - Participated in LNT focus group.
  - Uploaded data from engine experiments to CLEERS website.
- Continued ongoing discussions with industry peers and Manufacturers of Emission Controls Association (MECA) partner(s).
- Presented papers at 2005 SAE Fall Powertrain & Fluid Systems Conference and 2006 Congress:
  - Presented N_2 Selectivity paper (SAE 2005-01-3876) at SAE Fall Powertrain & Fluid Systems Conference.
  - Presented LTC regeneration paper (SAE 2006-01-1416) at SAE Congress.
- Submitted paper for 2006 SAE Fall Powertrain & Fluid Systems Conference.

Future Directions

- Study Sulfation/Desulfation:
  - Multiple catalysts with same formulation.
  - Desulfation frequency study.
- To investigate improved LNT regeneration strategy performance related to the following parameters:
  - Smoke
  - Torque perturbations
  - Reductant slip (HC and CO)
  - Engine out NOx flux
  - Attempt to increase the fuel specific NOx reduction (lower fuel penalty)

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 N_2. The momentary fuel-rich environment in the 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. NOx regeneration is normally a 2-4 second event and must be completed approximately every 30-90 seconds (duration and interval dependent on many factors; e.g., load, speed, and temperature).

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.

Different strategies for introducing the excess fuel for regeneration can produce a wide variety of hydrocarbon and other species. One focus of this work is to examine the effectiveness of various regeneration strategies in light of the species formed and the LNT formulation. Another focus is to examine the desulfation process and quantify catalyst performance after numerous sulfation/desulfation cycles. Both regeneration and desulfation will be studied using advanced diagnostic tools.

Approach

A 1.7-L Mercedes 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 hydrogen and NOx at five locations within the LNT monolith using a spatially resolved capillary inlet mass spectrometer (SpaciMS). Fourier transform infrared (FTIR) sampling capability has also been improved with dilution and intra-catalyst extraction options. In addition to these set-up changes, we've increased the statistical population size by (1) running the experiments in triplicate, (2) using dedicated engine-out (EO) and tailpipe (TP) five gas benches, with one bench that sweeps from EO to TP in six steps, providing six data sets of EO-to-TP NOx reduction efficiency (NRE), (3) utilizing a remotely operated sample switching system that allows for rapid data acquisition, and finally (4) developing MATLAB code to rapidly reduce the large quantities of data collected.

Three regeneration strategies have been studied with the goal of introducing a broad range of species to the LNT catalyst. Two of the strategies use throttling to reduce the intake air flow, and in turn they reduce the exhaust air:fuel ratio (AFR). Excess fuel is then introduced into the cylinder to produce a rich AFR. The first of these two strategies applies excess fuel by extending the main fuel pulse and delaying it in crank angle time (delayed extended main or DEM). The second strategy introduces the excess fuel in a late cycle post injection at 80 degrees ATDC (Post80). In addition to these two strategies, a third strategy uses EGR in place of throttling to reduce intake air flow and exhaust AFR. The EGR is increased to approximately 55% while the pilot injection is disabled and the main injection timing is advanced to stabilize the combustion. These changes drive the engine into an advanced combustion regime referred to as low temperature combustion (LTC). LTC is characterized by simultaneous low NOx and low PM emissions. Once the engine is operating in the LTC regime, a nominal amount of excess fuel is applied to the main fuel pulse to produce a rich AFR. These strategies are used to study catalysts under quasi-steady conditions, that is steady load and speed but with periodic regeneration.

Activities for FY 2006 can be categorized into three main areas:

- Assessment of the utilization of LTC for reducing fuel penalty associated with LNT regeneration.
- Quantification of the performance impacts of sulfation and desulfation.
- Assessment of catalyst formulation impacts using model and commercial LNTs.

Future work will include bench-scale and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) characterization of LNT monoliths, wafers, and/or powders. Results from the engine experiments will be used to help define more meaningful bench scale methods. The ability to correlate bench-scale and engine test stand measurements will be enhanced by using the exact same catalyst formulations in some cases.

Results

Summary of LTC Regeneration Reduced Fuel Penalty Study – Previous work at ORNL has shown that LTC regeneration has a superior fuel specific NOx reduction (FSNR – grams of NOx reduced per gram of

excess fuel used to regenerate) versus both DEM and Post80. This portion of the study focused on performing an in-depth investigation of the relative benefits of LTC regeneration, which had the lowest fuel penalty, to the DEM regeneration, which had the best NRE.

Integrating the engine-out molar reductants for the three strategies, a decreasing trend in H_2 mass was noted from DEM to Post80 (P80) to LTC, respectively. In addition, the NRE for these strategies follows the same trend. Previous observations have indicated that H_2 production for a given strategy dictates the NRE of the LNT [1]. As the LTC strategy has the lowest H_2 level, it is not surprising that it also has the lowest NRE. In order to capitalize on the superior FSNR but improve the NRE, methods were investigated that would lead to increased H_2 production for the LTC regeneration strategy. The first method studied involved doubling the rich period to increase the H_2 mass delivered per regeneration. The second method studied involved halving the lean period to reduce the mass of NOx stored and therefore, increasing the mass of H_2 delivered per gram of NOx.

Figure 1 shows the DEM (3/30) and LTC (6/30) cases. The nomenclature in parentheses indicates the rich period duration and the total cycle time in seconds (as such, 3/30 indicates a 3 second rich pulse on a 30 second cycle). DEM (3/30) has a NRE slightly below 90%, compared to the LTC (6/30) NRE of about 95%. Worthy of note is that, even with improved NRE, the LTC strategy still has on the order of five times better FSNR. Furthermore, although there is only a 6-7% difference in NRE, this DEM case would actually have twice the tailpipe emissions of this LTC strategy for equivalent engine-out NOx emissions.

Figure 2 compares DEM (3/60) and LTC (6/60). Under conditions in which there is only a need for 75% NRE, these two cases would be a closer comparison. For these data, the LTC strategy has nearly 35 times better FSNR. This research has been published in SAE 2006-01-1416 [2] and the reader is encouraged to review this publication for more detail.

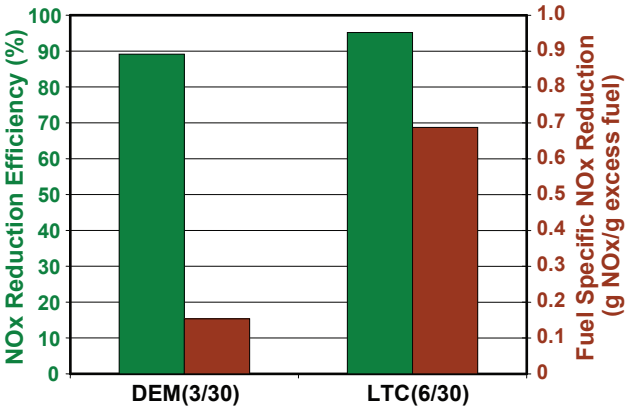

FIGURE 1. NRE and FSNR for DEM (3/30) and LTC (6/30) Strategies

Summary of Sulfation/Desulfation Effects – The deleterious impact of LNT sulfur poisoning is well known but not well understood. In order to better understand how sulfur affects LNTs performance, a set of experiments was completed to produce a range of sulfur poisoning levels. Following the sulfur poisoning measurements, the LNT was desulfated in order to study the effect of high temperature aging. Finally, an LNT of the same formulation, which had been exposed to several high temperature desulfations, was evaluated for comparison.

Figure 3 shows the NRE performance of four strategies as the LNT is progressively sulfur poisoned and then desulfated. The strategies included a DEM and Post80 regeneration with a 20 second cycle time and a DEM and Post80 with a 60 second cycle time. It can be seen that the 60 second Post80 strategy is not only the least effective strategy, it is also the strategy that is most affected by sulfur poisoning and desulfation aging.

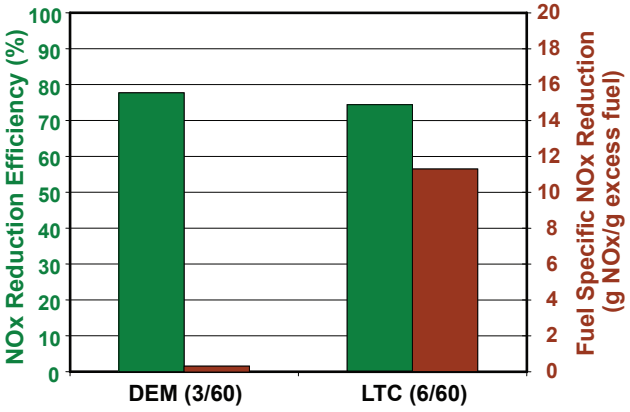

FIGURE 2. NRE and FSNR for DEM (3/60) and LTC (6/60) Strategies

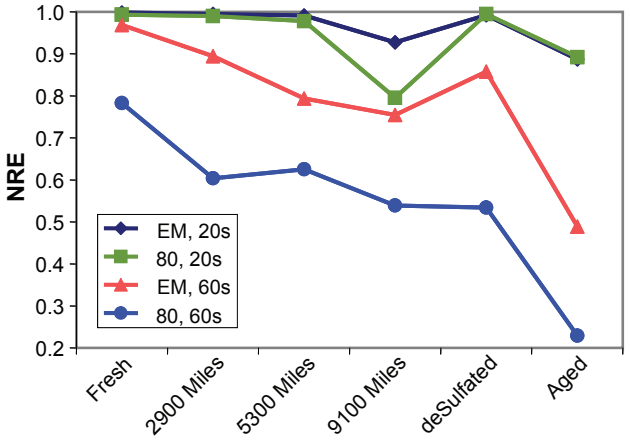

FIGURE 3. Sulfuation, Desulfation and Aging Effects on NOx Reduction Efficiency

When studying the utilization of the reductants as they progress through the LNT, the data indicate that the sulfur loading state has little effect on the level of unused reductants at the exit of the LNT. However, as seen in Figure 4 for the Post80 20 second cycle, the production of ammonia is affected by the level of sulfur. The ammonia formation after desulfation was higher for all four strategies. Since the reductant to NOx ratio did not change dramatically, it is suspected that thermal sintering of the sorbate may be the cause of the higher ammonia production. Findings reported by Castoldi et. al. [3] show that ammonia formation corresponds with higher sorbate loading.

Finally, in both the DEM and Post80 20 second cycles, it was observed that H_2 was being generated in the catalyst. This H_2 production is most likely due to catalytic processes such as partial oxidation of HCs or reforming processes such as the water-gas-shift reaction. Figure 5 shows the "excess intra-catalyst H_2 produced" in regeneration, defined here as the tailpipe H_2 minus the minimum intra-catalyst H_2. Internal H_2 production shows rapid degradation with sulfur loading, and a regain in production after desulfation for the 20 second strategies. The aged catalyst measurements indicate that multiple sulfation/desulfation cycles continue to reduce internal H_2 production. This indicates that LNT control strategies depending on internal H_2 generation to optimize reductant utilization may lose effectiveness with aging. This research has been published in SAE 2006-01-3423 [4] and the reader is encouraged to review this publication for more detail.

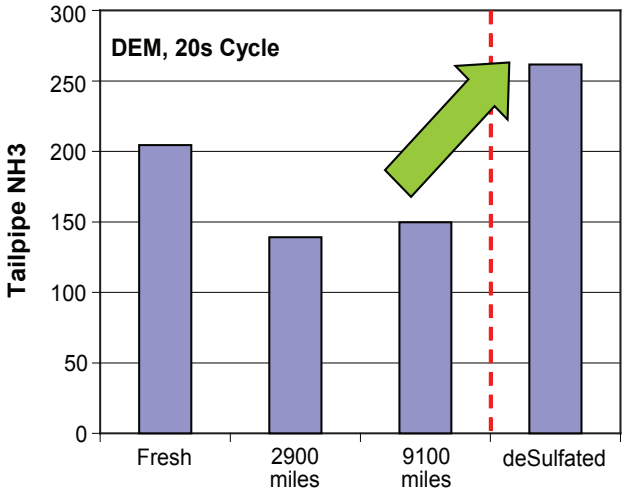

FIGURE 4. Tailpipe Ammonia Increases after Desulfation

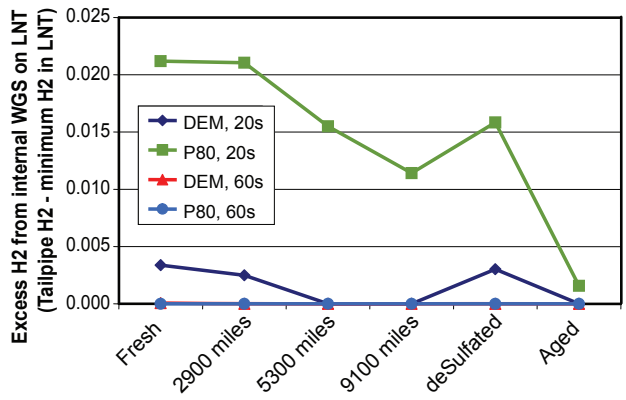

FIGURE 5. Excess Intra-Catalyst H_2 Production during Regeneration as a Function of Sulfation, Desulfation and Aging

Summary of Model and Commercial Catalyst Study – Experiments are underway to help understand the effects of catalyst formulation on NOx reduction performance. Two model LNT catalysts with differing barium loadings and a commercial GDI catalyst are being examined. These formulations have been suggested by the CLEERS LNT focus group. Full characterizations of these alternate formulations will be performed, including intra-catalyst measurements during four regeneration strategies. Preliminary results indicate similar trends for all three formualtions, although there are definite quantitative differences. The availability of the results for the two different model catalysts will also be a valuable contribution to CLEERS.

Conclusions

Strategies for in-cylinder regeneration have been developed for studying reductant chemistry effects on LNTs. Notable conclusions are as follows:

- LTC regeneration produces lower PM levels than typical lean/EGR operation, and considerably less than DEM.
- Low fuel consumption for LTC regeneration yields superior fuel specific NOx reduction:
  - Increasing frequency and duration of regeneration improves NOx reduction for LTC with minimal fuel penalty.
- Preliminary data indicates that regeneration with LTC has the potential for producing equivalent NOx reduction to DEM and P80 regeneration, but with 5x-35x more efficient fuel utilization:
  - Additional improvements in NOx conversion, fuel efficiency, PM generation, and torque smoothing are possible with further effort.
- In general, reductant utilization in LNT only slightly changed with sulfation/desulfation:
  - The LNT zone impacted by sulfur does tend to move downstream with repeated sulfation/desulfation and aging.

- NH_3 formation increased after desulfation:
  - There are indications that sorbate migration/ coarsening occurred at higher desulfation temperature.
- Strategies with high HC and low H_2/CO (Post80) may depend on intra-catalyst H_2/CO production for regeneration:
  - Sulfation/desulfation degradation of catalytic function may have greater impact on regeneration strategies that rely in intra-catalyst H_2/CO production.
- Preliminary model and commercial catalyst data with different formulations indicate similar trends but different quantitative performance.

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2. Shean Huff, Brian West, Jim Parks, Matt Swartz, Johney Green, Ron Graves, "In-Cylinder Regeneration of Lean NOx Trap Catalysts Using Low Temperature Combustion," *Society of Automotive Engineers Technical Series* 2006-01-1416 (2006).

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2. Jim Parks, Shean Huff, Josh Pihl, Jae-Soon Choi, Brian West, "Nitrogen Selectivity in Lean NOx Trap Catalysis with Diesel Engine In-Cylinder Regeneration," *Society of Automotive Engineers Technical Series* 2005-01-3876 (2005).

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4. Shean Huff, Jim Parks, Matt Swartz, Brian West, "Measurement and Characterization of LNT Regeneration - Posting Data on CLEERS Website For Model Development," 9th CLEERS Workshop, May 2006.

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

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- Josh Griffin (Sandia National Laboratories)

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

- Assembled, from literature and intuition, a comprehensive Chemkin-format reaction mechanism for LNT regeneration.
- Coupled the Chemkin plug flow reactor code with the Sandia-developed APPSPACK optimization code in order to automate the process of parameter estimation.
- Found an optimized, thermodynamically consistent set of kinetic parameters for the regeneration mechanism by fitting model predictions to the results of pseudo-steady state reactor experiments conducted at Oak Ridge National Laboratory (ORNL).

Future Directions

- Repeat the mechanism assembly and parameter optimization process for the NOx storage phase of normal LNT operation.
- Augment the regeneration mechanism with reactions for additional kinds of reductants, in particular hydrocarbons.
- Introduce reactions needed to describe sulfur poisoning and desulfation.

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. Lean NOx traps (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. However, 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 for both phases of LNT operation.

Our work thus far has been focused primarily on modeling the regeneration chemistry in an LNT. This is due to the existence of a large set of bench-scale reactor data taken at ORNL that is ideally suited to the modeling tools that we have available. For the same reason, we have treated the reduction of stored NOx only by H_2 and CO, even though hydrocarbon reductants are also used in practice. Needless to say, much remains to be done before a comprehensive kinetics model for LNT behavior is available.

Approach

The first step in constructing the regeneration mechanism is to assemble a tentative set of elementary reaction steps and associated mass-action kinetic parameters. Information from the catalysis literature is used where available, but some reactions and parameter values are simply hypothesized in order to obtain a comprehensive set. For a given proposed mechanism and a given set of experimental conditions, the steady-state flow through a single monolith channel is simulated with the Chemkin-based PLUG code to obtain a predicted set of exit concentrations for all gas-phase species. After this is done for all experiments in the ORNL data base, an overall average deviation between the predicted

and measured results is computed. This is used as the objective function in an optimization routine that adjusts the kinetic parameters in order to obtain the best possible fit to the data. Finally, superfluous reactions are identified by dropping candidates one at a time from the mechanism, repeating the optimization procedure, and observing the degradation in the overall fit.

A very significant complication in this parameter estimation process arises from the fact that not all of the parameters can be varied independently if thermodynamic consistency is to be maintained. Specifically, a well-defined number of the equilibrium constants for the surface reactions must be constrained so as to be consistent with the known thermodynamics of the gas-phase species. In addition, all of the activation energies, whether varied independently or computed from thermodynamic constraints, are required for physical reasons to be non-negative. The optimization of the kinetic parameters is therefore a very large and complex problem, but it is made feasible by the availability of the Sandia-developed APPSPACK code running on a massively parallel computing platform.

Results

While it is possible that the regeneration mechanism will undergo further refinements if necessary to accord with new data, the current version is quite acceptable in that it satisfies all constraints and provides a reasonably good fit to all of the ORNL data sets simultaneously. Even though all chemistry is assumed to occur on the catalyst surface, the mechanism involves both gas-phase and surface species. The former include the typical components of engine exhaust as well as the desired and unwanted products of aftertreatment: O_2, NO, NO_2, CO, H_2, CO_2, N_2, H_2O, N_2O, and NH_3. The surface species are those thought to exist on the precious metal (nominally Pt) sites responsible for regeneration: *(Pt), O(Pt), NO(Pt), NO_2(Pt), CO(Pt), H(Pt), N(Pt), OH(Pt), H_2O(Pt), NH(Pt), NH_2(Pt), NCO(Pt), and NH_3(Pt). The first of these is simply an empty site available for adsorption. Taking place among these species are 24 elementary reaction steps, all of them reversible; some are gas-surface interactions, while the remainder involve only surface species. In the former category are adsorption/desorption reactions for all gas-species except N_2O; the adsorptions of O_2, H_2, CO_2, and N_2 are assumed to be dissociative. The remaining gas-surface reactions are

$$H_2O(Pt) + CO(Pt) = 2H(PT) + CO_2$$
$$N(Pt) + CO = NCO(Pt)$$
$$NCO(Pt) + H_2O(Pt) = NH_2(Pt) + CO_2 + *(Pt)$$
$$2NO(Pt) = N_2O + O(Pt) + *(Pt)$$
$$NO_2(Pt) + CO(Pt) = NO(Pt) + CO_2 + *(Pt)$$
$$N_2O + H(Pt) = N_2 + OH(Pt)$$
$$NO(Pt) + NH_2(Pt) = N_2O + 2H(Pt)$$

The first of these is essentially the well-known water-gas-shift reaction, which can in principle account for the ability of CO to reduce NOx to NH_3 in the presence of H_2O. However, the experimental data suggest that a different route is actually operative at low temperatures, and the second and third reactions above provide such a pathway through an isocyanate surface intermediate. The existence of such a species has been confirmed by direct observation at ORNL.

The mechanism is completed by the following eight reactions involving only surface species:

$$NO(Pt) + O(Pt) = NO_2(Pt) + *(Pt)$$
$$NO(Pt) + *(Pt) = N(Pt) + O(Pt)$$
$$H(Pt) + O(Pt) = OH(Pt) + *(Pt)$$
$$H(Pt) + OH(Pt) = H_2O(Pt) + *(Pt)$$
$$N(Pt) + H(Pt) = NH(Pt) + *(Pt)$$
$$NH(Pt) + H(Pt) = NH_2(Pt) + *(Pt)$$
$$NH_3(Pt) + *(Pt) = NH_2(Pt) + H(Pt)$$
$$NH_3(Pt) + O(Pt) = NH_2(Pt) + OH(Pt)$$

With the exception of the last reaction, which is an atom transfer that provides a route for ammonia oxidation, these are simply surface decomposition/recombination processes that are almost certain to occur on the catalyst.

As noted above, the proposed mechanism is quite successful in reproducing a large body of experimental data generated at ORNL. Although the experiments were conducted separately from this project, a brief description of them should be given here in order to make clear the kind of situation that the mechanism was used in modeling. In each experiment, a reactant gas of specified composition was made to flow through a core sample of a commercially available LNT catalyst. Each feed mixture included CO_2, H_2O, and N_2 in amounts typical of engine exhaust, together with a lesser amount of one of the following reactant combinations: NO/H_2, NO/CO, NO_2/H_2, NO_2/CO, N_2O/H_2, N_2O/CO, NH_3/O_2, NH_3/NO, NH_3 alone, H_2 alone, or CO alone. During each experiment, the temperature was ramped slowly from below 100°C to 500°C in order to generate pseudo steady-state conversion data over a wide range of temperatures. Chemiluminescent analyzers and Fourier transform infrared (FTIR) spectroscopy were used to measure the concentrations of key species in the outlet stream, and these values provided the basis for comparison with the reactor simulations.

A comprehensive review of the modeling results is not possible here, so we will discuss just a few of the most interesting cases. Figures 1 and 2 show

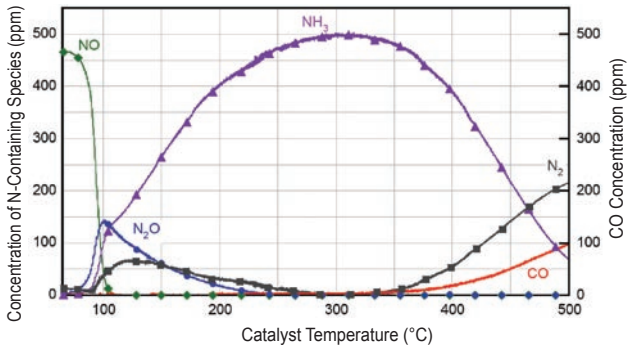

FIGURE 1. Experimental Outlet Concentrations for a Feed Stream Containing 1:2.5 NO/H_2

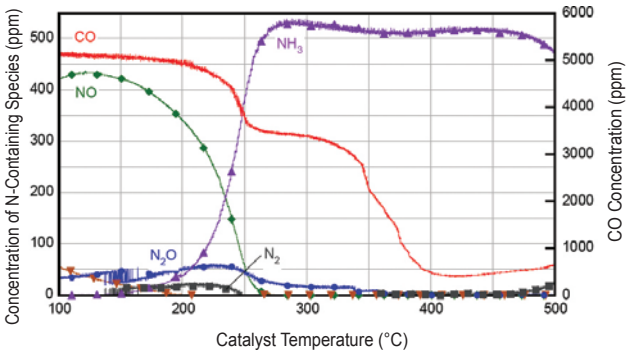

FIGURE 3. Experimental Outlet Concentrations for a Feed Stream Containing 1:10 NO_2/CO

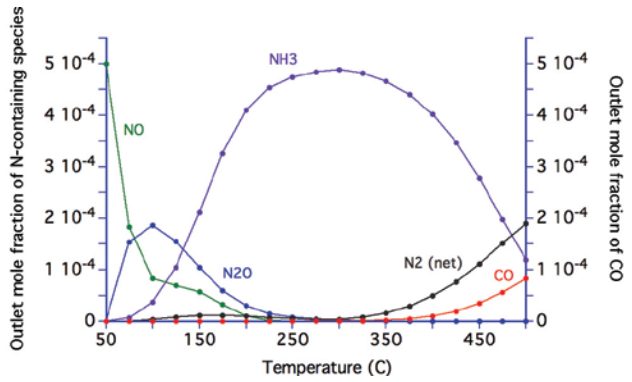

FIGURE 2. Computed Outlet Concentrations for a Feed Stream Containing 1:2.5 NO/H_2

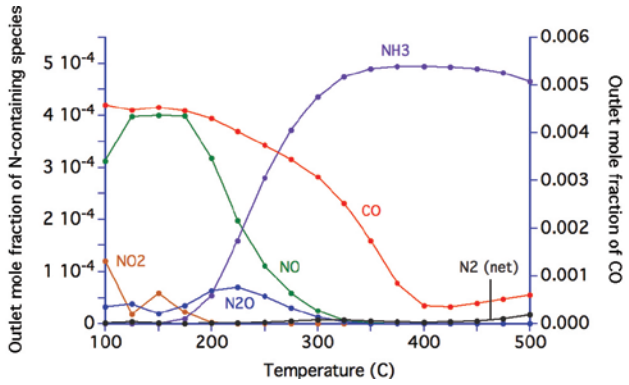

FIGURE 4. Computed Outlet Concentrations for a Feed Stream Containing 1:10 NO_2/CO

the experimental data and the model predictions, respectively, for the case in which the feed stream contains NO and H_2 in a 1:2.5 ratio. Obviously, the excess amount of H_2 gives rise to a strong tendency to form the reduction byproducts N_2O and NH_3 rather than the nominally desired N_2, although it should be mentioned that NH_3 is actually the desired product in some novel applications of this technology. In any case, it can be seen that the model (and, by inference, the chemical mechanism) is able to capture all of the general trends, including the eventual decomposition of NH_3 at high temperatures. The role of kinetics is crucial here, as equilibrium calculations show essentially no NH_3 at temperatures above 300°C.

