Mechanisms of Sulfur Poisoning of NOx Adsorber (LNT) Materials

Do Heui Kim, George Muntean, Chuck Peden
Institute for Interfacial Catalysis
Pacific Northwest National Laboratory

Neal Currier, Randy Stafford, John Stang (retired), Alex Yezerets
Cummins Inc.

Hai-Ying Chen, Howard Hess
Johnson Matthey

Program Managers: Ken Howden and Gurpreet Singh

The work was funded by the U.S. Department of Energy (DOE) Office of FreedomCar and Vehicle Technologies.

May 19, 2009

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Project ID: ace_24_peden

Project Overview

Timeline

- Start – February 2003
- Finish – September 2008
- 100% Complete

Budget

- Total project funding
  - DOE: ~$1,900K
  - Matched 50/50 by Cummins as per CRADA agreement
- DOE funding received in FY09:
  - $0K

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- Cummins, Inc.
  - w/Johnson Matthey

Barriers

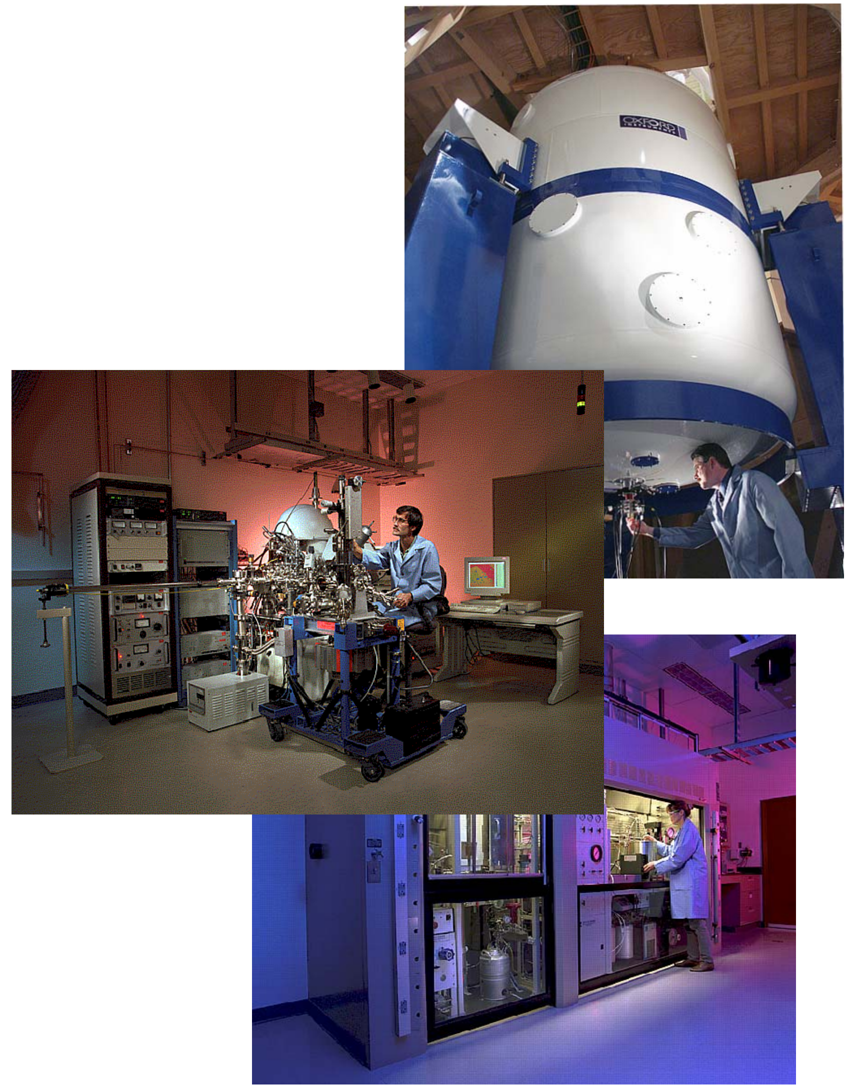
- Mechanisms for deactivation now better established. Still, the ability to accurately and routinely characterize catalyst condition in materials returned from the field remains a significant challenge.
- Optimizing sulfur removal strategies during regeneration processes that minimize damage to the catalyst material is an ongoing critical activity. This is an area where there is a particular need for more fundamental understanding.
  - How much sulfur has to be removed to prevent long term degradation that reduces performance below requirements prior to regulated lifetime of the system.
- Improve system performance to reduce system cost.

Goals and Objectives

- Develop an understanding of the mechanisms of Lean-NOx Trap (LNT, aka NOx adsorber) deactivation due to high temperatures and the presence of sulfur species in the exhaust.
- Apply the developing understanding to determine appropriate operating conditions and suggest areas for improvements in catalyst formulation; verify improved performance through materials characterization, lab and engine testing.
- Develop protocols and tools for catalyst state diagnosis of engine- and field-aged catalysts.

Approach

- **Prepare and Process Model NOx Adsorber Materials**
  - All catalysts have been provided by Johnson Matthey. We used '**Simple Model**' Pt-Ba-Al_2O_3, '**Enhanced Model**' materials, and the **current commercialized formulation**.
    - Fresh, as-received (AR)
    - Variably sulfated (including engine-aged)
- **Utilize expertise and state-of-the-art catalyst characterization and testing facilities at PNNL's IIC to address mechanisms and structure/function**
    - XRD, XPS, NMR, TEM/EDX and SEM/EDX
    - NO_2 TPD, H_2 TPRX
    - Lab reaction system
    - Synchrotron based techniques (XANES, EXAFS, and *in situ* time-resolved XRD)



