E. Microstructural Changes in NO_x Trap Materials under Lean and Rich Conditions at High Temperatures

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Contract No.: DE-AC05-00OR22725

Objective

- Facilitate the development of nitrogen oxides (NO_x) trap catalysts for lean gasoline or diesel exhaust treatment by
  - Investigating materials issues related to deterioration of NO_x traps performance upon aging as a result of thermal and sulfation-desulfation cycles.
  - Designing new lean NO_x trap (LNT) materials that are robust under the LNT operating conditions.

Approach

- Study microstructural changes in model LNT catalyst systems under normal operating conditions and accelerated aging using simulated diesel exhaust in a reactor system to understand the causes of failure.
- Correlate microstructural changes with performance by evaluating model LNT catalyst systems on a bench-top reactor
- Design new LNT catalysts that are robust under operating and aging conditions. Rapidly screen new catalysts for microstructural changes using an ex-situ reactor system and detailed evaluation on a bench-top reactor.

Accomplishments

- Tested the updated ex-situ reactor with simulated stoichiometric, lean, rich, and lean/rich cycling exhaust capability to treat transmission electron microscopy (TEM) samples by reproducing the results of the old reactor.
- Completed a study of microstructural changes in the model LNT catalyst, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)], and 2%Pt/γ-Al_2O_3 using simulated diesel exhaust (without sulfur oxides) under the following conditions:
  - 60-s/5-s lean/rich cycling at 500°C/4 h for 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)
  - 240-s/60-s lean/rich cycling at 500°C/4 h for the model catalysts and 2%Pt/γ-Al_2O_3
  - Accelerated aging at 700°C for 16 h using 60-s/5-s lean/rich cycling and 240-s/60-s lean/rich cycling for 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)

- Carried out a preliminary study of microstructural changes under accelerated aging conditions (700°C, 16 h) using simulated exhaust (with SO_2) at 240-s/60-s lean/rich cycling for 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3).
- Neared completion of the assembly of the bench-top flow reactor and installation of software. We will initiate experiments to correlate microstructural changes in LNT materials to LNT performance.

Future Direction

- Initiate correlation of microstructural changes with LNT performance by testing model catalysts on a bench-top reactor for performance.
- Guided by the results of correlation of microstructural changes with performance, design new LNT catalyst systems and carry out systematic evaluation.

Introduction

The introduction of diesel-engine–based heavy-duty trucks and passenger vehicles depends on the successful development of a strategy to treat NO_x emissions. There presently is no catalyst or combination of catalysts that can convert NO_x into inert gases under oxidizing conditions over a complete range of exhaust temperatures. Among NO_x treatment strategies, LNTs are the most likely candidates for early deployment because they are consumer-transparent (no action is needed on the part of consumers) and they can be system-integrated into current vehicle control strategies.[1]

NO_x traps collect engine-out NO_x during lean operation and treat it during short rich operation cycles.[2]] The NO_x traps can be considered to be derived from commercial three-way catalysts (TWCs) installed to treat stoichiometric emissions from engines operating at air-fuel ratios of ~14. Therefore, the basic components of NO_x traps are identical to TWCs. The advanced version of a TWC is a two-layer system on a honeycomb substrate with the inner layer based on platinum-alumina and the outer layer on rhodium-ceria-zirconia. The NO_x traps derived from advanced TWCs are identical to these with the exception of a high baria content (the upper limit being close to 20%) in the alumina layer.

Fresh NO_x traps work very well, but they cannot sustain their high efficiency over the lifetimes of vehicles. The gradual and persistent deterioration in the performance of commercial TWCs is quite well known.[3] The performance deterioration in NO_x traps is believed to be caused by aging due to high-temperature operation and sulfation-desulfation cycles necessitated by the sulfur oxides (SO_x) in the emissions from the oxidation of sulfur in fuel. The formation of barium aluminate is also considered to be a cause of performance deterioration since barium aluminate forms on thermal aging and is an inefficient NO_x adsorber. Until last year, the aging-related microstructural changes in precious metals components were not available in open literature. In our previous reports, we summarized our studies of fresh and aged supplier samples that clearly show changes that occur on aging under various operating conditions. The prominent changes are sintering and migration of precious metals and migration of barium, leading to reduced precious metal-adsorber surface area available for NO_x adsorption in lean cycles.