Figures 3 and 4 show results for a feed that contains NO_2 and CO in a 1:10 ratio. Again, the large excess of reductant causes large amounts of NH_3 to be formed at sufficiently high temperatures, although this is still a kinetically-driven phenomenon: ironically, NH_3 appears in significant amounts at equilibrium only *below* 250°C. However, the most interesting aspect of this case is the striking two-step drop in the outlet CO concentration that is seen experimentally. Clearly, the first step is closely tied to NH_3 formation, while the second is not. The experiment in which CO is fed by itself confirms that the high-temperature drop is due to the water-gas-shift reaction, so we conclude that the NH_3 formation seen here is attributable to some other pathway. The most reasonable choice is the isocyanate scheme mentioned earlier; its incorporation into the overall mechanism allows the model to reproduce the experiment fairly well, although the intermediate plateau in the CO level is largely absent.

Finally, Figures 5 and 6 show results for a feed stream containing a 1:2 mixture of NH_3 and O_2. Even though the primary purpose of the regeneration mechanism is to simulate reduction of NOx, these results show that the mechanism is sufficiently robust to describe a process as different as NH_3 oxidation; note that NH_3 is present at low temperatures and NO at high temperatures, in direct contrast with Figures 1 and 2.

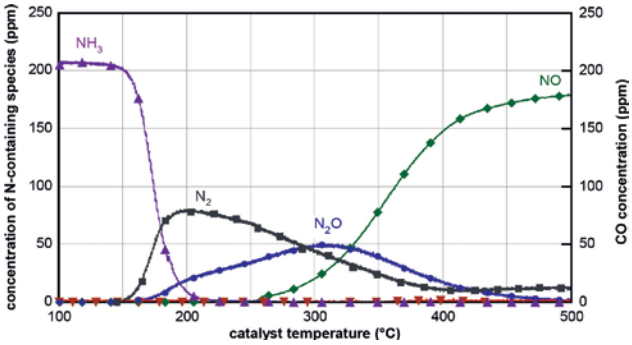

FIGURE 5. Experimental Outlet Concentrations for a Feed Stream Containing 1:2 NH_3/O_2

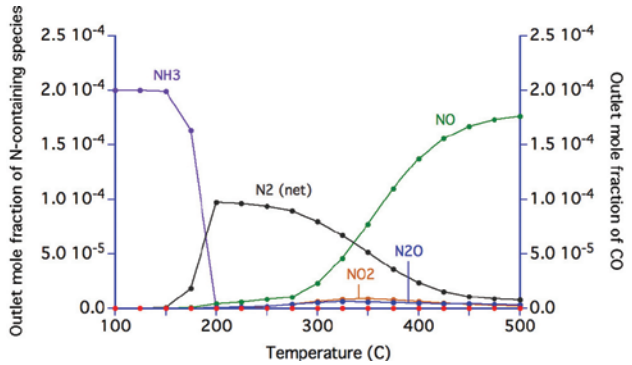

FIGURE 6. Computed Outlet Concentrations for a Feed Stream Containing 1:2 NH_3/O_2

Neither species is present at equilibrium, as all nitrogen appears simply as N_2.

Conclusions

- The chemistry occurring on the precious metal sites of a lean NOx trap can be simulated quite well with a reasonably compact (24-step) elementary reaction mechanism.
- Both water-gas-shift and isocyanate pathways for CO consumption are necessary to explain experimental results over a wide range of temperatures.
- Optimization of very large sets of kinetic parameters in the presence of constraints is time-consuming but feasible with newly available software and parallel processing machines.

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2. R. S. Larson, V. K. Chakravarthy, C. S. Daw, and J. A. Pihl, "Modeling Kinetics of NH_3 and N_2O Formation in Lean NOx Traps," Ninth CLEERS Workshop, Dearborn, MI, May 4, 2006.

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II.B.5 Advanced Engine/Aftertreatment System R&D

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Objectives

- Improve the effectiveness and efficiency of lean-NOx traps (LNTs) by understanding the role and fate of various hydrocarbon (HC) species in LNT regeneration through engine experiments.
- Define pathways to reduce catalyst deactivation and fuel penalty from sulfation and desulfation processes by examining fully-formulated LNT catalysts in bench reactors.
- Study advanced combustion regimes and thermodynamic cycles using infinitely variable intake and exhaust valve timing on a camless engine prototype.

Accomplishments

- Determined (in engine-based LNT experiments) that light alkenes are preferred HC species for LNT regeneration, followed by mono-aromatics. Branched alkanes are poorly utilized by LNTs.
- Examined engine-aged LNT samples in ORNL reactors. Results show sulfur remnants in front of the catalyst, as well as significant differences in front and rear surface area, NOx storage capacity, and NOx conversion.
- Removed camless engine prototype from International vehicle and installed in ORNL engine-dynamometer lab.

Future Directions

- Continue to study LNT chemistry at bench scale, to improve understanding of sulfation/desulfation. The ability to desulfurize the catalyst is foremost to commercial success of LNT technology.
- Commission camless engine at ORNL facility, explore interaction between advanced low-temperature combustion modes (lower NOx and PM) and overexpansion (improved efficiency).

Introduction

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 many open issues that must be resolved prior to commercialization. One of the most important issues is sulfur poisoning. Even with the nationwide availability of 15 ppm sulfur diesel fuel, the LNT will require effective sulfur management. The catalyst's high affinity for sulfur will require periodic desulfation. Desulfation requires high temperature and fuel-rich conditions. Managing the desulfation such that thermal damage is avoided is very important to the life of the aftertreatment system. Prior work in this Cooperative Research and Development Agreement (CRADA) project has focused on understanding the regeneration and desulfation processes through engine experiments with full-scale aftertreatment devices. Ongoing work with the LNT technology at ORNL will focus on bench-scale experiments to better understand the fundamentals.

A second focus of the CRADA will involve use of a unique camless engine prototype with infinitely variable valve timing, to study more conventional variable valve timing approaches. Using valve timing to trap exhaust gas (internal exhaust gas recirculation, or EGR) will be examined as a means to bring about advanced combustion modes such as low-temperature combustion. Overexpansion as a means to greater thermal efficiency or other thermodynamic cycles unique to the diesel engine will also be explored.

Approach and Results

Under this CRADA, experiments at ORNL have focused on in-pipe or in-exhaust (after turbo) fuel injection for LNT regeneration. ORNL developed a PC-based controller for transient electronic control of EGR valve position, intake throttle position, and actuation of fuel injectors in the exhaust system. Diesel oxidation catalysts (DOCs) in conjunction with a catalyzed diesel particle filter (CDPF) and LNT have been evaluated under quasi-steady-state conditions while sampling for HC species at multiple locations in the exhaust system.

Previously reported studies examined fuel cracking upstream of a 14 liter LNT by using the CDPF alone and in conjunction with a 5.0 liter DOC. Gas chromatograph mass spectrometry (GC-MS) and Fourier transform infrared (FTIR) spectroscopy were used to speciate the hydrocarbons entering and exiting the LNT catalyst. Results showed high utilization of light alkenes and mono-aromatics, and poor utilization of branched alkanes. Follow-on experiments utilized pure compounds (1-pentene, toluene, and iso-octane) to confirm the rank order of HC species for LNT regeneration [1].

The LNT was also desulfated on the engine, using throttling, EGR, and in-pipe injection of diesel fuel. This desulfation was conducted at a "road load" condition to demonstrate that desulfation might be accomplished during normal driving.

This year, small one-inch long core samples were taken from the front and rear of the 14 liter LNT as shown in Figure 1. These samples were analyzed by several methods to elucidate the desulfation effectiveness and aging effects. Figure 2 shows results of diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) analysis on the front and rear samples. A small amount of washcoat was scraped from each sample for DRIFTS analysis. The large sulfate peak noted on the front sample indicates the presence of sulfur, while the rear sample shows little or no sulfur. Additional analysis on fresh and sulfated samples is planned and will allow further understanding of the sulfation and desulfation processes for this catalyst formulation. Additional samples from the core of this catalyst will also be examined.

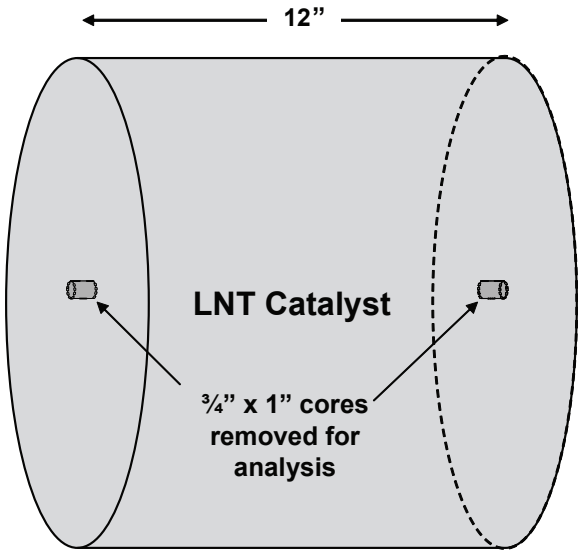

FIGURE 1. LNT Schematic Showing Location of Core Samples Removed for Bench Analysis

Other bench-scale analyses included N_2 physisorption for surface area measurements using a static constant volume sorption apparatus (method of Brunauer, Emmett and Teller), precious metal sizing by X-ray diffraction (XRD), and NOx storage and conversion using small cores in a microreactor. During desulfation, the temperature in the rear of the LNT was at least 50°C higher than in the front. This higher temperature apparently leads to a loss of surface area in the rear; the front sample measured some 23 m^2/g while the rear had been reduced to 16. Also, the average precious metal particle size in the front was 3.9 nm, while the rear showed signs of sintering with an increase to 4.5 nm. In addition, both XRD and DRIFTS analysis indicate the presence of $BaCO_3$ in the rear, while only trace amounts were observed in the front sample, most likely due to the overwhelming presence of $BaSO_4$.

Figure 3 shows the comparative NOx storage for the front and rear samples at three different temperatures. The figure shows that the stored sulfate causes a significant loss of storage capacity at 400°C on the front sample. The loss of storage capacity at 400°C directly relates to the most stable storage sites of the LNT, i.e., weak storage sites and stable storage sites are utilized at the lower temperatures, but only the more stable sites are utilized at the higher temperature. Therefore, these results show that the remaining sulfates are preferentially blocking the most stable sites of the LNT. These

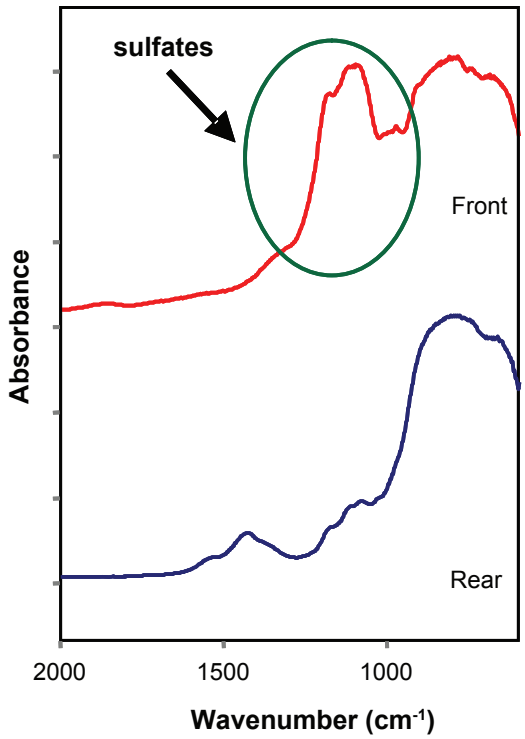

FIGURE 2. DRIFTS Spectra from Front and Rear LNT Samples Show Prominent Sulfate Peak in Front Sample

results also relate directly to the desulfation process. Because the front section of the catalyst did not reach temperatures high enough to remove the most stable sulfates, the most stable nitrate storage sites are thus preferentially blocked.

The presence of sulfate and the loss of surface area also impact the NOx conversion efficiency, shown in Figure 4. These data were collected using a modified CLEERS protocol [2]. The front of the catalyst has superior NOx conversion at the lower temperature, while the rear sample is better at the higher temperature. These results suggest that the precious metal sintering limits the performance at the lower temperatures more than the loss of NOx storage sites. This observation is supported by the fact that LNT performance is limited at lower temperatures by NO to NO_2 oxidation, a reaction that is heavily dependent on precious metal surface sites. Conversely, the improved performance for the rear of the catalyst at 400°C can be attributed to the higher

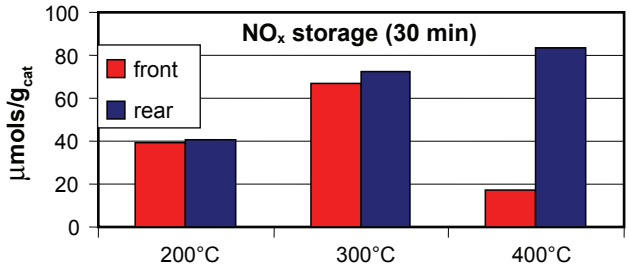

FIGURE 3. NOx Storage Capacity as a Function of LNT Temperature

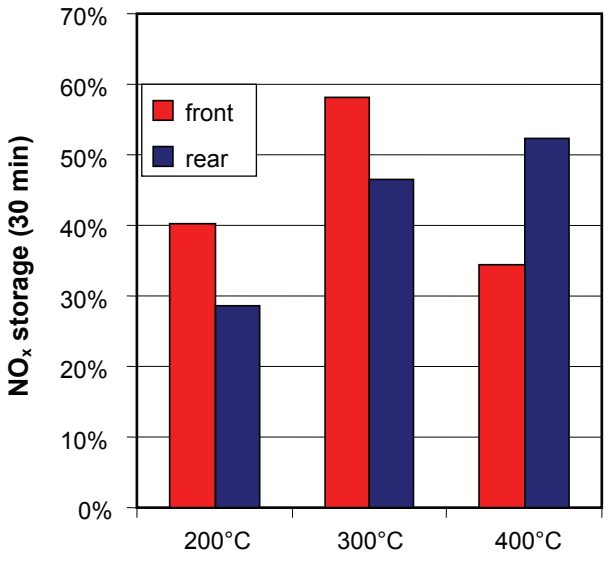

FIGURE 4. NOx Conversion of Front and Rear LNT Core Samples in Micro-reactor

NOx storage capacity. Again, analyses of fresh samples will provide more insight into the significance of these results.

In addition to the bench-scale LNT studies at ORNL, a camless engine prototype has been setup for advanced combustion studies. In FY 2006 this camless engine prototype was removed from an International truck and installed in place of the International T444E V8 diesel previously used in the engine-based LNT studies. Engineers from International visited ORNL on three occasions to train ORNL staff on the camless hardware and software, to assist with the engine removal, and to help commission the engine in the ORNL dynamometer cell. Difficulties with the transition from vehicle to dynamometer cell precluded engine operation before the end of the FY. These difficulties were resolved and the engine was successfully started early in FY 2007.

Conclusions

During this CRADA activity, experiments on LNT regeneration have been conducted with diesel fuel and three pure compounds to examine the HC sensitivity of the catalyst system. A LNT desulfation was conducted at a road-load condition with diesel fuel spray for reductant. Core samples from the engine-aged LNT have been examined in ORNL bench reactors. A camless engine prototype has been removed from an International truck and installed in an ORNL dynamometer cell. Notable conclusions are the following:

- Light alkenes and monoaromatics appear to be preferred by the LNT.
  - Pentene is the most efficient compound examined, followed by toluene.
  - Iso-octane is very poorly utilized by the LNT.
- Laboratory reactor analyses of engine-aged LNT samples suggest:
  - Higher temperatures at the rear of the catalyst during desulfation are believed to be responsible for more complete sulfur removal and precious metal sintering (coarsening).
  - Presence of sulfur in the front of the catalyst impacts performance at higher temperatures where storage capacity is most important.
  - Precious metal coarsening in the rear of the LNT catalyst impacts performance most notably at lower temperatures, where the NO to NO_2 oxidation and NO_2 to N_2 reduction limits performance.

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II.B.6 Advanced CIDI Emission Control System Development

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Kenneth Howden

Subcontractors:

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- ExxonMobil Research and Engineering Company (EMRE), Paulsboro, NJ

Objectives

Develop and demonstrate a highly efficient exhaust emission control system for light-duty compression ignition direct injected (CIDI) engines to meet Federal Test Procedure (FTP) Tier 2 emissions standards (0.07 g/mi NOx, 0.01 g/mi particulate matter, PM) with minimal fuel economy penalty and 120k mi durability.

Accomplishments

- The project was completed and the final technical progress report was filed.
- Tier 2 Bin 5 emission levels were achieved for non-methane hydrocarbons (NMHC), CO, and PM at 120k miles using a selective catalytic reduction (SCR) system and catalyzed diesel particulate filter (CDPF) with a mid-size diesel engine on a 6,000 lbs gross vehicle weight rating (GVWR) light-duty truck (LDT). Weighted tailpipe NOx on the FTP for light-duty vehicles (FTP-75) was 0.128 g/mi.
- With a more active diesel oxidation catalyst (DOC), the 120k mile SCR system reduced NOx emissions to 0.091 g/mi, which corresponded well to lower-mileage results under similar conditions. This confirmed the durability of the copper/zeolite SCR catalyst.
- Tier 2 Bin 5 levels for NOx were achieved using an improved SCR catalyst aged in the laboratory for the equivalent of 120k miles. The tailpipe NOx emissions were 0.061 g/mi when tested with a more active DOC.
- Post mortem analyses of the 120k mile catalysts revealed non-uniform aging.
- Improvements were made to the DOC and SCR models

Future Directions

The project is concluded. No further work is planned.

Introduction

Reducing particulate matter (PM) and NOx emissions are primary concerns for diesel vehicles required to meet 2007 Federal Tier 2 and California Low Emission Vehicle II (LEVII) emission standards (Table 1). These standards represent a 90-95% reduction from Federal Tier 1 diesel standards.

TABLE 1. 2007 FTP Emission Standards* (passenger cars and light-duty vehicles)

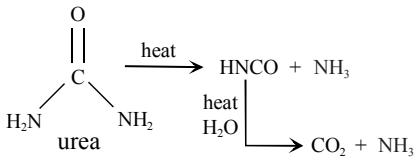
	50k mi		*120k mi*	
Standard (g/mi)	**NOx**	**PM**	**NOx**	**PM**
LEVII	0.05	----	0.07	0.01
Tier 2, Bin 5	0.05	----	0.07	0.01

*Supplemental FTP standards not included.

The high oxygen content of diesel exhaust makes onboard NOx control complicated. The technology with the most potential to achieve 90+% NOx conversion with minimal or no fuel economy penalty is SCR with an ammonia-based reductant such as aqueous urea. Ammonia-SCR has been used extensively for stationary source NOx control [1]. The main reactions are shown below:

Feasibility of using aqueous urea on vehicles has been proven by past work at Ford [2,3], Volkswagen [4], Mack Truck [5] and DaimlerChrysler [6].

urea decomposition:



NO_x reduction:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$$
$$2NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O$$

Control of diesel PM is accomplished with a periodically regenerated ceramic filter, usually called a catalyzed diesel particulate filter, or CDPF. The filter may be washcoated with precious metal to help oxidize HC and collected soot. A DOC may also be placed upstream of the filter to further aid in filter regeneration. The DOC also provides reduction in hydrocarbon (HC) and carbon monoxide (CO) emissions, as well as NO oxidation for more durable SCR function.

Approach

At Ford, improved supplier catalysts were tested in laboratory flow reactors for aged conversion levels. The best performing system that included a DOC, SCR catalyst, and CDPF was aged and tested on an engine dynamometer at FEV. Development and evaluation of improved SCR catalysts continued. Ultra-low-sulfur diesel fuel (<15 ppm S) was used for all aging and testing. Tests of the aged system were performed on a 6,000 lbs GVWR LDT. Appropriate exhaust gas sensors and control strategies were tested for durable system function. System modeling played an important role in design and analysis of performance.

Results

Catalyst system aging to the equivalent of 120,000 miles was completed on the engine dynamometer at FEV. Total time on the engine was 2,544 hours. The CDPF was regenerated a total 643 times, each typically lasting ten minutes, including six minutes with the SCR catalyst at high temperature (over 600°C). In all, the SCR catalyst spent 64 hours at high temperature during the durability phase.

The catalysts were installed on the LDT for emissions testing. Issues with engine control prevented using the rapid warm-up strategy that had proven effective in enabling NOx emissions approaching Tier 2 Bin 5 with fresh catalysts. Average tailpipe emissions from FTP-75 testing showed that non-methane organic gases (NMOG) and CO emissions were within Tier 2 Bin 5 limits, but the NOx emissions were higher than fresh and at 50k mi, with 74% conversion and 0.128 g/mi tailpipe NOx over the FTP-75 cycle (see Figure 1). The CDPF continued to be effective at meeting the regulated level of PM with 0.0012 g/mi, and it effectively converted any NH_3 slip from the SCR catalyst.

In order to determine which component was responsible for the decreased emission performance, combinations of low-mileage and 120k mi SCR and DOC catalysts were tested. The low mileage DOC with the aged SCR improved NOx emissions to the level reported at 50k mi: 0.091 g/mi NOx with 85% conversion efficiency. This indicated that the decreased performance of the aged emission system was due

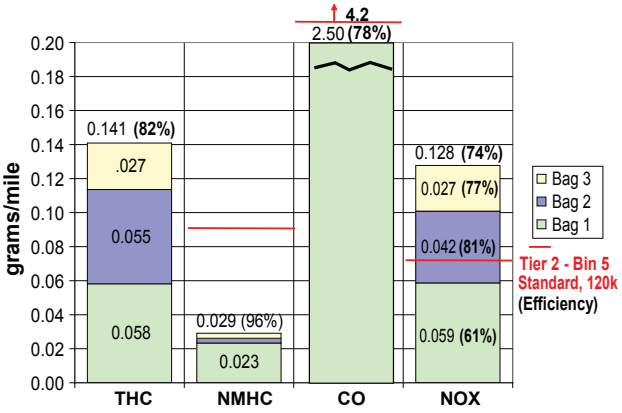


FIGURE 1. FTP-75 performance of the 120k mi aged catalyst system on the 6,000 lb light-duty truck without rapid system warm-up.

primarily to deterioration of the DOC, and that the copper/zeolite SCR catalyst was durable to 120k mi.

A newer SCR catalyst with improved low-temperature performance was aged in the laboratory at 670°C under lean conditions for 64 hours. This catalyst was installed on the LDT, and with the aged DOC NOx emissions were improved to 0.081 g/mi. With the more active DOC this catalyst met the Tier 2 Bin 5 NOx limit, with 0.061 g/mi over the FTP-75, even without an engine capable of running a rapid warm-up strategy (Figure 2).

A detailed post-mortem analysis of the 120k mi DOC, SCR and CDPF components showed non-uniform aging of the DOC and SCR catalysts due to exotherms from DPF regeneration and poisoning by oil additives. HC, CO, and NO oxidation activity and surface area of the rear portion of the DOC were reduced compared to the inlet, indicating exposure to high temperatures. The front face of the SCR was especially degraded in NOx performance compared with the rest of the brick. Laboratory flow reactor results are shown in Figure 3 for different parts of a core sample taken from the SCR. The activity of the outlet sample correlated well with a lab-aged sample. There was evidence to suggest contamination by urea-related deposits as an additional aging factor. The CDPF was intact and its washcoat showed evidence of thermal aging. Some ash and soot were found in the inlet channels, as expected.

Semi-empirical DOC and DOC+SCR system models were developed further during the course of the project. The DOC model was used to study the effect of formulation and volume on the amount of NO_2 generated and the resulting SCR NOx conversion. A more detailed SCR model was developed, incorporating energy and mass balances, NH_3 oxidation and several selective NH_3 reactions with NOx. The kinetic parameters were calibrated using NH_3 adsorption and desorption experiments and other laboratory flow

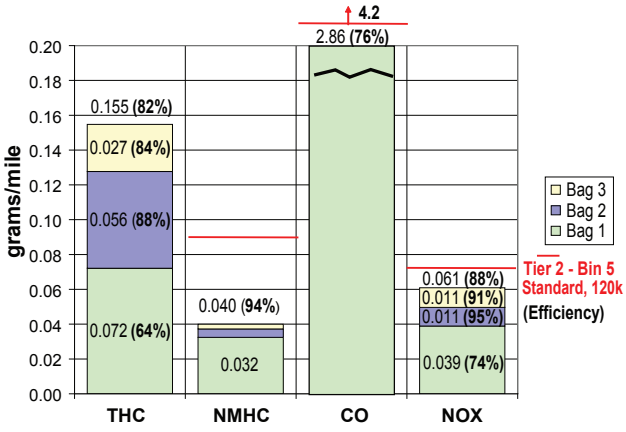


FIGURE 2. FTP-75 performance of the improved SCR catalyst with low-mileage DOC.