Technical Accomplishments/ Progress/Results

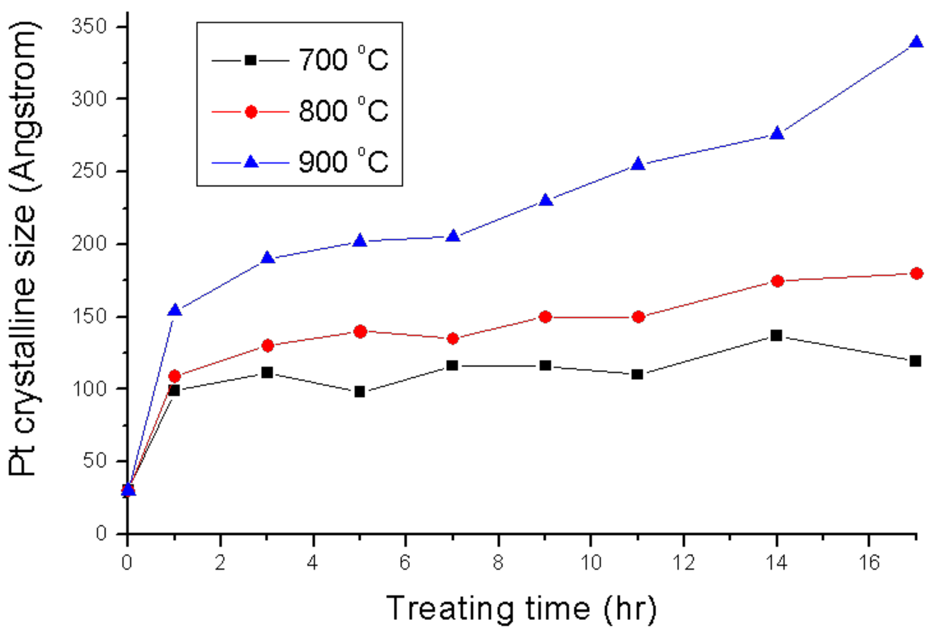
Some program highlights:

- **Precious metal sintering identified as a significant deactivation mechanism.**
  - Clear correlation between precious metal sintering and loss in activity with high temperature treatments in oxidizing environments
  - Presence of ceria in the catalysts shown to significantly inhibit precious metal sintering.
- **Performance testing procedure developed that allowed deactivation processes due to the effects of sulfur and high temperatures to be clearly distinguished.**
  - Experiments using this reaction 'protocol' provided optimum conditions for removing sulfur while also preventing precious metal sintering.
  - Catalysts containing ceria shown to be less sensitive to sulfur poisoning and could be desulfated at lower temperatures.
- **Deactivation due to formation of barium aluminate shown to be reversible and generally occurring at higher temperatures.**
  - The presence of water 'leached' Ba from the deactivating barium aluminate phase. The Ba could then be re-dispersed onto the alumina support material.

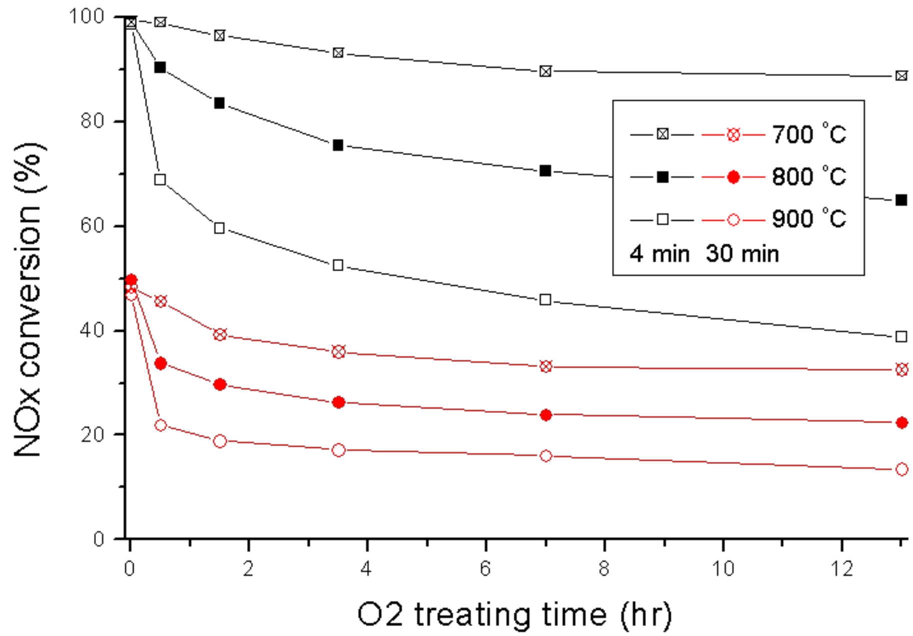
Technical Accomplishments/ Progress/Results

NOx storage performance was directly correlated with changing Pt particle size upon thermal treatments; greater NOx storage performance is observed for samples with small sized Pt particles, and deteriorates rapidly as the Pt particles sinter.

