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

C. K. Narula, K. Lester, H. Meyer, L. Allard
Oak Ridge National Laboratory
P.O. Box 2008, MS 6116
Oak Ridge, TN 37831-6116
(865) 574-8445; fax: (865) 576-6298; e-mail: narulack@ornl.gov

DOE Technology Development Area Specialist: Dr. Sidney Diamond
(202) 586-8032; fax: (202) 586-1600; e-mail: sid.diamond@ee.doe.gov
ORNL Technical Advisor: D. Ray Johnson
(865) 576-6832; fax: (865) 574-6098; e-mail: johnsondr@ornl.gov

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Objective

- Facilitate deployment of a nitrogen oxides (NO_x) trap for lean diesel or gasoline exhaust by
  - — investigating materials issues related to deterioration of the performance of NO_x traps upon aging as a result of thermal and sulfation-desulfation cycles
  - — investigating materials that are robust under the lean NO_x trap operating conditions

Approach

- Synthesize new model catalyst systems containing platinum (Pt): Pt/BaO.6Al_2O_3, [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)].
- Treat them under thermal, lean-diesel, and rich-diesel conditions at 500ºC for 4 h and monitor changes in microstructure. The next step involves evaluation under lean-rich cycles and aging under laboratory aging cycles.
- Evaluate the performance of the selected systems on a bench-top flow reactor.

Accomplishments

- Completed the microstructural evaluation of model catalysts Pt/BaO.6Al_2O_3, [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)]. The latter is a better representative of this class of NO_x trap systems.
  - — Completed and reproduced the study of microstructural changes on aging under diesel lean and rich conditions at 500ºC.
  - — Completed microstructural changes under thermal aging studies of these samples for comparison.
  - — Completed microstructural changes in thermally aged samples after extended exposure to lean and rich conditions.
- Began updating the ex-situ reactor to enhance its capabilities to enable treatment of transmission electron microscopy (TEM) samples under lean, rich, or, stoichiometric conditions, as well as lean-rich cycles. This reactor will be capable of rapid screening of the model catalyst powders for their durability in exhaust under the operating conditions for diesel and gasoline engines.
- Equipped the synthesis laboratory to enable preparation of NO_x trap materials. The bench-top-flow reactor is being set up.

Future Direction

- Evaluate model catalyst systems on a bench-top flow reactor for their efficiency and durability as NO_x traps under simulated diesel and gasoline conditions [with or without sulfur oxides (SO_x) in the simulated exhaust]. These results will provide a benchmark for evaluation of new materials.
- Carry out microstructural characterization of model NO_x trap powders after aging under lean, rich, or stoichiometric conditions on the bench-top flow reactor and TEM samples on an ex-situ microreactor.
- Investigate new materials that can withstand NO_x trap operating conditions without detrimental structural changes.

Introduction

NO_x traps are at the forefront of various strategies under investigation to treat NO_x from diesel and lean-gasoline engines.[1] NO_x traps collect engine-out NO_x during lean operation and treat it during short rich-operation cycles.[2] Fresh NO_x traps work very well but cannot sustain their high efficiency over the lifetime of a vehicle. The efficiency loss is believed to be caused by aging due to high-temperature operation and sulfation-desulfation cycles necessitated by the SO_x in the emissions from the oxidation of sulfur in fuel. 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.

NO_x traps are derived from commercial three-way catalysts installed to treat emissions from engines operating at stoichiometric air-fuel ratios. Therefore, the basic components of NO_x traps are identical to three-way catalysts. The advanced version of a three-way catalyst is a two-layer system on a honeycomb substrate with the inner layer based on Pt-alumina and the outer layer on rhodium-ceria-zirconia. The NO_x traps derived from advanced three-way catalysts are identical to the catalysts except for a high baria content (the upper limit being close to 20%) in the alumina layer. Thus aging can lead to intermixing of layers, crystallization of baria-containing phases that are not good NO_x absorbers, and sintering of precious metals. The first goal of this project is to determine if one or all of the microstructural changes take place and if these changes occur 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 lean conditions to determine the species formed during lean cycles.
- Complete microstructural characterization of fresh NO_x trap materials after exposure to rich conditions to determine the species formed during rich cycles.