In order to design a thermally durable NO_x trap, there is a need to understand the changes in the microstructures of materials that occur during various modes of operation (lean, rich, and lean/rich cycles). This information can form the basis for selection and design of new NO_x trap materials that can resist deterioration under normal operation. The first goal of the project is to determine if one or all of the microstructural changes take place during lean, rich, or lean/rich cycles.

The tasks to achieve this goal are as follows:

- Complete microstructural characterization of fresh and thermally aged NO_x trap materials to determine the species formed as a result of aging.
- Complete microstructural characterization of fresh NO_x trap materials after exposure to simulated lean, rich, and lean/rich cycling conditions with and without SO_x to determine the species formed during lean cycles.
- Complete microstructural characterization of fresh NO_x trap materials after exposure to

accelerated lean/rich aging conditions to determine the species formed as a result of elevated temperatures.

- Correlate microstructural changes with the performance of LNTs.

The second goal of the project is to investigate and design new catalyst materials that can withstand NO_x trap operating conditions without undergoing detrimental structural changes. The results from the first goal will provide insights into changes that occur in NO_x trap materials at a microstructural level upon extended exposure to NO_x trap operating conditions, enabling selection and design of materials for the second goal.

Approach

Our approach involves a detailed study of microstructural changes in model LNT catalyst systems using an updated ex-situ reactor under normal operating conditions, and accelerated aging using simulated diesel exhaust in a reactor system to understand the causes of failure and the deterioration mechanism.

The next step in this process is establishment of a correlation between microstructural changes and the performance of model LNT catalyst systems using a bench-top reactor.

Finally, we plan to design new LNT catalysts that are robust under operating and aging conditions. In this protocol, we will use microstructural changes as a rapid screening tool for new catalysts and will carry out detailed evaluation using a bench-top reactor.

Results

Our previous studies of the microstructural changes that occurred in a supplier LNT system (based on Pt/BaO–Al_2O_3 and CeO_2–ZrO_2 materials) upon aging on (1) a pulsator at Ford Motor Company (2) a dynamometer at Ford, and (3) vehicles in gasoline direct-injection spark-ignition engines in Europe show the following results.

After pulsator aging, lean and rich aged samples showed that the sintering of platinum particles occurs during aging and barium migrates into the ceria-zirconia layer. Both of these factors reduce the platinum-barium oxide surface area where NO_x adsorption and reduction takes place during lean and rich cycles, respectively. The stoichiometric aging also leads to the migration of barium into the ceria-zirocnia layer, but the sintering of platinum is less severe.

The dyno-aged samples showed extensive sintering of platinum and its migration in the ceria-zirconia layer. The sintering of rhodium was also observed. The migration of barium into the ceria-zirconia and the sintering of the precious metal component could explain the deterioration of performance.

The analysis of samples evaluated on a vehicle after 32,000 km and 80 km showed that the bulk of the sintering of precious metals occurred in the stages of on-vehicle aging.

These results primarily show precious metal sintering and barium migration to be causes of performance deterioration in NO_x trap materials in gasoline engine exhaust conditions.

While the laboratory aging protocols for diesel engines were in development, we compiled data showing early-stage changes in model NO_x trap materials under diesel conditions. We also reported the synthesis and characterization of three catalyst systems, i.e. (Pt/Al_2O_3), (2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)]), and (2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO.6Al_2O_3)]). Now that the laboratory aging protocols are in public domain, we have carried out a preliminary study of microstructural changes in LNT catalyst materials under the accelerated aging conditions. The results are summarized in the following paragraphs.

Microstructural Changes in Model Catalysts

The TEM samples of a model LNT catalyst, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)] and a standard 2%Pt/γ-Al_2O_3 were treated under lean/rich cycling at operating (500ºC) and accelerated aging (700ºC) conditions using a simulated diesel exhaust on the updated ex-situ reactor (Figure 1). The microstructural changes in the samples were analyzed by scanning TEM (STEM). The simulated diesel exhaust contained CO, CO_2, H_2, C_3H_6, NO, H_2O, and O_2 with N_2 as a balance gas. The SO_2 was added to the simulated exhaust stream in some accelerated aging studies. All tests were run at a gas flow of 100 cc/min. A summary of the results is presented in Tables 1 and 2.

