FreedomCAR & Fuel Partnership

Mechanisms of Sulfur Poisoning of NOx Adsorber (LNT) Materials

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Feb. 25, 2008

This presentation does not contain any proprietary or confidential information

Project Overview

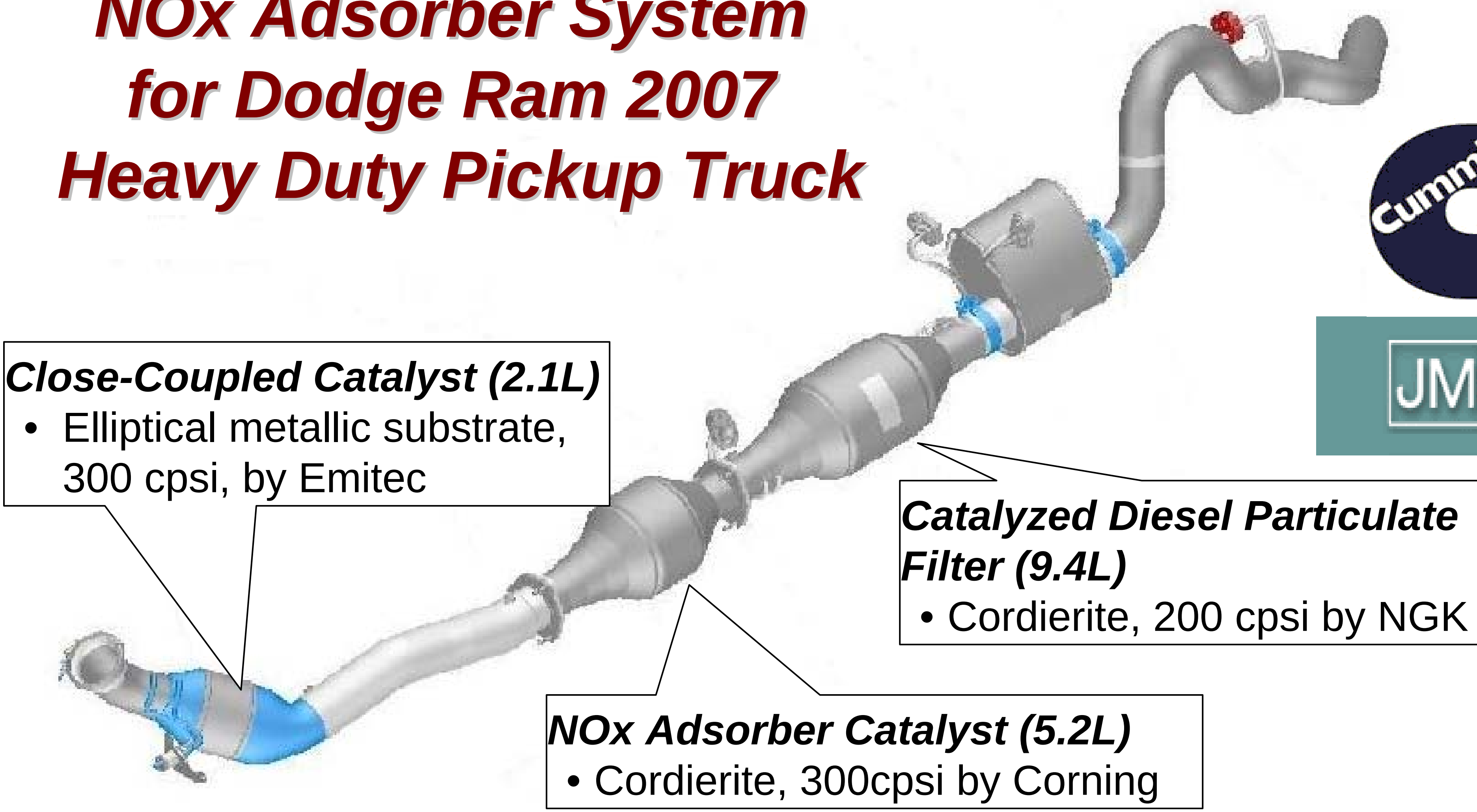
- The project is a CRADA between PNNL and Cummins Inc. It involves a significant collaboration with catalyst supplier, Johnson Matthey Environmental Catalyst Technology Division.