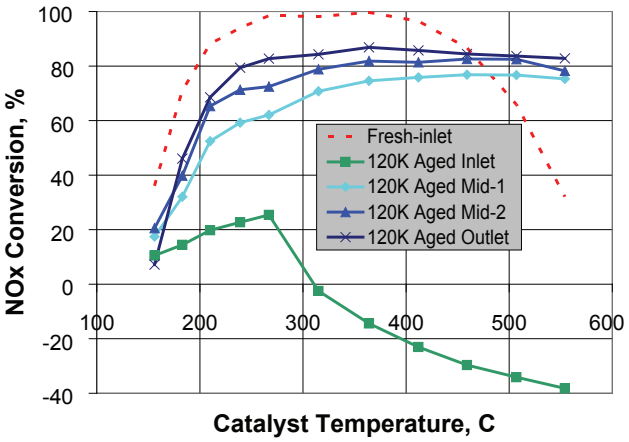


FIGURE 3. NOx activity of core taken from 120k engine-aged SCR catalyst, SV=30,000/hr, NO only.

reactor data. Model performance was validated by comparing predictions to vehicle test results, as in Figure 4. The model predictions gave direction for improving urea control and selecting catalyst components, and helped to explain the vehicle emission results.

Conclusions

- Catalyst system aged to the equivalent of 120k mi on an engine dynamometer met Tier 2 Bin 5 for NMHC, CO, and PM. The engine was not capable of running a rapid warm-up cold start strategy, resulting in a tailpipe NOx level of 0.128 g/mi.
- DOC deterioration was found to be responsible for most of the decrease in NOx performance, indicating that the copper/zeolite SCR was durable to 120k mi.

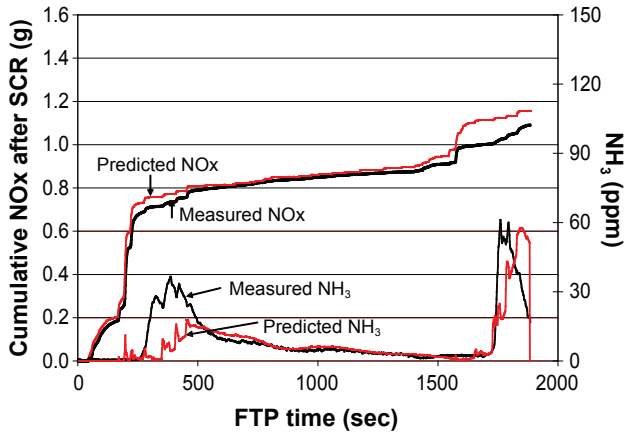


FIGURE 4. Vehicle NOx and NH_3 emissions measured after the improved lab-aged SCR catalyst, compared to model predictions for an FTP-75 test.

- The test vehicle met the Tier 2 Bin 5 NOx limit with a more active DOC and an improved SCR catalyst aged to 120k mi equivalent.

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2. Harnstoff SCR und CDPF System für einen Light-Duty Truck (Urea SCR and CDPF System for a Tier 2 Light-Duty Truck), Christine Lambert, Scott Williams, Brendan Carberry, Erik Koehler, Dr.-Ing. Dean Tomazic, 2006 Aachen Colloquium.

3. Tier 2 Bin 5 Emission Control System for a Light-Duty Diesel Truck, C. Lambert, SAE Government/Industry Meeting, May 10, 2006.

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II.B.7 Fundamental Sulfation/Desulfation Studies of Lean NOx Traps, DOE Pre-Competitive Catalyst Research

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DOE Technology Development Manager:
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Objectives

- Provide a better understanding of the fundamental deactivation mechanisms that result during regeneration and desulfation
  - Investigate ways to limit the impact of these mechanisms
- Transfer this information to teams to:
  - Improve the material
  - Improve the desulfation methods
  - Improve simulation of the processes

Approach

- Effort is pre-competitive
  - Allows open dissemination of results and data
- Study deactivation mechanism fundamentally
- Evaluate deactivation from sulfur poisoning and de-sulfation
  - Employ moderate levels of sulfur (15 ppm SO_2) to more accurately mimic engine levels
  - Desulfation under controlled temperature ramps
- Employ multiple analytical techniques to monitor activity and morphology effects
  - Investigate surface species (DRIFTS) and their reactivity
  - Monitor activity over typical operating range, 200-400°C with powder reactor
  - Investigate morphological effects with (BET, X-ray defraction [XRD], Chemisorption)

Accomplishments

- Presented recent efforts at Delphi, CLEERS, and ACE Review (poster)
- Identified multiple sulfate species on both Ba- and K-based lean-NOx traps (LNTs) that are dependent on time and temperature
- Titrated sulfur poisoning in both DRIFTS and kinetic reactor to evaluate poisoning potential of fast and slow sites.
- Correlated sulfation degree to desulfation species
- Demonstrated linear loss in storage sites with sulfation
- Published FY 2005 results in refereed journal (Catalysis Today)
- Characterized catalysts for morphological and bulk changes

Future Directions

- Verify sulfates form near Pt then migrate during rich phase
- Perform detailed sulfation/desulfation experiments on washcoated catalyst sample in translational diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) reactor with spatially resolved capillary inlet mass spectrometer (Spaci-MS)
  - Investigate fast desulfation to potentially drive off weakly bound sulfates before they convert to strongly bound sulfates
- Determine sulfation/desulfation behavior of mixed Ba/K model catalysts
  - Investigate which phase preferentially adsorbs sulfates first
- Investigate effects of doping storage phase with other alkali/alkaline components to affect sulfate stability

Introduction

Several efforts previously investigated under the Cummins/Oak Ridge National Laboratory (ORNL) Cooperative Research and Development Agreement (CRADA) which are pre-competitive have been transferred to this project. This allows

open dissemination of those research results, without confusing issues of CRADA protected information, and frees up CRADA funds to investigate protected topics. The transferred efforts connect kinetic rates with optical spectroscopy areas. Nevertheless, the two projects will continue to work closely to address both competitive and pre-competitive research issues.

The complex heterogeneous nature of production catalyst washcoats critically obscures research of fundamental mechanisms. Model catalyst materials represent only a component of production materials, but allow isolation of individual fundamental processes; these include detailed mechanisms for desorption and poisoning, intermediate existence and role, and reduction details. Hence, this project primarily employs model catalyst materials for experimental investigation of fundamental catalyst phenomena.

Approach

Under future vehicle regulations, the efficiency of a diesel engine system will also be correlated to the efficiency of the catalyst system since a fuel penalty is sustained to achieve the emissions requirements. Therefore, it is essential to have an efficiently functioning catalyst system in conjunction with a diesel engine. Modeling/simulating processes is an effective way to develop efficient 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 emphasis of this project is to improve detailed understanding of mechanisms limiting catalyst performance. Work closely 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, poisoning processes and the 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.

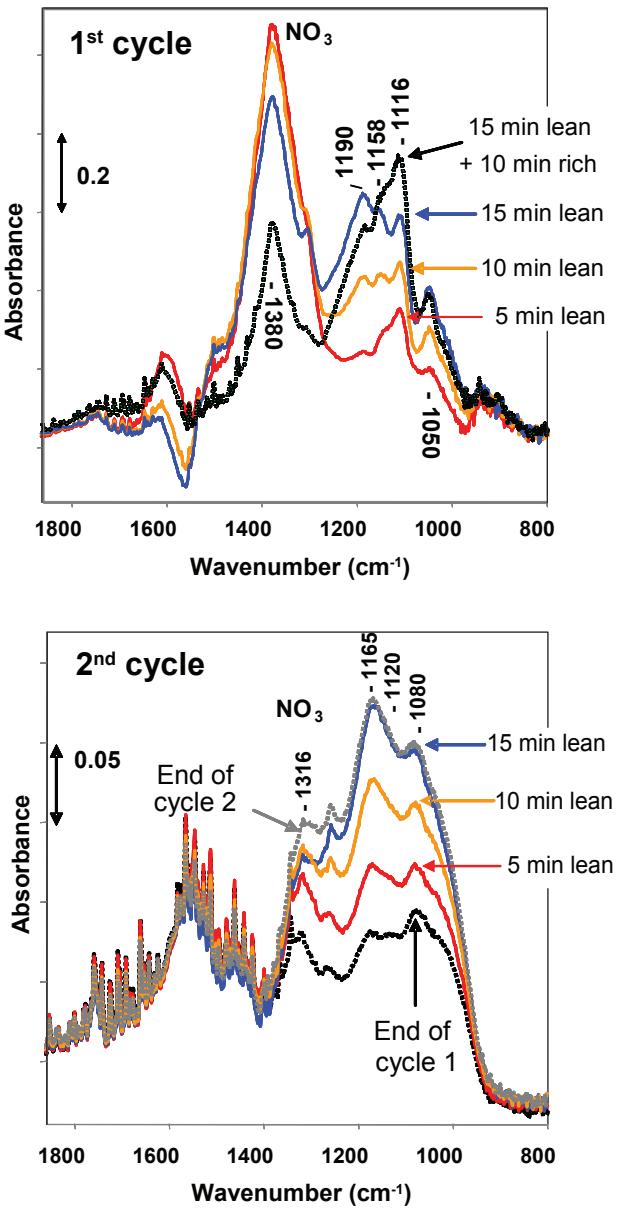

FIGURE 1. DRIFT spectra of sulfation on K-based LNT during cycles of 15 minutes lean and 10 minutes rich. (a) First cycle shows initial sulfation, and (b) second cycle shows LNT as it becomes completely poisoned and nitrate formation ceases.

Results

The results this year have been focused on studying SO_2 adsorption on the storage (Ba or K) and catalytic (Pt) sites of LNTs. We have identified a precursor to permanent sulfate formation on both Ba- and K-based LNTs using DRIFTS. This is illustrated for the K-based LNT in Figure 1a where sulfates are initially observed forming at 1116 cm^{-1} in conjunction with the nitrates at 1380 cm^{-1}; eventually the sulfates at 1158 and 1190 cm^{-1} begin to form as the nitrates begin to diminish. When all nitrate formation ceases during the second cycle (Figure 1b) the sulfate at 1165 cm^{-1} dominates the spectra. Also of interest in these initial spectra is the transformation of sulfates when switching from lean to rich (peaks at 1190 and 1158 cm^{-1} decrease while 1116 cm^{-1} increases). This view contrasts the widely held notion that sulfates are highly stable and immobile, i.e they form in the storage medium and do not change until desulfation. These initial findings were the basis for the bulk of the efforts this year and attempted to answer key questions regarding sulfate stability with respect to degree and temperature of sulfation.

The Ba-based LNT effort this year was focused in the DRIFTS reactor by performing 6.5-minute lean and 30-second rich cycles with 15 ppm of SO_2 flowing at all times; temperatures evaluated were 200, 300, and 400°C. Multiple sulfur groups were observed for these experiments, but specific spectral identification has not been finalized to date. The first observation for Ba-based LNTs regarded sulfur's impact on nitrate storage. At 200°C, the overall nitrate storage was not impacted by SO_2 until the LNT was heated to 500°C, i.e. the sulfur adsorbed as a spectator that required "activation" at higher temperatures to remove nitrates and impact storage capacity. At 300°C, surface nitrates were immediately impacted upon SO_2 addition, and at 400°C bulk nitrates incurred the largest impact. Observations were also detected with respect to Pt surface sites. The Pt-CO bond is visible during the rich-phase of these experiments; it can be an indicator of active Pt sites. When SO_2 is included in the flow the intensity of this bond steadily decreases at all temperatures; however, when SO_2 is removed it recovers. This is indicative of SO_2 masking the Pt surface sites and limiting reactivity.

The K-based LNT effort this year included efforts in the DRIFTS reactor and the powder-based microreactor. Three distinct sulfate forms were observed with DRIFTS on the K-based LNT (listed in order of increasing stability): ionic sulfate, monodentate sulfate and bidentate sulfate. Figure 2 shows the peak areas associated with these sulfates while sulfating at 200, 300, and 400°C with an intermittent mild desulfation at 500°C (the max allowed temperature in the DRIFTS reactor). These plots indicate for each temperature the degree of sulfation continues throughout the experimentation, i.e. no sulfate groups are removed during the mild "desulfation" at 500°C. Also, although the less-stable ionic sulfate is a dominant feature initially, heating tends to transform it into the more stable bidentate sulfate. These two key observations are somewhat disappointing, but continue to illustrate that the sulfate forms on LNTS continue to be mobile, and in future experiments we are hoping to demonstrate the possibility to desulfate the less stable form quickly before it can transform into the more stable bidentate sulfate. This will also more accurately mimic engine-based desulfation efforts, but will require some reactor modifications.

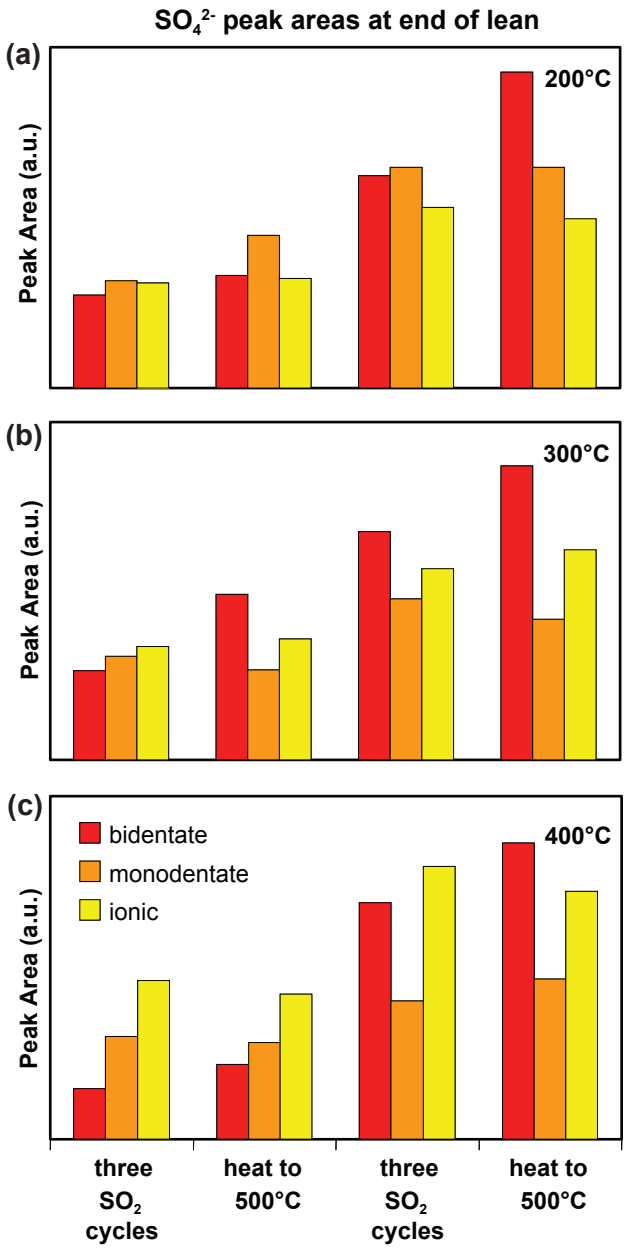

FIGURE 2. DRIFTS peak areas of sulfur groups—(■) bidentate, (■) monodentate, and (■) ionic—that form during incremental sulfation of K-based LNT catalysts. Areas are determined at the end of the lean cycle.

Analyzing sulfates only describes part of the process, thus it is important to also analyze the effects on nitrates. The general observations at 200 and 300°C for the K-Based LNTs are that the active NOx storage, i.e. the amount of NOx that is stored and then released for a given cycle, is relatively constant during the initial sulfation experiments. This is depicted graphically in Figure 3 using the light bars. The impact of sulfur on the overall amount of nitrates stored on the LNT, i.e. the nitrates that are stored but not necessarily released during the rich-phase, is depicted in Figure 3 using the dark bars. It is evident at all temperatures that the overall capacity begins to decrease as soon as SO_2 is introduced; however, the effective storage is not immediately impacted at 200 and 300°C. At 400°C, where nearly all of the storage sites are participating in active NOx storage, the impact on overall storage is immediately observed. This DRIFTS reactor-based observation is also observed in the micro reactor results. Figure 4 shows the overall NOx conversion in the microreactor as a function of exposure time.

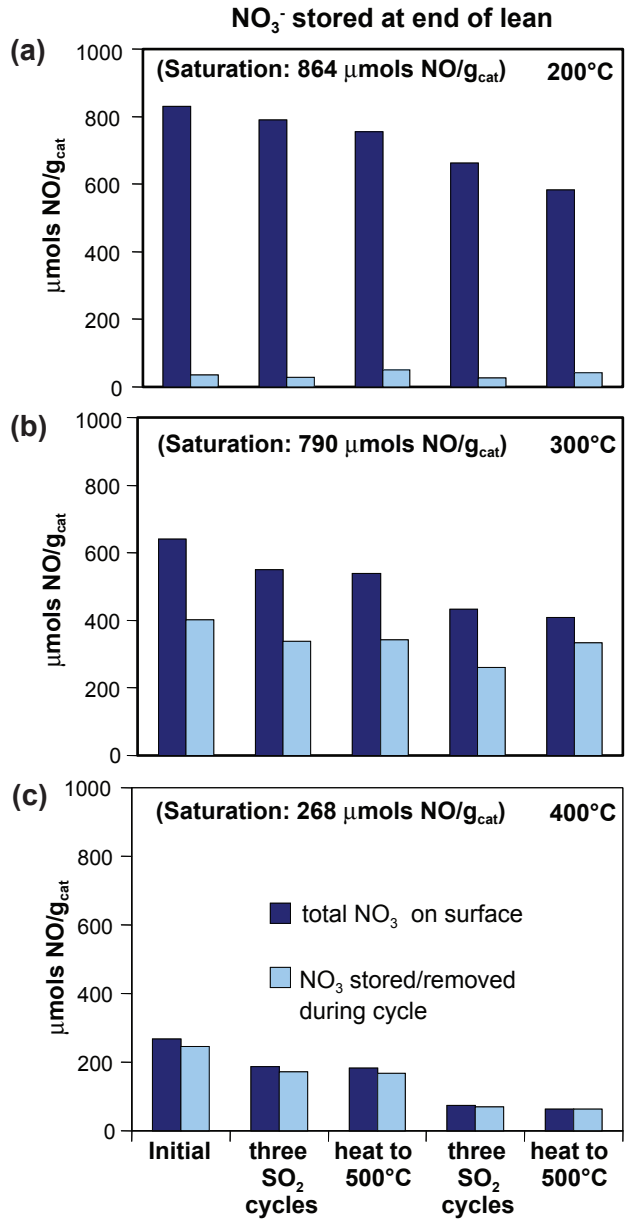

FIGURE 3. Quantified DRIFTS analysis of active nitrates (▭) and overall nitrate storage (■) during incremental sulfation of K-based LNT catalysts. Values are determined at the end of the lean cycle.

At each temperature there is a level period where the NOx conversion is not impacted, then after a period of about 4 hours the NOx conversion decreases almost linearly; the rate of deactivation varies proportional to temperature.

The low levels of SO_2 used to sulfate the catalyst did not allow for accurate measurements of sulfur uptake, so it was difficult to monitor the degree of sulfation directly. However, during the desulfation a large amount of SO_2 and H_2S are desorbed and detection possible. From this, a sulfur collection efficiency can be estimated based

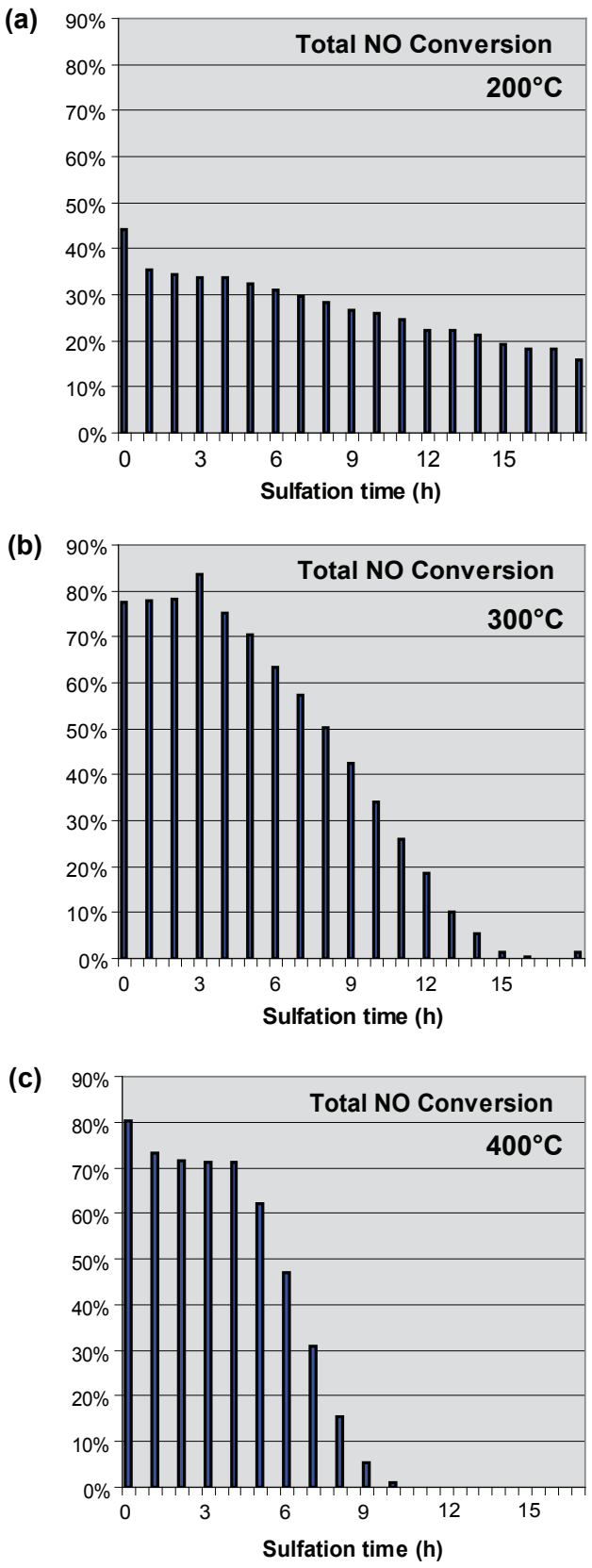

FIGURE 4. NOx Conversion as a function of LNT poisoning using 15 ppm SO_2 at (a) 200°C, (b) 300°C, and (c) 400°C.

on time and temperature. The desulfation results are listed in Table 1, where it is apparent sulfur is trapped much more effectively at 300°C, and much of the SO_2 is not collected at 200°C and 400°C. The desulfation procedure regains much of the activity as demonstrated in Figure 5.

TABLE 1. Summary of desulfation products and their respective temperature of peak formation. Desulfation conditons: 400 to 800°C at 10°C/min, 5,625 ppm CO, 3,375 ppm H_2, 5% H_2O, 5% CO_2, and 30k, h^{-1}.

Sulfation Temperature (°C)	Sulfation Time (h)	H_2S Released (μmols)	Peak Temperature (°C)	SO_2 Released (μmols)	Peak Temperature (°C)
200	18	1.4	750	5.7	760
300	3	1.8	760	1.3	760
300	18	5.0	750	18.0	500+760
400	18	1.1	750	2.6	760

Incremental sulfation studies in the DRIFTS reactor show that the initially formed sulfate generally transitions to the more stable sulfate upon heating to 500°C rather than being removed. Powder reactor efforts corroborated this result as the lightly sulfated LNT does not desulfate below 750°C. A key observation from the sulfation studies was the ability of the LNT to maintain its active sites during the incremental addition of SO_2. This has implications to modeling efforts and consequently systems control, since it suggests that sulfates that form near Pt can migrate to another less-active site. This view contrasts the notion of sulfates being highly stable and immobile, and suggests that LNTs can withstand a significant level of sulfur without a major impact on overall conversion. This observation is most significant at 200 and 300°C where there are a significant number of storage sites that are not used during lean/rich cycling. This result has also been independently corroborated in the powder reactor for all temperatures. The powder reactor study also showed that the collection efficiency of SO_2 varied significantly with temperature with the most efficient collection of sulfur at 300°C; however, sulfur has the fastest and most significant impact on NOx conversion at 400°C.

The reduced funding level this year did not allow for efforts to go forward with our DRIFTS reactor that enables *in-operando* investigation of surface species along the length of washcoated sample. The reactor is designed to allow flow between the infrared window and the sample. The catalysts sample can have dimensions that are 25 mm wide and a length of up to 300 mm. This reactor is designed to allow surface investigations along the axial length of washcoated samples. When coupled with Spaci-MS this reactor will be a powerful tool that will allow a direct correlation between observed surface species and gas-phase concentrations.

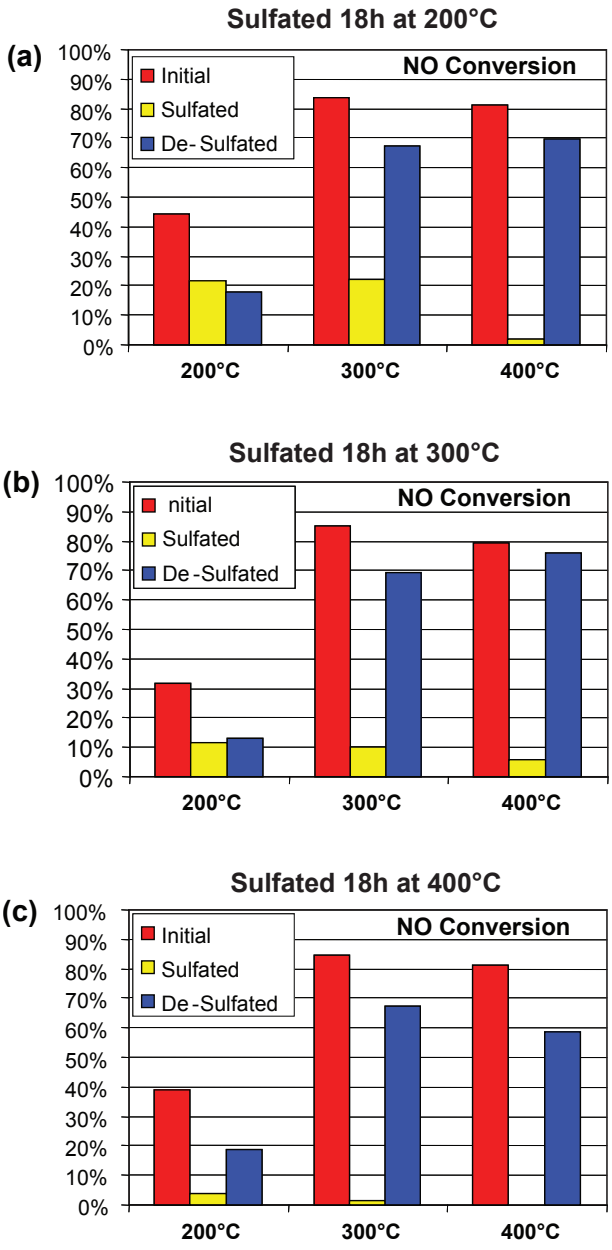

FIGURE 5. NOx conversion before sulfation (■), while completely poisoned (■), and after 800°C desulfation (■); sulfation using 15 ppm SO_2 at (a) 200°C, (b) 300°C, and (c) 400°C.