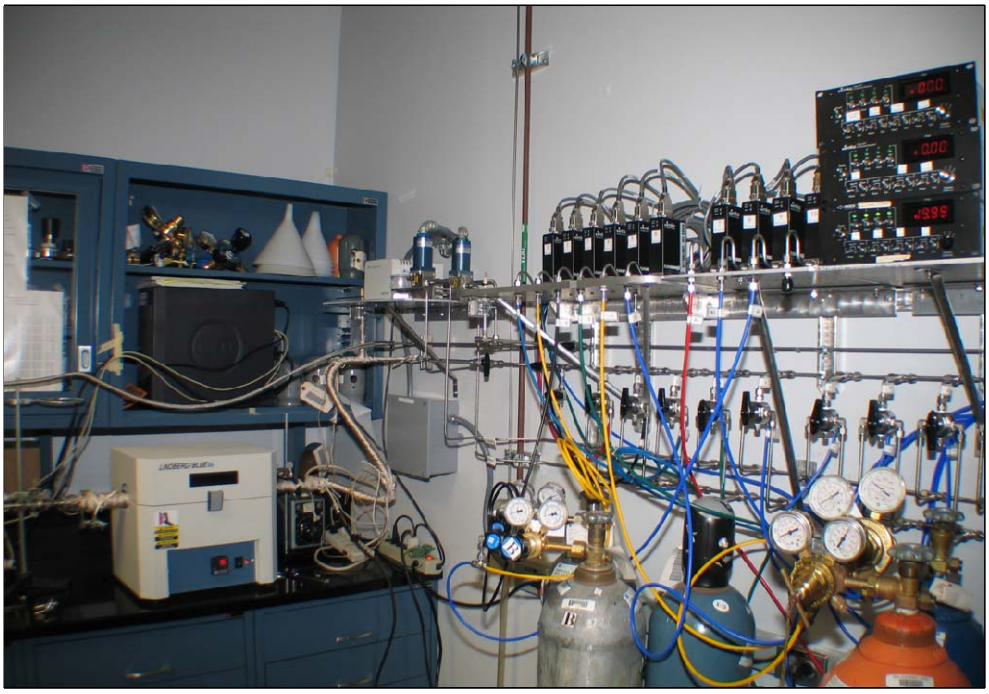

Figure 1. Ex-situ reactor set-up.

Table 1. Platinum particle size change under lean/rich cycle treatment at 500°C/4 h using simulated exhaust without SO_2

Catalyst	Fresh sample	Lean/rich diesel aging	
		60 s/5 s	240 s/60 s
2%Pt/γ-Al_2O_3	0.9–2.3 nm	—	0.7–2.7 nm
2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	0.7–2.2 nm	0.7–2.8 nm	0.7–2.1 nm

Table 2. Platinum particle size change under lean/rich cycle treatments at 700°C using simulated exhaust

Catalyst	Aging time	Lean/rich diesel exhaust		
		60 s/5 s	240 s/60 s	
		w/o SO_2	w/o SO_2	w/ SO_2
2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	Fresh	0.6–2.9 nm	0.9–2.5 nm	1.0–2.1 nm
	4h	0.5–5.0 nm	0.6–4.4 nm	1.0–3.7 nm
	8h	0.6–5.4 nm	0.8–5.3 nm	0.8–4.6 nm
	12h	0.6–5.9 nm	0.7–4.7 nm	—
	16h	—	0.7–4.7 nm	—

Operating conditions—lean/rich cycling at 500°C on ex-situ reactor: After 4 h of treatment in a simulated exhaust flow without SO_2, no platinum sintering was observed regardless of lean/rich pulse time (Figure 2).