Pt Crystallite Size by XRD



NOx Conversion Deactivation



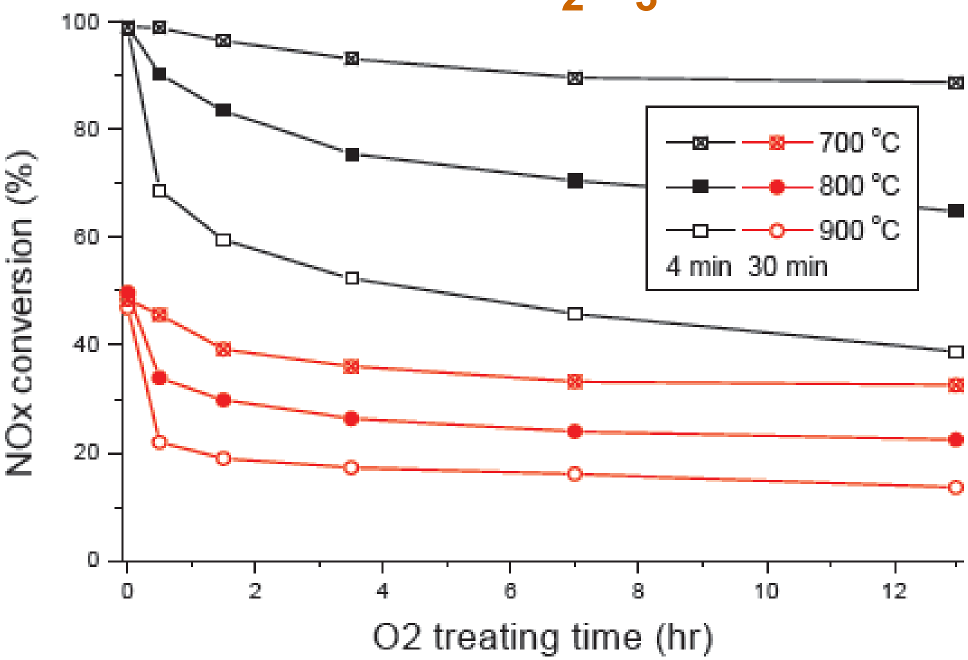
D.H. Kim, Y.-H. Chin, G.G. Muntean, A. Yezerets, N.W. Currier, W.S. Epling, H.-Y. Chen, H. Hess, and C.H.F. Peden, Ind. Eng. Chem. Res. **45** (2006) 4415.

Pacific Northwest NATIONAL LABORATORY | Institute for INTERFACIAL CATALYSIS

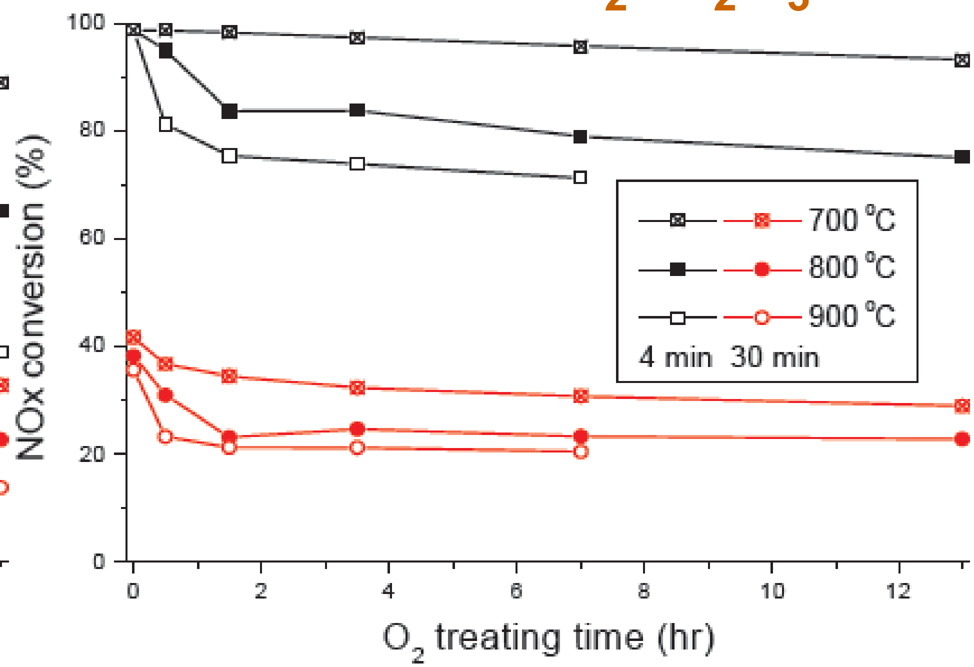
Technical Accomplishments/ Progress/Results

Ceria-containing catalysts display significantly reduced levels of deactivation during oxidative 'aging'. A primary reason for this is likely markedly reduced Pt sintering. Even for 900 °C-aged ceria-containing catalyst, Pt particles are very difficult to find in TEM.

'Simple Model' Pt-BaO/Al_2O_3 LNT



'Enhanced Model' Pt-BaO/CeO_2-Al_2O_3 LNT



D.H. Kim, G.G. Muntean, C.H.F. Peden, A. Yezerets, N.W. Currier, J. Stang, H.-Y. Chen, and H. Hess, DEER Meeting Presentation, August, 2008.

Technical Accomplishments/ Progress/Results

Some program highlights:

