II.B Energy Efficient Emission Controls

II.B.1 Assessing Reductant Chemistry During In-Cylinder Regeneration of Diesel Lean NO_x Traps

Shean Huff (Primary Contact), James Parks, Stuart Daw, John Storey, Brian West, Bill Partridge, Sam Lewis, Jae-Soon Choi, Todd Toops
Oak Ridge National Laboratory
2360 Cherahala Boulevard
Knoxville, TN 37932

DOE Technology Development Manager: Ken Howden

Objectives

- Enable light-duty diesel market penetration through the development of energy-efficient aftertreatment.
- Establish a relationship between exhaust species and various regeneration strategies on a fully controlled engine.
- Characterize effectiveness of in-cylinder regeneration strategies.
- Develop stronger link between bench- and full-scale system evaluations.
    - Provide data through the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) focus group to improve models. Use models to guide engine research.

Approach

- Characterize H_2, carbon monoxide (CO), and hydrocarbons (HCs) generated by the engine.
    - Use Fourier transform infrared (FTIR) spectroscopy, gas chromatography/mass spectrometry (GC/MS), and spatially resolved capillary inlet mass spectrometry (SpaciMS) to characterize engine strategies.
- Characterize candidate lean NO_x traps (LNT) for performance and degradation.
    - Correlate various reductants with catalyst performance.
- Develop and execute rapid sulfation/desulfation experiments.
- Develop experiments for bench-scale work to further characterize LNT monoliths, wafers, and/or powders.

Accomplishments

- Received full-size catalysts (diesel oxidation catalyst and NO_x adsorber) from the Manufacturers of Emission Controls Association (MECA) in August 2003.
    - LNT cores for bench flow (same formulation)
- Defined and procured 2 “model catalysts” (via CLEERS & Emerachem).
    - Engine and bench samples
- Diagnosed engine problem; replaced engine (unplanned).
- Investigated effects of fuel chemistry and regeneration strategy on exhaust species, exhaust species on LNT performance, and regeneration strategy on PM.
- Examined 3 fuels and 2 strategies with full speciation, SpaciMS.
    - Further examine other temperatures.

  - Examine regeneration in the midst of low-temperature combustion (LTC) operation.
- Developed desulfation strategy, desulfurized LNT.
- Coordinating experimental plans with CLEERS and bench reactor teams.

Future Directions

- Conduct similar experiments with catalysts in fresh, heavily sulfated, and desulfated conditions and across a wider temperature range to understand if the conclusions hold for broader cases.
- Further investigate regeneration during “LTC”.
- Conduct rapid sulfation/desulfation with speciation and SpaciMS.
- Examine model catalysts and other MECA catalysts.
- Share results and coordinate research plans through CLEERS LNT focus group.

Introduction

NO_x emissions from diesel engines are very problematic, and the U.S. Environmental Protection Agency (EPA) emissions regulations require ~90% reduction in NO_x from light- and heavy-duty diesel engines in the 2004-2010 timeframe. An active research and development focus for lean-burn NO_x control is in the area of LNT catalysts. LNT catalysts adsorb NO_x very efficiently in the form of a nitrate during lean operation, but must be regenerated periodically by way of momentary exposure to a fuel-rich environment. This rich excursion causes the NO_x to desorb and then be converted by more conventional three-way catalysis to N_2. The momentary fuel-rich environment in the exhaust can be created by injecting excess fuel into the cylinder or exhaust and/or throttling the intake air and/or increasing the amount of exhaust gas recirculation (EGR). The controls methodology for LNTs is very complex, and there is no clear understanding of the regeneration mechanisms. NO_x 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 NO_x, they also have a high affinity for sulfur. As such, sulfur from the fuel and possibly engine lubricant (as SO_2) can adsorb to NO_x adsorbent sites (as sulfates). Similar to NO_x 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 NO_x performance. There is much to be learned with regard to LNT 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 examine 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 (Figure 1). The engine is equipped with an electronic engine control system that provides full bypass of the original equipment manufacturer (OEM) engine controller. The controller is capable of monitoring and controlling all the electronic devices associated with the engine (i.e., fuel injection timing/duration/number of injections, fuel rail pressure, turbo wastegate, throttle, and EGR).

Two regeneration strategies [delayed extended main (DEM) and Post80] and three fuel compositions (ECD1, BP15, and DECSE) have been studied with the goal of introducing a broad range of species to the LNT catalysts. The DEM strategy uses intake

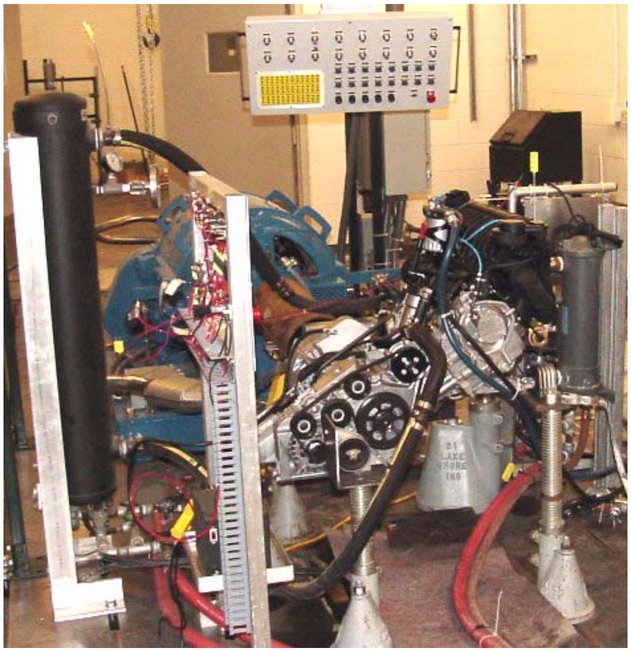

Figure 1. Experimental Setup Including Engine, Control System, Motoring Dyno, and Exhaust System

throttling to lower air:fuel ratio. The main injection duration is extended to achieve rich conditions and retarded a few crank angle degrees to reduce the torque increase associated with excess fueling. Figure 2a shows several oscilloscope trace snapshots in time that illustrate the approach. The traces show injector current versus time. Post80 involves adding an injection event after the main injection event to achieve rich operation. The strategy studied here uses a throttle strategy identical to that of the DEM strategy and excess fuel injection at 80 degrees after top dead center (ATDC), as shown in Figure 2b. Note that the pilot is disabled during the post injection. Concerns about injector durability led to the strategy shown in the figure. Catalysts are being studied under quasi-steady conditions, that is, steady load and speed but with periodic regeneration, as shown in Figure 3.

Ultra-low sulfur fuels were used in this study, with sulfur (S) contents at or below the 15 part per million (ppm) limit set by EPA for 2006. Selected properties of the fuels are shown in Table 1. Chromatograms of the 3 fuels are shown in Figure 4. The peaks labeled C10-C25 are normal alkanes. The Diesel Emission Control Sulfur Effects (DECSE) program defined a fuel that has been widely used in diesel emission control research. This fuel is a mix of refinery streams blended to yield properties representative of 1999 industry average fuel in all respects except for sulfur level. The initial batch of DECSE base fuel was around 3 ppm S; the DECSE fuel used in this study was less than 1 ppm S. The BP15 fuel is a much broader refinery cut and, as shown in the chromatogram, contains a much wider array of HC species than the DECSE fuel. BP15 is a one-time refinery run by BP to produce a “2007-like” fuel, with 15 ppm S (refined for the Advanced Petroleum-Based Fuels – Diesel Emission Control Program). The ECD-1 is a commercially available fuel that has been approved for use in California. As shown in Table 1 and Figure 4, ECD-1 and BP15 are very similar in their HC species, varying only in aromatics, cetane, and S level.