- 60-s/5-s lean/rich cycling: 2%Pt-98% [10%CeO2-ZrO2-90%(2%La2O3-98%BaO•6Al2O3)]: STEM of the fresh sample showed platinum particles in the 0.7–2.2 nm range. The electron microscopy images show no significant growth in particle size, 0.7–2.7 nm, after aging.
- 240-s/60-s lean/rich cycling: 2%Pt-98% [10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)]: STEM images of the fresh sample showed platinum particles in the 0.7–2.2 nm range. The particles showed no increase in particle size range after aging. STEM images of the fresh 2%Pt/γ-Al_2O_3 showed platinum particles in the 0.9–2.3 nm range, and no growth in particle size was seen after 4 h.

Accelerated aging—lean/rich cycling at 700°C: The accelerated aging of a model catalyst, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)], was carried out using simulated exhaust without SO_2 under 60-s lean/5-s rich pulses or 240-s/60-s rich pulses, and no significant difference was noted. Interestingly, platinum sintering was evident after only 4 h of sample treatment under accelerated aging conditions. A gradual growth in platinum particles in the 2.0–5.0 nm range was seen after each additional 4 h of treatment. Addition of SO_2 to the simulated exhaust did not lead to any additional noticeable platinum sintering. Figures 3 and 4 depict the results of the accelerated aging study at 240 s/60 s lean/rich cycling with and without SO_2, respectively.

60-s/5-s lean/rich accelerated aging treatment using simulated exhaust without SO_2:

- STEM images of the fresh sample showed platinum particles in the 0.6–2.9 nm range.
- After 4 h of aging, sintering of the particles could be seen in the STEM images by the appearance of particles in the 2.0–5.0 nm range.
- After each of the remaining four increments, STEM images showed further platinum sintering with a gradual increase in the number of 2.0–5.0 nm particles.

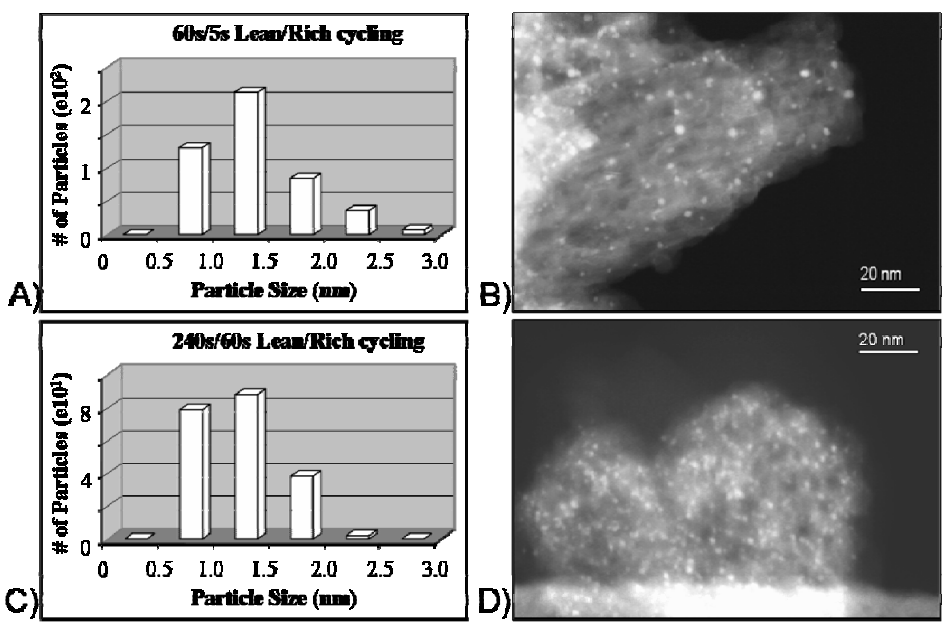

Figure 2. (a) Particle size distribution of multiple areas of a model LNT catalyst, 2%Pt-98% [10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)], after lean/rich cycling and 60-s/5-s pulse using simulated exhaust without SO_2. (b) A STEM image of one area recorded in (a). (c) Particle size distribution of multiple areas of a model LNT catalyst after lean/rich aging at a cycling time of 240 s/60 s. and (d) A STEM image of one area recorded in (c).