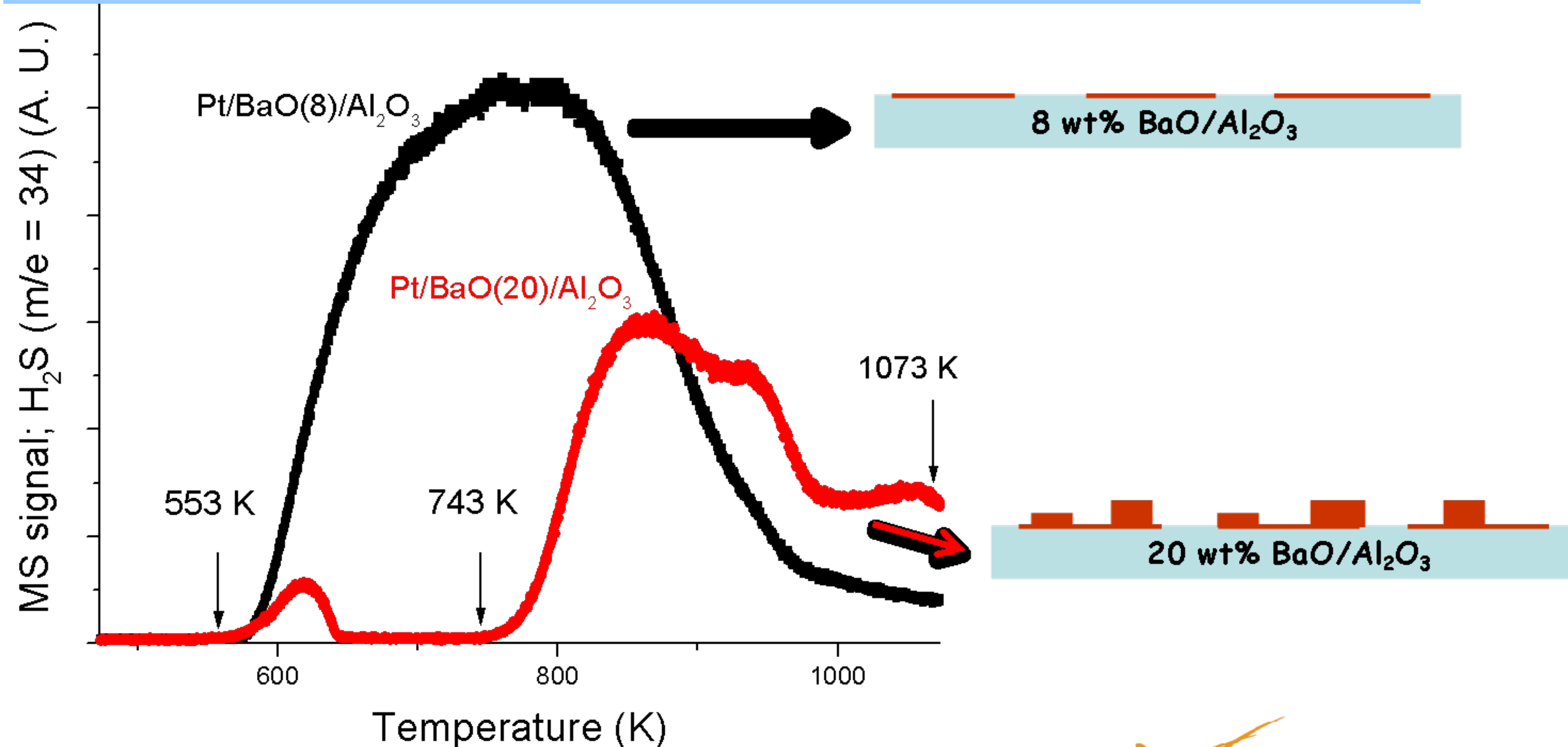
- **Precious metal sintering identified as a significant deactivation mechanism.**
  - Clear correlation between precious metal sintering and loss in activity with high temperature treatments in oxidizing environments
  - Presence of ceria in the catalysts shown to significantly inhibit precious metal sintering.
- **Performance testing procedure developed that allowed deactivation processes due to the effects of sulfur and high temperatures to be clearly distinguished.**
  - Experiments using this reaction 'protocol' provided optimum conditions for removing sulfur while also preventing precious metal sintering.
  - Catalysts containing ceria shown to be less sensitive to sulfur poisoning and could be desulfated at lower temperatures.
- **Deactivation due to formation of barium aluminate shown to be reversible and generally occurring at higher temperatures.**
  - The presence of water 'leached' Ba from the deactivating barium aluminate phase. The Ba could then be re-dispersed onto the alumina support material.

Some program highlights:

- **Desulfation behavior is strongly dependant on both the barium loading and the degree of sulfation. For example, catalysts with lower Ba-loading:**
  - Desulfate at lower temperature;
  - Desulfate much more completely at a given temperature; and
  - Are much less prone to formation of a refractory BaS phase.
- **We found both positive and negative roles for water in desulfation processes:**
  - Positive: BaS readily converts to BaO and H_2S by reaction with H_2O.
  - Negative: H_2O promotes irreversible Pt sintering behavior.
  - Sequential desulfation steps: reduction to BaS at high temperature, followed by water treatment at lower temperature where Pt sintering is not significant.
- **In recent work, several the-state-of-the-art characterization tools have been applied to investigate material changes in field-aged monolith-type commercial catalysts.**
  - Seeking readily applied characterization of deactivation.
  - Most of these results contain proprietary information about catalyst composition and structure.

Technical Accomplishments/ Progress/Results

Sulfated Pt-BaO(8)/Al_2O_3, consisting of predominantly of “surface” (monolayer) BaO/$BaCO_3$ species, displays more facile desulfation by H_2 at lower temperature than sulfated Pt-BaO(20)/Al_2O_3, a material containing primarily “bulk” (particulate) BaO/$BaCO_3$ species.



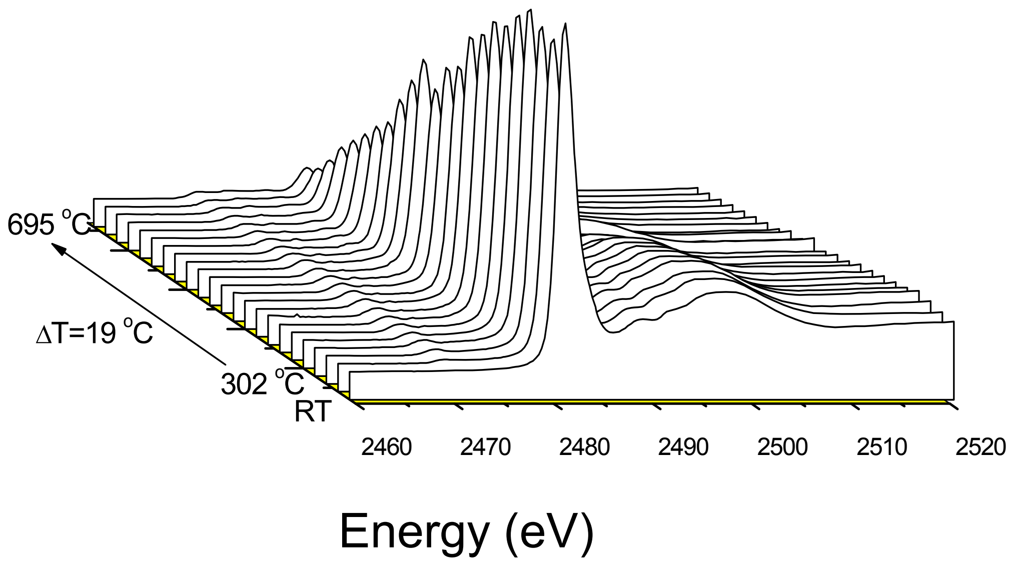
D.H. Kim , J. Szanyi, J.H. Kwak, T. Sailer, J.C. Hanson, C.M. Wang, C.H.F. Peden, J. Phys. Chem. B **110** (2006) 10441.