- **Project first initiated in February 2003; CRADA agreement signed through September of 2008**

- 'Tech transfer' via
  - Regular (approximately monthly) conference calls.
  - Annual face-to-fact CRADA Reviews (first and 4th held in 2004 and 2007 at PNNL, second in 2005 at Johnson-Matthey and third in 2006 at Cummins). **Fifth annual review held on Feb 21st and 22nd, 2008 at Johnson-Matthey in Wayne, PA.**

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



Purpose of the Work

- Develop an understanding of the mechanisms of Lean-NOx Trap (LNT) 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 dynamometer and field aged catalysts.

Responses to Previous Year Reviewers' Comments

- We thank the reviewers for recognizing the importance of the work and are gratified that they noted good progress even though a significant amount of the work is proprietary.
  - → A reviewer's comment about the continuing critical nature of the issue of sulfur poisoning, a major focus for this program, was also appreciated.
- While we understand the comments about incomplete presentation of all of the work on this CRADA (e.g., "this reviewer wished his company could share the detailed results"), we also sensed that this situation was understandable and acceptable to the reviewers.

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.

Approach

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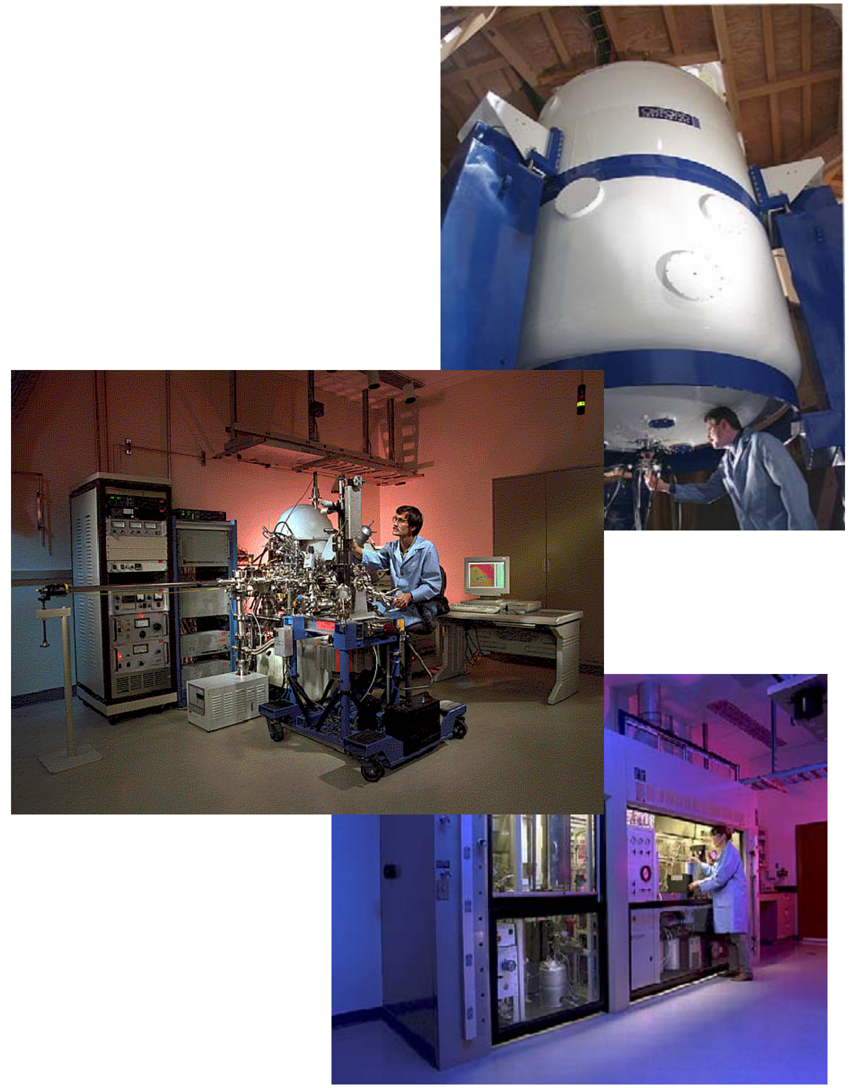
- Prepare and Process Model NOx Adsorber Materials
  - All catalysts have been provided by Johnson-Matthey. We are using a 'Simple Model' Pt-Ba-Al_2O_3, an 'Enhanced Model' material, and the current commercialized formulation.
    - Fresh, as-received (AR)
    - Variably sulfated (including engine-aged)
- 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)