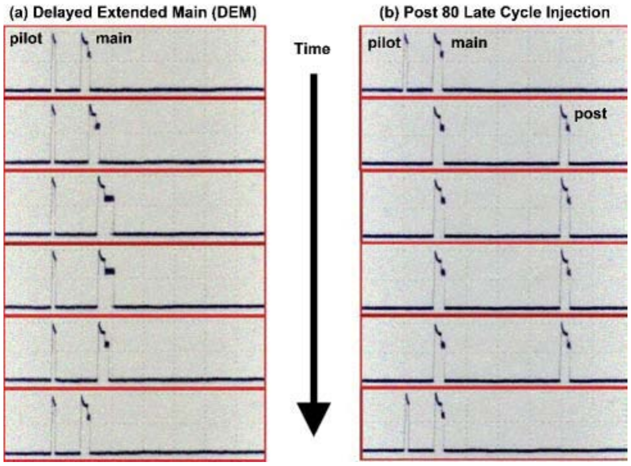

Figure 2. Oscilloscope Traces Showing (a) DEM and (b) Post80 Fuel Injection Strategies

Table 1. Selected Fuel Properties

Fuel/Property	BP15	ECD-1	DECSE
Cetane No.	50	54	44
Aromatics, % ASTM D1319	29	24	27
Sulfer, ppm ASTM D5453 (as tested)	14	9	<1
H/C Ratio	1.86	1.87	1.84

Advanced tools such as H_2-SpaciMS and GC/MS are being used to characterize the species produced in the engine or in upstream catalysts. The H_2-SpaciMS is being used for both in-pipe and in-situ measurements within the catalyst monoliths. In addition, catalysts and exhaust species will be

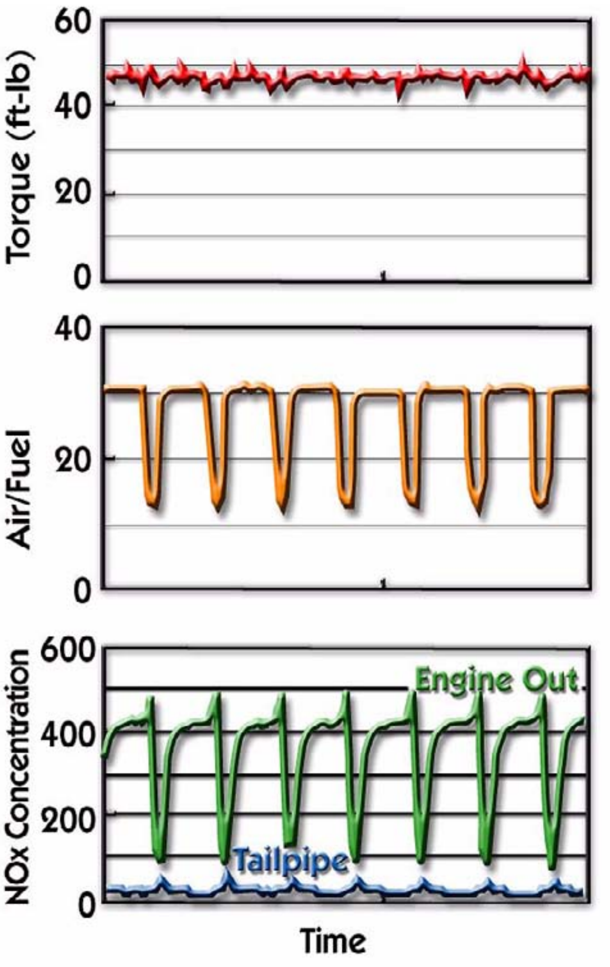

Figure 3. Quasi-Steady-State LNT Regeneration Trace

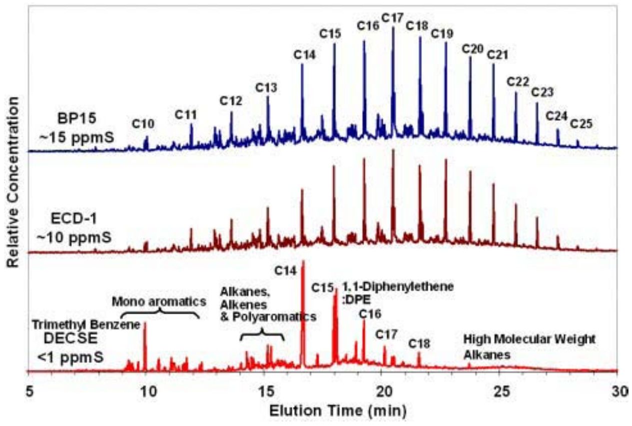

Figure 4. GC/MS Chromatograms Showing Raw Fuel HC Species

characterized after rapid sulfation and during desulfation. LNT catalysts have been provided by some MECA members. "Model" catalysts will also be characterized.

Finally, bench-scale work will be used to further characterize LNT monoliths, wafers, and/or powders using our bench-scale reactor and the diffuse reflectance Fourier transform infrared spectroscopy reactor. Results and characteristics of the engine experiments will be used to help define more meaningful bench-scale studies. In some cases, the exact same catalyst formulation characterized on the engine stand will also be examined in the bench studies.

<u>Results</u>

Summary of Fuel and Strategy Effects

Figures 5a and 5b show the differences in CO and H_2 production for the DEM and Post80 strategies for all three fuels evaluated at the same nominal 1500 RPM, 50 ft-lb_f, 300°C exhaust temperature condition. The DEM strategy produces consistently more CO and H_2 than the Post80, regardless of fuel. The total HC emissions for each strategy and fuel are summarized in Figure 5c. It is interesting to note that while we observed differences in the detailed HC species produced by the strategies and fuels, there appears to be no significant fuel effect on total CO, HC, or H_2 for any given strategy. Figure 5d indicates that the DEM strategy consistently produces better NO_x reduction than the Post80 strategy for all fuels. Moreover, the strategy-dependent LNT efficiency correlates with that of CO and H_2 concentration, but not HC. This result suggests that for the conditions reported here, H_2 and CO have a greater effect on LNT efficiency than do all other HCs present. These results are consistent with bench-scale experiments in the literature that have shown H_2 to be the preferred reductant, followed by CO, then propene.

In-Situ Analysis of H_2 Utilization

In-situ intra-catalyst speciation was used to further investigate the role of reductants in the LNT regeneration process. The H_2-SpaciMS was used to measure transient total NO_x, O_2, and H_2 concentrations at ¼, ½, and ¾ catalyst-length locations within the LNT. These results are combined with conventional LNT-in and -out CO

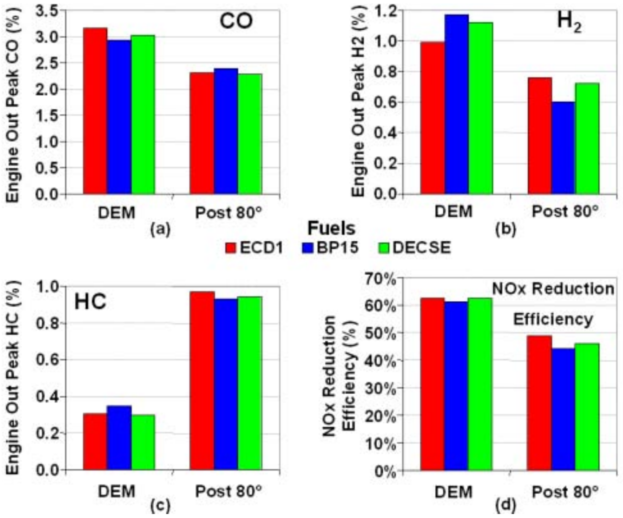

Figure 5. Summary of Fuel and Strategy Effects on CO, H_2, and HC Emissions and Average NO_x Reduction

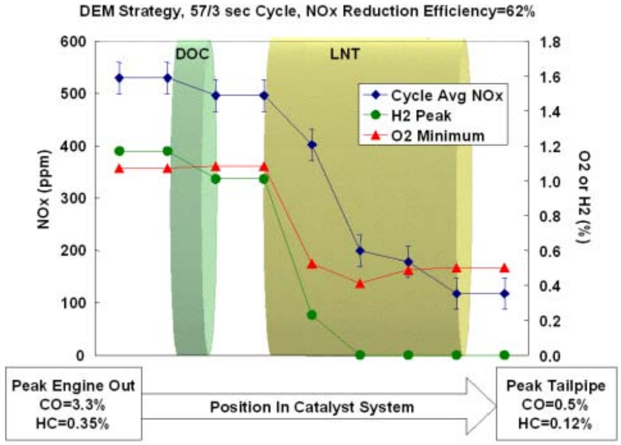

Figure 6. In-Situ Measurements through the Catalyst System for DEM Strategy, BP15 Fuel

and HC measurements from standard bench analyzers and are shown in Figures 6 and 7 for the DEM and Post80 regeneration strategies, respectively. The figures show peak H_2, CO, and HC levels and minimum O_2 during regeneration as well as average NO_x levels over the sorption cycle; similar results were obtained for each fuel studied (data from BP15 fuel is shown).

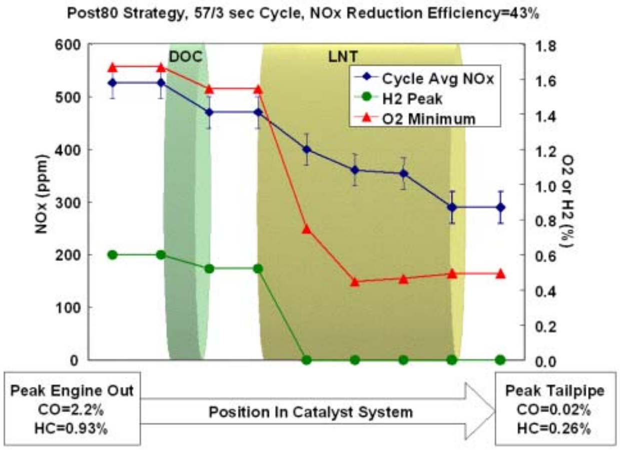

Figure 7. In-Situ Measurements through the Catalyst System for Post80 Strategy, BP15 Fuel

The data from the DEM strategy (Figure 6) shows little change in exhaust chemistry across the diesel oxidation catalyst (DOC) during regeneration. Some decrease in the reductant levels occurs, but the primary decrease in reductant concentration occurs in the LNT catalyst. The strategy is effective in consuming oxygen since engine-out O_2 levels drop to 1.1%; however, the DOC is not effective in completely removing the remaining O_2 since the 1.1% level remains downstream of the DOC. Measured O_2 levels drop to 0.5% at ¼ length inside the LNT and remain at that level throughout the LNT. Oxygen levels of 0% are difficult to measure considering the fact that O_2 levels drop for 2-3 seconds intermittently between lean exhaust O_2 levels of 12.6%; thus, it is assumed that the 0.5% level is representative of O_2 depletion in the catalyst. Note that any remaining O_2 going into the LNT catalyst may influence regeneration since reductants must be consumed to complete the O_2 depletion process. The measured H_2 level drops inside the LNT during the first ½ length of the catalyst, which corresponds with the largest drop in NO_x level. Once H_2 is depleted (during the downstream ½ of the catalyst), little NO_x reduction occurs despite the fact that both CO and HCs are plentiful in the catalyst as evident from measurements at the LNT outlet.