The second goal of the project is to investigate and design new 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 synthesizing new model catalyst systems; treating them under thermal, lean, and rich conditions; and monitoring microstructural changes to understand the deterioration mechanism. In order to rapidly screen model catalyst systems, we have designed an ex-situ reactor system that is being further upgraded to enhance its capabilities. The updated system will operate in the 25–1000°C range and will have the ability to introduce periodic rich pulses while the catalyst is being treated under lean or stoichiometric conditions.

The information from this study will be used to design thermally durable catalyst systems and will be tested on a bench-top flow reactor system.

Results

Over the last 2 years, we determined the microstructural changes that occurred in a supplier lean NO_x trap system (based on Pt/BaO-Al_2O_3 and CeO_2-ZrO_2 materials) upon being aged on (1) a pulsator at Ford Motor Company, (2) a dynamometer at Ford, and (3) vehicles with gasoline direct-injection, spark-ignition (DISI) engines in Europe.

- After pulsator aging, lean and rich aged samples showed that the sintering of Pt particles occurs during aging, and barium migrates into the ceria-zirconia layer. Both of these factors reduce the Pt-barium oxide surface area where NO_x adsorption and reduction take place during lean and rich cycles, respectively. The stoichiometric aging also leads to the migration of barium into the ceria-zirconia layer, but the sintering of Pt is less severe.
- The dyno-aged samples showed extensive sintering of Pt and its migration into the ceria-zirconia layer. The sintering of rhodium was also observed. The migration of barium into ceria-zirconia and the sintering of the precious metal component could explain the deterioration of performance
- The analysis of the samples evaluated on-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 the cause of performance deterioration in NO_x trap materials in gasoline engine exhaust conditions. While the laboratory aging protocols for diesel engines are in development, we have compiled data showing early-stage changes in model NO_x trap materials under diesel conditions. We assumed that lower-temperature simulated diesel exhaust would slow down the aging compared with gasoline engine exhaust. Thus we completed a series of thermal aging, diesel lean aging, and diesel rich aging cycles of a model NO_x trap and a model NO_x trap modified with manganese oxide, as well as Pt/Al2O3, for comparison purposes. The results are summarized in the following paragraphs.

Synthesis of New Model Catalysts

Pt/Al_2O_3: The Pt/alumina was prepared by the impregnation method using H_2PtCl_6 salt. X-ray powder diffraction (XRD) shows broad diffraction peaks for alumina and no peaks due to Pt, as expected because of the small particle size of Pt in the freshly prepared sample (Figure 1).

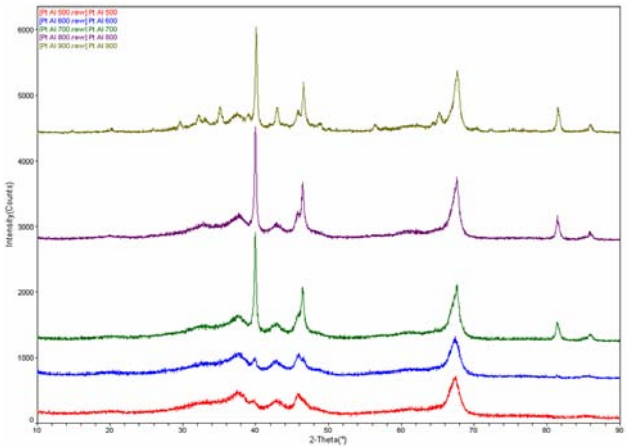

Figure 1. X-ray diffraction patterns of Pt/Al_2O_3.