Technical Accomplishments/ Progress/Results

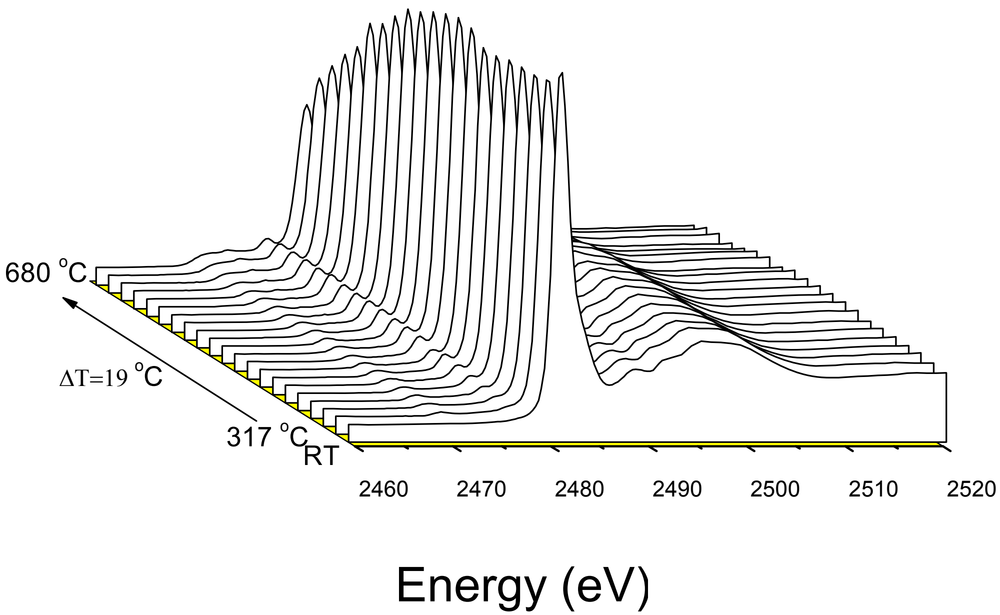
FreedomCAR & Fuel Partnership

TR-XRD results confirm that catalysts with lower Ba loading desulfate at lower temperatures, desulfate more completely, and result in a much lower amount of a refractory BaS phase.

Pt-BaO(8)/Al_2O_3, 5 g/L, with H_2 only



Pt-BaO(20)/Al_2O_3, 5 g/L, with H_2 only



D.H. Kim , J. Szanyi, J.H. Kwak, T. Sailer, J.C. Hanson, C.M. Wang, C.H.F. Peden, J. Phys. Chem. B **110** (2006) 10441.

Pacific Northwest NATIONAL LABORATORY

Institute for INTERFACIAL CATALYSIS

FreedomCAR & Fuel Partnership

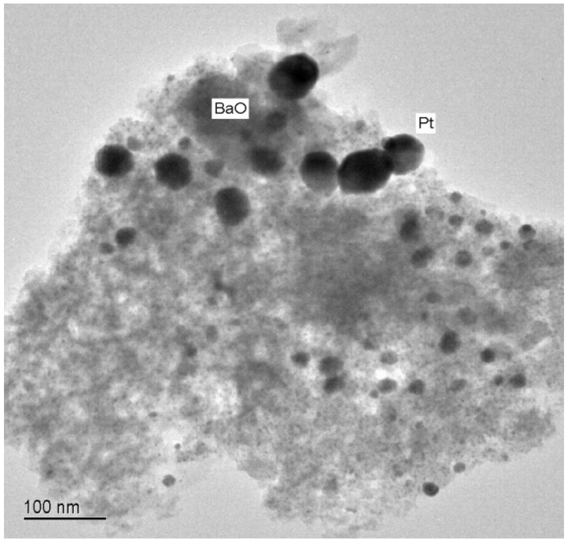
Some program highlights:

- **Desulfation behavior is strongly dependant on both the barium loading and the degree of sulfation. For example, catalysts with lower Ba-loading:**
  - Desulfate at lower temperature;
  - Desulfate much more completely at a given temperature; and
  - Are much less prone to formation of a refractory BaS phase.
- **We found both positive and negative roles for water in desulfation processes:**
  - Positive: BaS readily converts to BaO and H_2S by reaction with H_2O.
  - Negative: H_2O promotes irreversible Pt sintering behavior.
  - Sequential desulfation steps: reduction to BaS at high temperature, followed by water treatment at lower temperature where Pt sintering is not significant.
- **In recent work, several the-state-of-the-art characterization tools have been applied to investigate material changes in field-aged monolith-type commercial catalysts.**
  - Seeking readily applied characterization of deactivation.
  - Most of these results contain proprietary information about catalyst composition and structure.

