Heavy-Vehicle Propulsion Materials

Microstructural Changes in NO_x Trap Materials

Project ID (PM_9138)

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Microstructural Changes in NOx Trap Materials

21CTP Technical Goal: **Develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system efficiency from ~42% today to 50% by 2010.**

Project Objectives

Our objectives is to understand the changes in the microstructure of NO_x trap materials that occur during various modes of operation (lean, rich, and lean-rich cycles). This information forms the basis for selection and design of new NO_x trap materials that can resist the deterioration under normal operation.

FY 2005 Focus

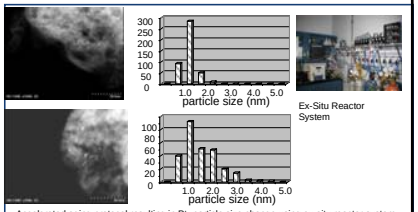
Our focus has been to understand microstructural changes in NO_x trap materials under accelerated aging conditions.

Planned Duration

October 2003 to September 2007

DOE Funding/Industry Cost Share

FY04: $100K; FY05: $95K



Accelerated aging protocol resulting in Pt- particle size change using ex-situ reactor system

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Collaborators
J. Hoard, G. Graham, Ford Motor Co.
L.F. Allard, ORNL

Accomplishments

- We updated the ex-situ reactor to include lean-rich cycling capability and used it to examine selected areas repeatedly for microstructural changes under accelerated aging protocol at 240s/60s and 60s/5s lean-rich cycles at 700ºC using simulated diesel exhaust without SO_2 (6/30). We expect to complete accelerated aging protocol using simulated exhaust with SO_2 by 9/30. The results suggest significant sintering at early stages of aging.
- We have completed a study of microstructural changes in model lean NO_x trap catalysts in air, lean, and rich using sulfur free simulated diesel exhaust using the ex-situ reactor at 500ºC. The results suggest minimal aging at this temperature.

Significant Future Milestones

- Correlate microstructural changes with NO_x trap efficiency and establish microstructural changes as indicators for high-throughput screening of new catalyst materials. (9/30/06)

Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_9138	Materials Technology	HV Propulsion Materials	Applied Research	8-15-05

Objectives

- Determine changes in the microstructure of NO_x trap materials that occur during various modes of operation (lean, rich, and lean-rich cycles).
- Correlate the performance of lean NO_x trap model catalysts with the microstructural changes.
- Guided by the "Catalysts by First Principles" results and correlation of performance with microstructure, design, synthesize and evaluate new NO_x trap materials that can resist deterioration under normal operation.

Relevance to 21CTP Goals

- Develop and demonstrate an emissions compliant engine system for class 7-8 highway trucks that improve the engine system efficiency from ~42% today to 50% by 2010
- In order to improve the durability of LNT's, we have developed the understanding of microstructural changes during operating conditions leading to persistent performance loss.
- We are initiating microstructure-performance correlation experiments on model catalyst system.
- This information is essential for the design of durable catalysts for LNTs

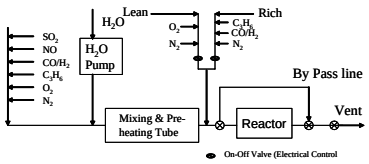
Technology Transfer

- Collaborators
  - J. Hoard, G. Graham, Ford Motor Co.
  - M. Moses, Post-doctoral fellow
- Fundamental Studies
  - Presentations and Publications in open literature

Approach

- Analyze production catalysts aged on a pulsator, dyno, and on-vehicle to determine microstructural changes
- Design Ex-situ reactor to expose TEM samples to lean, rich, and lean-rich cycles under simulated exhaust
- Synthesize model catalysts and conduct studies of microstructural changes using ex-situ reactor
- Correlate microstructural changes with LNT performance
  - This approach will also allow for high-throughput screening of new catalysts
- Design and evaluate durable LNT catalysts