The Post80 strategy data (Figure 7) is similar to the DEM strategy data in terms of O_2 depletion; however, a higher engine-out O_2 level (1.7%) is indicated. Hydrogen depletion occurs earlier in the Post80 case, with H_2 fully consumed by the ¼ length position. The lower available LNT-in H_2 concentration with the Post80 strategy corresponds with the lower NO_x reduction efficiency shown in Figure 5d. The lower H_2 and CO levels combined with the higher O_2 level at LNT-in may contribute to the degraded regeneration efficiency for the Post80 strategy; less of the apparently preferable reductants are available, and more of these are required for O_2 depletion. Note that in the Post80 case, CO is fully depleted across the LNT. HC levels are greater at both the engine-out and LNT-out positions for the Post80 strategy. The consumption of HCs inside the LNT catalyst may contribute to some NO_x reduction since both CO and H_2 are consumed in the LNT; however, the HCs appear less effective for NO_x reduction since no large drop in NO_x levels was observed in the LNT after the H_2 was consumed.

Conclusions

Two strategies for in-cylinder regeneration have been developed for studying reductant chemistry effects on LNTs. Each strategy was evaluated with three fuels: BP15, ECD-1, and DECSE.

Notable conclusions are the following:

- Fuel chemistry has a definite effect on exhaust HC speciation, but negligible effect on engine-out CO and H_2 emissions for the fuels evaluated.
- For 14:1 minimum indicated air:fuel ratio, the Post80 strategy produces 3 times the HCs, with a much broader mix of HC species than DEM.
- The DEM strategy produces higher engine-out CO and H_2 and lower HC emissions than Post80.
- The DEM strategy produces much higher PM emissions than the Post80 strategy.
- For the conditions studied with a minimum air:fuel ratio of 14:1:
  - DEM yields higher NO_x conversion than the Post80 strategy, implying that CO and H_2 are the key reductants and that HC effects on regeneration are secondary.
  - The correlation between hydrogen depletion and NO_x reduction inside the LNT catalyst indicates H_2 may be the most reactive reductant for LNT regeneration.
  - Although both the DEM and Post80 strategies yield engine-out O_2 levels below 2%, the higher O_2 concentrations for the Post80 strategy may contribute to poorer regeneration performance as reductant supply is consumed to complete depletion of O_2 in the exhaust.

II.B.2 Dedicated Sulfur Trap for Diesel Engine Control

David King (Primary Contact), Liyu Li
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

DOE Technology Development Manager: Ken Howden

CRADA Project with Caterpillar Inc.

Objectives

- Develop a low-cost dedicated SO_x trap with capacity exceeding 40 wt.% (SO_2 basis) that can be removed and replaced during periodic vehicle servicing.
- Provide high capacity for both SO_2 and SO_3 removal at temperatures of 200°C and below.
- Demonstrate compatibility with NO_x trap operation (lean-rich cycling).

Approach

- Prepare absorber candidate materials and characterize their properties.
- Test performance with SO_2-containing feedstocks over range of temperatures and with feedstock compositions anticipated under lean-rich cyclic operation.
- Correlate absorbent properties with performance in SO_2 uptake tests.

Accomplishments

- Cryptomelane, an octahedral molecular sieve based on manganese cations, has been identified as a stoichiometric SO_2 absorber having total capacity of approximately 70 wt.% and a breakthrough capacity of 60 wt.% at 325°C. The capacity of the material is virtually unaffected with realistic feeds under cyclic lean-rich conditions.
- Performance of this material has exceeded the 40 wt.% milestone set for SO_2 capacity for the project and is far superior to that of any other reported SO_2 absorber or adsorber. With cryptomelane at 200°C, exit concentration of SO_2 has been maintained at or below 10 ppb until the breakthrough (100 ppb) point, with breakthrough capacity ~2 wt.%.
- A novel metal-modified cryptomelane material has been identified that has resulted in an increase in SO_2 breakthrough capacity to 27 wt.% at 200°C.

Future Directions

- Continue studies with metal-modified cryptomelane to further increase SO_2 uptake capacity at 200°C and below.
- Develop and characterize alternate SO_2 adsorbents having moderate SO_2 capacity that can be regenerated on the vehicle during the rich cycle.
- Demonstrate similar performance of such adsorbers with realistic exhaust conditions and in monolith form.

Introduction

The emission of NO_x from on-road diesel trucks is an important environmental problem. Major efforts are underway to reduce these emissions through the implementation of NO_x conversion devices such as regenerable NO_x traps, which store NO_x as surface nitrates. Sulfur oxides (primarily SO_2) that are present in the diesel exhaust will gradually decrease the effectiveness of NO_x traps. SO_2 is oxidized to SO_3 over the NO_x trap catalyst, and SO_3 reacts to form sulfates that block NO_x adsorption sites. The sulfates are not removed during the rich gas regeneration period that converts adsorbed nitrates to N_2; thus, a high-temperature desulfation step is needed. This results in a gradual degradation of the NO_x trap over the course of many cycles.

One possible approach to improving NO_x trap longevity is to develop a high-capacity, dedicated sulfur oxide-specific trap that is located upstream and can be replaced at regular intervals during engine maintenance. We have identified a promising class of absorbents based on manganese oxide octahedral molecular sieves (OMS). These materials comprise MnO_6 octahedra that are assembled to share faces and edges, resulting in a family of porous absorbents. The most effective of these OMS materials for SO_2 adsorption is the 2x2 member, cryptomelane.

Approach

Following initial results with cryptomelane in which we demonstrated a high SO_2 capacity, we investigated a number of experimental parameters (temperature, space velocity, SO_2 concentration) to further define performance of this material. We then examined the effect of other components in the feed (NO, CO, hydrocarbons) to determine if these species reacted with cryptomelane or were similarly adsorbed. We also examined the performance of other members of the OMS family to compare performance and gain insights into the absorption process. We then studied the capacity and performance of this material under conditions simulating lean-rich cyclic operation. Finally, we examined SO_2 uptake performance at lower temperatures (to 150°C) and developed alternate materials to improve this low-temperature performance.

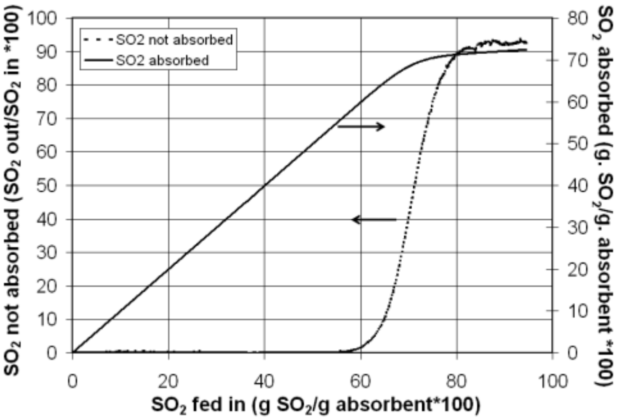

Figure 1. SO_2 Absorption by Cryptomelane at 325 °C at 8000 h^{-1} GHSV

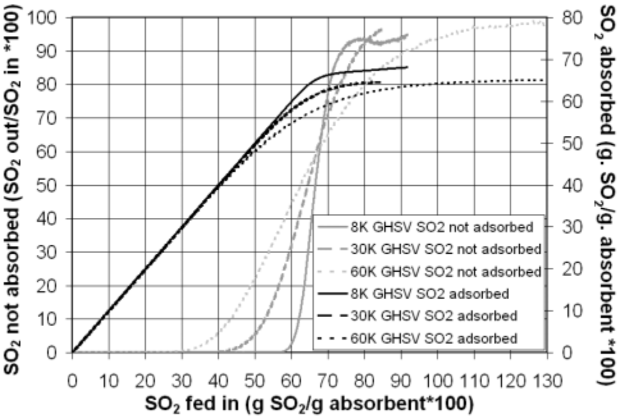

Figure 2. Effect of Feed Gas Space Velocity (GHSV) on SO_2 Absorption by Cryptomelane