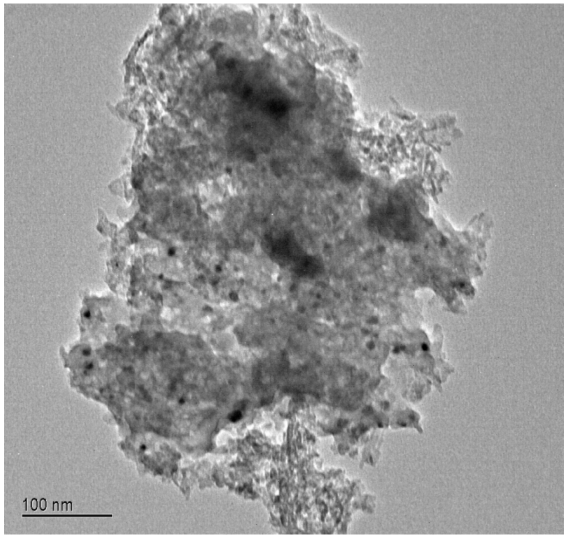
Technical Accomplishments/ Progress/Results

Positive and Negative roles of water during desulfation steps

- Positive effect: BaS + H_2O → BaO + H_2S ↑ (extra removal of sulfur)
- Negative effect: facilitate the Pt sintering esp. at higher temperature



Cooperatively desulfated with H_2/H_2O up to 800 °C



Sequentially desulfated with H_2 up to 800 °C, followed by H_2O at 300 °C

The TEM data showed that Pt sintering was significantly inhibited due to the absence of H_2O during the desulfation at high temperatures, and also demonstrates the similar NO_x uptake with the desulfated sample cooperatively with H_2 and H_2O.

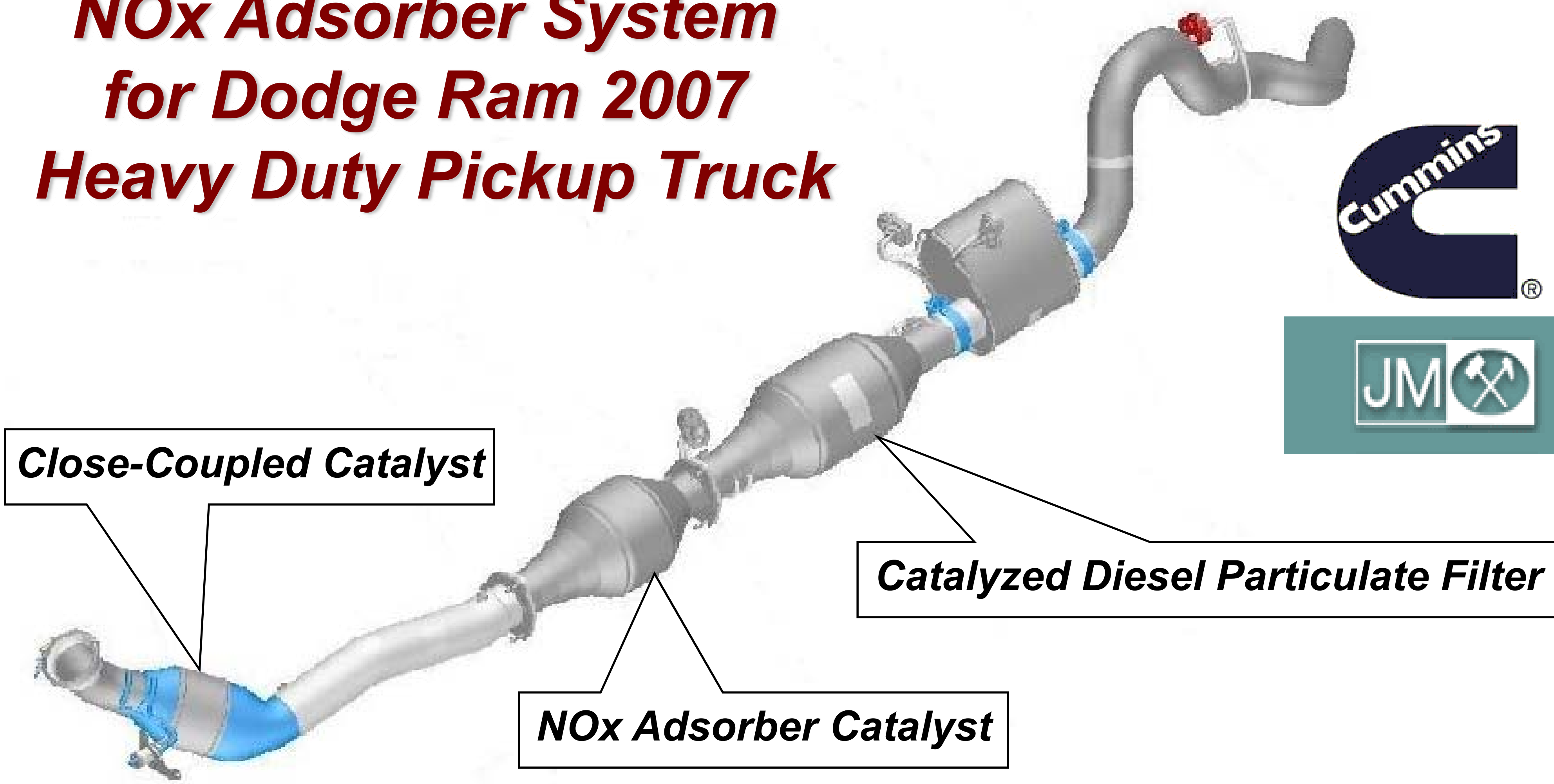
D.H. Kim, J.H. Kwak, X. Wang, J. Szanyi and C.H.F. Peden, Catal. Today **136** (2008) 183.