2%Pt, 5%MnO2, 93%[10%CeO2-ZrO2, 90%(2%La2O3, 98% BaO.6Al2O3)]: The model catalyst was synthesized by impregnating 2%Pt, 97%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98% BaO.6Al_2O_3)] with manganese nitrate and subsequent decomposition.

Microstructural Changes in Model Catalysts

The microstructural changes in model catalysts (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)]) after thermal treatment at 500, 600, 700, 800, and 900ºC; lean treatment at 500ºC for 4 h; and rich treatment at 500ºC were followed with XRD and transmission electron microscopy (TEM). Here lean and rich treatment refers to exposure of sample in an ex-situ reactor (Figure 7a, described previously) to diesel lean and diesel rich conditions. A summary of changes in the precious metal (Pt) is presented in Table 1.

Table 1. Summary of Pt particles size changes under various treatment conditions in model catalysts I, II, and III

Sample	Treatment conditions				
	Fresh	Thermal treatment (XRD of powders)	Thermal treatment at 500°C on ex-situ reactor	Treatment under lean conditions on ex-situ reactor	Treatment under rich conditions on ex-situ reactor
Pt/Al_2O_3	1–1.2 nm	600ºC, 3.4 nm 700ºC, 17.1nm 800ºC, 26.1nm 900ºC, 39.5nm	2–4 nm	8–10nm	2–4 nm
Model NO_x trap catalyst I: 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)]	1–2nm	600ºC, 2.6 nm 700ºC, 21.3nm 800ºC, 37.2nm 900ºC, 48.4nm	1–2 nm	1–2nm	1.5–3.5 nm
Model NO_x trap catalyst II: 2%Pt, 5%MnO_2–93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO.6Al_2O_3)]	1–2 nm	700ºC, 20.7nm 800ºC, 27.0nm 900ºC, 34.0nm	1–2 nm	2–3nm	1–2nm

Thermal Treatment

- Thermal treatment of samples was carried out at 500, 600, 700, 800, and 900ºC in a bench-top furnace in air.
- Pt/Al_2O_3: In XRD patterns (Figure 1) of Pt/Al_2O_3, diffraction peaks due to Pt particle size start to grow in 500–900ºC range. The calculated Pt particle sizes (using the Scherrer formula, assumes spherical particles) are 3.4, 17.1, 26.1, and 39.5 nm at 600, 700, 800, and 900ºC, respectively. At 500ºC, the alumina is a mixture of γ-alumina and hydrated γ–alumina. At 800ºC, a broad peak assignable to the alpha phase can be seen. At 900ºC, the diffraction peaks due to α– and γ – alumina are observed. TEM of the fresh sample shows that the Pt particle size is in the 1–1.2 nm range (Figure 2). This particle size grows to 2–4 nm on thermal treatment in a furnace at 500°C for 4 h.
- 2%Pt, 98%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98%BaO.6Al_2O_3)]: In XRD patterns (Figure 3), diffraction peaks due to Pt particle size start to grow in the 500–900ºC range. The calculated Pt particle sizes (using the Scherrer formula, assumes spherical particles) are 2.6, 21.3, 37.2, and 48.4 nm at 600, 700, 800, and 900ºC, respectively. TEM of the fresh sample shows that the Pt particle size is ~1 nm (Figure 4). This

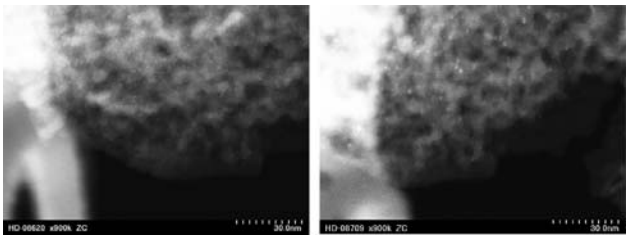

Figure 2. TEM of fresh and thermally aged (500ºC, 4 h) Pt/Al_2O_3.