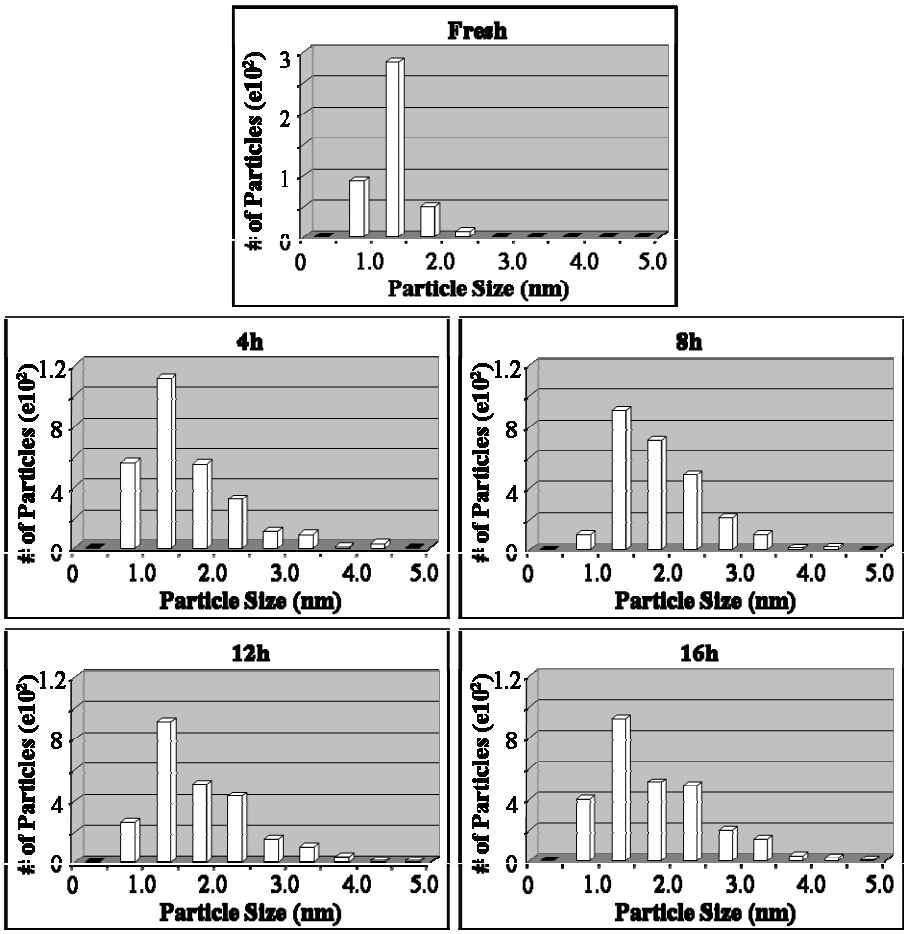

Figure 3. These graphs show platinum particle size distribution of the model LNT catalyst, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)], fresh and after accelerated aging at 700°C in 4-h increments for 16 h and 240-s/60-s lean/rich pulse using simulated diesel exhaust without SO_2. The same four areas of the sample were used for each distribution.