Results

Cryptomelane was prepared by the reaction of manganese sulfate with potassium permanganate following a method described by DeGuzman [1]. The adsorption of SO_2 from air (250 ppm SO_2, 325°C, 8000 h^{-1} GHSV) is shown in Figure 1. The figure has plots to show both the instantaneous SO_2 measured in the effluent (SO_2 not absorbed) as well as the cumulative quantity of SO_2 absorbed. The former curve allows clear visualization of the SO_2 breakthrough capacity (approximately 60 wt.%), while the latter curve shows total capacity (approximately 72 wt.%). Such high SO_2 uptake capacities have not been previously described with any material. The effect of space velocity is shown in Figure 2 (250 ppm SO_2, 325°C), indicating that with increasing flow rate the breakthrough capacity

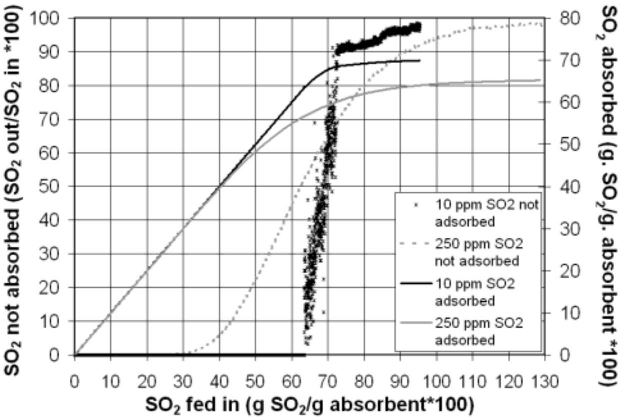

Figure 3. Effect of SO_2 Concentration on Absorption Capacity of Cryptomelane at 325°C and 60,000 h^{-1} GHSV

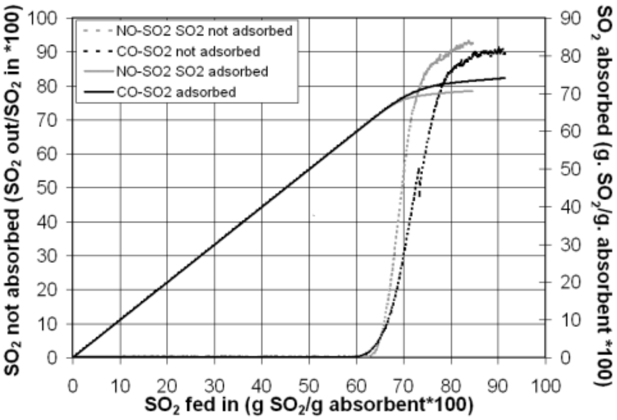

Figure 4. Effect of NO (178 ppm) or CO (250 ppm) on the SO_2 Absorption over Cryptomelane at 325°C and 8000 h^{-1} GHSV

(defined as the point at which SO_2 out = 1% of SO_2 in) shows a significant decrease, whereas the total capacity is affected by only a small percentage. SO_2 concentration in the feed is also an important parameter, as shown in Figure 3. As the SO_2 concentration in the feed is reduced from 250 to 10 ppm (at 325°C, 60,000 h^{-1} GHSV), the breakthrough capacity increases substantially, as does the total capacity. It is clear there are kinetic limitations to the SO_2 uptake process, which we believe proceeds through the following steps: oxidation of SO_2 to SO_3 by the high valent manganese cations in the cryptomelane followed by reaction of SO_3 with the resulting lower valent manganese cations to form manganese sulfate. Since the final product is a bulk manganese sulfate, we refer to this process as absorption rather than adsorption.

For operation in emissions control, the SO_x trap will be exposed to other species such as NO and CO. As was the case with SO_2, it is possible that the cryptomelane can oxidize NO to NO_2 and CO to CO_2, and these reactions could result in loss of oxidizing capacity toward SO_2 and possibly loss of absorption capacity from manganese nitrate and carbonate, respectively. Figure 4 shows that neither NO (178 ppm) nor CO (250 ppm) adversely affects the uptake of SO_2. We have separately demonstrated that cryptomelane does indeed oxidize both NO and CO under the conditions of operation of the test, but they are not absorbed. Since capacity of cryptomelane is maintained, this indicates that the cryptomelane is reoxidized by oxygen in the feedstream and that cryptomelane has catalytic and redox properties.

Cryptomelane is one of a class of octahedral molecular sieves based on manganese. The cryptomelane molecular sieve pore is characterized by a square channel having two manganese octahedra on a side (hence a 2x2 structure). Since there are a number of other members of the OMS family, we investigated their SO_2 absorption properties for comparison with cryptomelane at 325°C. We also investigated for comparison a non-OMS MnO_2 sample that has a high manganese oxidation state similar to that found in cryptomelane. The results are shown in Table 1. Although other OMS materials show high capacity, such capacities are only achieved at low space velocities and low packing densities. These low-density materials would have low volumetric capacity. At comparable packing density, cryptomelane is superior. The non-OMS MnO_2 sample has low SO_2 uptake. It appears that the OMS structure is important for SO_2 absorption, and cryptomelane is the best OMS material for SO_2 adsorption.

A lean-rich cycle experiment was carried out with cryptomelane to determine whether the capacity of the material toward SO_2 could be maintained despite being exposed to periods of reducing gases. Extended exposure of cryptomelane to reducing gases converts the sample to MnO and Mn_2O_3. The cycling treatment employed a lean phase (12% O_2, 10% CO_2, 0.05% NO, 10% H_2O, balance He) for 6

Table 1. SO_2 Absorption Performance of Manganese Oxides OMS Materials at 325 °C

Material	Packing density, g/cm^3	SO_2 break-through capacity (100 x g. SO_2/g absorbent)	SO_2 total capacity (100 x g. SO_2/g absorbent)	GHSV[1]
1x1 pyrolusite	1.34	<0.1	2.7	18K
2x2 cryptomelane A	0.66	59	71	8K
2x2 cryptomelane B	0.99	50	60	8K
2x3 romanechite	0.29	57.5	70	3.4K
2x3 romanechite	0.43	31	51	5.1K
2x3 romanechite	0.92	12	40	11K
2x4 sodium manganese oxide	0.90	33	42	11K
3x3 torodokite	0.87	1.5	48	11K
EMD MnO_2[2]	0.99	3.5	8.7	12K

1) Feed gas flow for cryptomelane B was 67 sccm, and 100 sccm for all others.

2) EMD MnO_2 is not an OMS material. Source: Comilig, Inc.; BET surface area: 30 m^2/g.

minutes followed by a rich phase (1.5% O_2, 4% CO, 1.3% H_2, 10% CO_2, 10% H_2O, 0.05% NO, 0.4% C_3H_6, balance He) of 30 seconds. The cyclic treatment was carried out at 450°C for 6 hours at 26,000 h^{-1} GHSV. X-ray diffraction showed that the cryptomelane structure remained, although scanning electron microscopy (SEM) showed some coarsening of the particles. The subsequent SO_2 uptake experiment at 325°C and 8000 h^{-1} GHSV showed breakthrough capacity of 45 wt.% and total capacity of 60 wt.%. Although these capacities have decreased somewhat relative to the fresh material, performance remains very good, especially in light of the high temperature of the lean-rich cycling experiment and the duration of the rich period. More realistic conditions of lean-rich cycling (rich period ~10 seconds) are likely to be less detrimental to performance. We believe that the redox properties of the cryptomelane in the presence of oxygen account for its good performance under lean-rich cycling.

Low temperature performance of the SO_2 trap is also critically important under conditions where the diesel exhaust may not attain 325°C or higher. We have evaluated cryptomelane for SO_2 absorption as low as 150°C. The results, provided in Table 2, clearly show that breakthrough capacity decreases significantly with decreasing temperature. This may be a result of lower kinetic activity at lower temperature or a slower rate of diffusion of the manganese sulfate from the surface to the bulk of the material. During the course of this latter investigation, we carried out modification of the cryptomelane by metal modification, and this resulted in an improved low temperature uptake of SO_2, also shown in Table 2. This is a promising lead that may provide guidance to the development of onboard regenerable adsorbents.

Table 2. SO_2 Breakthrough Capacity of Cryptomelane and Metal-Modified Cryptomelane at 60,000 hr^{-1} GHSV as a Function of Absorption Temperature[1]

Absorbent	150°C	200°C	250°C
Cryptomelane	1.54	1.60	2.90
Metal-doped cryptomelane, lower loading	2.20	5.20	38.1
Metal-doped cryptomelane, higher loading	8.75	26.84	33.42

[1] Feed gas: 10 ppm SO_2 in air. Breakthrough capacity (100 x g SO_2/g absorbent) is defined as the point where SO_2-out exceeds 1% of SO_2-in (100 ppb).

Conclusions

The octahedral molecular sieve material cryptomelane is an attractive SO_x absorber for a replaceable trap concept. It possesses the following properties:

- SO_2 total capacity of 70 wt.% and breakthrough capacity of 60 wt.%, which is very high compared to other adsorber materials.
- Capacity is unaffected by the presence of NO or CO in the feedstream.