Some program highlights:

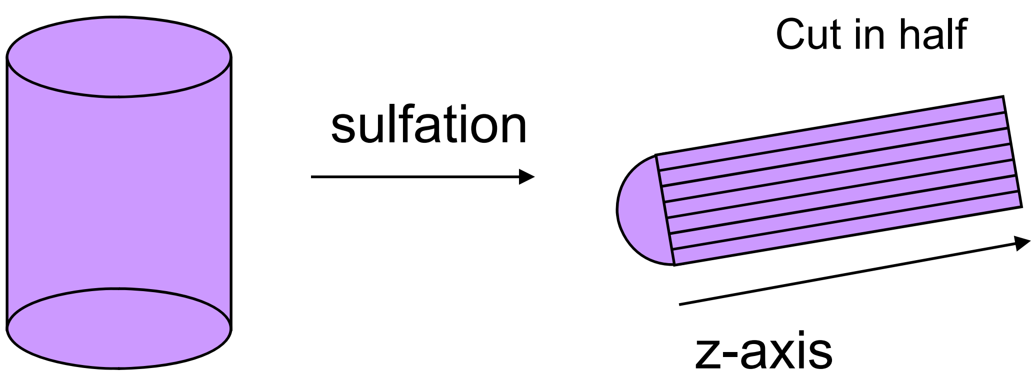
- **Desulfation behavior is strongly dependant on both the barium loading and the degree of sulfation. For example, catalysts with lower Ba-loading:**
  - Desulfate at lower temperature;
  - Desulfate much more completely at a given temperature; and
  - Are much less prone to formation of a refractory BaS phase.
- **We found both positive and negative roles for water in desulfation processes:**
  - Positive: BaS readily converts to BaO and H_2S by reaction with H_2O.
  - Negative: H_2O promotes irreversible Pt sintering behavior.
  - Sequential desulfation steps: reduction to BaS at high temperature, followed by water treatment at lower temperature where Pt sintering is not significant.
- **In recent work, several the-state-of-the-art characterization tools have been applied to investigate material changes in field-aged monolith-type commercial catalysts.**
  - Seeking readily applied characterization of deactivation.
  - Most of these results contain proprietary information about catalyst composition and structure.

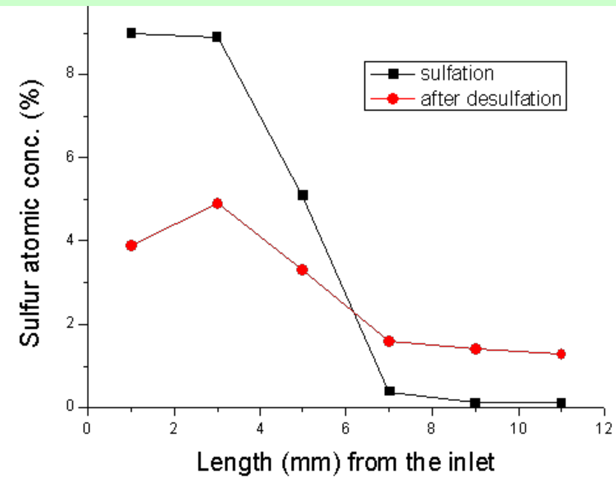
LEV II-ULEV Certified System with Cummins 6.7L Engine and A/T System

NOx Adsorber System for Dodge Ram 2007 Heavy Duty Pickup Truck

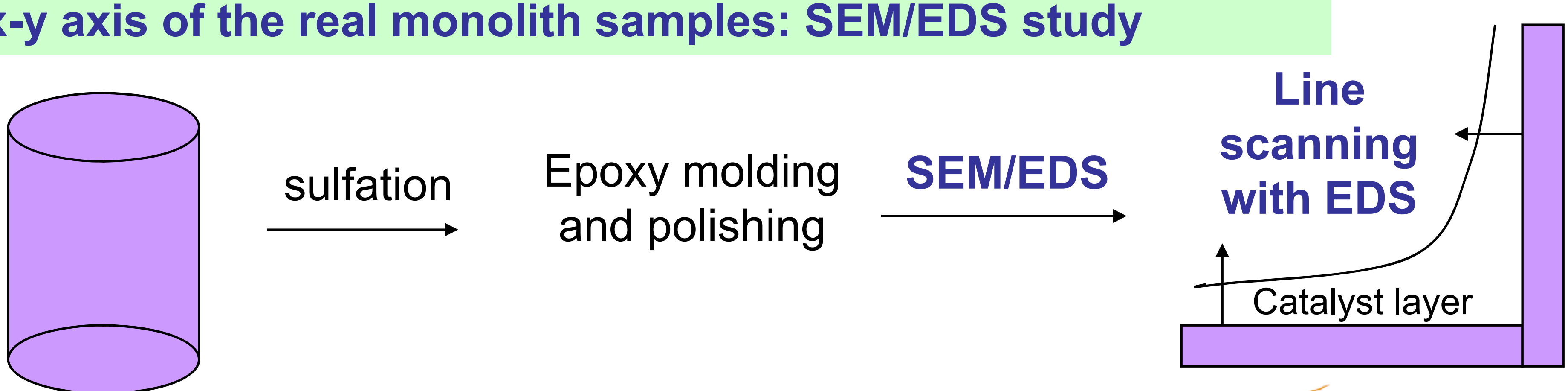


Spatial analysis of species distributions during sulfation/desulfation along the z-axis of the real monolith samples: XPS study





Cross-sectional analysis of sulfur species during sulfation along the x-y axis of the real monolith samples: SEM/EDS study



Activities for This Next Year

- This CRADA has been completed and a new CRADA with the same partners has just been signed.

Alex Yezerets, Cummins, Keynote Address at the 20th Meeting of the North American Catalysis Society:

- "*Diesel after-treatment technology is still in its infancy* – no evidence that diesel catalysis research is yet approaching mass-transport limitations"
- "Unlike '3-way' catalysis for gasoline engines, diesel catalysis is *unlikely* to converge to a single solution!"