FY 2008 Objectives/Activities

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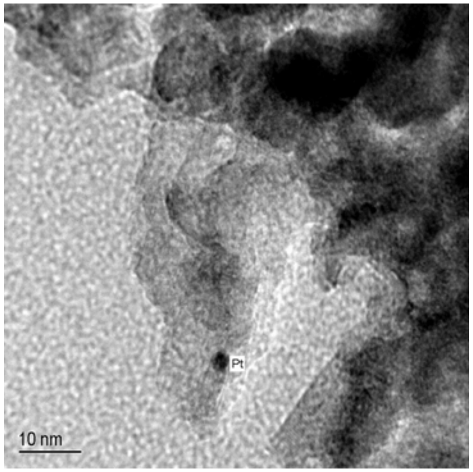
Two primary areas of focus:

- Determine most appropriate tools and procedures for catalyst state diagnosis of field-tested materials.
  - One aspect of these studies is to identify relatively simple, robust, and cost-effective methods: SEM/EDX line scanning and spatio-resolution XPS successfully applied so far
  - Results obtained in this part of the work contain proprietary information regarding catalyst composition and structure.



- Identify the chemical mechanisms of sulfation/desulfation processes to avoid the deactivation arising from these processes
  - *In-situ* sulfur XANES, Pt EXAFS, and TR-XRD techniques provide information on sulfur and Pt oxidation states, and Ba-phase structural changes.
  - Investigate the roles of water during desulfation, focusing on Pt sintering.

Technical Accomplishments/ Progress/Results

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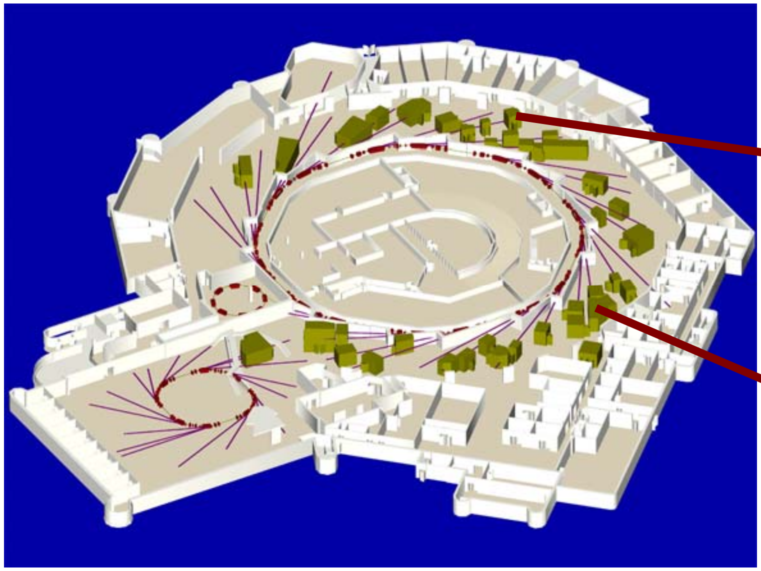
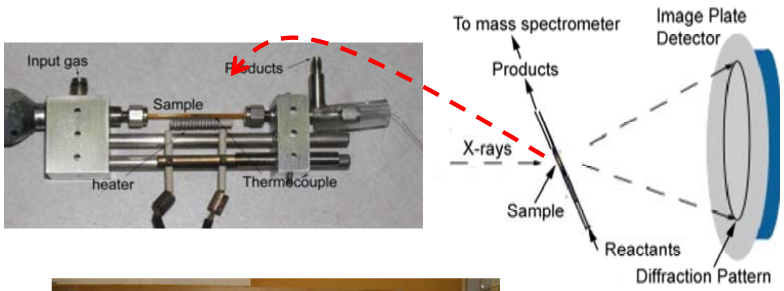
State-of-the-art *in-situ* synchrotron experiments performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Specific techniques used include:

- X-ray absorption near-edge structure (XANES);
- Extended x-ray absorption fine structure (EXAFS); and
- Time-resolved x-ray diffraction (TR-XRD)