- Cryptomelane is stable to lean-rich cycling conditions with minimal loss of capacity.
- Breakthrough and total capacity increase as SO_2 concentration is decreased, which is favorable for operation with projected 15 ppm sulfur diesel fuel.
- The breakthrough capacity decreases as temperature decreases from 325°C, but alternate materials show promise for increasing low temperature capacity.

FY 2004 Publications/Presentations

1. Li, L.Y.; King, D.L. Method for Determining Performance of Sulfur Oxide Adsorbents for Diesel Emission Control Using Online Measurements of SO_2 and SO_3 in the Effluent, *Ind. Eng. Chem. Res.,**2004**, 43, 4452.*
2. Li, L.Y.; King, D.L. High Capacity Sulfur Dioxide Absorbents for Diesel Emissions Control, submitted for publication (*Ind. Eng. Chem. Res.*).
3. Li, L.Y.; King, D.L. Sulfur Oxide Adsorbents and Emissions Control, U.S. patent application, filed January 2004.
4. D.L. King and Liyu Li, “Development of SO_x Trap For Diesel Emissions Control”, DOE Annual Review, Argonne National Laboratory, Chicago, May 2004.

References

1. DeGuzman, R.N.; Shen, Y.F.; Neth, E.J,; Suib, S.L.; O’Young, C.K.; Levine,S.; Newsam, J.M. Synthesis and Characterization of Octahedral Molecular Sieves (OMS-2) Having the Hollandite Structure, *Chem. Mater. **1994,** 6, 815.*

II.B.3 In-Pipe Regeneration of NO_x Adsorber Catalysts for Heavy-Duty Applications

Brian H. West (Primary Contact), John Thomas, John Storey, Sam Lewis
Oak Ridge National Laboratory
2360 Cherahala Boulevard
Knoxville, TN 37932

Industrial Partner:
Xinqun Gui, International Truck and Engine Corporation

DOE Technology Development Manager: Kevin Stork

Objectives

- Develop NO_x adsorber regeneration and desulfation strategies for diesel aftertreatment systems (including diesel oxidation catalysts and diesel particle filters).
- Improve understanding of role/fate of different exhaust hydrocarbons in advanced diesel aftertreatment systems for several reductant delivery systems. International Truck and Engine Corporation will focus on in-cylinder strategies while Oak Ridge National Laboratory (ORNL) will examine in-manifold and in-pipe strategies.

Approach

- NO_x adsorber regeneration strategies will be developed for several steady-state conditions. Electronic control of the intake throttle and exhaust gas recirculation (EGR) valve will be used to lower air:fuel ratio prior to reductant (fuel) delivery in-pipe (into exhaust, upstream of catalysts).
- System performance will be measured for a variety of regeneration conditions. Hydrocarbon speciation and other advanced ORNL analytical tools will be used to improve system understanding.

Accomplishments

- Developed PC-based system for transient electronic control of intake throttle, EGR valve, wastegate, and in-exhaust reductant (fuel) delivery.
- Developed strategy for regenerating NO_x adsorber at rated load (600°C) condition for NTE (not-to-exceed); measured hydrocarbon (HC) species entering and exiting the NO_x adsorber for mild, moderate, and aggressive reductant oxidation schemes.
  - Achieved 70% NO_x reduction at rated power, with acceptable CO and HC emissions and very low fuel penalty (<2.5%).
  - Confirmed degree of fuel cracking in oxidation catalysts; observed improved NO_x adsorber performance with aggressive fuel cracking to generate lighter HC species.
  - Showed potential fuel savings with more aggressive in-pipe fuel reforming.
  - Developed air-assisted in-pipe fuel spray for enhanced fuel/air mixing and observed greater degree of fuel cracking.
- Developed strategy for regenerating NO_x adsorber at a road load (400°C) condition; measured hydrocarbon (HC) species entering and exiting the NO_x adsorber with and without an upstream diesel oxidation catalyst (DOC).
  - Demonstrated >80% NO_x reduction at 400°C condition with sulfated catalyst.

Future Directions

- Desulfurize NO_x adsorber catalyst and measure sulfur compounds.
- Re-examine NTE and lower temperature conditions with in-pipe injection of pure compounds.
  - Configure system for multiple in-pipe reductant delivery locations. Reductant upstream of the DOC will consume excess oxygen, while downstream reductant will provide the bulk of HC species for regeneration. This approach will remove any temperature effect of adding or removing the DOC.
  - Speciate hydrocarbons at adsorber inlet and outlet; clarify HC sensitivity as a function of temperature.

Introduction

Heavy-duty emissions standards call for a 90% reduction in NO_x and particulate emissions by 2010, as shown in Figure 1. These new regulations include certification at any and all engine operating conditions, wherein emissions may not exceed 150% of the emissions standard. This regulation is known as not-to-exceed (NTE) and includes steady operation at the rated load condition. The NO_x adsorber catalyst is a promising technology to help meet these stringent new NO_x standards, but there are many open issues that must be resolved prior to commercialization. The (lean-burn) diesel engine does not readily run rich, but rich exhaust conditions are required to regenerate the NO_x adsorber catalyst. With more flexible fueling systems and other advanced engine control schemes, engineers are devising means to run these engines rich during "normal" operation to regenerate NO_x adsorber catalysts. However, the NTE points can include operating conditions at which rich engine operation could be detrimental to the engine and/or aftertreatment system. It is a challenge to produce rich exhaust, and doing so can potentially cause durability problems, excessive fuel consumption, and excess PM, HC, and/or CO emissions.

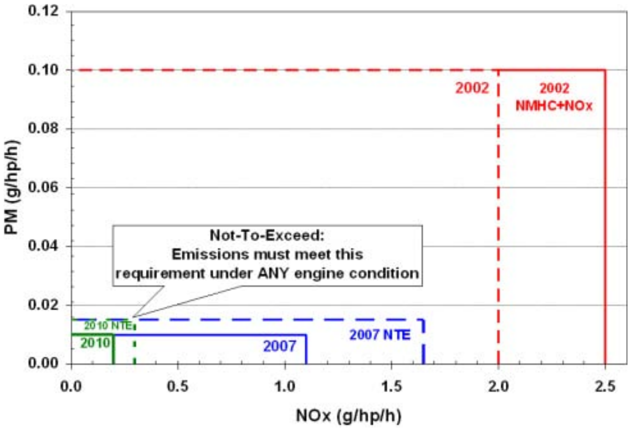

Figure 1. Impending Heavy-Duty Emissions Standards

Additionally, the NO_x adsorber catalyst is very sensitive to sulfur in the exhaust; therefore, effective sulfur management schemes must be developed that will ensure full useful life of the aftertreatment systems. This Cooperative Research and Development Agreement (CRADA) with International Truck and Engine Corporation aims to help resolve some of the problems and unknowns with the NO_x adsorber technology.

Approach and Results

International Truck and Engine is pursuing engine-based (in-cylinder) approaches to adsorber regeneration, while complementary experiments at ORNL are focusing on in-pipe or in-exhaust (after turbo) fuel injection. ORNL has 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 (Figure 2). Aftertreatment systems consisting of different diesel oxidation catalysts in conjunction with a diesel particle filter and NO_x adsorber are

Figure 2. In-Pipe Fuel Injection for NO_x Adsorber Regeneration

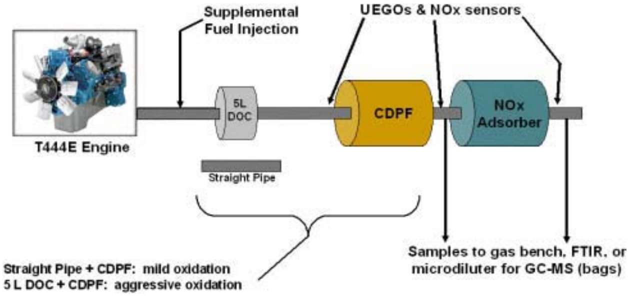

Figure 3. Aftertreatment System Schematic Diagram

being evaluated under quasi-steady-state conditions with sampling for HC species at multiple locations in the exhaust system.

A catalyzed diesel particulate filter (CDPF) was installed just upstream of the NO_x adsorber catalyst for all experiments, as shown in Figure 3. Fuel cracking upstream of the 14.0 liter NO_x adsorber was examined by using the CDPF alone and in conjunction with a 5.0 liter oxidation catalyst. Gas chromatograph mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR) were used to speciate the hydrocarbons entering and exiting the NO_x adsorber catalyst for the rated load condition (450 ft-lb, 2300 RPM, ~600°C catalyst temperatures) and for a lower-temperature “road load” condition (200 ft-lb, 1800 RPM, ~400°C catalyst temperatures).