Conclusions

- Three sulfate forms observed on LNTs
  - Form depends on temperature, degree of sulfation and lean/rich condition
- All sulfur leaving the engine is not trapped
  - Rates of sulfation vary with temperature
  - Additional T-dependent data being generated

- Model must account for two types of sites
  - Fast and slow sites are relevant to rates of sulfation
  - Fast sites appear to be less impacted by initial sulfation
  - Surface mobility is a key factor
- Sulfation degree and relative impact is temperature dependent
  - SO_2 stored at 400°C is more detrimental to performance than SO_2 collected at 200 or 300°C

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II.B.8 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

- Characterized detection limit of various analytical methodologies for real-time on-engine measurement of oil dilution.
- Quantified details of CO regeneration of lean-NOx traps (LNTs) and function of the water-gas-shift reaction (WGSR). Regeneration CO pulsing results in dynamic surface carbonate formation which displaces surface water resulting in dynamic gas-phase water pulses. Comparing isocyanate (NCO) and WGSR pathways for NH_3 formation; WGSR does not appear to be a primary pathway.
- Characterized nature of spatially resolved capillary inlet mass spectrometer (SpaciMS) capillary flow, for improved calibrations and system design for mitigation of intra-capillary condensation.
- Improved the robustness of phosphor thermography fiber probe tips, and signal-to-noise ratio (SNR) of the instrument.

Future Directions

- Apply oil-dilution diagnostic for real-time on-engine measurements with various operating conditions.
- 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

A combination of improved technologies for in-cylinder and aftertreatment control of NOx emissions are required to efficiently meet 2010 emission regulations. These include advanced combustion and associated engine hardware and controls, improved catalyst systems, and overall system management improvements. The development and application of enhanced diagnostic tools is required in order to realize these technology improvements. For instance, unique diagnostics developed in this Cooperative Research and Development Agreement (CRADA) have been used by the partners to resolve the network, sequence and distribution of catalyst reactions via intra-reactor species and temperature measurements; this detailed understanding in combination with other more conventional analysis has proven critical to system implementation. Similarly, the partners have applied these diagnostics outside the CRADA to quantify the performance of EGR and other hardware for improved system efficiency. These types of applications of advanced analytical techniques are required to obtain the detailed understanding of specific system components and the integrated systems in order for the manifold of technologies required for meeting efficiency and emissions targets to work effectively in concert.

Approach

- Apply advanced analytical capabilities to improve the efficiency of diesel-engine-catalyst systems.
- Engine-based research focuses on detailed barriers to diesel market penetration.

- Bench-based research is focused on detailed catalyst reactions, interactions of various reactions, their distribution through the device, and the efficacy of various operation strategies.
- Both the engine and bench research are designed to provide the requisite insight necessary to improve the efficiency of diesel systems.

Results

DOE goals support development of robust and deployable engines using advanced combustion regimes that provide simultaneous high efficiency and low particulate and NOx emissions. Certain advanced combustion regime approaches can result in dilution of engine oil with fuel resulting in chronic irreversible hardware degradation. Current analytical approaches for quantifying oil dilution (e.g., ASTM D 3524-04) are off-line measurements and do not provide the desired detection limit. On-engine real-time measurements of oil dilution would hasten development of robust advanced engine systems that meet DOE goals.

The CRADA team has evaluated a range of analytical approaches to assess their applicability for the desired *in situ* oil-dilution measurement. Optical (ultra-violet/visible, near-infrared, mid-infrared, laser-induced fluorescence, total synchronous fluorescence) and electrical impedance spectroscopy methods based on natural diesel and oil mixtures have a detection limit of approximately 1% v/v diesel in oil which is not sufficient. Compared to our previous work with oil dilution in gasoline systems [1], diesel dilution of oil is complicated by the similarity of the two constituents. Bench results based on incorporation of commercial fuel dyes indicate this to be a possible route for realizing the analytical specifications. This methodology is amicable to optical-fiber based systems, on-engine and real-time analytical systems.

In previous CRADA work the nature of CO regeneration of LNT catalysts and the role of the WGSR has been investigated. That work demonstrated that CO appears to directly regenerate LNT catalysts, and that the WGSR is a lower-priority reaction that apparently occurs in the wrong place and at the wrong time to effect regeneration (see publications). That work also indicated several interesting intra-catalyst water dynamics. The first of these is that when available, the WGSR initially uses surface water and may ultimately cause a gas-phase water sink as the surface is rehydrated to continue the reaction. The second is that dynamic gas-phase water sources can occur spatially and temporally coincident with oxidizing fronts. These results suggest that gas-phase CO_2 generation from oxidation of CO results in catalyst-surface carbonate formation and subsequent displacement of surface water into the gas-phase; this was indicated by gas-phase water generation synchronous with missing gas-phase CO_2. In follow-on work we eliminated several complicating reactions by pulsing CO_2 or oxygen directly into a stream of humidified nitrogen. In a manner consistent with the interpretation of earlier results, gas-phase water generation scaled with the amplitude of the CO_2 pulse. Catalyst temperature had little effect on the efficiency of surface-species displacement, and no displacement was observed with oxygen pulsing. This is further evidence that surface carbonate formation can displace water from the catalyst surface into the gas phase. Consequently, the obtained results further support our conjecture that the water-gas-shift reaction is probably not relevant to primary NOx release/reduction during LNT regeneration: CO acts directly to release/reduce NOx and the resulting CO_2 product displaces surface H_2O which cannot be consumed via water-gas-shift reaction.

WGSR is also potentially relevant to NH_3 generation, and experiments were performed to investigate WGSR and NCO pathways during LNT regeneration. Figure 1 shows species transients from a LNT under various flow conditions. From 900 to ~960 s the feed consists of NO_2+H_2O+N_2. From ~960 to ~1150 s the feed is CO+N_2. From ~1150 to ~1270 s the feed is N_2, and beyond ~1270 s the feed is H_2O+N_2. An NH_3 puff is observed at the first flow switching event that could be attributable to WGSR or NCO pathway; however, the amplitude of this feature does not scale with the temperature dependence of the WGSR. There is no NH_3 formation in the absence of water during regeneration conditions. Transient NH_3 generation is also observed at the final feed switch without CO and as H_2O is turned on. The results suggest surface NCO hydrolysis to be the primary pathway for NH_3 generation.

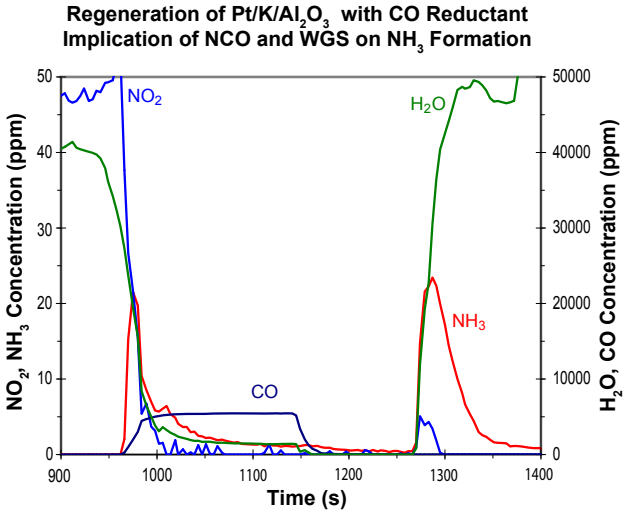

FIGURE 1. FTIR Measured Transient LNT-Effluent Species Pool with Varying Feed Composition to Investigate the Origin of NH_3

The SpaciMS is an instrument developed in the CRADA that has been applied extensively both within and outside the CRADA and on DOE and industry sponsored projects to further DOE energy efficiency goals. Experiments were performed to better understand the nature of sample flow in the SpaciMS capillaries. This improved understanding is needed to improve measurement quantification and better specify capillary conditions to mitigate intra-capillary sample condensation. Capillary flow is generally not well understood based on discussions with industry leaders in the vacuum and capillary technologies areas, university professors and a Fellow of the American Vacuum Society. Experiments were performed to characterize the transit time of various gas mixtures. These measurements show that capillary flow follows mixture bulk viscosity; hydrogen and methane flow faster than oxygen and nitrogen, and helium behaves more like nitrogen than hydrogen. Moreover, little chromatography effect was observed. A step-edge of H_2 in N_2 flow faster than does N_2, but the mixture constituents arrive at approximately the same time; in the mixture H_2 arrives slightly earlier than N_2, but the predominant effect is from mixture composition and hence viscosity. This work will continue in conjunction with flow modeling to better understand capillary flow and its implications on SpaciMS measurements.

Optical-fiber based phosphor thermography has been refined and used in the CRADA to quantify *in situ* intra-catalyst transient temperature distributions. In combination with the SpaciMS this provided a rich description of the catalyst chemistry in terms of local species and temperature. This significantly benefits the understanding and modeling of these complex systems important to DOE's efficiency goals. Methodologies to produce robust, minimally invasive, phosphor-tipped optical fibers have been investigated. Deposition methodologies for multi-component oxide phosphors can change the nature of the phosphor and be limited. A method using fine attrition-milled phosphor in conjunction with a thermally cured ceramic adhesive has proved superior to previous methodologies. Using the new method, coated fibers have survived repeated experiments up to 1,000°C and involving fiber-probe translation.

Conclusions

- Dye additives appear to provide a pathway to realizing oil-dilution specifications
- CO appears to directly regenerate LNT catalysts
- WGSR is of secondary importance to LNT-catalyst regeneration
- WGSR is not a primary pathway for NH_3 generation
- SpaciMS capillary flow does not appear to follow Hagen-Poiseuille flow
- SpaciMS capillary flow is proportional to sample bulk viscosity
- SpaciMS capillary flow shows little chromatography effect
- Improved phosphor deposition methods provide more robust phosphor-thermography probes

References

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FY 2006 Publications/Presentations

1. Jae-Soon Choi, William P. Partridge and C. Stuart Daw (2005). "Spatially-resolved in situ measurements of transient species breakthrough during cyclic, low-temperature regeneration of a monolithic $Pt/K/Al_2O_3$ NOx storage-reduction catalyst," Applied Catalysis A 293, 24-40; doi:10.1016/j.apcata.2005.06.025.

2. Jae-Soon Choi, William P. Partridge, William S. Epling, Neal W. Currier, and Thomas M. Yonushonis (2006). "Intra-channel evolution of carbon monoxide and its implication for the regeneration of monolithic $Pt/K/Al_2O_3$ NOx storage-reduction catalyst," Catalysis Today 114, 102-111; doi:10.1016/j.cattod.2006.02.011.

3. William P. Partridge, "Spatially Resolved Capillary-Inlet Mass Spectrometry: Instrument Details and Applications," Centre for the Theory and Application of Catalysis (CenTACat), Queen's University Belfast, Belfast, Ireland, June 7, 2006.

4. Bill Partridge, Jae-Soon Choi, William S. Epling, Neal W. Currier, Tom Yonushonis, "Intra-Reactor Measurements of Transient Species Distributions," The Instrumentation, Systems and Automation Society EXPO 2006, Houston, Texas, October 17, 2006.

5. Jae-Soon Choi, Vitaly Prikhodko, Kalyan Chakravarthy, Stuart Daw, "Assessing Monolith Length Effect on LNT Performance," 9th CLEERS Workshop, University of Michigan, Dearborn, May 4, 2006.

Special Recognitions & Awards/Patents Issued

1. Invited seminar at Queen's University Belfast, Ireland, Centre for the Theory and Application of Catalyst (CenTACat) on in-operando intra-reactor SpaciMS species measurements; see item 3 in FY 2006 Publications/Presentations.

II.B.9 Off-Highway Engine Emission Control with High System Efficiency

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Objectives

- Demonstrate Tier 3 emission levels with fuel consumption at 195 g/kWh or less by optimizing injection control with urea-SCR.
- Achieve particulate matter emission levels less than 0.02 g/kWh.
- Optimize NOx emissions using an advanced urea-SCR system.

Accomplishments

- Achieved interim Tier 4 NOx emissions and final Tier 4 particulate matter (PM) emissions for an off-highway diesel engine using a combination of advanced injection control coupled with urea selective catalytic reduction. This represents a >90% reduction in NOx and PM emissions over the baseline setting.
- Discovered that the total PM emissions are reduced by 50% by the urea-SCR catalyst. This effect was maintained during high rates of urea application (up to stoichiometric level flow). Evaluated the influence of fuel sulfur concentration on the performance of a urea-SCR system and PM emissions.
- Evaluated the influence fuel sulfur level, injector orifice design and catalyst systems.

Future Directions

- Conduct an investigation of particulate formation and chemistry as a function of rail pressure and urea-SCR dosing.
- Optimize the efficiency of a 2007 Deere diesel engine equipped with open control, variable geometry turbocharger (VGT), and exhaust gas recirculation (EGR) to enable excursions into advanced combustion regimes.
- Assess waste heat recovery potential using a combination of experimental evaluation and advanced modeling.
- Install and evaluate a prototype reformer for a lean-NOx (LNT) study on the 2007 Deere engine.

Introduction

Tier 3 federal standards for new off-highway diesel engines require that NOx and PM levels be regulated to 4 g/kWh and 0.2 g/kWh, respectively, for engines between 130 and 560 kW. The phase-in period for Tier 3 compliance is set to begin in 2006 and to be completed by 2008. Urea-SCR has been shown to effectively reduce NOx emissions for on-highway applications, but needs to be thoroughly evaluated for off-highway engines since both engine design and operating conditions are different. The utilization of advanced injection systems and controls are to be evaluated for improvements in both PM emissions and fuel efficiency. This project seeks to develop and evaluate emission control methodologies with the goal of identifying pathways to meet interim Tier 4 and retrofit solutions.

Approach

During FY 2006, this Cooperative Research and Development Agreement with Deere & Company was renewed with a focus on maintaining or improving fuel economy while meeting Tier 4 emissions levels for NOx and PM. The initial approach was to assess the efficacy of utilizing high fuel rail pressures to lower PM emissions. Because NOx emissions increase with high rail pressure, an advanced urea-SCR system was evaluated to determine its effectiveness to lower NOx emissions to Tier 4 levels. The test protocol followed the ISO 8178 C1 test cycle for off-highway engines. Data were collected for a range of urea delivery rates, up to and exceeding the stoichiometric value. The particulate matter was evaluated as a function of rail pressure. The PM was also evaluated during the urea-SCR process to determine chemistry changes that might result during the urea-SCR process.

Results

The influences of rail pressure and urea-SCR on the resulting NOx and PM emissions are shown in Figure 1. Increasing the rail pressure to values approaching

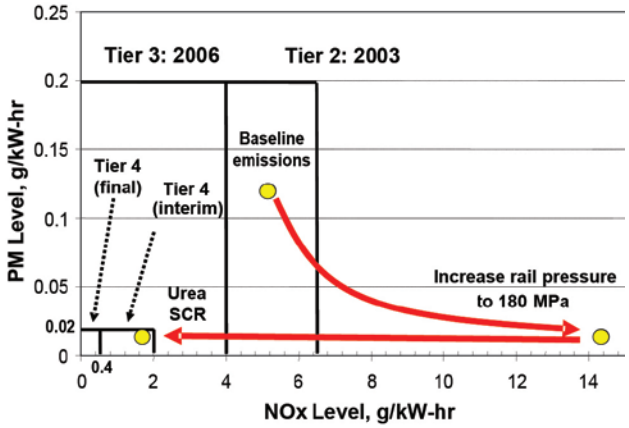

FIGURE 1. PM versus NOx Emissions for an Off-Highway Diesel Operated at High Fuel Rail Pressures and Utilizing Urea-SCR

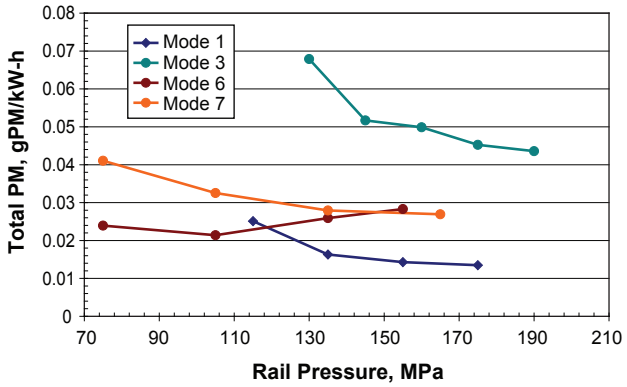

FIGURE 2. Total PM as a Function of Rail Pressure and Engine Operation

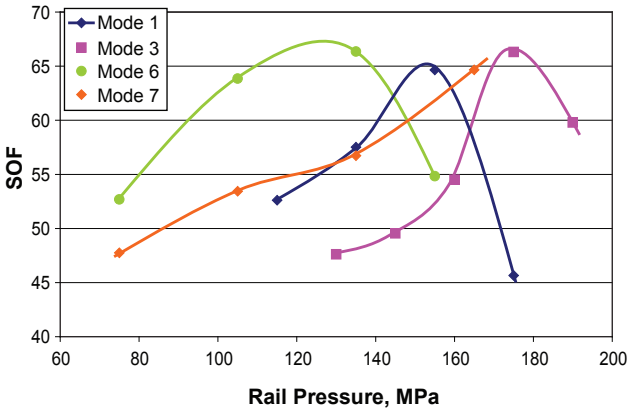

FIGURE 3. SOF of the Collected PM as a Function of Rail Pressure and Engine Operation

180 MPa decreased the total PM to less than 0.02 g/kWh; however, the NOx emissions were increased from a starting value of 5 g/kWh to almost 15 g/kWh. Under high rail pressure, the application of urea-SCR was effective at lowering the NOx emissions to 1.75 g/kWh, which meets the interim Tier 4 limits. The results show that the high rail pressure/urea-SCR approach was successful at meeting the Tier 4 PM and interim Tier 4 NOx emissions for off-highway diesels.

Further analysis of the PM structure and chemistry were performed as a function of rail pressure for four of the ISO 8178 test points shown in Table 1. The total PM and SOF results are shown as a function of rail pressure in Figures 2 and 3, respectively. Although the total PM mass was observed to decrease for Modes 1, 3, and 7 with increasing rail pressure (as shown in Figure 2), the effect appears to be marginal. For Mode 6 the mass initially decreased slightly when raising the pressure to 100 MPa. At high pressures however, the Mode 6 PM mass was observed to gradually increase with higher rail pressures. Analysis of the collected PM indicated that the soluble organic fraction (SOF) was very high for each condition as shown in Figure 3. For modes 1, 3, and 6 the SOF of the PM was observed to increase initially, reach a peak value, and then decrease with increasing rail pressure. The reason for this is not known, but is probably related to fuel droplet size and jet penetration distance.

TABLE 1. Description of Modal Test Points

ISO 8178 Mode	Engine Speed, rpm	Torque, ft-lbs
1	2,400	400
3	2,400	200
6	1,400	352
7	1.400	235

The total PM was also collected for Mode 6 while applying urea to lower the NOx emissions. The results shown in Figure 4 indicate that the total PM mass can be significantly reduced by the urea-SCR catalyst. This reduction is significant even during high rates of urea application, up to and including overspray conditions. The accompanying gas chromatography-mass spectrometry results indicate that high pressures generate a large SOF, which is eliminated (via oxidation) by the catalysts is relatively unaffected during urea-dosing.

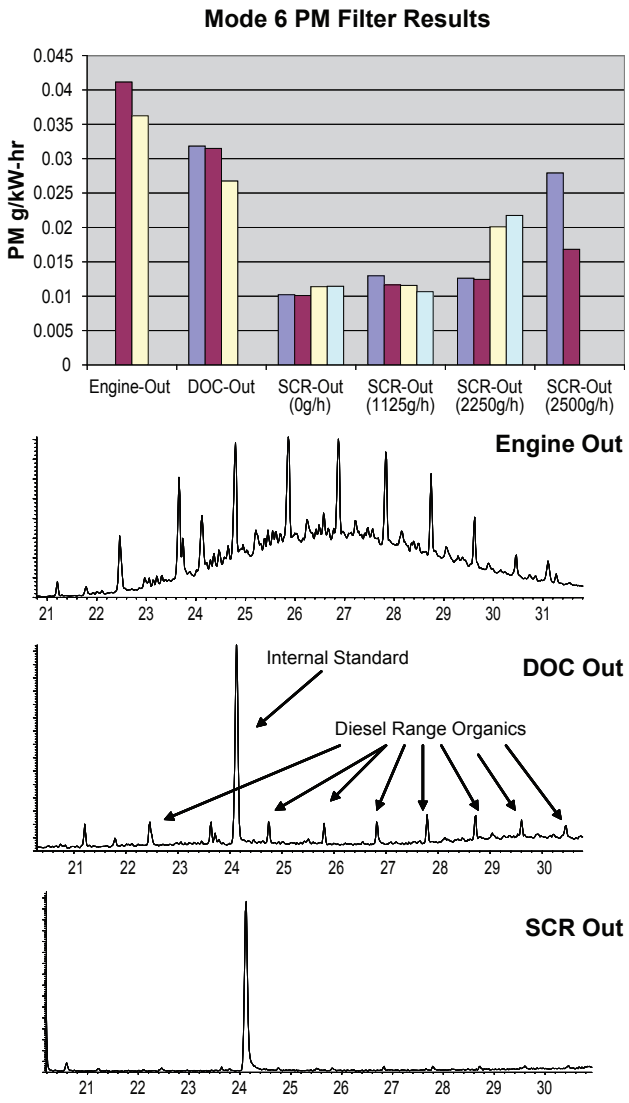

FIGURE 4. Brake Specific PM Emissions and Chemistry During the Application of Urea to the SCR Catalyst

Conclusions

- The combination of high rail pressure and urea-SCR was effective at lowering PM and NOx emissions from an off-highway diesel engine to within Tier 4 and interim Tier 4 levels, respectively. This approach is considered to have better fuel efficiency compared to reformer-based systems
- Total PM mass for Modes 1, 3, and 7 decreased gradually with increasing rail pressure; however, for Mode 6, the mass actually increased with high rail pressure.
- The SOF of the particulates was high. For modes 1, 3, and 6 the SOF increased initially, reached a peak value, and then decreased with increasing rail pressure.

II.B.10 Discovery of New NOx Reduction Catalysts for CIDI Engines Using Combinatorial Techniques

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Subcontractors:
- BASF Catalysts LLC (formerly Engelhard Corporation, Iselin, NJ)
- 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 (i.e., hydrocarbon-SCR, HC-SCR).
- Have 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 120k standard.

Accomplishments

- Tested over 5,600 materials for NOx reduction potential since the initiation of the project and testing of materials with simulated diesel fuel is the standard.
- Twenty full-size catalysts have been coated to use for engine studies.
- Conversions of 92% (Highway Cycle), 76% (US06 Cycle) and 60% (Federal Test Procedure, FTP) have been measured (V6 common rail diesel).
- Sulfur poisoning has been evaluated and regeneration strategies have been identified using both reactor studies and engine evaluations.
- Laboratory thermal aging studies have been completed.
- Phosphorus poisoning studies have been initiated.
- Discovery testing with a simulated gasoline fuel has been started.

Future Directions

- Use the discovery system to refine the downselected catalysts to make them production viable.
- Use the discovery system to evaluate materials for gasoline applications using simulated gasoline fuel.
- Dyno evaluate the downselected catalysts to identify control strategies that satisfy the emission control standards, resist or regenerate from poisoning and coking.
- Develop a production feasibility analysis for one of these catalyst systems.
- Produce the final report and conclude the project.

Introduction

This GM project was initiated on August 16, 2002. 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

Selective catalytic reduction (SCR) with reductants from the fuel (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 (Engelhard, now a division of BASF), informatics to mine the data arising from the fast throughput experimentation (Accelrys and GM) and classic reactor evaluation to determine the suitability of the new materials for automotive applications (GM and BASF).

Results

To date at BASF, over 5,600 new materials have been evaluated on the discovery system since the initiation of the project. To date the results from this approach have identified at least two catalysts for

coatings that have been downselected for detailed analysis that would identify if these coatings might have the potential for engine applications. Issues considered in these analyses include effects of poisoning (sulfur and phosphorus poisoning), propensity to coke, thermal aging and engine control strategies that would allow a diesel powertrain to satisfy emission standards. These studies have included reactor studies with a simulated diesel fuel (67 vol% n-dodecane and 33 vol% m-xylene), coating and canning of the materials on full size monolith bricks and engine testing of these catalysts.

The catalyst/dyno setup is shown in Figure 1. This design includes a DOC to clean up the engine-out hydrocarbons and a dosing system for controlled addition of hydrocarbon to the SCR catalysts. The mixer is added to ensure full vaporization of the fuel before the HC-SCR catalyst.