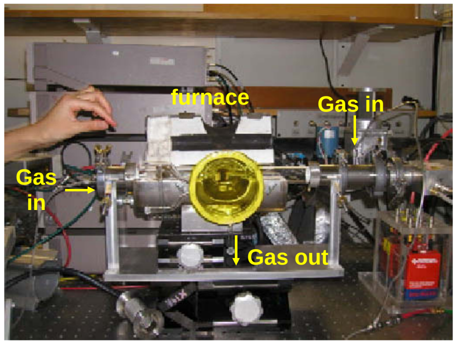
BROOKHAVEN NATIONAL LABORATORY
NSLS NATIONAL SYNCHROTRON LIGHT SOURCE



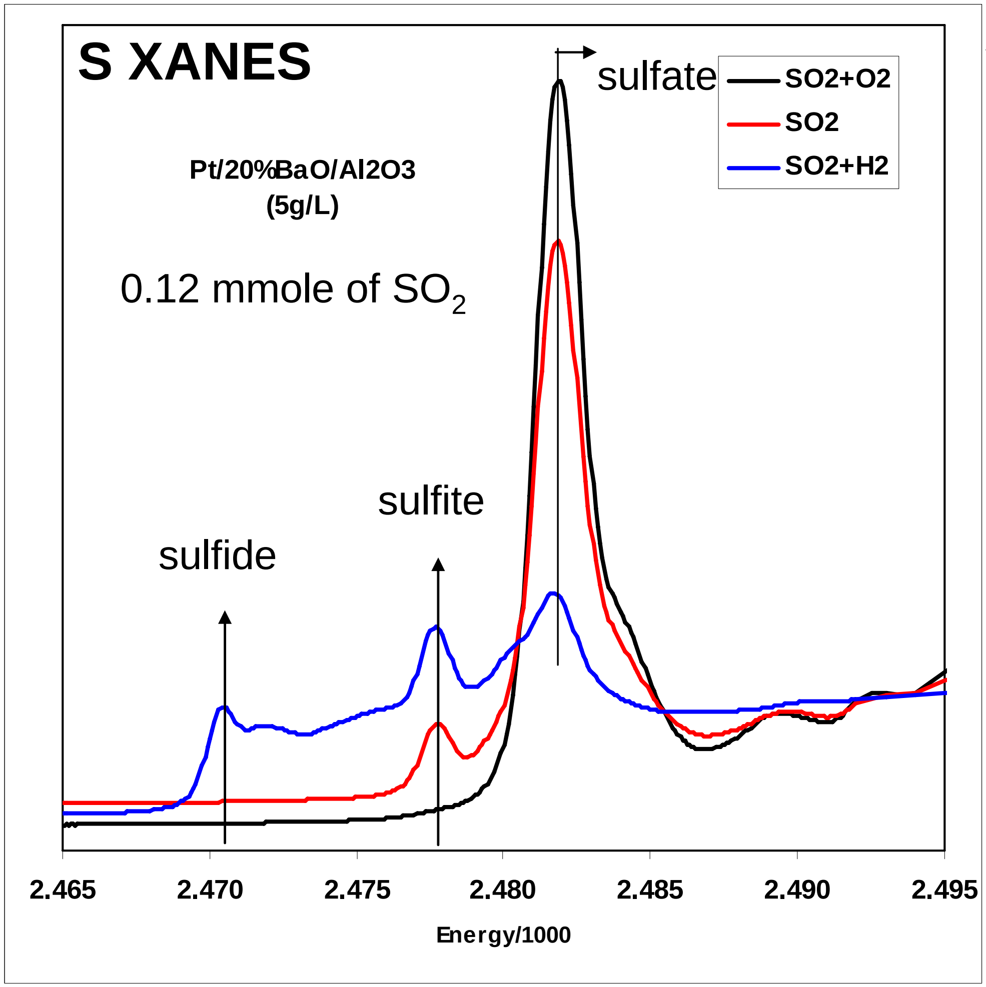
In-situ
TR-XRD



In-situ
S XANES
&
Pt EXAFS

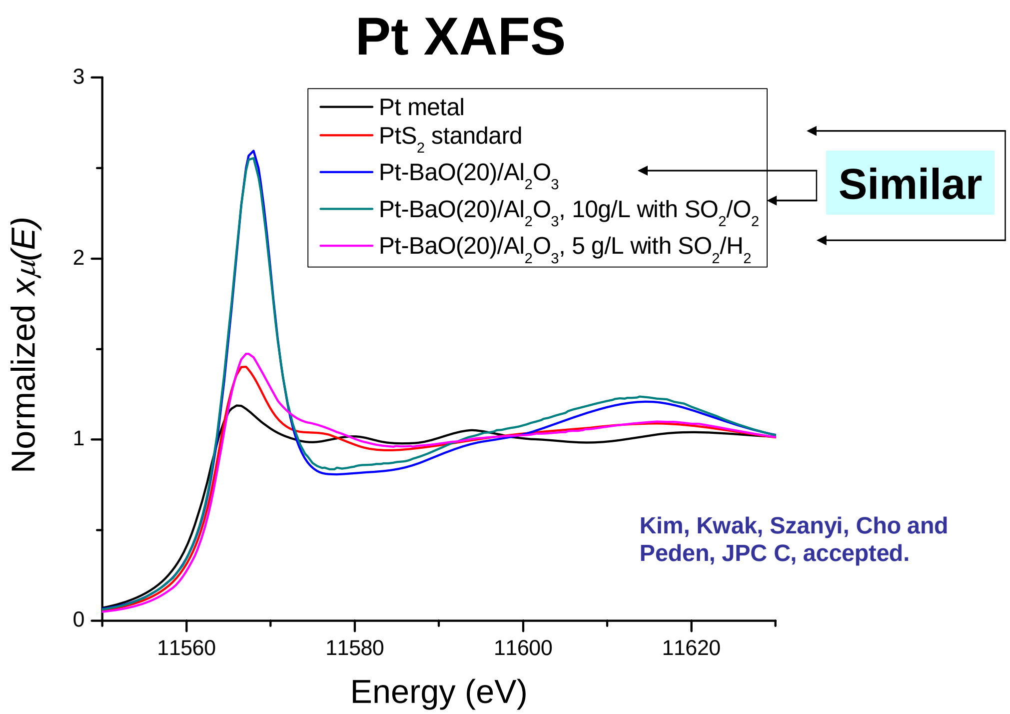


Effect of oxidizing or reducing sulfation conditions on the sulfur species over Pt-BaO/Al_2O_3



Oxidizing: sulfate only

Reducing: **sulfide**, sulfite and sulfates