GC-MS and FTIR are used to identify and quantify the various HC species in the exhaust. With the DOC upstream of the CDPF, we find many cracked HC compounds (cracked HCs that are not prevalent in raw fuel) at the NO_x adsorber inlet during regeneration. The apparent benefits of fuel cracking in the diesel oxidation catalyst for the rated load condition (600°C) are shown in Figure 4. The fuel penalty on the x-axis is the amount of fuel used for regeneration, expressed as a fraction of the fuel used for normal lean operation. It is clear in this figure that for an equivalent level of NO_x reduction, 10-20% less fuel is needed for regeneration when an oxidation catalyst is added upstream of the CDPF. From these data we presume that the lighter HC species are more effective reductants than the heavier HC compounds in raw diesel fuel. The GC-MS data indicate that the light alkenes (propene, butenes, pentenes) and mono-aromatics are more readily consumed, whereas a larger fraction of the branched alkanes pass through the NO_x adsorber catalyst. The experiments represented in Figure 4 used a conventional automotive fuel injector for delivering excess fuel (reductant) into the exhaust (shown in Figure 2). Concerns about fuel evaporation and mixing, particularly at the lower-temperature road load condition, led to development of an air-assist fuel injector, shown in Figures 5a and 5b. As the schematic (5a) shows, the conventional injector sprays into an air chamber, which then sprays into the exhaust through an orifice, assisted by compressed air. As shown in Figure 5b, atomization was greatly improved as compared to the conventional spray in Figure 5c.

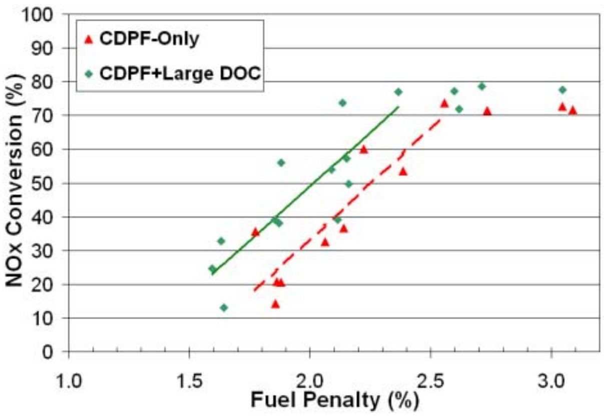

Figure 4. NO_x Conversion Versus Fuel Penalty for Rated Load Condition, CDPF-Only vs. CDPF+DOC (600°C catalyst temperature)

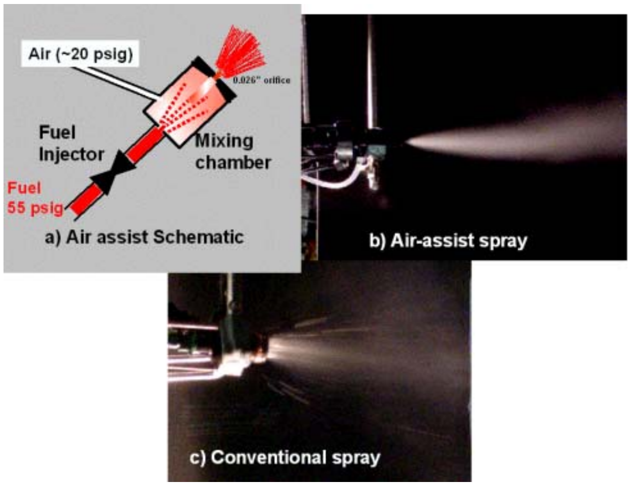

Figure 5. a) Schematic of Air-Assist Injection, b) Air-Assisted Fuel Spray, c) Conventional Injector Spray

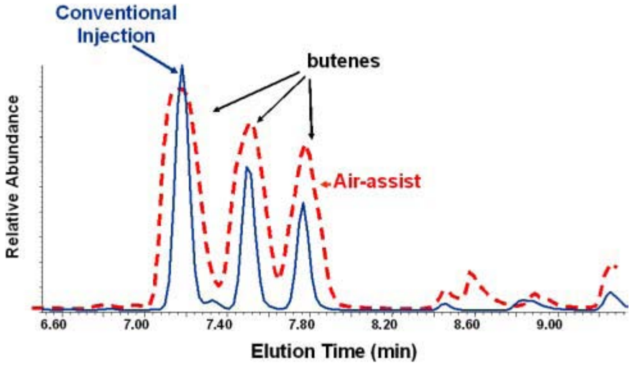

Figure 6. Gas Chromatogram Showing Butene Peaks at NO_x Adsorber Inlet During Regeneration for Conventional and Air-Assist Injection (rated load condition)

The use of the air-assist injector improved the fuel cracking in the upstream DOC, as indicated in Figure 6. The figure shows butene peaks at the NO_x adsorber inlet from GC-MS for regeneration using the air-assist and the conventional injector at the rated load condition (600°C). Note that the butene area counts with the air-assist injector are over double the area counts with the conventional injector, and these higher counts are saturated (above the maximum detection), so the concentration ratio is much higher than 2. Similar results were noted for other species as well, including propene. For the 600°C rated load condition, the improved fuel cracking with the air-assist injector resulted in a small improvement in NO_x conversion; perhaps 5-8% less fuel nets the same NO_x reduction, as shown in Figure 7. The NO_x conversions shown in Figure 7 are not as good as those shown in Figure 4 due to sulfur poisoning of the NO_x adsorber. Exhaust sulfur (largely SO_2) is readily stored on the NO_x storage sites in the NO_x adsorber catalyst as a sulfate. These sulfated sites are rendered ineffective for NO_x storage until they are "desulfurized" by a process similar to regeneration, except with higher temperatures and longer times required. The NO_x adsorber was sulfur-poisoned through the normal course of running the engine on an ultra-low sulfur fuel containing 10 ppm (parts per millon) sulfur.

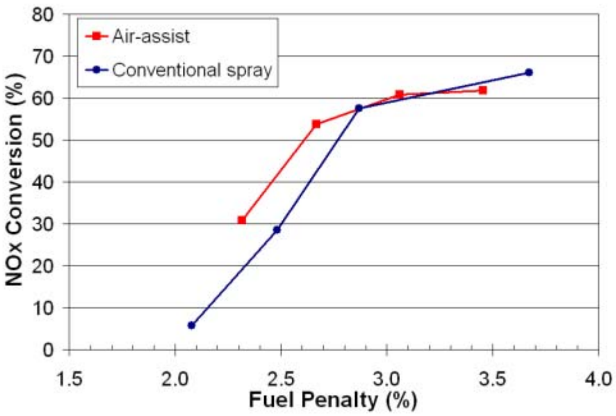

Figure 7. NO_x Conversion Versus Fuel Penalty for Rated Load Condition, Conventional vs. Air-Assist Injection (600°C catalyst temperature)

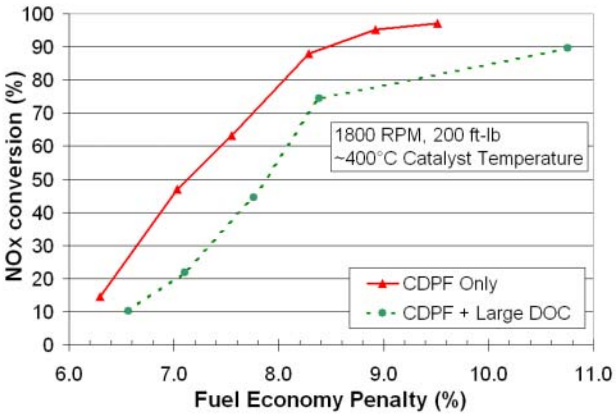

Figure 8. NO_x Conversion Versus Fuel Penalty for Road Load Condition, CDPF-only vs. CDPF+DOC (~400°C catalyst temperature)

Figure 8 summarizes the results of experiments at the road load condition. In contrast to the rated load condition (Figure 4), note that this figure implies that the "CDPF Only" case actually provides equivalent NO_x reduction at a lower fuel penalty than the "CDPF + DOC" case. While GC-MS and FTIR data indicate that the DOC also enhances fuel cracking at this lower temperature, thereby providing lighter HC species to the NO_x adsorber, any benefits of these lighter species on NO_x adsorber regeneration are confounded by other differences in the two cases. The variations in the NO_x adsorber temperature, as shown in Figure 9, probably contribute to some of this difference. Note (in the top half of the figure) that with the DOC present, the exotherms in the NO_x adsorber catalyst are very small, resulting in a fairly steady temperature of 385-390°C. When the DOC is removed, the regeneration event produces a large exotherm in the front core of the NO_x adsorber

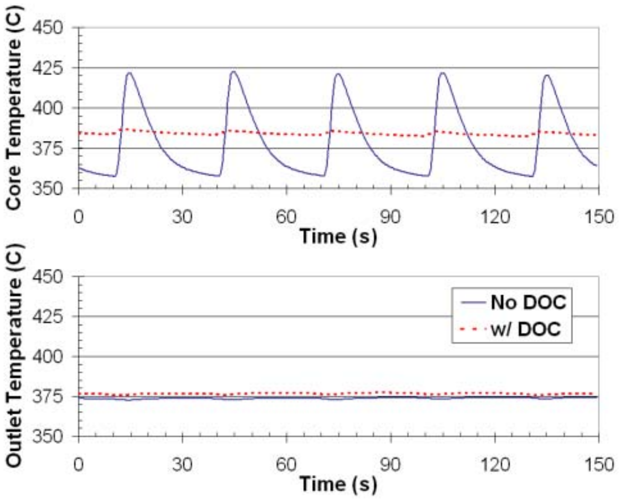

Figure 9. NO_x Adsorber Temperatures for Road Load Condition (Top: NO_x Adsorber Core Temperature; Bottom: NO_x Adsorber Outlet Temperature)