This dyno test system (V6 common rail diesel) has been used to evaluate the effects of hydrocarbon dosing (carbon to nitrogen ratios, C/N), oxygen concentrations, space velocities and transient effects in the engine environment. Instantaneous NOx conversions measured (2005) over the US06 Cycle (Figure 2) shows conversions consistent with the high conversions observed from the laboratory reactor experiments. Subsequent engine studies using the same dyno setup with a larger catalyst volume have measured conversions of 92% (Highway Fuel Economy Test, HWFET), 76% (US06) and 60% (Federal Test Procedure, FTP).

Thermal aging of the same catalytic coating as was used in the engine test were performed (Figure 3). For air aging the sample is held at the specified temperature (650°C) for varying times in air with 10% water vapor added to gases. The air aging at 16 hours is the standard aging used for all the discovery samples. As can be seen from the figure there is little loss in activity for the sample. The redox aging cycle between rich and lean feeds is more representative of the aging that would occur for the stoichiometric three-way catalyst. This aging cycle typically causes exotherms within the catalyst. These exotherms can often exceed the inlet gas temperature by several hundred degrees. Consequently, redox aging can expose the catalyst to temperature variations that exceed the temperatures the catalyst "sees" with air aging. As can be seen in the figure the redox aging does cause a greater loss in activity than air aging; however, with a gas temperature

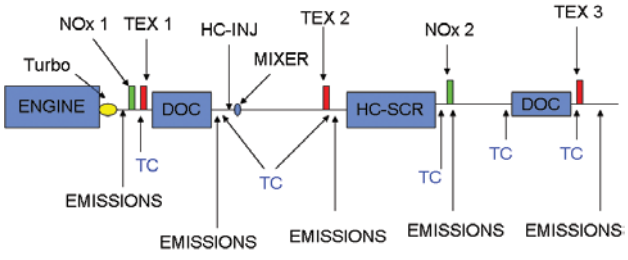

FIGURE 1. Schematic shows the test cell design for measurement of emission reduction technology using the full-size HC-SCR converters. TEX indicates species detectors for the emissions at various points within the aftertreatment system. HC-INJ indicates a system for controlled injection of hydrocarbons into the exhaust stream.

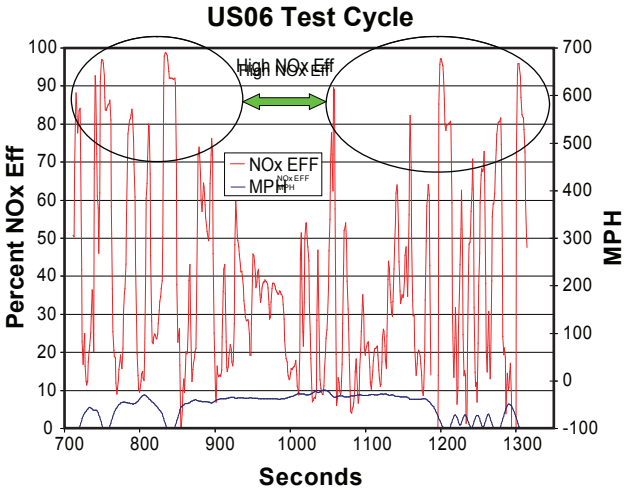

FIGURE 2. Graph of the instantaneous NOx conversion for this HC-SCR dyno measurement over a part of the US06 test cycle. For presentation convenience, the miles per hour in the test cell is multiplied by -100 to move it off the graph of the NOx conversion.

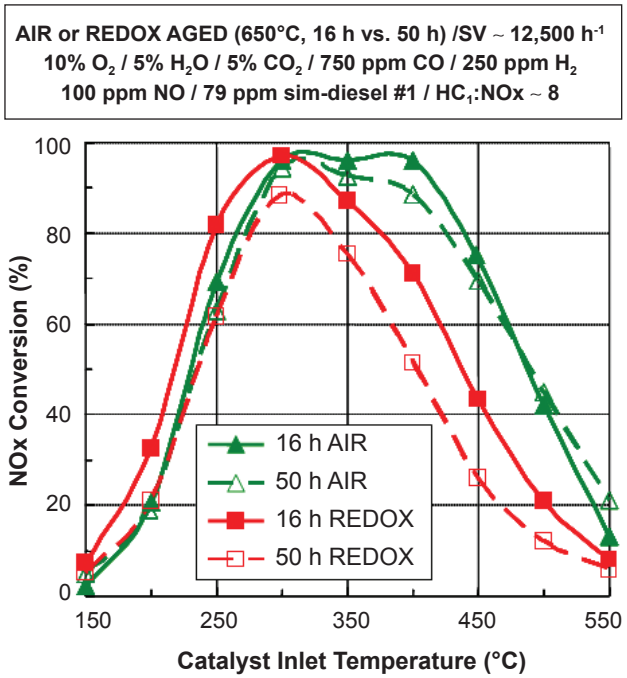

FIGURE 3. Comparison of the activity of monolith samples after aging. The air aging at 16 hours is the standard aging used for all the discovery samples. Redox aging cycles between rich and lean feeds.

of 650°C it does not cause much more damage. Other aging data does show that these catalysts are quite sensitive to temperature, and higher aging temperatures cause significantly more damage. However, 650°C is a common upper limit to the exhaust temperatures of today's modern diesels.

Sulfur in modern diesel fuels has been significantly reduced. We have evaluated the effects of sulfur poisoning on the downselected catalyst coating used in the engine tests. A range of regeneration conditions were examined. This particular catalyst sample was sulfated and desulfated multiple times over approximately three months. Optimum exhaust gas conditions were developed for desulfation. The activity of the catalyst was evaluated at the beginning of that phase of the project. These catalysts similar to all the catalysts in this project were aged at 650°C in steam for 16 hours. At the end of that extensive study the activity of the desulfated catalyst was measured and compared with the initial activity (see Figure 4). There was some small loss of overall activity; however these results do show that this catalyst for coating can be regenerated from sulfation and is relatively stable to multiple regenerations.

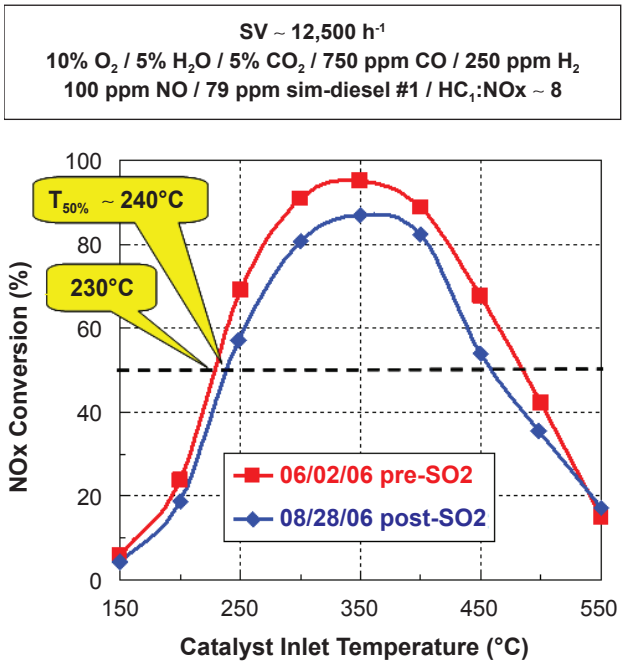

FIGURE 4. Comparison of the activity of a monolith sample after sulfur poisoning and regeneration. This sample was used to test a range of regeneration strategies. There is very little loss of activity from these tests.

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.

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.

Special Recognitions & Awards/Patents Issued

1. Five records of invention were filed based on work from this project during this year.

II.B.11 Efficient Emissions Control for Multi-Mode Lean DI Engines

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DOE Technology Development Manager:
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Objectives

- Examine benefits of HC emissions from low-temperature combustion to support hydrocarbon selective catalytic reduction (HC-SCR).
- Investigate unusual engine control approaches to enhance catalyst performance.
- Assess potential for combining aftertreatment technologies (such as SCR with lean-NOx trap, LNT) to provide aftertreatment solution for multiple operational modes (e.g., low-temperature combustion [LTC] vs. conventional diesel combustion).

Accomplishments

- Modified LNT regeneration strategies to generate engine-out hydrogen and other reformate products under net-lean conditions.
  - Individual cylinder control provides up to 0.8% hydrogen with over 1% CO, and 3,000 ppm cracked HCs with 9% oxygen in exhaust.
- Evaluated commercial HC-SCR catalysts on engine.

Future Directions

Evaluate commercial HC-SCR catalysts (Pt, Cu, and Ag), and Pacific Northwest National Laboratory (PNNL) HC-SCR catalyst

- Bench reactor experiments
  - Promotional effect of hydrogen
  - Temperature sweep
  - Investigate CO or HC masking
- Engine-based study
  - Conventional diesel combustion
  - High Efficiency Clean Combustion (HECC) modes
  - Late-cycle post injection or in-pipe injection
  - Individual cylinder control

Introduction

New combustion regimes are being investigated as a means to improve the efficiency of diesel engines. 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. Additionally, new combustion regimes are sought that will result in improvements in brake specific fuel consumption (BSFC). While these regimes will be implemented whenever possible in future production engines, it is expected that diesels will still run in the more conventional modes at certain operating conditions. The wide range of operating conditions provides a challenging environment for the aftertreatment system. Multi-mode operation of the engine will almost certainly require a multi-mode aftertreatment system. This project aims to leverage existing combustion and aftertreatment R&D at ORNL, collaborating with industry partners to develop and characterize advanced catalysts to fill this need. While lean-NOx trap and urea-SCR technology show great promise for reducing NOx under conventional diesel combustion conditions, the lighter load, low NOx regimes may require different catalyst technology. Treatment of the HC and CO emissions during low temperature combustion is of concern even when engine-out NOx is low enough to not require further treatment. Because of the relatively high HC to NOx ratio in LTC modes, HC-SCR may be an attractive option to augment the LNT or urea-SCR 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 modest activity. Experiments to date have shown that LTC can result in an order of magnitude reduction in NOx, with PM emissions and BSFC comparable to levels at "factory" calibrations. Under these combustion modes, HC emissions have been speciated, and a wide range of reactive compounds have been found, including light alkenes, oxygenates, and other compounds known to be effective HC-SCR reductants. As these HC emissions must be treated, it is logical to use them to reduce NOx rather than simply oxidizing them. When operating in traditional combustion regimes, the HC requirements of the aftertreatment system might be fulfilled by injecting additional fuel by a number of means, including in-cylinder injection. The

ongoing LNT studies at ORNL (described separately within this annual progress report) have developed strategies for periodic rich operation (necessary for LNT regeneration). Variations of these strategies were developed (under this "Multimode Catalysis" project) to investigate reformate production under net lean conditions. Results of these experiments will be discussed in the Results section. Commercial HC-SCR catalysts have been obtained from a Manufacturer of Emission Controls Association (MECA) partner and were evaluated under a variety of conditions in FY 2006 using a slipstream for screening 2-inch diameter catalyst cores.

Strategies developed for LNT regeneration have included a late-cycle post injection (80 degrees after top dead center, or Post80), and a delayed extended main (DEM) strategy in which the main injection pulse is extended into the rich regime and retarded to offset any torque increase associated with overfueling. These strategies have been well characterized under the auspices of the related LNT project, and the results have been published [1]. The regeneration strategies study showed that while the reductant levels from the DEM strategy decreased with increasing air:fuel ratio (AFR), only the HC level changed significantly with leaner AFR for the Post80 strategy. That is, the carbon monoxide (CO) and hydrogen (H_2) peaks were relatively constant across the rich AFR sweep for Post80.

Another reported application of reformate is to enhance HC-SCR catalyst function [2-4]. Researchers have shown reformate, or more specifically H_2, to significantly improve NO conversion over Ag/Al_2O_3 catalysts across a wide temperature range. Additionally, H_2 has been shown to offset performance losses of HC-SCR catalysts associated with increased space velocity and sulfur presence. The presence of H_2 in lean exhaust can also serve to accelerate catalyst light-off [5-7].

These LNT strategies were exercised at several lean AFRs to examine whether the H_2 production trend could be extended into the lean regime. Hydrogen was produced in the lean regime close to stoichiometry, but dropped off quickly as AFR was increased. Individual cylinder control was then explored to generate higher levels of reformate under net lean conditions. The strategy commands one cylinder rich, while the other three cylinders remain lean. To preclude engine imbalance and perhaps premature engine wear, each cylinder is programmed to run rich for only 400 milliseconds (ms), although this parameter is adjustable. For example, cylinder 1 runs rich for 400 ms while cylinders 2-4 run lean. When cylinder 1 transitions back to lean operation, cylinder 3 (the next cylinder in firing order) transitions into the rich regime. This control strategy is referred to as ICDEM (Individual Cylinder Delayed Extended Main). Results of these experiments were reported last year [8]. A preliminary catalyst experiment was also conducted using a slipstream of the richest ICDEM strategy through a 2-inch core of a Pt/Al_2O_3 HC-SCR catalyst, highlighting the potential benefit of such a strategy to enhance catalyst light-off [9].

Experiments this year again used the 2-inch core engine exhaust slipstream for evaluating catalysts, as shown in Figure 1. The combination of sample pumps induced a flow of 43 liters per minute (lpm), for a space velocity of 30,000 hr^{-1}. Thermocouples were deployed at the inlet, core, and outlet of the catalyst sample. Both the Pt/Al_2O_3 sample described previously [9], and a Ag/Al_2O_3 sample from the same MECA supplier were evaluated in this setup.

Results

Based on the published results that show a remarkable improvement in NOx reduction at low temperatures for Ag/Al_2O_3 with the addition of H_2 [2-4], the objective was to investigate the benefits of reformate on HC-SCR catalyst performance. The initial experiments were conducted at an engine condition that produced catalyst inlet temperatures in the 200-240°C range. Individual cylinder control was used to run both DEM and Post80 (P80) strategies on one cylinder at a time, denoted ICDEM and ICP80, respectively. The ICDEM produced the most hydrogen and allowed a study of the promotional effect of H_2 on the NOx reduction. The ICP80 produced mostly HCs, and was considered more of a conventional HC-SCR strategy. A third set of experiments used ICP80 at a higher engine load, to increase exhaust temperature. In order to maintain a similar level of NOx, some EGR (exhaust gas recirculation) was used at this higher load. These experiments are denoted ICP80 w/EGR in the figures that follow. Figures 2-4 show the engine-out concentration of the reductants produced by each strategy as a function of the fuel injection pulsewidth of the excess fuel. This parameter is the duration of the post injection event (at 80 degrees after top dead center), or the additional pulsewidth added to the normal main

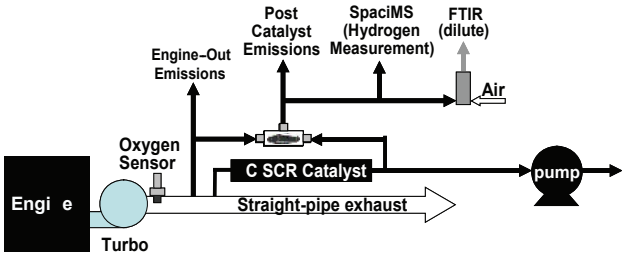

FIGURE 1. Experimental Schematic Showing Slipstream Approach used for Evaluating Catalyst Cores

injection for ICDEM. Note in Figure 2 that the ICDEM produces the most engine-out hydrogen, while Figure 4 shows that ICP80 produces the most hydrocarbons. The NOx level for all experiments was on the order of 500 ppm (parts per million). The ICDEM and ICP80 experiments had 10-12% oxygen in the exhaust. The higher load and use of EGR for the ICP80 w/EGR experiments resulted in about 6% oxygen in the exhaust.

The HC:NOx ratio is shown in Figure 5 as a function of pulsewidth for each strategy for reference purposes. The remaining figures in this report will use HC:NOx ratio for the x-axis. The best NOx conversion noted was approaching 30% for the Pt/Al_2O_3 using the ICP80 strategy at a HC:NOx ratio of 9, as shown in Figure 6. The figure also shows that this catalyst effectively treats the HC and CO emissions. Figure 7 shows the same information for the Pt/Al_2O_3 catalyst with the ICDEM strategy. There does not appear to be any promotional effect of the hydrogen on this catalyst. While the H_2 and CO are consumed, the HC conversion is below 90% and the NOx conversion is below 20%. Reasons for this drop in performance under this condition are presently unclear. In particular, at similar HC:NOx ratios, the NOx conversion is only about half for ICDEM versus ICP80 for this catalyst.

Figure 8 shows the performance of the Ag/Al_2O_3 catalyst with the ICDEM strategy. As noted earlier,

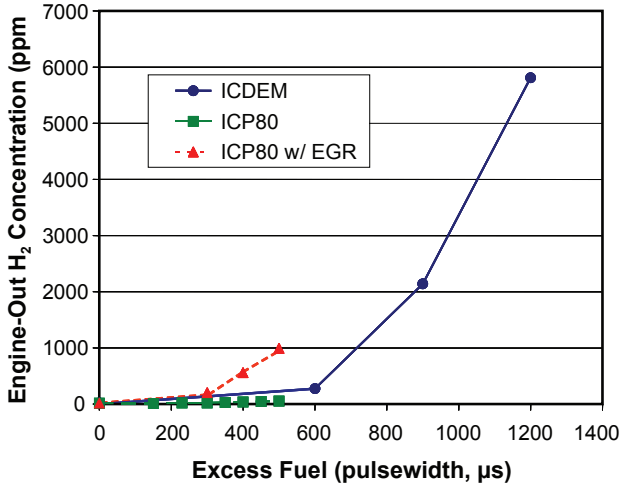

FIGURE 2. Engine-Out Hydrogen Concentration as a Function of Excess Fuel Pulsewidth

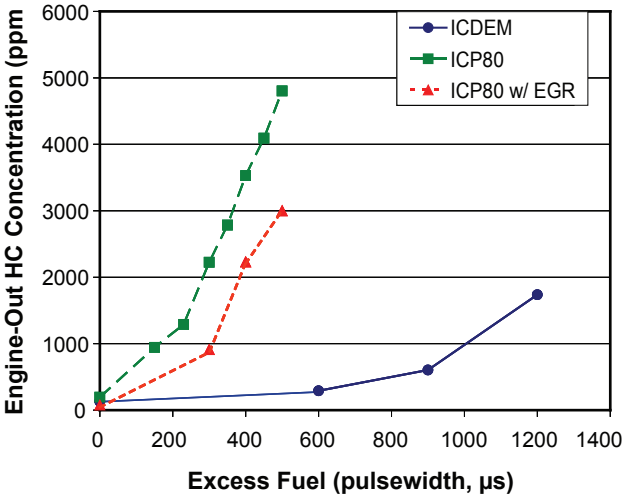

FIGURE 4. Engine-Out HC Concentration as a Function of Excess Fuel Pulsewidth

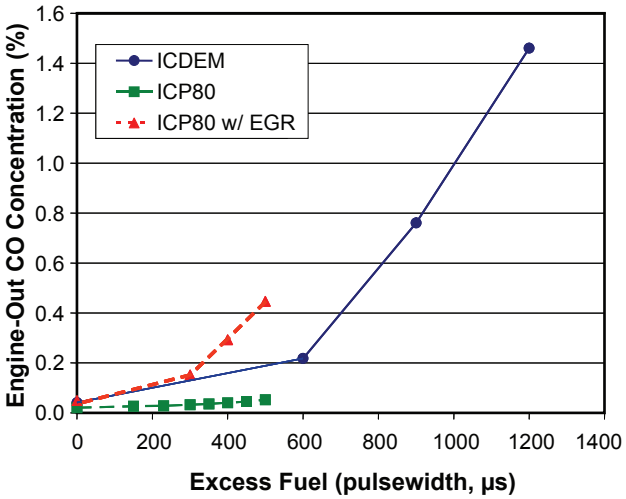

FIGURE 3. Engine-Out CO Concentration as a Function of Excess Fuel Pulsewidth

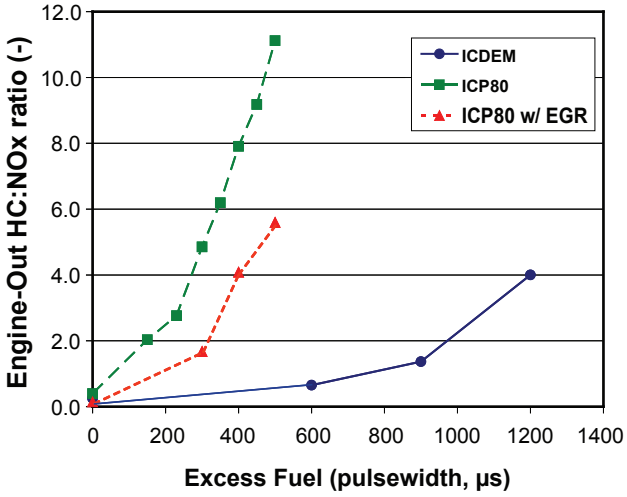

FIGURE 5. Engine-Out HC:NOx Ratio as a Function of Excess Fuel Pulsewidth

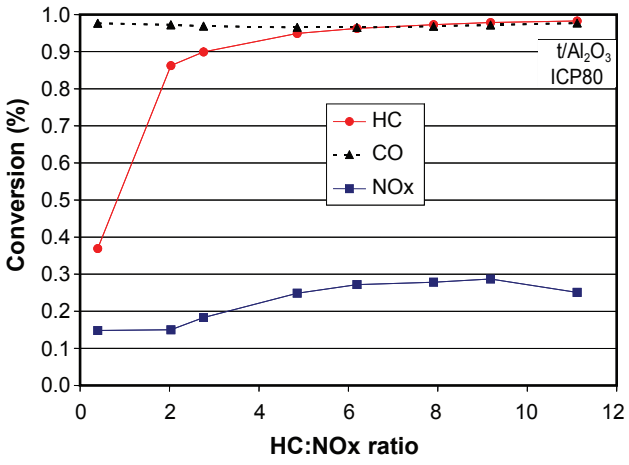

FIGURE 6. Conversion Efficiency Versus HC:NOx Ratio for Pt/Al_2O_3 Catalyst Using ICP80 Strategy

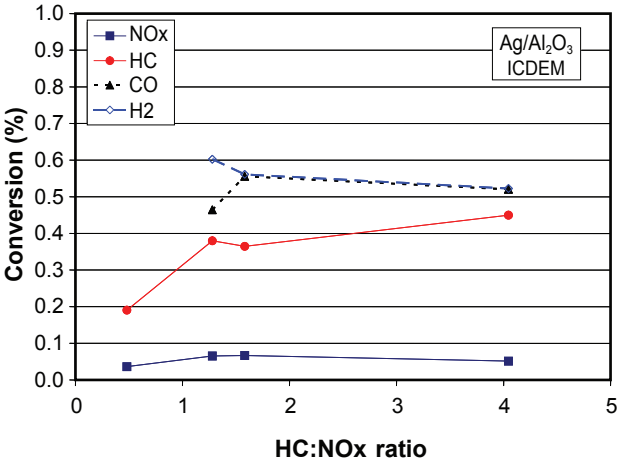

FIGURE 8. Conversion Efficiency Versus HC:NOx Ratio for Ag/Al_2O_3 Catalyst Using ICDEM Strategy

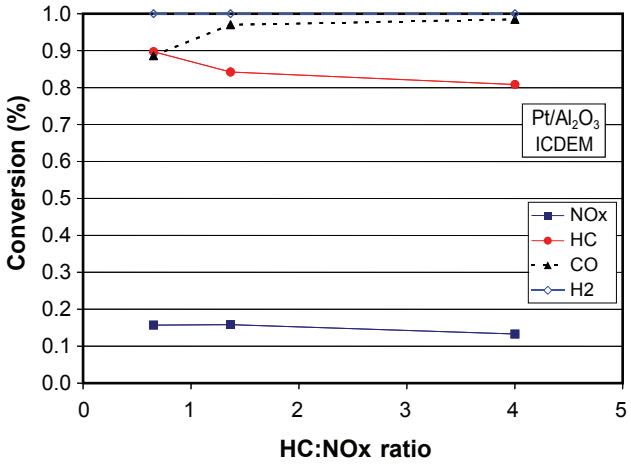

FIGURE 7. Conversion Efficiency Versus HC:NOx Ratio for Pt/Al_2O_3 Catalyst Using ICDEM Strategy

bench-scale experiments have shown Ag/Al_2O_3 catalysts to display remarkable improvements in NOx conversion when small amounts of hydrogen are added to the feed [4], so the results in Figure 8 were not anticipated. As the figure shows, the exhaust feed from the ICDEM strategy netted less than 10% NOx conversion and less than 50% HC conversion. Hydrogen and CO conversion were also very poor.

While there does not appear to be any promotional effect of the hydrogen on this Ag/Al_2O_3 catalyst for the ICDEM case, results for the ICP80 were even worse, with comparable NOx conversion and almost undetectable changes in CO or HC. In order to raise the catalyst inlet temperature, experiments were conducted with ICP80 at a higher load, with EGR to trim the engine-out NOx to a comparable level. As shown in Figures 3 and 4, the higher load and use of EGR results in comparable HC emissions and higher CO emissions. The higher temperature did promote conversion of 10-20% of the CO and HC, but NOx conversion was again negligible, in the 5-8% range. Reasons for the poor performance of this catalyst are unclear, but there are several hypotheses:

- Hydrocarbon Masking. The referenced Ag/Al_2O_3 experiments were conducted on flow reactor benches with bottled gas feed [2-4]. Perhaps the nature of real engine exhaust hydrocarbon species and particulate matter are "masking" active catalyst sites.
- CO Inhibition. Engine-out CO concentration is about three times that of the engine-out hydrogen. The CO may be chemisorbed onto the active metal sites; the chemisorbed CO may prevent H_2 and other gas species from interacting with the active sites and thereby inhibiting the activity of the catalyst.
- Catalyst Loading/Formulation. Details regarding the loading or formulation of the MECA-supplied Ag/Al_2O_3 catalyst are not known. Bench reactor experiments with this catalyst will help elucidate whether "real" exhaust was inhibiting the promotional effect of the hydrogen documented in the literature [2-4].