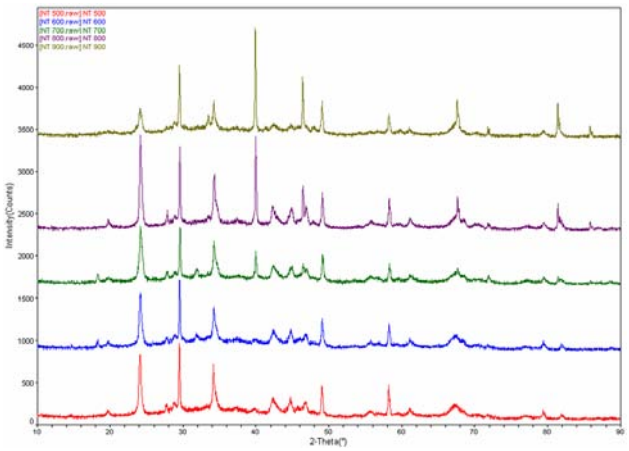

Figure 3. XRD patterns of 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)].

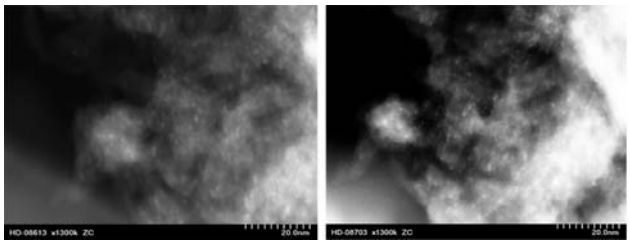

Figure 4. TEM of fresh and thermally aged (500ºC, 4 h) 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%$BaO.6Al_2O_3$)].

particle size grows to 1–2 nm upon thermal treatment in a furnace at 500ºC for 4 h.

- 2%Pt, 5%MnO_2, 93%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98% $BaO.6Al_2O_3$)]: In XRD patterns (Figure 5), diffraction peaks due to Pt particle size start to grow in the 500–900ºC range. The calculated Pt particle sizes (using the Scherrer formula, assumes spherical particles) are 20.7, 27, and 34 nm at 700, 800, and 900ºC respectively. TEM of the fresh sample shows that the Pt particle size is ~1 nm (Figure 6). This particle size grows to 1–2 nm upon thermal treatment in a furnace at 500ºC for 4 h.

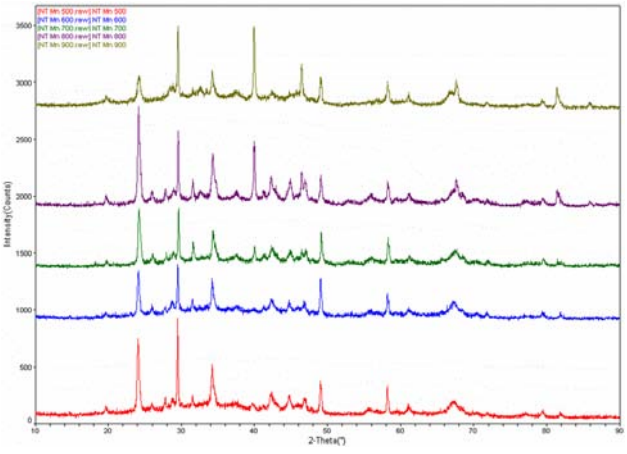

Figure 5. XRD patterns of 2%Pt, 5%MnO_2–93% [10%CeO_2-ZrO_2-90%(2%La_2O_3-98% $BaO.6Al_2O_3$)].