(previously in the DOC), causing the NO_x adsorber temperature to climb rapidly to over 420°C, then cool to a minimum temperature below 360°C before the next cycle. This core temperature is measured with a 0.020 inch diameter thermocouple at the center of the front 3-inch monolith of the NO_x adsorber catalyst, which is composed of four 3-inch monoliths. The actual surface temperature swings inside the catalyst could be more pronounced due to the relatively slower transient response of the thermocouple. As the bottom half of the figure shows, the temperatures out of the NO_x adsorber are very similar for either case; thus, on a net basis, the same amount of energy is deposited into the catalyst system during regeneration even though the position of energy deposition (heat release) differs. For the case with no upstream DOC, the higher thermal dynamics may contribute to improved NO_x conversion. Catalytic activity varies with temperature, and these effects can be different for various processes. For example, HC oxidation rates and NO_x reduction rates increase with increasing temperature, while nitrate stability and, thereby, NO_x storage is improved at lower temperatures. One theory derived from the observed data follows: the higher temperature during regeneration improves reaction rates for HC utilization and/or nitrate decomposition (which leads to more NO_x storage sites recovered) and the lower temperature during lean operation improves nitrate stability and/or NO oxidation (which leads to more NO_x storage site utilization). Thus, temperature modulations in the NO_x adsorber catalyst can alter NO_x reduction performance.

The exotherm is caused by oxidation of a portion of the reductant (fuel) in depleting any remaining engine-out oxygen. This oxidation reaction must occur before the chemical reduction can take place in the NO_x adsorber. If this oxidation takes place in the DOC, then the NO_x adsorber temperature is more constant. If the DOC is not in place, the bulk of this oxidation and exotherm occurs in the NO_x adsorber, generating the temperature swings noted in Figure 9. This interesting result highlights another challenge in designing and operating these complex systems. While lighter HC species are probably more desirable under any regeneration condition, the presence of a small amount of oxygen during regeneration may also enhance NO_x reduction by momentarily increasing temperature. In addition, with the DOC removed, a small amount of engine-out CO (800-900 ppm) was present at the NO_x adsorber inlet during regeneration. With the DOC installed, this CO and remaining exhaust gas oxygen were largely consumed while also cracking the raw fuel HC into lighter species. Follow-on experiments in FY 2005 will examine desulfation and attempt to clarify the HC species sensitivity as a function of temperature.

Conclusions

Cracking of raw fuel with DOCs can provide the NO_x adsorber catalyst with HC species not present in raw fuel. Observations from experiments to date include the following:

- Providing the NO_x adsorber with preferred HC species can lower the fuel penalty associated with NO_x adsorber regeneration for a given level of NO_x reduction, shown at the rated load condition.
- Mono-aromatics and light alkenes have been found to be readily consumed in the NO_x adsorber catalyst, while a large fraction of the branched alkanes are passed through.
- The heavy-duty not-to-exceed (NTE) regulations are extremely demanding. For 70% NO_x reduction to be adequate in the 2010 timeframe, engine-out NO_x emissions will have to be reduced to below 1.0 g NO_x/(hp•h).

- Momentary exotherms from oxidation of raw fuel in the NO_x adsorber catalyst during regeneration can improve NO_x conversion, overwhelming any benefit associated with cracking the fuel in an upstream DOC.

Publications/Presentations

1. West, Brian H., John F. Thomas, Mike Kass, John Storey, and Sam Lewis, “NO_x Adsorber Regeneration Phenomena in Heavy-Duty Applications,” U.S. Department of Energy Advanced Combustion Engines Merit Review, May 13-15, 2003, Argonne, IL.
2. West, Brian H., John F. Thomas, Mike Kass, John Storey, and Sam Lewis, “NO_x Adsorber Regeneration Phenomena In Heavy Duty Applications: ORNL/ITEC CRADA,” presented at 9th Diesel Engine Emissions Reduction Workshop, August 2003.

II.B.4 Hydrocarbon-Based NO_x Catalysts for Diesel Applications

Christopher L. Marshall
Chemical Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, CMT/205
Argonne, IL 60439-4837

DOE Technology Development Manager: Ken Howden

Objectives

- Test the use of deNO_x catalysts developed for stationary source applications for use in diesel vehicle emission reduction. Use realistic feeds and conditions typical of diesel emissions (temperature, space velocity, oxygen content) to appraise the ability of the catalyst to work under these conditions.
- Optimize the deNO_x catalyst and processing conditions for high conversion and selectivity to N_2 as the desirable nitrogen product.
- Demonstrate the integration of the catalyst system to work onboard a diesel vehicle.
- Set up a formal Cooperative Research and Development Agreement (CRADA) between Argonne National Laboratory (ANL) and a diesel manufacturer and a catalyst manufacturer. The goal of the CRADA will be to complete commercialization of the catalyst package for onboard NO_x reduction using diesel fuel as the reductant.

Approach

- **Task 1.** Work with a diesel engine manufacturer and a catalyst manufacturer to develop catalyst testing protocols and conditions that will both adequately test the range of the catalysts and properly simulate realistic diesel conditions. These conditions will include the proper hydrocarbon, space velocity, and fuel-to-air ratio.
- **Task 2.** The current catalyst testing system will be optimized to test catalysts using the protocols developed under Task 1. In addition, under this task we will construct a combinatorial screening unit that will allow us to test as many as 12 catalysts per day. Such a unit will speed the optimization of catalyst parameters and feed considerations to be tested in Tasks 3 and 4.
- **Task 3.** Continue the synthesis of new catalyst materials begun for stationary source applications. The catalyst formulations will be optimized for use in diesel applications. Variables to be studied include zeolite type, exchange metal type and amount, and additive composition and means of addition.
- **Task 4.** Catalyst formulations developed under Task 3 will be tested for NO_x conversion under simulated diesel conditions using the protocols developed under Tasks 1 and 2. Product yields will be recorded, concentrating not just on the conversion levels (as reported) but also on the exact composition of the exhaust stream. We are especially interested in the makeup of the nitrogen compounds and will concentrate on complete conversion of all nitrogen to N_2. Composition of CO_x will also be studied under this task.
- **Task 5.** Utilize the in situ characterization tools developed for testing the stationary source catalysts. These include in situ extended x-ray adsorption fines structure spectroscopy/x-ray adsorption near edge spectroscopy (EXAFS/XANES) and Fourier transform/infrared (FT/IR) techniques, which reveal the state of the metals and the adsorbed species on the surface of these metals under true reaction conditions. The Heterogeneous Catalysis Group at ANL has worked to develop both the techniques and the reactor cells that can examine the working catalysts under realistic conditions (see, e.g., "In Situ EXAFS Analysis of

the Temperature Programmed Reduction of Cu-ZSM--5," M. K. Neylon, C. L. Marshall, A. J. Kropf, J. Amer. Chem. Soc., 124(19), p 5457 [2002]).

- **Task 6.** Catalysts being tested under Tasks 3 and 4 will also be studied using ex situ temperature-programmed techniques such as temperature-programmed reduction (TPR) and temperature-programmed oxidation. TPR has been especially effective in monitoring the ease of reduction of the metals, which is directly related to both the activity and selectivity of the catalyst.
- **Task 7.** Report results to DOE and collaborators. The project progress reporting procedure will conform to the requirements of the Office of FreedomCAR and Vehicle Technologies.

Accomplishments

- Catalytic tests showed that when using feeds containing only paraffins (~70% of diesel fuel), the current catalyst was ineffective in converting NO_x to N_2. $DeNO_x$ activity was not achieved below the hydrocarbon combustion temperature. Nitrogen selectivity still remained near 100%. These results suggest that the paraffinic portion of diesel fuels cannot be effectively used as the reductant.
- Tests with aromatic feeds (toluene and xylenes) were very effective in converting NO_x to N_2 over the current catalyst. $DeNO_x$ light-off activity was achieved far below the hydrocarbon combustion point. Nitrogen selectivity to N_2 still remained near the 100% mark. These results suggest that the aromatic fraction of diesel fuels (~20%) is a prime candidate as the reductant for $deNO_x$ catalysts.
- The data from the bullet above was extended to low-sulfur jet fuel (JP-8). JP-8 was tested as a reductant for the CeO_2/Cu-ZSM-5 catalyst, both neat and with added aromatics. The catalyst converted 80% of the NO_x to N_2 at a 40,000 hr^{-1} space velocity (Figure 1). JP-8 also improved the high-temperature activity of the catalyst. The activity improvement over using propylene as a feed is 195% at 400°C and 212% at 450°C (Figure 2). Spiking studies with xylenes show that the improvements are related to the wider variety of boiling points of the JP-8 fuels. This wider temperature range meets the industry needs for both low-temperature $deNO_x$ for low- and normal-load operations and high-temperature $deNO_x$ for higher-temperature, high-load operations.