Follow-on experiments will be complemented by flow reactor bench evaluations. Comparing results in the "ideal" gas bench environment to those from further engine experiments will elucidate the possible functional mechanisms. Furthermore, additional catalyst formulations will be requested from MECA suppliers.

Conclusions

Strategies previously developed for in-cylinder regeneration of LNTs have been modified to allow production of H_2 and other reformate products (e.g., CO, light HCs) under net-lean exhaust conditions by overfueling individual cylinders. These strategies were used to provide reductant to HC-SCR catalysts in slipstream experiments on core samples of two MECA-supplied catalysts. Notable conclusions are the following:

- A commercial Pt/Al_2O_3 HC-SCR catalyst was shown to effectively remove HC, CO, and hydrogen from low-temperature (<240°C) diesel exhaust gas. Maximum observed NOx conversion approached 30% with a HC:NOx ratio in the 7-10 range.
- In-cylinder production of hydrogen with the ICDEM strategy does not appear to enhance low temperature performance of the Pt/Al_2O_3 catalyst under quasi-steady conditions.
- An Ag/Al_2O_3 HC-SCR catalyst was found to provide poor NOx, HC, CO, and H_2 conversion for either the ICDEM or ICP80. Follow-on experiments will attempt to discern the contradictions between bench and engine experiments.

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9. Brian West, Shean Huff, James Parks, Matt Swartz, and Ron Graves, "In-Cylinder Production of Hydrogen During Net-Lean Diesel Operation," Society of Automotive Engineers Paper No. 2006-01-0212, April 2006.

FY 2006 Publications/Presentations

1. Brian West, Shean Huff, James Parks, Matt Swartz, and Ron Graves, "In-Cylinder Production of Hydrogen During Net-Lean Diesel Operation," Society of Automotive Engineers Paper No. 2006-01-0212, April 2006. (Oral presentation at SAE Congress)

2. Brian West, Shean Huff, James Parks, Matt Swartz, and Ron Graves, "In-Cylinder Production of Hydrogen During Net-Lean Diesel Operation," Invited speaker to Diesel Crosscut Team Meeting, Detroit Michigan, November 2005.

Special Recognitions & Awards/Patents Issued

1. Provisional Patent filed, "Advanced Engine Management for Control of Exhaust Species," Ron Graves, Brian West, Shean Huff, and James Parks, 3/30/2006.

II.B.12 NOx Control for High Power Density Hydrogen Engine

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Objectives

- Demonstrate applicability of compression ignition direct injection (CIDI) aftertreatment systems for H_2 internal combustion engine (ICE) applications
  - Lean NOx traps (LNTs), urea (NH_3) selective catalytic reduction (SCR), H_2 SCR
- Determine what key catalytic chemistry is affected by carbon-free exhaust
  - Impacts modeling parameters; both H_2 ICE models and CIDI models
  - Reactor sizing, precious metal cost, and engine operation

Approach

- Initial experimentation on powder catalysts
- Evaluate promising candidates on bench-scale reactor with washcoated cores
  - LNT catalyst: Umicore High Temperature European LNT for SIDI
    - CLEERS LNT focus group reference material
  - Urea (NH_3) SCR catalyst: Iron (Fe) and zeolite-based
    - CLEERS SCR focus group reference material
- Generate data specific for modeling requirements
  - PSAT submodels
  - CLEERS global kinetics model

Accomplishments

- Completed powder catalyst evaluation
  - LNT, urea (NH_3) SCR, and H_2 SCR
  - Down-selected LNT and urea (NH_3) SCR for bench-core reactor
- Results presented at Ford H_2 ICE meeting in March 2006
- Evaluated LNT catalyst performance on ORNL bench-core reactor
  - Two reductant concentrations; 300-500°C evaluation
  - Direct comparison to conventional exhaust (with CO and CO_2)
  - Excellent overall performance–70-100% NOx conversion
  - N_2 selectivity and performance better with H_2 than CIDI exhaust
    - Up to 90% less NH_3 (undesirable by-product) formation
    - 11-33% improvement in NOx conversion

Future Directions

- With remaining funds from FY 2006, we will evaluate SCR catalysts with waschcoated cores
  - Investigate NO:NO_2 ratio
    - Ratio impacts global reactions
    - 1:1 is ideal ratio for fastest reaction path
  - Determine byproduct formation dependence
    - Vary NH_3:NOx ratio
  - Vary temperature from 300-600°C
- With any remaining funds, or if project is funded in FY 2007, the following expanded evaluation will be performed:
  - Evaluate space velocity requirements for H_2 ICE LNT and NH_3-SCR
  - Characterize effect of periodic high NOx dose
    - NOx concentration can reach 0.8-1.0% at $\Phi = 0.8$
    - NH_3-SCR and LNT

Introduction

An increasing national focus on moving towards a hydrogen economy calls for hydrogen-enabled internal combustion engines as a near-term transition technology. While there is potential for these engines to reduce carbon emissions from vehicles, NOx emissions are still problematic [1], and control of NOx emissions with aftertreatment will most likely be required. Oak Ridge National Laboratory's support to the systems analysis program has for several years focused on providing

data for important engine and emissions control related systems for use in larger systems-analysis models that estimate the fuel economy and emissions potential of multiple vehicle configurations. This area is a unique strength of ORNL and is the area in which ORNL can contribute the most to the FreedomCAR and Vehicle Technologies Program. ORNL's involvement with the fuels, engines, and emissions control research areas put ORNL in a unique position to bring input from these areas to the Systems Analysis Program.

Approach

Since little work has been performed in the area of lean NOx reduction for hydrogen ICEs, it is not clear which NOx reduction strategy is best suited to meet the emissions requirements. It is expected that one of the systems being studied for CIDI engines, i.e. lean NOx traps, urea SCR, or H_2 SCR catalysts will be required for hydrogen ICEs. The ORNL team will investigate these strategies with bench flow reactors under typical operating conditions to determine which is best-suited to hydrogen-fueled vehicles. The catalyst or trap materials and cores for the experimental work will be sought from major suppliers through informal collaborations. Additionally, ORNL can formulate catalyst samples (model catalysts) for bench-scale work as needed.

Urea SCR depends on the decomposition of urea into ammonia (NH_3) to reduce NOx in oxidative conditions. Current models of urea SCR catalysts in CIDI exhaust conditions will need to be evaluated and modified for lean-burn hydrogen engines. H_2 SCR and NOx adsorber catalysts can make use of on-board fuel (H_2) to reduce NOx. Successful expansion of current CIDI models of these catalysts for hydrogen applications will require in-depth investigation of the interaction of hydrogen with the catalysts under lean-burn hydrogen engine exhaust conditions, specifically with respect to how the chemistry varies from CIDI. NOx adsorber catalysts are expected to adsorb NOx in a similar fashion to CIDI applications, but NOx reduction ("regeneration") with pure hydrogen fuel will be a dynamic chemical and thermal process that will require thorough evaluation and study for efficient and safe catalyst operation.

Results

The Umicore high-temperature LNT catalyst was evaluated for NOx conversion, N_2 selectivity, and reductant reactivity at a space velocity of 30k h^{-1}. Two reductant concentrations and two exhaust conditions were used while studying the LNT chemistry from 300 to 500°C. The high reductant concentration introduced during the rich phase is 3.1 times the required reductant to reduce the NOx fed to the reactor during the lean phase; the low reductant is 1.1 times the required amount. The exact concentrations for all gases are displayed in Table 1. NO and NO_2 are measured using a chemiluminescence detector (CLD), CO, CO_2, NH_3, N_2O, and H_2O are measured using a Fourier transform infrared (FTIR) instrument with a gas cell attachment, and intra-catalyst measurements of H_2 are made with a spatially resolved capillary inlet mass spectrometer (Spaci-MS).

Excellent NOx conversion was observed for the high reductant concentration at all temperatures and for both the conventional CIDI and the H_2 ICE exhaust conditions; the results are summarized in Figure 1a. The most interesting result from this comparison is the 70% NOx conversion observed with conventional exhaust at 500°C. Compared to the 100% reduction observed with H_2 ICE conditions this is a considerable decrease in activity. Figure 2 shows that the NOx conversion is limited by the regeneration chemistry, as there is a very large amount of NOx released that is not converted. This result suggests that CO is considerably less effective than H_2 at reducing NOx, and thus H_2 ICE has a better regeneration environment for LNT aftertreatment. N_2 selectivity, i.e. the percentage of stored NOx that is converted to N_2, is also a key concern with LNTs. N_2O and NH_3 are by-products that have been observed in conventional CIDI exhaust, and in general they are undesirable. Figure 3a shows the percentage of stored NOx that is converted to both NH_3 and N_2O as measured by FTIR; the remainder is presumed to form N_2. H_2 ICEs have significantly less byproduct formation than CIDI exhaust at 300 and 500°C, especially with respect to NH_3. This suggests that precise reductant

TABLE 1. Gas concentrations used in for the LNT evaluation in the bench-core reactor.

	NO	O_2	CO	H_2	CO_2	H_2O
Conventional Diesel Exhaust						
High Reductant (2.8% total)						
Lean (60s)	300 **ppm**	10%	-	-	5%	5%
Rich (5s)	-	-	1.75%	1.05%	5%	5%
Low Reductant (1.0 % total)						
Lean (60s)	**300** ppm	10%	-	-	5%	5%
Rich (5s)	-	-	0.675%	0.325%	5%	5%
H_2 ICE Exhaust						
High Reductant (2.8% total)						
Lean (60s)	**300** ppm	10%	-	-	-	5%
Rich (5s)	-	-	-	2.8%	-	5%
Low Reductant (1.0% total)						
Lean (60s)	300 ppm	10%	-	-	-	5%
Rich (5s)	-	-	-	1.0%	-	5%

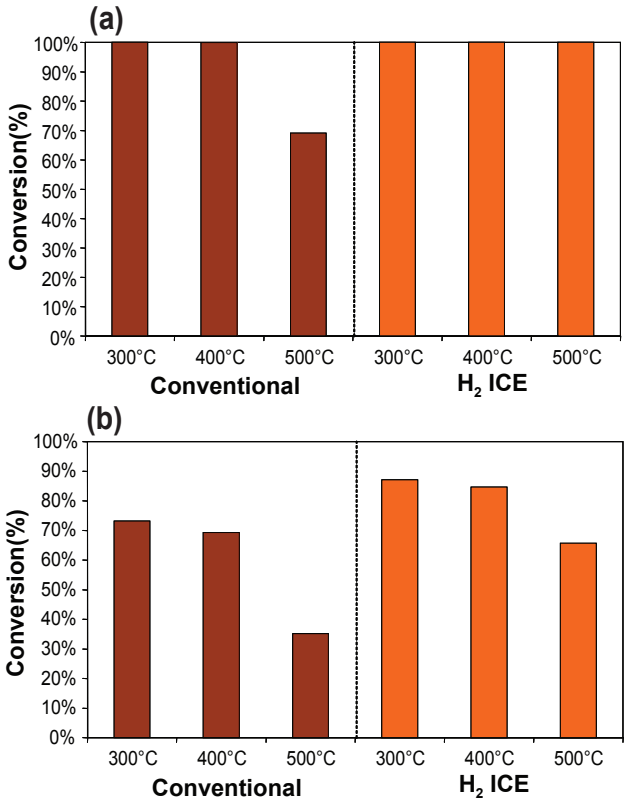

FIGURE 1. Comparison of NOx conversion for H_2 ICE and conventional CIDI exhaust using either (a) 2.8% of total reductant or (b) 1.0% of total reductant.

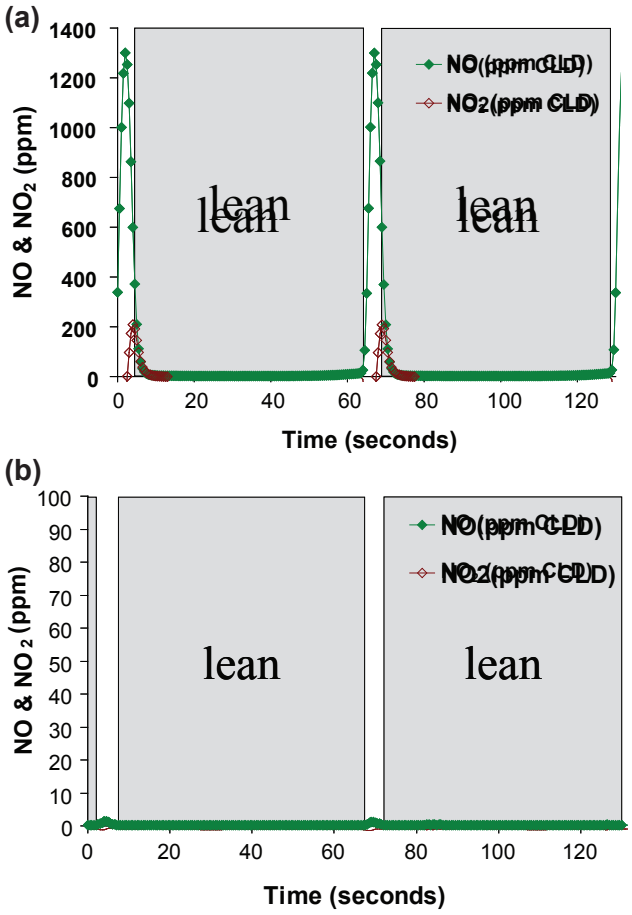

FIGURE 2. NO and NO_2 profiles at 500°C during 60 s lean and 5 s rich cycles for (a) conventional CIDI exhaust and (b) H_2 ICE exhaust.

control relative to NOx production is not as crucial for H_2 ICEs as it is for CIDI. The high reductant, intra-catalyst H_2 profiles for both conditions at 500°C are displayed in Figure 4. The key observation in these measurements is that the front quarter of the LNT is in contact with significantly more H_2 in the H_2 ICE case compared to the CIDI case. The CIDI exhaust undergoes the following water-gas-shift reaction (WGS) to produce H_2:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

However, this reaction is too slow to produce H_2 that is kinetically relevant to NOx reduction [2]. The result in this study further supports evidence that the CO does not have a significant contributing role in most CIDI applications, and H_2 is the most important reductant for efficient regeneration of LNTs.

When evaluating the LNT with low reductant concentrations the NOx conversion was 11-33% higher at all temperatures with H_2 ICE exhaust compared to conventional CIDI exhaust as displayed in Figure 1b. At this reductant concentration it is evident that H_2 ICE conditions increase the effective storage capacity of the LNT either from better reduction and removal of the stored NOx, or due to a competition for sites with CO_2, possibly both. Figures 5a and 5b show the NOx level at 300°C during the lean-phase is considerably higher in the CIDI case compared to H_2 ICE, which illustrates the increase in effective storage. Figures 5c and 5d show the significantly higher NOx pulse during the rich-phase which continues to illustrate the better regeneration efficiency observed with H_2ICE exhaust. Figure 3b shows that the selectivity is moderately better for the H_2 ICE case and the formation of NH_3 has been eliminated for the low reductant concentration. Intra-catalyst measurements demonstrated that all of the H_2 had reacted one-quarter of the way through the core for both cases and at all temperatures (see Figure 6). This is another very favorable result for H_2 ICE, since this suggests that smaller and less expensive reactors can be implemented to achieve 90% conversion, especially if sulfur levels are maintained at the ppb-level in the H_2 source.

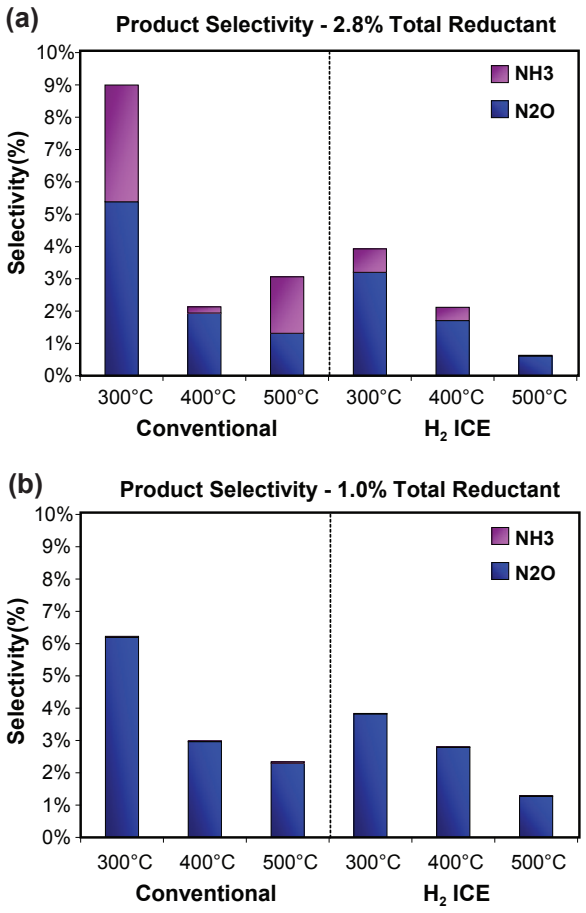

FIGURE 3. Nitrogen-based product selectivity for H_2 ICE and conventional CIDI exhaust using either (a) 2.8% of total reductant or (b) 1.0% of total reductant.

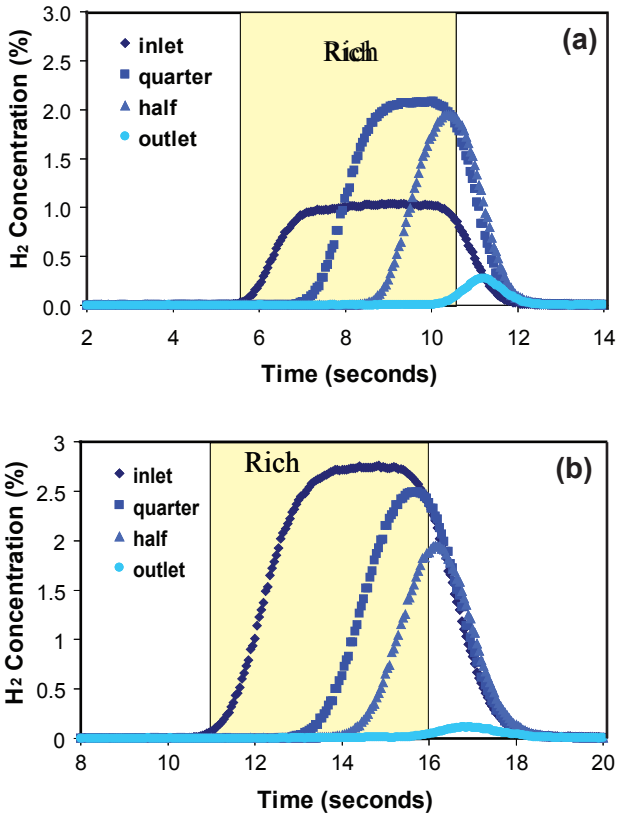

FIGURE 4. Intra-catalyst measurements of H_2 during the high reductant concentration (2.8% total reductant) experiments at 500°C for (a) conventional CIDI exhaust and (b) H_2 ICE exhaust.

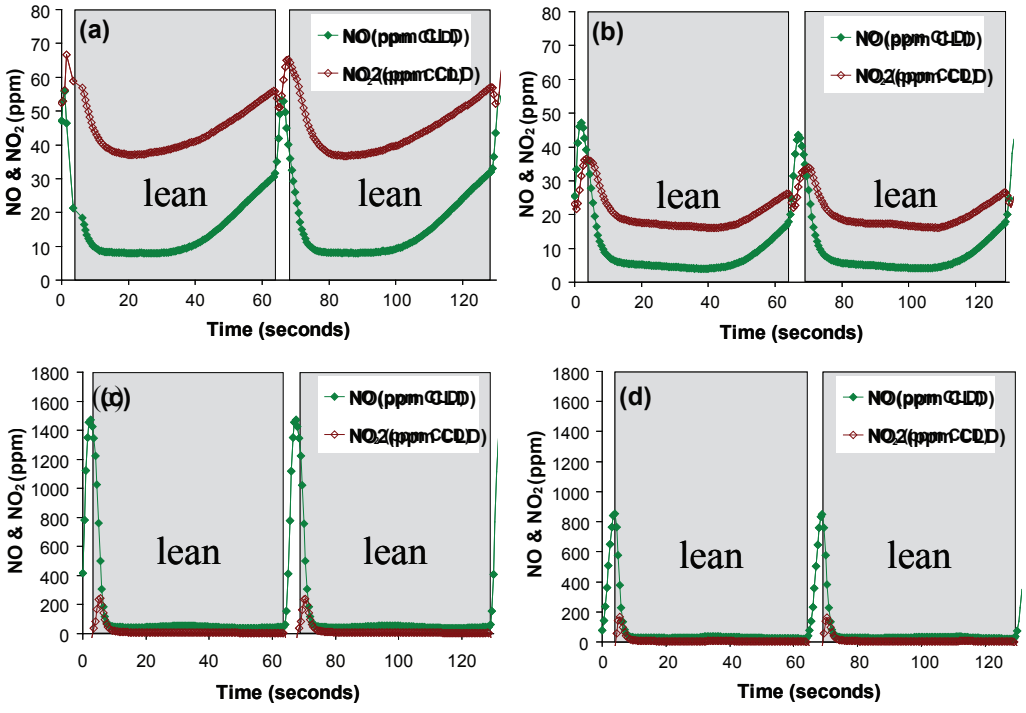

FIGURE 5. NO and NO_2 profiles at 300°C during 60s lean and 5s rich cycles for (a) conventional diesel exhaust and (b) H_2 ICE exhaust; similar profiles are also shown at 500°C for (c) conventional CIDI and (d) H_2 ICE exhaust.

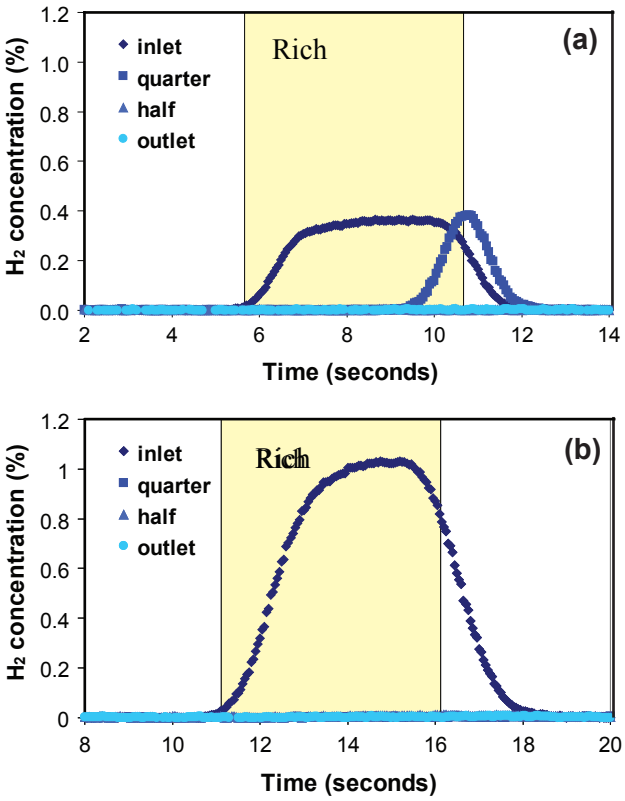

FIGURE 6. Intra-catalyst measurements of H_2 during the low reductant concentration (1.0% total reductant) experiments at 500°C for (a) conventional CIDI exhaust and (b) H_2 ICE exhaust.

Conclusions

- LNTs are a viable solution for H_2 ICE NOx aftertreatment
  - NOx conversion always higher than conventional diesel exhaust
    - Results suggest conventional CIDI exhaust is limited due to insufficient H_2
  - Field application will still depend on sulfur
    - level of H_2 source
    - Lube-oil consumption rate
- H_2-ICE based LNTs demonstrate better N_2 selectivity than CIDI applications
  - N_2O moderately lower
  - NH_3 significantly lower
  - Precise reductant control not as crucial for H_2 ICE
    - Less NH_3 slip with excess reductant
    - Dependence on accurate NOx map less critical than with diesel
    - Effort also improves understanding of LNTs with conventional diesel exhaust

FY 2006 Publications/Presentations

1. T.J. Toops, "H_2 Internal Combustion Engine NO_x Aftertreatment", H_2 ICE meeting at Ford, December 8, 2006, Dearborn, MI.

2. T.J. Toops, J.A. Pihl, "H_2 Internal Combustion Engine Research: Evaluation of NO_x Aftertreatment Systems", Advanced Combustion and Emissions Control Meeting, November 9, 2006, Southfield, MI.

References

1. R. Natkin et al., SAE 2002-01-0242.

2. J.-S. Choi, W.P. Partridge, W.S. Epling, N.W. Currier, T.M. Yonushonis, Catal. Today 114:1 (2006) 102.

II.B.13 Cross-Cut Lean Exhaust Emission Reduction Simulation (CLEERS)

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The following report is for two separate activities included under CLEERS:

- Administrative Support (Stuart Daw and Vitaly Prikhodko)
- Joint Development of Benchmark Kinetics (Stuart Daw, Kalyana Chakravarthy, Todd Toops, Jae-Soon Choi, Jim Parks, Josh Pihl, and Vitaly Prikhodko)

Objectives

Administrative Support

Provide coordination of the CLEERS activity for the Diesel Cross-Cut Team in accomplishing the following:

- Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.
- 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 R&D needs and priorities.

Joint Development of Benchmark Kinetics

- Coordinate ORNL's collaboration with Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL) in the development of kinetics information needed for aftertreatment component simulation.
- Provide benchmark laboratory measurements of NOx reduction chemistry and reaction rates.
- Coordinate laboratory measurements of lean-NOx trap (LNT) and selective catalytic reduction (SCR) materials with ongoing test-stand/vehicle studies in the National Transportation Research Center (NTRC) facility.
- Develop and validate global chemistry and (low-order) models for LNT and SCR kinetics.