Lean and Rich Treatment in Ex-situ Reactor

The aging of model catalysts was carried out in our ex-situ reactor system (schematics in Figure 7) under lean or rich diesel exhaust conditions at 500°C for 4 h [CO, CO_2, H_2, HC, NO_x, H_2O, flow rate 100cc/min] showed some sintering of Pt particles,

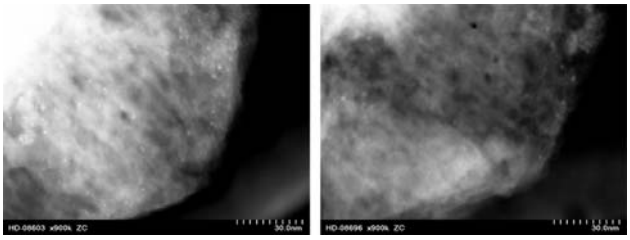

Figure 6. TEM of fresh and thermally aged (500ºC, 4 h) 2%Pt, 5%MnO_2–93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% $BaO.6Al_2O_3$)].

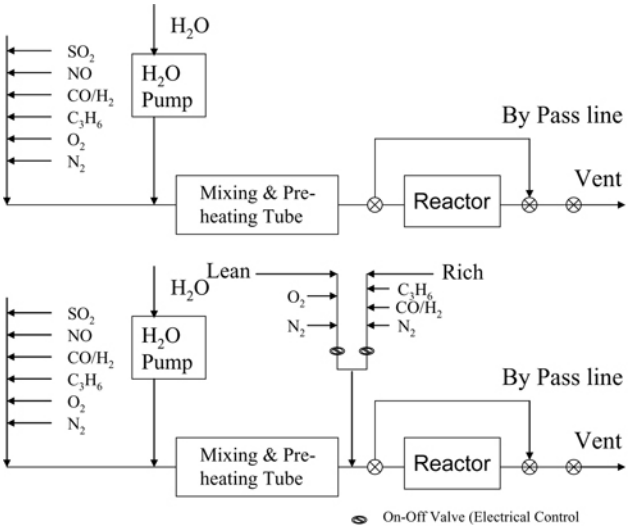

Figure 7. a. Schematics of current ex-situ reactor; b. Schematics of modified ex-situ reactor.

and the size grew to ~2.5nm. However, the sintering was significantly less than that observed upon thermal aging (~30–40nm) at 500°C in air.

It is important to note that the experiments in the ex-situ reactor system do not precisely duplicate the aging of NO_x traps during normal operation. The alternating lean/rich conditions are not present in our experiments; instead, our samples are exposed to lean conditions, and a lack of control of space velocity due to the very small amount of catalyst leads to NO_x absorber saturation conditions. The saturation condition persists throughout our treatment.

Lean Treatment

- Pt/Al_2O_3: TEM of the fresh sample shows that the Pt particle size is in the 1–1.2 nm range (Figure 8). This particle size grows to 8–10 nm in diesel lean simulated exhaust in the ex-situ reactor at 500ºC for 4 h.

- 2%Pt, 98%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98%BaO.6Al_2O_3)]: TEM of the fresh sample shows that the Pt particle size is ~1 nm (Figure 9). This particle size grows to 1–2 nm upon lean treatment in the ex-sit reactor at 500ºC for 4 h.
- 2%Pt, 5%MnO_2, 93%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98% BaO.6Al_2O_3)]: TEM of the fresh sample shows that the Pt particle size is ~1 nm (Figure 10). This particle size grows to 2–3 nm in diesel lean simulated exhaust in the ex-situ reactor at 500ºC for 4 h.

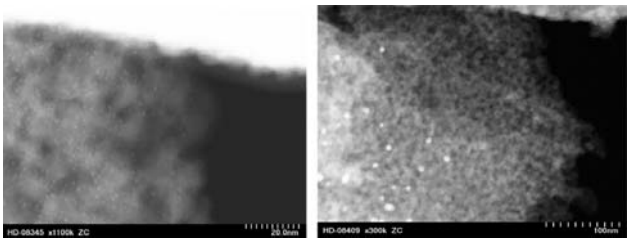

Figure 8. TEM of fresh and lean aged (500ºC, 4 h) Pt/Al_2O_3.