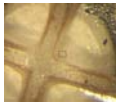
Ex-Situ Reactor



*The **ex-situ reactor** is designed to expose TEM samples to lean, rich, or lean-rich cycles of simulated diesel or gasoline exhaust.*

Technical Accomplishments/ Progress/Results

Production LNTs



Two-Layer System:
- Pt-BaO-Al_2O_3 inner layer (dark orange)
- Rh-CeO_2-ZrO_2 outer layer (light orange)

Dyno Aging
- The dyno aged samples showed extensive sintering of platinum and its migration in ceria-zirconia layer.
- The sintering of rhodium as well as the migration of barium into ceria-zirconia was also observed
- These observation explain the deterioration in LNT performance over time

Passenger Vehicle (DISI Fleet) Aging
- The analysis of on vehicle evaluated samples after 32K km and 80K km showed that the bulk of precious metal sintering occurred in the early stages of on vehicle aging

Model Catalysts

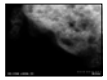
Model Catalyst	Fresh Sample[1]	Thermal Aging In Air (XRD of powder)	Lean Diesel Aging 500 °C/ 4h	Rich Diesel Aging 500 °C/ 4h	Lean/ Rich Cycle Diesel Aging 500 °C/ 4h[1]	
					60s/5s	240s/60 s
2% Pt / γ -Al_2O_3	0.8 – 2.0 nm (1.4 nm)	600ºC, 3.4nm 700ºC, 17.1nm 800ºC, 26.1nm 900ºC, 39.5nm	1.0 – 2.0[1]nm (1.5 nm)	2.0 - 4.0 nm	N/A	0.6 – 3.0 nm (1.5 nm)
2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	0.6 – 2.9 nm (1.4 nm)	600ºC, 2.6 nm 700ºC, 21.3nm 800ºC, 37.2nm 900ºC, 48.4nm	1.0 -2.0 nm	1.5 - 3.5 nm	0.5 – 4.3 nm (1.7 nm)	0.8 – 3.5 nm (1.7 nm)
2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	0.7 – 2.6 nm (1.6 nm)	700ºC, 20.7nm 800ºC, 27.0nm 900ºC, 34.0nm	2 – 3 nm	1 – 2nm	0.7 – 3.2 nm (1.7 nm)	-------

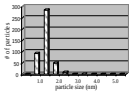
Pt particle size change under lean, rich, and lean-rich cycles (60s/5s and 240s/60s) using simulated exhaust to treat TEM samples in ex-situ reactors

Pt-particle size distribution of Model Catalyst 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)] after exposure to Lean-Rich cycle (240 sec, 60 sec) at 700ºC

(ADF STEM images of same sample area for all treatments)

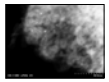
Fresh Sample

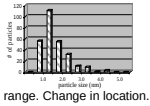




Pt Particles in 0.5-2.5 nm range

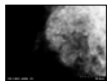
After 4 hours

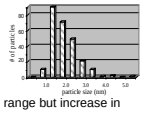




Pt Particles in 0.5-4.5 nm range. Change in location.

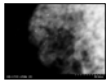
After 8 hours

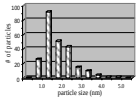




Pt Particles in 0.5-4.5 nm range but increase in average size. No change in location.

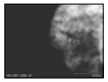
After 12 hours

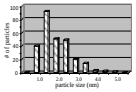




Pt Particles in 0.5-5.0 nm range. No change in location.

After 16 hours





. No change compared with "after 12 h".

- Presented results at CLEERS and DEER workshops
- Invited review article on NO_x treatment for *Int. J. Amer. Ceram. Tech. [Enviromental Issue]* (in press)

Future Work

- Correlate microstructural changes with the performance of LNT
- Establish microstructural changes as indicators for high-throughput screening of new LNT catalyst materials
- Guided by the "Catalysts by First Principles" results and correlation of performance with microstructure, design, synthesize and evaluate new NO_x trap materials that can resist the deterioration under normal operation