Accomplishments

Administrative Support

- Continued co-leading the CLEERS Planning Committee.
- Assisted in facilitating the SCR, LNT, and diesel particulate filter (DPF) Focus Group telecons with strong domestic and international participation.
- Continued co-leading LNT Focus Group and dissemination of standard LNT materials protocol.
- Continued identification of key technical priorities from CLEERS community.
- Provided regular update reports to DOE Diesel Crosscut Team.
- Held 9th CLEERS workshop at University of Michigan, Dearborn on May 2-4.
- Maintained website functionalities, security, and data to facilitate web meetings and serve Focus Group interactions.

Joint Development of Benchmark Kinetics

- Continued testing and validation of the LNT material characterization protocol in conjunction with the LNT Focus Group, SNL, PNNL and collaborating suppliers.
- Continued benchmarking of Umicore commercial reference LNT material in LNT standard protocol.
- 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 refinement of instrumentation on the ORNL bench-flow reactor to enhance capabilities for highly resolved measurements of key species (e.g., O_2 and NH_3).
- Initiated DRIFTS measurements of Umicore reference catalyst to study relationship of S poisoning to multiple storage sites.

Future Directions

Administrative Support

- 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 10th CLEERS workshop in the spring of 2007.
- Continue maintenance and expansion of CLEERS website.
- Continue providing regular update reports to the DOE Diesel Crosscut team.

Joint Development of Benchmark Kinetics

- Continue expansion of the capabilities of the ORNL bench-flow reactor.
- 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 material at multiple scales and transmit results to the LNT Focus Group as they become available.
- Update and post revised global LNT 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 the U.S. Environmental Protection Agency (EPA) emission standards scheduled to take effect in 2007 and again in 2010. Simulation and modeling are recognized by the DOE Diesel Crosscut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity (Crosscut Lean Exhaust Emissions Reduction Simulation) was initiated to promote development of improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. While CLEERS does not directly support the development of extensive full-emissions-system performance simulation codes, it does provide explicit support for the following activities:

- Public workshops on key emissions control topics;
- Collaborative interactions among Crosscut Team members, emissions control suppliers, universities, and national laboratories under specially organized topical focus groups;
- Development of experimental data, analytical procedures, and computational tools that are directly useful for understanding component performance and the behavior and durability of catalytic materials;
- Development of consistent frameworks for sharing information about emissions control technologies; and
- Development of explicit recommendations to DOE and the DOE Crosscut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is currently involved in two separate DOE-funded tasks that support CLEERS:

- Overall administrative support; and
- Joint development of benchmark LNT kinetics with SNL and PNNL.

Previous work on micro-scale catalyst modeling for performance and durability has been terminated due to funding reductions.

In the administrative task, ORNL staff members coordinate the CLEERS Planning Committee, the CLEERS Focus groups, the public workshops, and the CLEERS website (www.cleers.org). The joint kinetics development task involves collaboration among ORNL, SNL, and PNNL to produce key kinetics information needed for predicting the performance of LNTs both individually and integrated with catalyzed particulate filters and ammonia-based selective catalytic reduction. 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. The collaboration is structured to build on the strengths of each lab and leverages against other DOE-funded activities to maximize benefits.

Approach

Administrative Support

In FY 2006 ORNL continued acting as the lead coordinator of the overall functions of the CLEERS Planning Committee and Focus Groups. Stuart Daw of ORNL is responsible for providing general assistance to each of the Focus Groups and is a co-leader (with Dick Blint of GM) of the LNT Focus Group. George Muntean and Darrell Herling from PNNL are co-leaders of the DPF and SCR Focus groups, respectively, and report on their activities elsewhere. ORNL organizes and implements the public workshops under guidance from the Focus Groups and Planning Committee, providing both technical and secretarial support. The CLEERS website is maintained (under direction of Sreekanth Pannala) on an ORNL server accessible via the internet. Both public and restricted areas have been set up on this website to facilitate distribution of technical information, workshop information and presentations, and interactive web meetings. Stuart Daw provides assistance to Dick Blint (GM) in presenting periodic status updates and summary reports to the Crosscut Team. Both Stuart and Vitaly at ORNL respond to general requests and inquiries about CLEERS from the public and technical community.

Joint Development of Benchmark Kinetics

ORNL's responsibility in this activity is to set up and conduct experimental measurements of LNT chemistry and reaction rates that will help to define the critical physical characteristics of LNT materials responsible for determining practical performance (i.e., NOx emissions reduction and energy efficiency). In this function, ORNL utilizes reference non-competitive adsorber materials in the ORNL bench-flow and DRIFTS reactors. Where possible, these bench measurements are also supplemented with other specialized measurement capabilities such as high-resolution microscopy at the ORNL High Temperature Materials Laboratory (HTML). ORNL maintains regular interactions with PNNL and SNL and the industry collaborators through the LNT Focus Group in order to maximize the value of the data generated and provide feedback that can be considered in planning future experiments. Where possible, laboratory results are compared with and analyzed in the context of test-stand/vehicle LNT measurements generated in parallel projects at ORNL's NTRC facility. For assistance in interpreting trends, ORNL utilizes simplified computer LNT codes that can be used to evaluate the laboratory and test stand data. Results are published in peer-reviewed journals, presented in public meetings, and/or posted on the CLEERS website.

Results

Administrative Support

The ninth CLEERS workshop was held May 2-4 at the Dearborn campus of the University of Michigan. As with the previous workshop, there were more than 110 registrants, including many researchers from emissions controls suppliers, universities (both foreign and domestic), software vendors, and consultants. All three emissions control technology areas (LNTs, DPFs, and SCR) were highlighted as indicated in the technical program and presentations available on the website (www.cleers.org). More detailed summaries of the workshop discussions were also provided to the Diesel Crosscut Team in subsequent CLEERS updates. Key observations coming from the workshop included the following:

- There have been exciting new developments in the integration of LNTs with NH_3-based SCR. In some instances, the utilization of LNTs to generate NH_3 may reduce or eliminate the need for urea injection.
- Major progress has been made in defining a detailed kinetic mechanism for LNT regeneration, including the generation of NH_3, for a realistic commercial catalyst.
- More needs to be done to develop refined kinetic models of urea-SCR including the effects of NH_3 storage and hydrocarbon poisoning.
- More information about the modeling of pre-catalyst mixing devices for urea-SCR is needed.
- Oxidation catalysts are assuming increasingly important roles in integrated emissions control systems, and additional studies of the kinetics are needed for these new contexts.
- Integrated system performance (including combinations of SCR, LNT, and DPF) is now a high priority.

The LNT, SCR, and DPF Focus Groups have continued regular phone/web meetings throughout the year, and summary reports of the meetings have been provided to group members and the Diesel Crosscut Team. As in previous years, meeting topics have included reviews of experimental data donated by members, technical presentations by outside invited experts (e.g., from non-member universities), and discussions of technical needs and priorities among the Crosscut member companies. After much discussion, it has been decided that we will implement a trial change in the Focus Group meeting format such that the three individual meetings held each month will be reduced a single combined meeting. Responsibility for meeting coordination will alternate among the three individual LNT/SCR/DPF Focus Groups. It is believed that this

alternative meeting schedule will more effectively utilize the time commitment of the participants and also allow more effective discussions targeted on system integration issues. After a three-month trial period, the effectiveness of this new format will be re-assessed.

Technical priorities identified by the CLEERS Crosscut members have been updated in discussions among the Planning Committee and Focus Group leaders and on the basis of an anonymous survey held over the summer of 2006. The results have been summarized in a single CLEERS priorities document, which has been distributed to the Diesel Crosscut Team and which will be posted early in FY 2007 on the CLEERS website. Highlights of the updated priorities include:

- The importance of device interaction and systems integration simulation as key issues.
- Recognition that oxidation catalysts are extensively utilized in integrated systems and that additional kinetics models for these devices in a multi-component context is needed.
- Potential synergies between the chemistry of LNTs and conventional three-way catalysts.
- Increased emphasis on modeling of 3-D spatial details inside each type of device.
- Emphasis on resolving transport effects, hydrocarbon and ammonia storage, and spray modeling for urea SCR.
- Expansion of the available kinetics for particulate oxidation in DPFs to include particulates produced by more advanced engines operating in low temperature combustion modes.

Due to other commitments, Prof. Harold Kung (from Northwestern University) felt it necessary to resign from his position on the CLEERS Planning Committee. After an extensive review of potential candidates, the Crosscut Team has accepted Prof. Louise Olsson (from Chalmers University) as his replacement, and she has graciously agreed to accept the position. Her very active prior participation in CLEERS and her strong familiarity with current European aftertreatment R&D are important attributes she will be bringing to the role.

A tentative date for the next (10^{th}) CLEERS workshop has been set for May 1–3, 2007. The planned venue will again be the University of Michigan, Dearborn campus, with Prof. Tariq Shamim acting as host.

Joint Development of Benchmark Kinetics

Further improvements have been made to the ORNL bench flow reactor to allow more consistent LNT catalyst experimentation over a range of operating conditions. Specifically, a balancing system has been installed to prevent sudden pressure swings in the reactor outlet pressure during lean/rich cycling, where the composition of the inlet gas stream undergoes very rapid transitions in fractions of a second. Also, improved seals have been installed on the quartz reactor tube so that much higher temperature conditions (e.g., >1,000°C) can be studied.

Monolith length effects on LNT performance have received considerable attention this year in bench reactor studies. LNT performance changes associated with monolith length differences (at constant space velocity) have been reported anecdotally for some time, but careful studies of the causes have not been reported in the open literature. Such changes can be extremely relevant to simulations of practical LNT systems because many catalytic reactor models commonly assume that performance is controlled by residence time (i.e., the inverse of space velocity) rather than the specific dimensions (e.g., the diameter and length). Likewise, there has been an ongoing debate among the CLEERS LNT group concerning the need to specify the dimensions of the sample cores used in the standard bench protocol. So far, our experiments confirm that at least some operating conditions, monolith length and/or the internal linear gas velocity can have a significant impact on performance. Specifically, it appears that shorter monoliths exhibit higher NOx breakthrough during fast cycling when there is insufficient reductant for complete regeneration. An example of this effect as revealed in bench flow reactor measurements is illustrated in Figure 1. The reasons behind this difference appear to be related to reductant depletion by stored or gaseous oxygen and are still being investigated. But it is already clear that this effect is real and needs

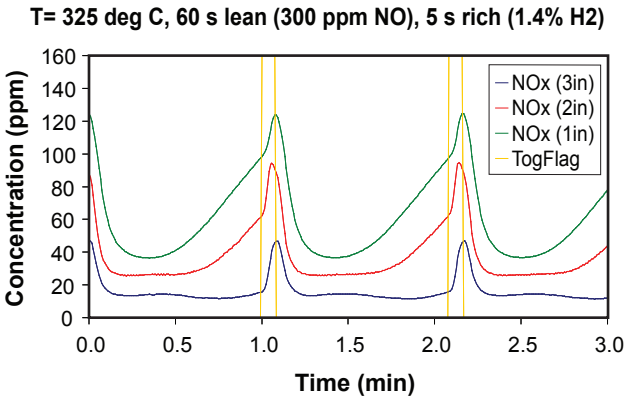

FIGURE 1. Example performance differences seen for different length monolith cores of the Umicore LNT reference catalyst under fast cycling conditions in the ORNL bench flow reactor. The yellow line indicates the beginning and end of regeneration. Even though gas flow has been adjusted in each case to keep the space velocity constant at 30,000 (1/hr), there is still greater NOx breakthrough as monolith length decreases from 3 to 2 to 1 inch.

to be properly addressed in evaluating kinetic data and simulating device performance.

Studies of the generation of N_2O and NH_3 byproducts during LNT regeneration have continued with the objective of developing an explicit and detailed kinetic mechanism for device simulation. This is particularly relevant in the context of commercial implementations of LNT-SCR combination systems, where the LNT is now used to generate NH_3 that is subsequently utilized for SCR NOx reduction. Special steady-state bench reactor experiments (under reducing conditions) have continued this year with the objective of measuring the relative reaction rates of NO with H_2 and CO to form N_2, N_2O, and NH_3 in the absence of O_2 and NOx storage reactions. Figures 2-4 illustrate the general trend observed for NH_3 and N_2O generation from NO reaction with H_2 over the Umicore catalyst as a function of temperature. Companion DRIFTS reactor studies (Figures 5 and 6) suggest that NCO (isocyanate) is an important intermediate species in NH_3 formation. As noted below, the role of isocyanate seems to be confirmed in the kinetic mechanisms developed from these bench data. The steady-state experiments have also revealed that the two main 'sinks' for NH_3 are oxidation by O_2 and NO to N_2O and decomposition to N_2 and H_2 at temperatures above 350°C.

Combining the steady-state reducing condition trends with observations from cycling experiments suggests the transient regeneration scenario depicted in Figure 7. Here we observe that at locations downstream from the propagating reductant front there is little or no NH_3 because any that is formed is rapidly oxidized. Near the center of the reductant front, NOx reduction to N_2 and NH_3 compete with each other as NOx is rapidly released from storage sites. However, upstream of the reductant front, NH_3 continues to be generated by the reduction of NOx from 'slow' release storage sites. Thus NH_3 only becomes visible at the reactor exit when the reductant front has completely passed through and regeneration is mostly complete. We speculate that increasing the population of 'slow' NOx storage sites

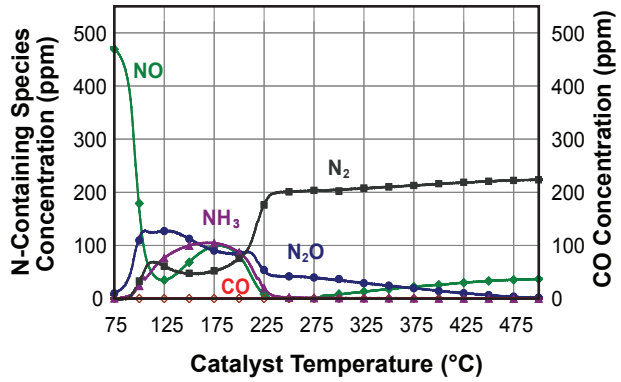

FIGURE 2. Pseudo-steady-state bench reactor conversion of N species and CO with a feed ratio of 1:1 NO/H_2 in water vapor, CO_2, and N_2 as temperature is ramped at 5°C/min.

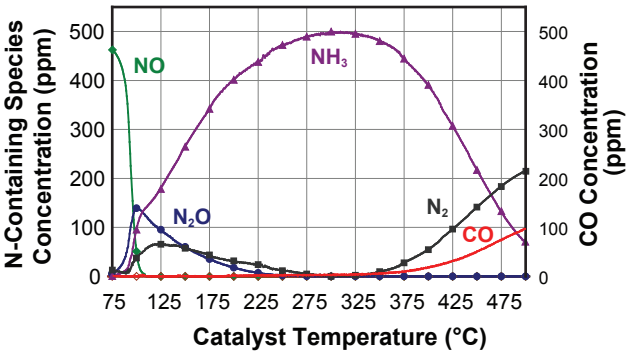

FIGURE 3. Pseudo-steady-state bench reactor conversion of N species and CO with a feed ratio of 1:2.5 NO/H_2 in water vapor, CO_2, and N_2 as temperature is ramped at 5°C/min. Note the higher NH_3 production compared to Figure 2.

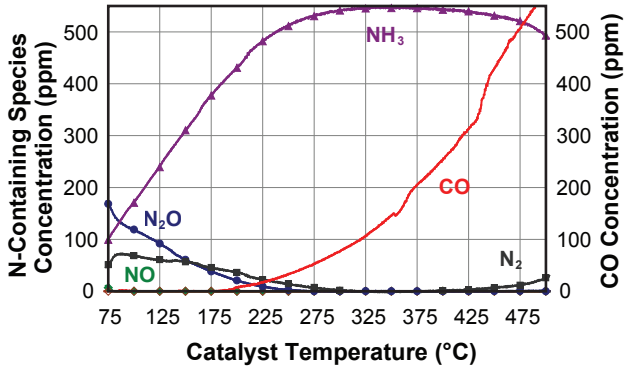

FIGURE 4. Pseudo-steady-state bench reactor conversion of N species and CO with a feed ratio of 1:10 NO/H_2 in water vapor, CO_2, and N_2 as temperature is ramped at 5°C/min. At such high H_2 concentrations, NH_3 generation dominates even at high temperature.

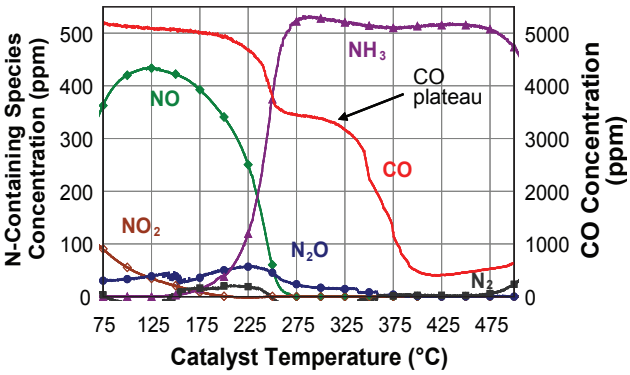

FIGURE 5. Pseudo-steady bench reactor conversion measurements for 1:10 NO_2/CO in water vapor, CO_2, and N_2 as temperature is ramped at 5°C/min. The second CO plateau above 250°C correlates with the rise of NH_3.

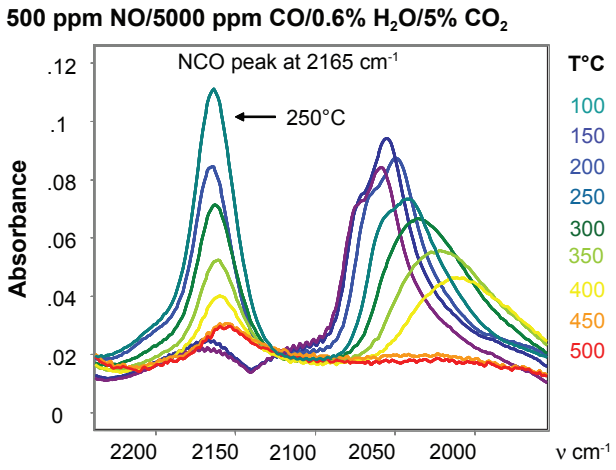

FIGURE 6. DRIFTS spectra illustrating evidence for NCO hydrolysis as prominent source for NH_3 generation. Here the feed gas is NO and CO in water vapor, CO_2 and N_2. At the same temperature that NH_3 formation jumps in the bench flow experiment, the DRIFTS measurement indicates a sharp decrease in NCO on the catalyst surface.

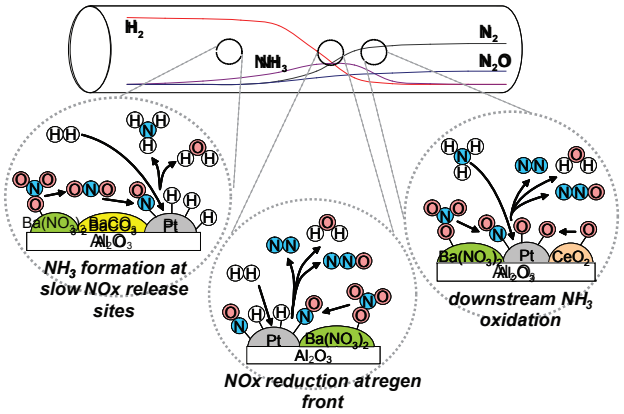

FIGURE 7. Proposed scenario for the stages involved in LNT regeneration as the reductant front progresses axially down the monolith.

might lead to enhanced NH_3 generation for situations where the latter is the desired result.

The above steady-state data are now being collaboratively studied by SNL and ORNL to develop a detailed kinetic mechanism for reducing conditions that is consistent with the observations. So far, this effort has been successful in developing a relatively compact mechanism that does a remarkably good job reproducing both the steady-state and transient features described above. An example of this good fit produced by this mechanism for steady-state reduction is illustrated in Figure 8. Highlights of the mechanism developed to date include:

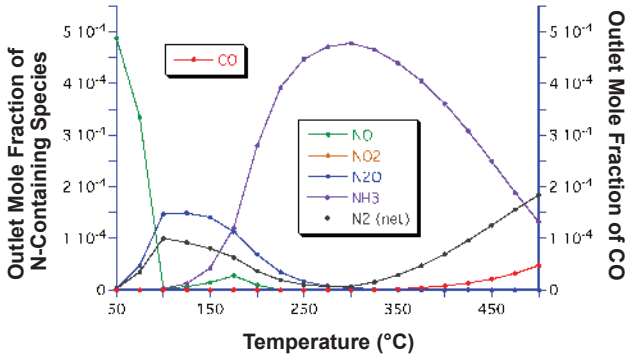

FIGURE 8. Predicted steady-state conversion for 1:2.5 NO/H_2 in water vapor, CO_2, and N_2 as a function of temperature based on the recently developed regeneration kinetic mechanism. Compare with Figure 3.

- Twenty three thermodynamically consistent surface reactions (all reversible);
- Elementary mass-action kinetics with no altered reaction orders or coverage dependent activation energies; and
- Important roles for both isocyanate formation and water-gas-shift reactions.

Additional details on this mechanism are reported in the SNL annual report. Current LNT modeling studies are focused on coupling this mechanism with a corresponding lean-phase mechanism that can be utilized to capture the main features of fast LNT cycling.

Initial studies of LNT sulfation and desulfation have utilized a Ba-based model catalyst in the DRIFTS reactor. At 200°C, initially formed sulfur groups appear to form that do not impact NOx storage sites until the samples have been further heated. Heating to 500°C drives the sulfates from their "observer" sites to active storage sites. Sulfation also impacts the active Pt surface area. At 300°C, the level of stored nitrates decrease readily with SO_2 in the feed stream; and additional heating is not necessary to impact storage. At 400°C, the effect of the SO_2 is most pronounced in the bulk-phase, where nitrates are readily decreasing. At all temperatures, CO adsorption on Pt diminishes with increasing sulfation, indicating loss of active Pt sites. When SO_2 is removed from the gas-phase these sites are recovered.

Conclusions

Administrative Support

Approximately 120 representatives from automotive and engine manufacturers, emissions controls suppliers, universities, and national laboratories attended the ninth international CLEERS workshop on May 2–4 at the University of Michigan, Dearborn campus. The

complete technical program, meeting summary, and most of the presentations are available on the website (www.cleers.org). Important new developments in emissions controls simulation and shifts in R&D priorities were identified, leading to subsequent discussions among the CLEERS Planning Committee, the LNT, DPF, and SCR Focus Groups, and the DOE Diesel Crosscut Team. These discussions are expected to be reflected in adjustments in national lab R&D in FY 2007. The next CLEERS workshop is planned for May 1–3, 2007.

The LNT, SCR, and DPF Focus Groups have continued regular phone/web meetings throughout the year with considerable international participation. The meeting topics have included reviews of experimental data donated by members, technical presentations by outside invited experts (e.g., from non-member universities), and discussions of technical needs and priorities among the Crosscut member companies. A trial change of the monthly meeting format will be implemented starting this October for a period of three months. During this period, all three groups will participate in a single joint monthly meeting.

An updated list of CLEERS R&D priorities has been developed and approved by the DOE Diesel Crosscut Team. The updated list includes an increased emphasis on emissions control device interaction and system integration and more extensive modeling of details in oxidation, DPF, and urea-SCR catalysts.

Joint Development of Benchmark Kinetics

ORNL LNT bench reactor studies have revealed important new insights regarding monolith length effects, the detailed mechanisms of regeneration and NOx reduction (including the formation of N_2O and NH_3), and the mechanisms of catalyst sulfation and desulfation. The impact of monolith length on NOx conversion is most apparent when the amount of reductant supplied is insufficient for regeneration. Under these circumstances, shorter monoliths suffer a significant penalty in NOx conversion efficiency and thus an increased potential fuel penalty. Generation of large quantities of NH_3 typically is associated with over regeneration (i.e., excess reductant). A relatively compact but detailed kinetic mechanism has been developed for regeneration based on the bench reactor measurements for the Umicore reference LNT catalyst.

Sulfur poisoning of LNT catalyst appears to occur in two stages, the first of which has minimal impact on NOx storage sites. The second sulfation stage is much more irreversible and is promoted by higher temperatures.

The above insights are currently being incorporated into improved LNT kinetic mechanisms, experimental characterization procedures and device simulation models. Future plans include the investigation of combined LNT-SCR device simulation.

Publications/Presentations

1. J.-S. Choi, W.P. Partridge, W.S. Epling, N.W. Currier, and T.M. Yonushonis, "Intra-channel evolution of carbon monoxide and its implication on the regeneration of a monolithic $Pt/K/Al_2O_3$ NOx storage-reduction catalyst, "Southeastern Catalysis Society Fall Symposium, Asheville, North Carolina, September 25–26, 2005.

2. J.A. Pihl, "Byproduct formation during regeneration of Lean NOx Traps," Master's Thesis, University of Wisconsin, November 2005.

3. J. Pihl and Todd Toops, "DRIFTS Studies of Lean NOx Trap Sulfation and Desulfation," 9th CLEERS Workshop, May 2–4, 2006, www.cleers.org.

4. J.-S. Choi, V. Prikhodko, K. Chakravarthy, and C.S. Daw, "Assessing Monolith Length Effect on LNT Performance," 9th CLEERS Workshop, May 2-4, 2006, www.cleers.org.

5. J. Pihl, J. Parks, T. Toops, S. Daw, and T. Root, ""Experimental studies of NH_3 and N_2O formation in lean NOx traps," 9th CLEERS Workshop, May 2–4, 2006, www.cleers.org.