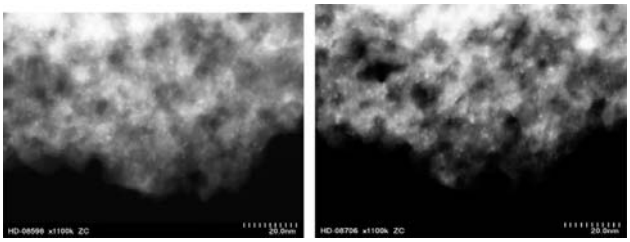

Figure 9. TEM of fresh and lean aged (500ºC, 4 h) 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)].

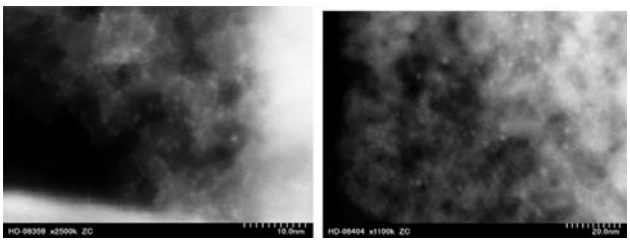

Figure 10. TEM of fresh and lean aged (500ºC, 4 h) 2%Pt, 5%MnO_2–93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO.6Al_2O_3)].

Rich Treatment

- Pt/Al_2O_3: TEM of the fresh sample shows that the Pt particle size is in the 1–1.2 nm range (Figure 11). This particle size grows to 2–4 nm in diesel rich simulated exhaust in the ex-situ reactor at 500ºC for 4 h.
- 2%Pt, 98%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98%BaO.6Al_2O_3)]: TEM of the fresh sample shows that the Pt particle size is ~1–1.2 nm (Figure 12). This particle size grows to 1.5–3.5 nm in diesel rich simulated exhaust in the ex-situ reactor at 500ºC for 4 h.
- 2%Pt, 5%MnO_2, 93%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98% BaO.6Al_2O_3)]: TEM of the fresh sample shows that the Pt particle size is ~1 nm (Figure 13). This particle size grows to 1–2 nm in diesel rich simulated exhaust in the ex-situ reactor at 500ºC for 4 h.

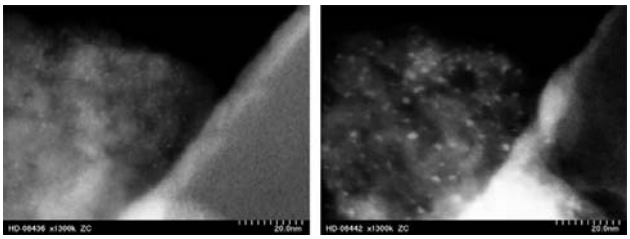

Figure 11. TEM off fresh and rich aged (500ºC, 4 h) Pt/Al_2O_3.

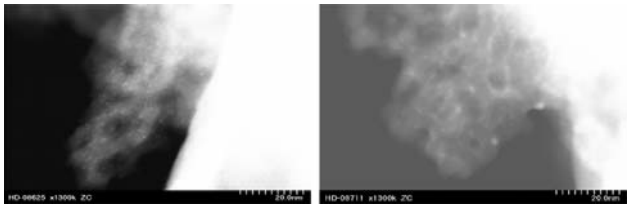

Figure 12. TEM of fresh and rich aged (500ºC, 4 h) 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)].

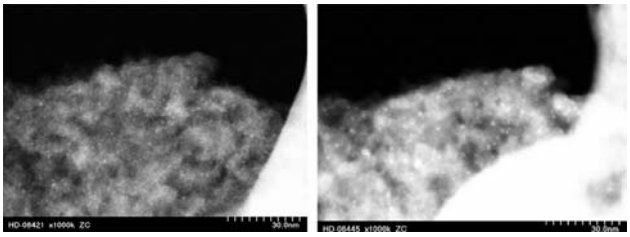

Figure 13. TEM of fresh and lean aged (500ºC, 4 h) 2%Pt, 5%MnO_2–93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO.6Al_2O_3)].