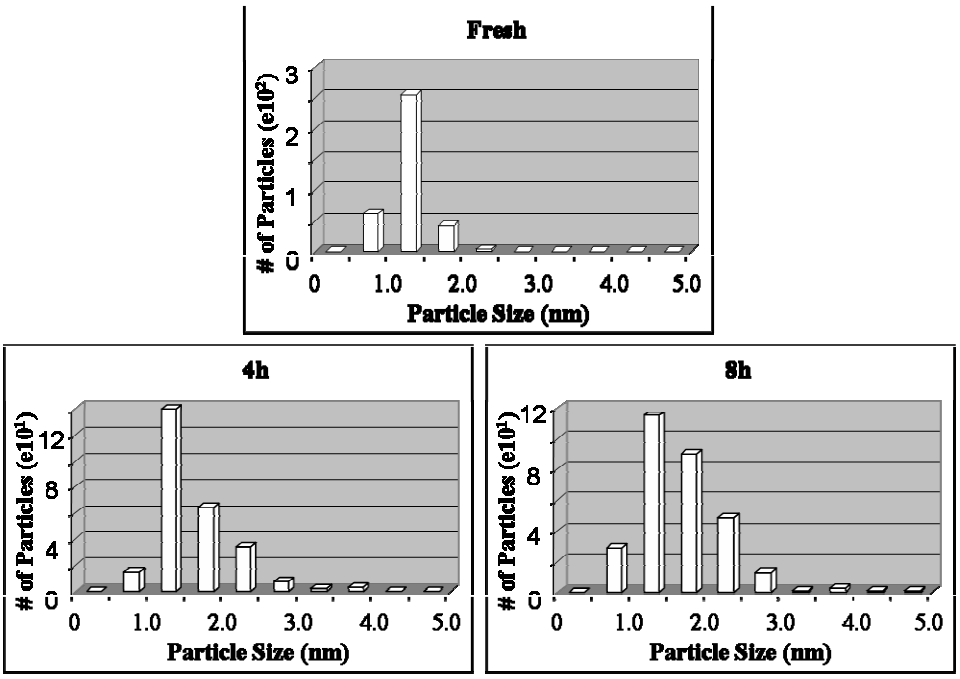

Figure 4. These graphs show platinum particle size distribution of the model LNT catalyst, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3)], fresh and after accelerated aging at 700°C in 4-h increments for 8 h and 240-s/60-s lean/rich pulse using simulated diesel exhaust with SO_2. The same three areas of the sample were used for each distribution.

240-s/60-s lean/rich accelerated aging treatment using simulated exhaust without SO_2: STEM images of the fresh sample showed platinum particles in the 0.6–2.5 nm range.

- After 4 h of aging, sintering of the particles could be seen in the STEM images by the appearance of particles in the 2.0–5.0 nm range.
- After each of the remaining 4-h increments, STEM images showed further platinum sintering with a gradual increase in the number of 2.0–5.0 nm particles.

240-s/60-s lean/rich accelerated aging treatment using simulated exhaust with SO_2:

- STEM images of the fresh sample showed platinum particles in the 1.0–2.1 nm range.
- After 4 h of aging, sintering of the particles could be seen in the STEM images by the appearance of particles in the 2.0–4.0 nm range.
- After another 4 h of aging, STEM images showed further platinum sintering with a gradual increase in the number of 2.0–5.0 nm particles.

Modifications to Ex-situ Reactor

Final modifications to the ex-situ reactor were completed this year to include the ability to cycle through lean and rich conditions. This involved the use of a bench-top flow furnace and the installation of additional gas-flow controllers and solenoid valves that could be controlled through a computer using LabView software. A picture of the modified ex-situ reactor setup is shown in Figure 1.

Assembly of Bench-Top Flow Reactor

The assembly of the bench-top flow reactor and installation of software is nearing completion. We will initiate experiments to correlate microstructural changes in LNT materials to LNT performance.

Conclusions

Our results for microstructural changes clearly show that LNT materials are relatively stable under normal operating conditions of diesel engines. Practically no sintering of precious metals is observed that could cause performance deterioration. However, our accelerated aging studies demonstrate that

rapid sintering of precious metals can take place, leading to performance deterioration. Interestingly, SO_x appears to place an indirect role in the performance deterioration of LNTs. Since there is no significant difference in precious metal sintering during accelerated aging using simulated exhaust with or without sulfur, it would appear that SO_x plays no role in precious metal sintering, but high-temperature treatment is required only for desulfation. Thus if there were no SO_x in diesel exhaust, there would be no need for high-temperature desulfation and the LNT would be quite durable.

Our next goals are to finish accelerated aging tests in the presence of SO_2 and to start evaluating new model catalyst systems for their performance and correlate them to microstructural changes.

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Presentations and Publications

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C. K. Narula, L. F. Allard, M. Moses, Y. Xu, W. Shelton, W. F. Schneider, G. Graham, and J. Hoard, "Lean NO_x Traps—Microstructural Studies of Real World and Model Catalysts," DEER 2005, Chicago, August 21–25, 2005.

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