6. R. Larson, K. Chakravarthy, C.S. Daw, and J. Pihl, "Modeling Kinetics of NH_3 and N_2O Formation in Lean NOx Traps," 9th CLEERS Workshop, May 2–4, 2006, www.cleers.org.

7. J.-S. Choi, W.P. Partridge, W.S. Epling, N.W. Currier, and T.M. Yonushonis, "Intra-channel evolution of carbon monoxide and its implication on the regeneration of a monolithic $Pt/K/Al_2O_3$ NOx storage-reduction catalyst," Catalysis Today, vol. 114, p. 102, 2006.

8. T. Toops, D.B. Smith, W.P. Partridge, "NOx Adsorption on $Pt/K/Al_2O_3$", *Catalysis Today*, vol. 114, p. 112, 2006.

9. Y. Ji, T.J. Toops, U.M. Graham, G. Jacobs, and M. Crocker, "A Kinetic and DRIFTS Study of Supported Pt Catalysts for NO Oxidation," *Catalysis Letters*, vol. 110, no. 1–2, pp. 29–37, August 2006.

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

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

Special Recognitions & Awards/Patents Issued

1. Special recognition for collaborative R&D under CLEERS from U.S. CAR presented to R. Blint, May 2006.

II.B.14 CLEERS DPF Modeling

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DOE Technology Development Manager:
Kenneth 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, morphology.
  - Develop improved sub-grid representations of the local soot oxidation reactions in diesel soot filters, e.g. oxidation mechanisms, detailed kinetics, global rates.
- Coordinate and lead the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) diesel particulate filter (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

- Developed tools for digital reconstruction of three-dimensional filter substrate microstructures from a small set of two dimensional images.
  - The use of fewer two-dimensional images dramatically decreases the time and expense involved with analyzing a new substrate, allowing additional different materials to be studied
  - Statistical metrics are used to verify the fidelity of the reconstructions
  - Reconstructions of any shape or volume can be produced
- Added soot oxidation kinetics to the micro-scale lattice-Bolzmann filter model.
  - Kinetics include separate temperature dependent rates for oxidation by NO_2 and oxygen
  - Rates can be adjusted according to the presence of soluble organic fraction (SOF) and changes in soot reactivity as it is oxidized
  - Initial parametric studies highlight the importance of catalyst placement with respect to the porous filter micro-structure
- Further developed single-channel experimental techniques.
  - Multiple filtration studies were carried out, including catalyzed and uncatalyzed Corning Duratrap RC filter material
  - Studies were conducted to differentiate the contributions of channel flow and wall flow resistance to overall pressure drop through a DPF device
- Developed techniques for observing regeneration on the surface of uncatalyzed and platinum catalyzed single channel filter samples.
- Coordinated and led monthly teleconferences for the CLEERS DPF sub-team.

Future Directions

- Extend micro-scale regeneration model to include surface catalytic reactions which convert NO to NO_2, allowing studies of phenomena such as 'NOx recycle' and optimization of catalyst loading and placement.
- Extend micro-scale regeneration model to include coupled heat transfer and oxidation exotherms, allowing studies of 'light-off' conditions during active filter regeneration.
- Conduct single channel experiments with catalyzed and uncatalyzed samples in parallel, in order to better quantify the effect of catalyst loading on regeneration behavior.

Introduction

High efficiency diesel engines provide an important short to medium-term strategy for meeting the nation's transportation needs while minimizing emissions implicated in global climate change. However, concerns over the health effects of particulate emissions from diesel engines have prompted legislation in the U.S.,

Europe, and Asia which has set challenging limits on vehicular exhaust soot concentrations. DPFs have emerged as an important enabling technology to comply with these new limits. DPFs have a negative impact on fuel efficiency because they introduce back-pressure to the exhaust system and, in the case of active regeneration systems, require energy to burn away collected soot. These factors must be minimized in order for high efficiency diesel engines to provide their maximum economic and environmental benefits.

Mechanisms taking place during filtration and regeneration at the microscopic scale of pores in filter substrates are critical to DPF performance. Many different porous substrate materials have been explored by industry, each with their own set of advantages and disadvantages. Currently, ceramic materials such as cordierite and silicon carbide are considered to be the most practical for near-term application. 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, in many cases, active gaseous species such as NO_2. Filtration efficiency can vary dramatically by particle size. This has important implications for human exposure to ultra-fine nanoparticles, which are suspected of posing significant health risks. The project described in this report seeks to elucidate pore-scale mechanisms involved in DPF operation through sub-scale computer simulation in order to promote more effective and reliable DPF devices which introduce 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. Detailed digital maps of the microscopic pores in various substrate materials are created using a novel stochastic reconstruction technique. The lattice-Boltzmann method is used to solve for the flow field of exhaust through the substrate microstructure as soot deposits form. The paths of simulated soot particles are derived from the exhaust flow field and include random Brownian motion. Simulations with various DPF substrates, including cordierite and silicon carbide, show how the substrate microstructures affect filtration performance. The micro-scale model has recently been extended to include the transport of active gaseous species and oxidation of accumulated soot. Parametric studies were conducted to examine the effect of substrate microstructure on net rates of soot consumption.

Experimental methods have been developed to observe the loading and regeneration of external surfaces of individual channels, allowing meaningful comparisons to model predictions. 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. Visible and infrared video cameras were used to observe loaded surfaces of filter samples during regeneration experiments in an effort to quantify the effect of catalysts on the initiation of 'light-off' during active regeneration events and to gain insight into pore scale phenomena which might promote faster and more efficient oxidation of collected soot.

Results

Pursuant to the overarching goal of the CLEERS project to promote improved device scale modeling of diesel after-treatment technologies, Pacific Northwest National Laboratory (PNNL) has continued to coordinate monthly teleconferences in order to discuss current CLEERS DPF research with various stakeholders, including OEMs, 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.

Over the course of FY 2006, tools were developed for faster and more flexible characterization of substrate microstructures. Detailed modeling of pore-scale phenomena requires accurate, high resolution characterization of the three-dimensional structure of porous filter substrates. Three-dimensional digital geometries were previously obtained using scanning electron microscopy of repeatedly polished substrate samples. This resulted in a series of two-dimensional grayscale micrographs. The 2-D images had to be precisely aligned, and the 3-D volume was then reconstructed by interpolation. Reconstructing a volume of any thickness required a large number of polishing steps. This procedure, while in principle allowing exact reconstruction of a given volume, had several drawbacks. The multiple polishing and microscopy steps made it relatively expensive and time-consuming to characterize new substrates. Also, subsequent analyses were constrained to the size and shape of the exact substrate volume examined.

To overcome these difficulties, a stochastic reconstruction technique was developed whereby a given substrate could be characterized from a small set of micrographs, all of which may be obtained during

a single scanning electron microscopy (SEM) session. Computer algorithms scan through the digitized 2-D images and tabulate statistical properties of the porous structure, including local porosity and chord length distributions. Local porosity must be accounted for because the porosity of some substrates (e.g. cordierite) has been observed to vary across the thickness of a filter wall. Chord length distributions are a statistical metric which have been widely used in the reconstruction of porous materials such as soils and rocks [1]. Chord length distributions contain information about pore size, shape, and connectivity.

A stochastic algorithm is then used to generate a 3-D reconstruction of the porous material by randomly placing a collection of solid grain shapes. The same statistical metrics are measured for the reconstructed volume, and the reconstruction process is iterated until there is satisfactory agreement between the reconstructed volume and the 2-D images. In this way, a volume of any size or shape can be generated which matches the observed structural characteristics of a given substrate. Using this technique, the microstructures of several current commercial substrate materials were reconstructed, including Corning Duratrap RC and Ibidin silicon carbide. Figure 1 shows the chord length distributions from original micrographs of a cordierite sample and those from a corresponding reconstruction. A somewhat similar approach has been taken to reconstruct DPF microstructures in proprietary modeling software [2, 3].

The shape and location of soot deposits in a filter substrate's microstructure are important not only for predicting filtration performance of various filter materials, but also for predicting regeneration behavior and perhaps other important phenomena like ash accumulation. Precious metal catalysts convert NO to NO_2, which is important for oxidation of soot in many filter regeneration strategies. How these gaseous species move from catalyst to soot within the 3-D flow field may be an important factor in getting the most benefit from a given catalyst loading. Pore-scale simulations of individual soot particle motion and deposition during loading were carried out in order to predict the location and morphology of soot deposits. These simulations have been carried out for several common DPF substrate materials, including cordierite and silicon carbide. Figures 2 and 3 show a small section of reconstructed cordierite filter wall before and after loading with soot. Figure 4 shows corresponding pressure drop predictions as a function of total soot loading. Figure 5 shows predicted depth of soot penetration into a silicon

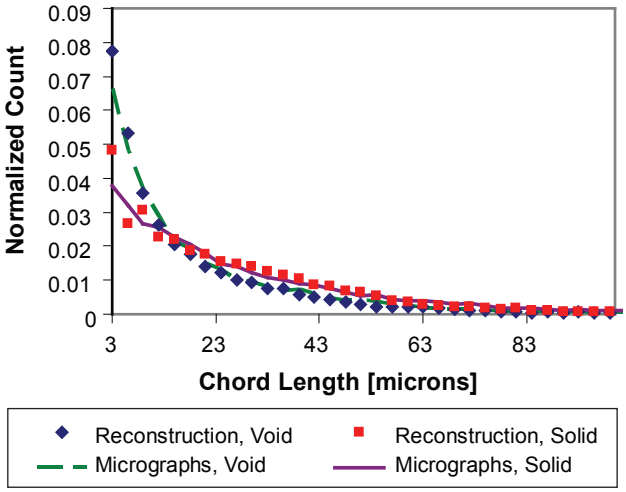

FIGURE 1. Chord Length Distributions from Cordierite Micrographs and 3-D Reconstruction

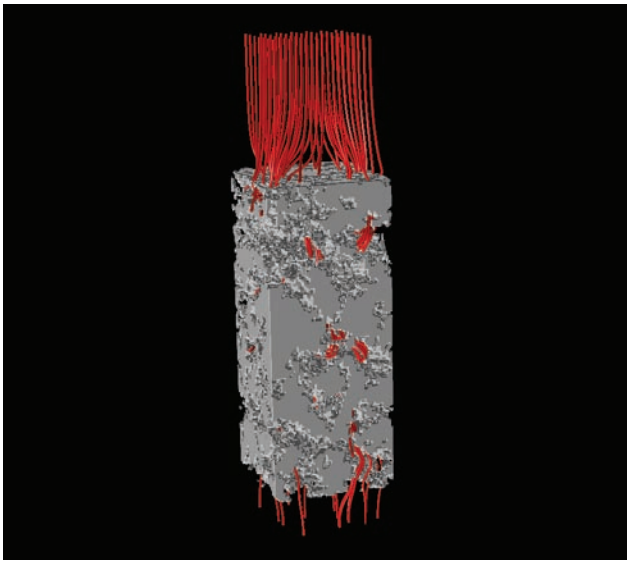

FIGURE 2. Volume of Reconstructed Cordierite before Loading with Soot

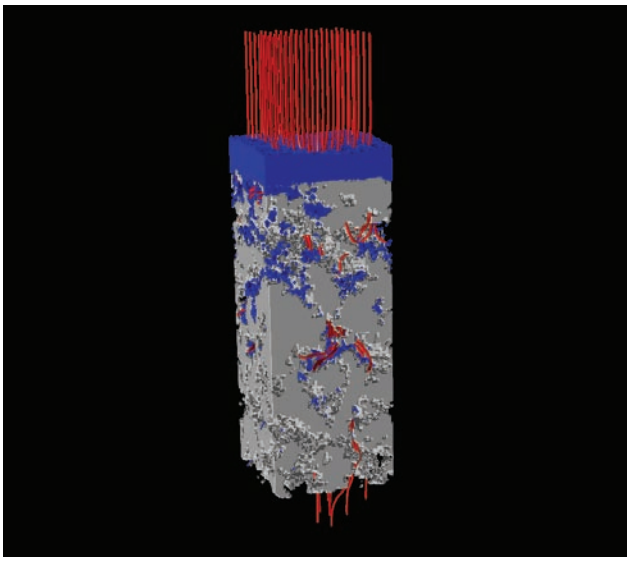

FIGURE 3. Volume of Reconstructed Cordierite after Loading with Soot

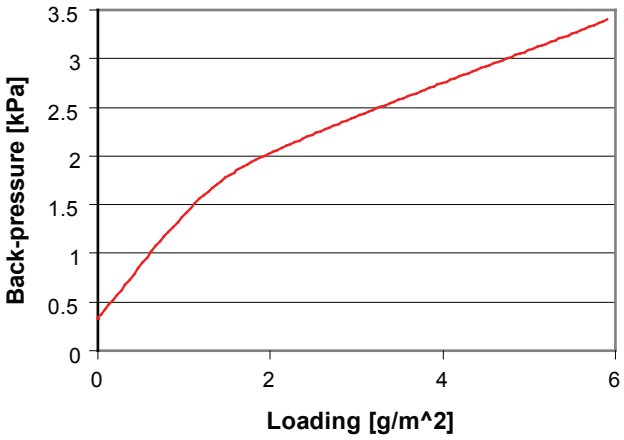

FIGURE 4. Predicted Pressure Drop across a Cordierite Filter Wall as a Function of Loading

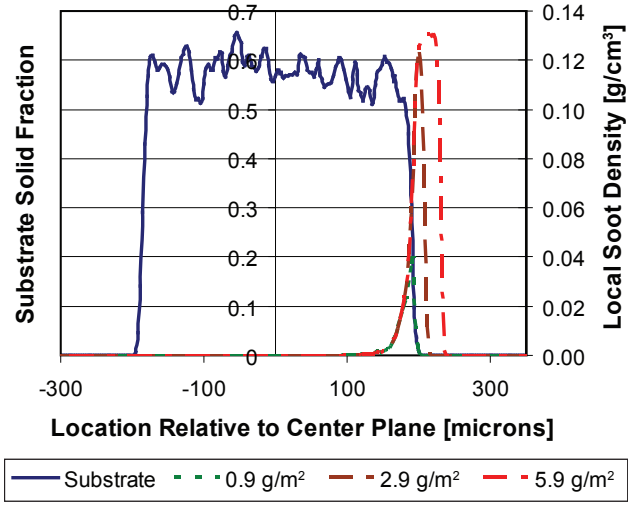

FIGURE 5. Predicted Penetration of Soot into Filter Wall during Loading

carbide filter wall at three different total loadings. The solid line, representing local substrate solid fraction, corresponds to the scale in the center, and the dashed lines, representing local soot density, correspond to the scale on the right side.

Recently published soot oxidation chemistry was also incorporated into the pore-scale filter model in FY 2006. The correlation employed was published by Messerer and associates in the Journal Carbon [4]. It includes temperature dependent terms for both NO_2 and O_2 oxidation as well as changes in the oxidation rates as the soot is consumed. Initial parametric studies using these kinetic relationships were conducted by introducing NO_2 at a fixed rate in three locations: upstream of the loaded filter, at the loaded filter surface, and on the back side of the filter wall (which would represent a worst case for catalyst location). Oxidation rates for the first two cases were similar, but

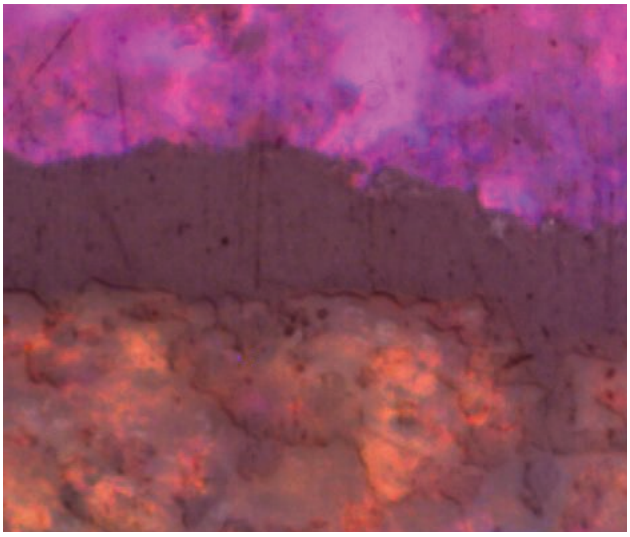

FIGURE 6. Thin Section Image of a Loaded Duratrap RC Filter Wall

were reduced almost by a factor of four in the third case. These results indicate that some NO_2 can migrate upstream from catalytic sites within the filter wall, but that the porous microstructure of the filter wall can be a significant barrier to transport of active gaseous species during regeneration.

Single channel loading experiments were carried out for a number of substrates, and the associated techniques were further refined over the course of FY 2006. Other experimental work focused on three areas:

1. Improving visualization techniques for soot within the substrate using a thin section technique. This method involves the use of vapor adhesives to stabilize soot deposits, allowing preparation of thin sections which can be examined using visible light refractometry (Figure 6). This work could allow direct observation of soot penetration into filter walls and is documented in detail in a forthcoming publication (SAE draft - publication 4).
2. Isolating individual contributions to overall pressure drop in DPF devices. Experimental techniques have been developed to directly measure the pressure drop across individual channel walls and pressure drop due to flow along DPF channels. These contributions to overall pressure drop are intertwined in most test data, and methods for measuring them separately could dramatically improve DPF models at all scales.
3. Developing a parallel measurement apparatus that allows testing of two single channel samples under identical exhaust conditions. This technique can be used to observe pressure drop and thermal changes in catalyzed and un-catalyzed single channel samples during loading and regeneration, allowing quantitative observation of catalytic action during soot oxidation.

Conclusions

- Stochastic reconstruction techniques may be used to economically generate three-dimensional geometries for simulation of pore scale phenomena in DPF substrates.
- Penetration of soot into filter walls of DPFs is dependent upon substrate pore geometry, and can be qualitatively predicted using micro-scale modeling.
- The degree of soot penetration into filter walls and the interaction between deposits and the substrate micro-structure can have a significant impact on overall back-pressure.
- Active gaseous species like NO_2 can migrate upstream through the porous substrate to take part in soot oxidation reactions.
- The porous substrate microstructure nevertheless constitutes an significant barrier to transport of gaseous species from catalytic locations within the filter wall.
- New experimental techniques have provided insights into soot stabilization and visualization, and into phenomena contributing to the total pressure drop across DPF devices.

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II.B.15 Innovative Emission Control Device Renewal

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Objectives

The objective of this project is the development of a diesel particulate filter (DPF) regeneration technique that minimizes:

- Impact on engine operation
- Power consumption
- Cost

Accomplishments

- Developed a microwave heating technique that uniformly heats the DPF, and eliminates parasitic soot absorption.
- A number of materials have been evaluated as possible microwave absorbing candidates.
- Lab demonstration of microwave regeneration of a soot-loaded DPF.
- A range of different spot configurations have been modeled for their effectiveness in initiating and propagating soot oxidation.
- A proprietary microwave absorbing configuration has been designed and patent applications have been filed.
- Engine control strategies for microwave assisted regeneration have been identified.
- The DPF was successfully regenerated on a vehicle using the alternative heating strategy.
- The soot ignition and energy deposition techniques developed from the microwave work have been applied to investigate alternative heater concepts.

Future Directions

The future direction of the project will examine an alternative regeneration technique which builds off the knowledge gained from the microwave regeneration work, and may provide an economy benefit over it.

Introduction

The goal of this project is to leverage the exotherm of soot oxidation during DPF regeneration in order to regenerate the DPF with a minimum amount of added energy. Instead of heating the entire DPF to the soot oxidation temperature, only selected spots are heated to the oxidation temperature of the soot. The resulting oxidation wave is allowed to propagate throughout the length of the DPF. To accomplish this, an effective heat source must be identified to start the PM oxidation process. This heater must be energy efficient, and be compatible with the typical vehicle electrical architecture. Furthermore, an engine control strategy must be developed to optimize the performance of this type of regeneration. The current project activities address each of these needs.

Approach

This project aims to develop a new approach to regenerate particulate filters in compression-ignition, direct injection (CIDI) diesel engines. This project has investigated the technology of spot heating within a DPF using various techniques in order to ignite the soot and leverage the heat from the soot oxidation to propagate a complete regeneration of the DPF. This project has investigated:

- A range of microwave active materials for both activity and stability in the DPF environment.
- A series of spot configurations within the DPF to identify those with the highest efficiency in soot ignition.
- Modeling has been used to predict the efficiency of spots to absorb energy.
- Modeling has also been used to predict the optimum spot positioning to ignite and propagate the soot oxidation with the minimum energy input.
- An alternative heating approach was also investigated to evaluate competitive heating technologies.

Results

An effective heating strategy must be developed to start the soot ignition. Microwave heating was evaluated by HRL Laboratories. A wide range of diesel exhaust compatible materials were evaluated for their microwave absorption properties and Curie temperature (the temperature where the material no longer absorbs the magnetic field component of the microwave source). The materials were typically in the form of a ceramic coating and included silicon carbide, indium tin oxide, nickel oxide, and iron or lithium-based ferrites. The figures of merit for the materials examined were the following:

1. Stable under diesel engine exhaust conditions.
2. Able to be heated with microwaves at 2.45 GHz to the soot ignition temperature.
3. For configurations relying on magnetic absorption, the material has a high Curie temperature.

To avoid parasitic absorption of microwaves by the soot in the DPF, set-up configurations were devised that confined heating to the front region of the trap. Using this configuration, lab experiments demonstrated 75% regeneration efficiency with respect to soot removal under controlled air flow conditions. Further work is required to reduce power consumption and to increase the compatibility of the microwave system with automotive designs.

An alternative strategy to microwave heating was also developed that concentrated the thermal energy to the front of the DPF to start particulate ignition. The alternative approach was applied to a vehicle to evaluate the effectiveness of this system

By only heating the front of the DPF, a much smaller amount of energy is used to ignite the particulate matter compared to raising the temperature of the entire DPF. This technique relies on leveraging the particulate oxidation energy to continue the soot burning as a flame front travels down the DPF channel (see Figure 1).

This approach has been demonstrated on a running diesel truck with a heavily loaded DPF. The DPF was then cut into 1" segments to analyze the effectiveness of this regeneration approach (see Figure 2).

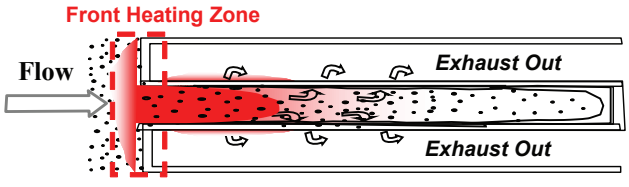

FIGURE 1. Front-Ignited DPF Regeneration

Figure 2 illustrates that nearly 85% on the soot was removed during this regeneration cycle. This outcome was also predicted by our DPF model as illustrated in Figure 3. Soot oxidation on the front face creates a propagating wave that was simulated using the DPF regeneration model developed by Michigan Technological Institute (MTU). Figure 3 is an example of one of these simulations. Figure 3 shows the evolution of the temperature in a DPF from the addition of heat. The different colored lines represent the temperature and soot levels at a specific point in time as the flame front propagates down the length of the DPF.

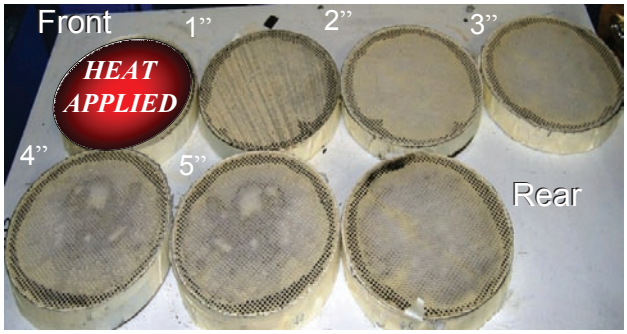

FIGURE 2. Segmented DPF After Regeneration

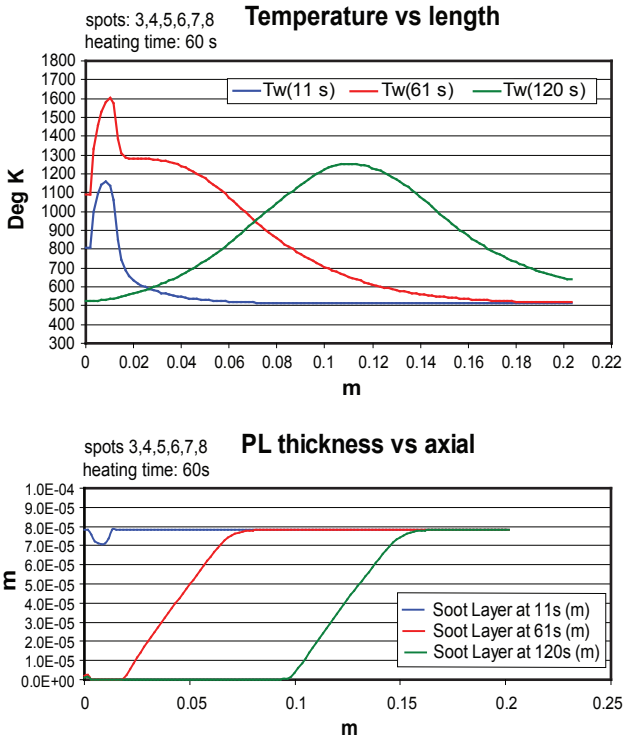

FIGURE 3. DPF Model Regeneration Results

Presently we are evaluating this selective heating regeneration technique on cordierite DPFs where substrate durability is an issue. Several heating designs and engine control strategies are being developed to address the substrate durability concerns.

Conclusions

The goal of this project was to develop a very robust and energy efficient approach to regenerate a DPF. Experimental results with the current heating and control strategy has been effective in reducing the fuel penalty required to regenerate a particulate filter. Additional benefits include: reduced tailpipe temperatures during regeneration, shorter regeneration times, and overall higher regeneration efficiencies. Several experimental regenerations have been successful and the technique looks increasingly promising.