Future Directions

- The results with JP-8 will be extended to low-sulfur diesel (e.g., BP-15; 15 ppm sulfur).
- Conduct tests with BP-15 and JP-8 under high O_2 concentrations in order to optimize the processing conditions under realistic feed conditions.
- Coat several optimized materials and test the activity with BP-15 and JP-8, with the aim to optimize process conditions towards making a working catalyst.
- Coat the best material onto a large monolithic support and test on an engine using a slip stream of the diesel feed as the reductant. Optimization will include maximizing space velocity while minimizing the catalyst volume.

Introduction

The oxide forms of nitrogen (NO, NO_2, and N_2O, collectively called NO_x) are some of the most difficult but important pollutants yet to be eliminated from exhaust streams. A key problem is that the most active commercial catalysts use ammonia to convert NO_x to nitrogen in the exhaust. Not only is ammonia difficult to store, but if conversion is not complete, ammonia can be released to the atmosphere - a problem worse than the release of NO_x. Catalysts are needed that will convert NO_x using a more readily available, more environmentally benign reductant.

One of the most promising catalysts is a metal-exchanged form of the zeolite ZSM-5. In the copper (Cu) exchanged form (Cu-ZSM-5), this catalyst shows a significant ability to reduce NO_x to N_2 using hydrocarbons such as propylene as the reductant.

Many published studies have shown that Cu-ZSM-5 has high selectivity for NO_x conversion with very low hydrocarbon slippage. A major disadvantage to Cu-ZSM-5 is that it is effective only when the exhaust stream is dry. The addition of water (a common component in all exhaust streams) renders the catalyst inactive. For this reason, most commercial development of Cu-ZSM-5 has been stopped.

We have been working on new additives to extend the life of catalysts such as Cu-ZSM-5. One of these additives (cerium oxide, CeO_2) has not only proven effective in eliminating the water stability problem for Cu-ZSM-5, but actually improves its activity.

Approach

The Heterogeneous Catalysis Group at Argonne National Laboratory has developed a series of additives that significantly lower the effective temperature for hydrocarbon-based NO_x reduction. These same catalysts have been recently examined under conditions closer to diesel engine applications and have shown great promise. The conditions used were around 500 ppm NO, a C:N ratio of 6:1, and a high O_2 concentration (8%). These conditions were suggested to us during discussions with diesel engine manufacturers. Tests were performed using n-hexane as the reducing gas for the deNO_x catalyst. The Argonne catalyst selectively converted NO_x (NO/NO_2) into N_2 (95+% selectivity) at temperatures of 300°C and higher. Throughout these tests, no coking was observed on the catalyst material and no catalyst deactivation was observed.

These catalysts can reduce NO_x emissions from diesel engines while saving energy. The energy savings come about from using hydrocarbons already "on-board" the diesel vehicle rather than manufacturing urea off-line which requires secondary storage, shipping, and delivery systems.

In FY 2004, we examined the further development of these catalysts for diesel engine applications. Development included improving means of adding the oxidation additive, investigating the effects of space velocity and air/fuel mixture changes, and determining the effects of potential poisons such as sulfur. Reaction kinetics was examined in order to optimize the stoichiometries of the fuel, air, and water.

Results

The CeO_2/Cu-ZSM-5 system shows significant activity for NO to N_2 conversion when JP-8 fuel is used as reductant (Figure 1). The unusual enhancement in activity observed in C_3H_6-SCR by the addition of water to the feed is also observed with this type of reductant. JP-8 improves the high-temperature activity of the catalyst. Unlike the C_3H_6 system, the middle distillate fuels increase the temperature window of activity while exhibiting no NO_2 breakthrough. The activity improvement over using propylene as a feed is 195% at 400°C and 212% at 450°C (Figure 2). It is proposed that in the CeO_2/Cu-ZSM-5 system, the aromatic components of the fuel are responsible for the greater part of the NO conversion.

Conclusions

The use of onboard fuel as the reductant for NO_x abatement in diesel and lean-burn engines is an attractive alternative to adding a reductant requiring additional onboard storage, as in the case of urea or light hydrocarbon selective catalytic reduction (SCR). The work has shown JP-8 to be effective and preferable for high-temperature (high-load) operation of the catalyst. Work will continue to investigate the use of low-sulfur diesel as a reductant.

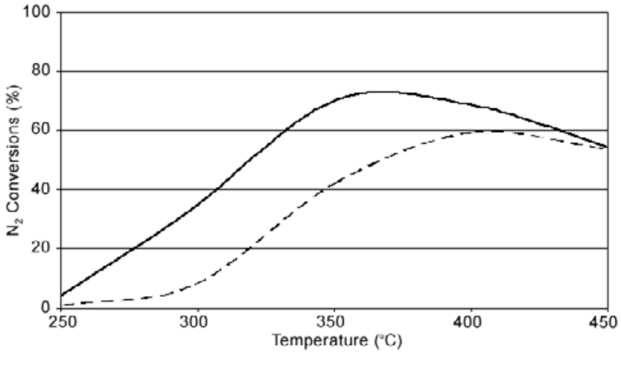

Figure 1. NO to N_2 Conversion for CeO_2/Cu-ZSM-5 with JP-8 as Reductant [Solid line: 10% water in stream. Dashed line: Dry stream. Conditions: 1000 ppm NO, 2% O_2, 2000 ppm JP-8 (based on average molecular weight). GHSV: 32,000 hr^{-1}.]

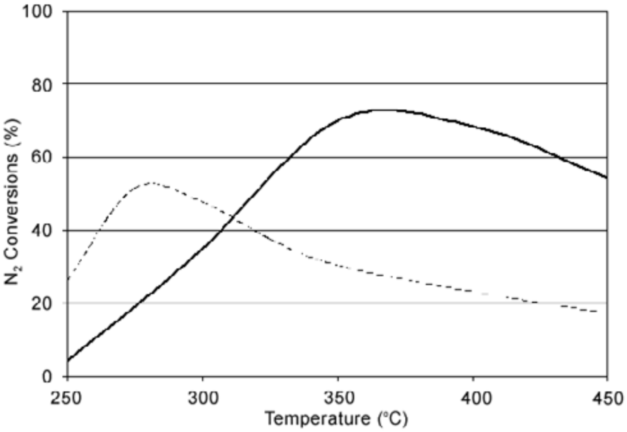

Figure 2. NO to N_2 Conversion for CeO_2/Cu-ZSM-5 with JP-8 or Propylene as the Reductant (Solid line: JP-8 as the reductant. Dashed line: Propylene as the reductant. Conditions: 1000 ppm NO, 2% O_2, 32,000 hr^{-1}.)

Special Recognitions & Awards/Patents Issued

1. "Novel Catalyst for Selective NO_x Reduction Using Hydrocarbons," C. L. Marshall and M. K. Neylon (European patent application WO 03/031781 A1; April 17, 2003).
2. "Novel Catalyst for Selective NO_x Reduction Using Hydrocarbons," C. L. Marshall and M. K. Neylon (U.S. patent application 2003/0073566 A1; April 17, 2003).

FY 2004 Publications/Presentations

1. "Coated Bifunctional Catalysts for NO_x SCR with C_3H_6 - Part I: Water-Enhanced Activity," Michael K. Neylon, Mario J. Castagnola, Norma B. Castagnola and Christopher L. Marshall, Catalysis Today, **96** (2004) 53-60.
2. "Coated Bifunctional Catalysts for NOY SCR with C_3H_6 - Part II: In situ Spectroscopic Characterization," Mario J. Castagnola, Michael K. Neylon, A. Jeremy Kropf and Christopher L. Marshall, Catalysis Today, **96** (2004) 61-70.
3. "Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons," C. L. Marshall, M. K. Neylon, M. J. Castagnola, and A. Jeremy Kropf, Annual Peer Review Meeting, Argonne National Laboratory, Argonne, IL, May 18, 2004.
4. "Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons," C. L. Marshall, M. K. Neylon, M. J. Castagnola, and A. Jeremy Kropf, 10th Diesel Engine Emissions Reduction Conference, San Diego, CA, August 31, 2004.

References

1. Shimizu, K., Shibata, J., Yoshida, H., Satsuma, A., Hattori, T. Appl. Catal. B: Environmental, 30, 151 (2001).
2. Klingstedt, F., Eranen, K., Lindfors, L. E., Andersson, S., Cider, L., Landberg, C., Jobson, E., Eriksson, L., Ilkenhans, T., Webster, D. Topics Catal. 30-31, 27 (2004).
3. Neylon, M. K., Castagnola, M. J., Castagnola, N. B., and Marshall, C. L. Catal. Today, 96, 53 (2004).
4. Castagnola, M. J., Neylon, M. K, and Marshall, C. L. Catal. Today, 96, 61 (2004).