Modifications in Ex-situ Reactor

The ex-situ reaction is under modification to include the ability to cycle through lean and rich conditions. This involves the addition of a gas-flow controller and installation of solenoid valves that can be controlled through a computer using the Labview

software system. The installation of plumbing is complete, and the new ex-situ reactor should be in operation shortly. The schematics of the modified reactor are shown in Figure 7b.

Surface Studies of Fresh and Aged Model NO_x Trap Catalyst

The results of X-ray photoelectron spectroscopy analysis (XPS) of 2%Pt, 98%[10%CeO_2-ZrO_2, 90%(2%La_2O_3, 98%BaO.6Al_2O_3)] are presented in Table 2. Powder samples of the fresh, thermally aged (500ºC in air for 4h), and lean simulated exhaust-exposed (after thermal aging) catalysts were pressed onto an indium foil and then analyzed. The high concentration of Pt and lathanum in fresh samples is due to the migration of these elements to the surface. Thermally aged samples probably achieve a redistribution of elements, leading to a reduced concentration of these elements on the surface. When a thermally aged sample is exposed to simulated lean NO_x conditions for about 4 h at 500ºC, the surface composition does not change significantly. The lack of a significant increase in nitrogen or carbon after extended exposure to lean diesel exhaust is puzzling. Further experiments are in progress to determine if it is just a surface phenomenon, or if the bulk material loses nitrate during our cooling protocol.

Conclusions

Our results from the study of microstructural changes in a supplier lean NO_x trap system (based on Pt/BaO-Al_2O_3 and CeO_2-ZrO_2 materials) upon aging on (1) a pulsator at Ford, (2) a dynamometer at Ford, and (3) vehicles in gasoline DISI engines in Europe show that precious metal sintering and barium migration occurs. This could be a cause of performance deterioration in NO_x trap materials.

We have successfully employed an ex-situ reactor to study aging in model NO_x trap catalysts. This system has allowed us to study changes in samples in a selected area under thermal, lean diesel, or rich diesel conditions. We have updated the ex-situ reactor to a lean–rich cycle NO_x trap system. This protocol will allow us to rapidly screen catalyst systems without having to do start-and-stop experiments to understand aging.

Our next goal is to complete the bench-flow reactor and start evaluating new model catalyst systems for their performance and relate them to microstructural changes.

References

1. N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sigiura., and K. Kasahra, "Development of New Concept Three-Way Catalyst for Automotive Lena-Burn Engines," SAE paper 95-0809, Society of Automotive Engineers..

2. N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, S. Tateishi, and K. Kasahara, "The New Concept 3-Way Catalyst for Automotive Lean-Burn Engine: NO_x Storage and Reduction Catalyst," *Catalysis Today* **27**, 63–69 (1996).

Table 2. XPS analysis of 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)]

Element	Fresh		Thermally aged at 500ºC in air for 4 hours		Aging under simulated lean diesel exhaust at 500ºC for 4 hours	
	Atomic %	Wt %	Atomic %	Wt %	Atomic %	Wt %
O	57.8	33.5	59.3	34.9	61.7	37.7
Al	26.6	26.0	27.6	27.4	26	26.8
C	6.3	2.7	3.7	1.6	4.1	1.9
Ba	3.9	19.4	5.9	29.8	5.1	26.7
La	2.2	11.0	0.5	2.5	0.6	3.2
N	0.3	0.2	0.2	0.1	0	0
Pt	1	7.1	0.5	3.6	0.5	3.7

Presentations

C. K. Narula, "Recent Advances in Lean NO_x Treatment in Automotive Exhaust," invited seminar at Purdue University, West Lafayette, Indiana, April 22, 2004.

C. K. Narula, "Applied Catalysis Program," a presentation of results to the Science and Technology Technical Review Panel, National Transportation Research Center, Oak Ridge, TN, 2004.