- A significant issue for all current viable technologies is expanding lean NOx performance to higher temperatures. The new CRADA between PNNL, Cummins and Johnson Matthey will address this problem with a specific focus on the lean NOx trap (LNT) technology.

Focus of New CRADA

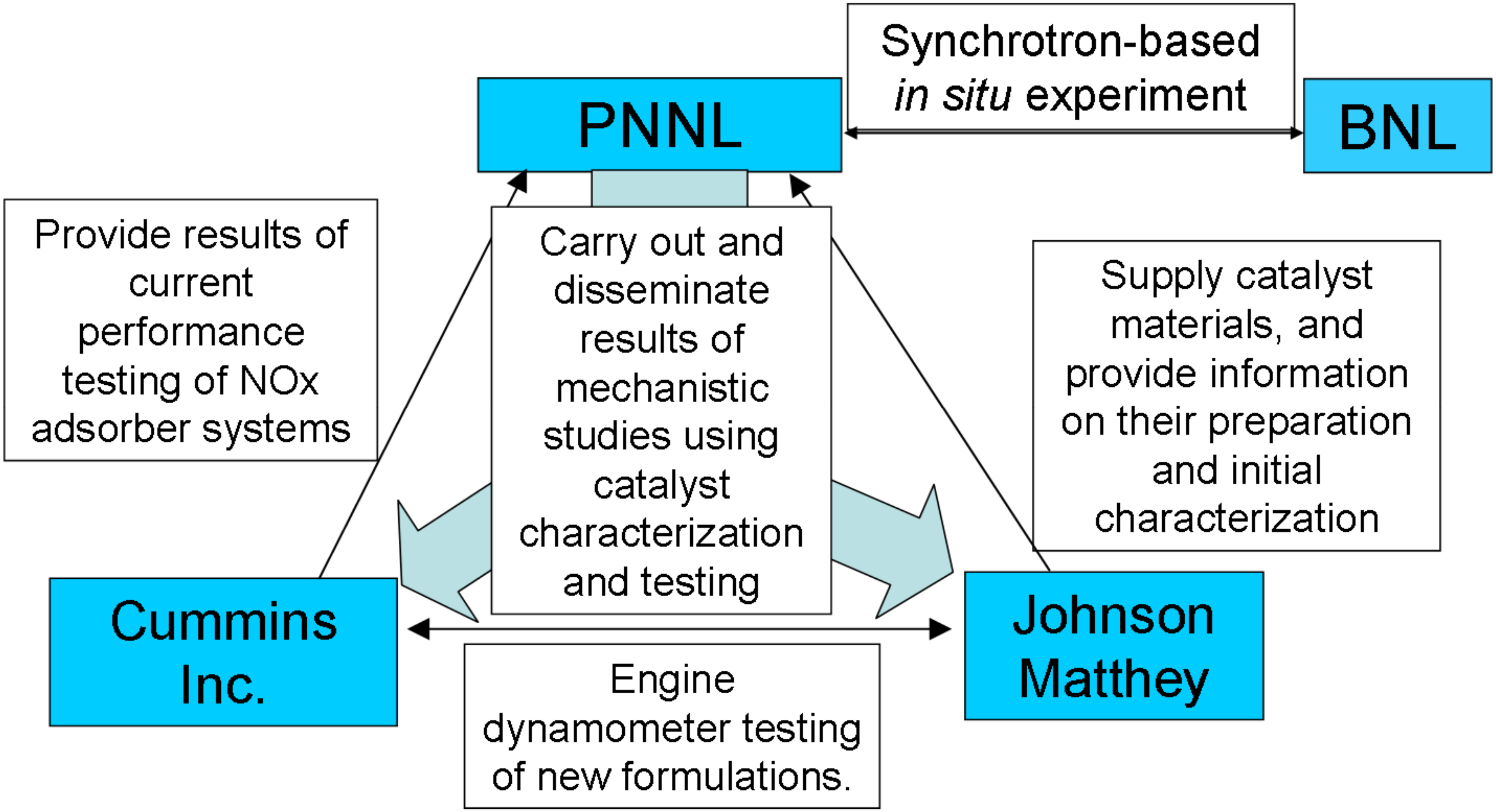
Higher Temperature Lean NOx Performance:

- Better NOx storage at higher temperatures
  - Modify the LNT and/or support material to expand NOx trapping at higher temperatures?
  - Improved NOx storage means enhanced SOx stability – enhance thermal stability to higher temperature deSOx?
  - Develop selectivity to NOx over SOx?
- Do something else at higher temperature for lean NOx removal rather than trapping?

Summary

- The LNT technology has now been commercialized enabling more wide-spread adoption of fuel-efficient diesels that meet upcoming NOx emissions regulations.
- PNNL’s role has been to provide fundamental insights into specific issues concerning LNT deactivation identified from Cummins’ and J/M’s experiences during system development.
- Technical highlights from this project included:
  - PNNL thanked by Cummins for their role in moving forward the commercialization of the LNT technology for the Dodge Ram pick-up truck.
  - Studies of engine dynamometer and field aged samples helped understand an observed but unexpected deactivation mode.
  - Fundamental studies of sulfur-removal mechanisms yielding insights important for optimizing desulfation strategies.
- This has been a highly interactive program which will now transition to a new CRADA focused on high temperature performance of the LNT technology.

Collaborations/Interactions



- ***Conference Calls were held typically once every month or two to discuss the results.***
- ***Annual face-to-face CRADA Reviews (1st and 4th held in 2004 and 2007 at PNNL, 2nd and 5th in 2005 and 2008 at Johnson-Matthey and 3rd in 2006 at Cummins).***