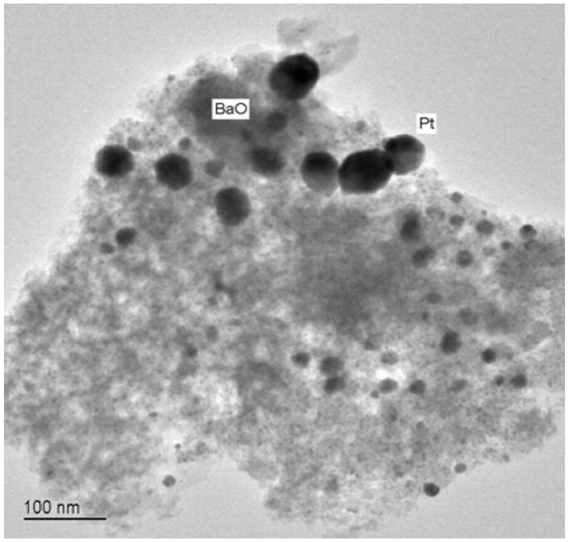
SO_2/O_2 sulfation → Pt-O bond

SO_2/H_2 sulfation → Pt-S bond

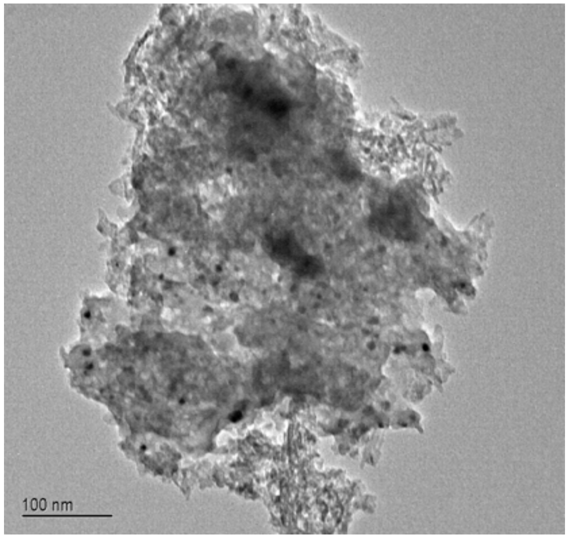
Technical Accomplishments/ Progress/Results

Positive and negative roles of water during desulfation steps

- Positive effect: $BaS + H_2O \rightarrow BaO + H_2S \uparrow$ (extra removal of sulfur)
- Negative effect: H_2O facilitates Pt sintering, esp. at higher temperature



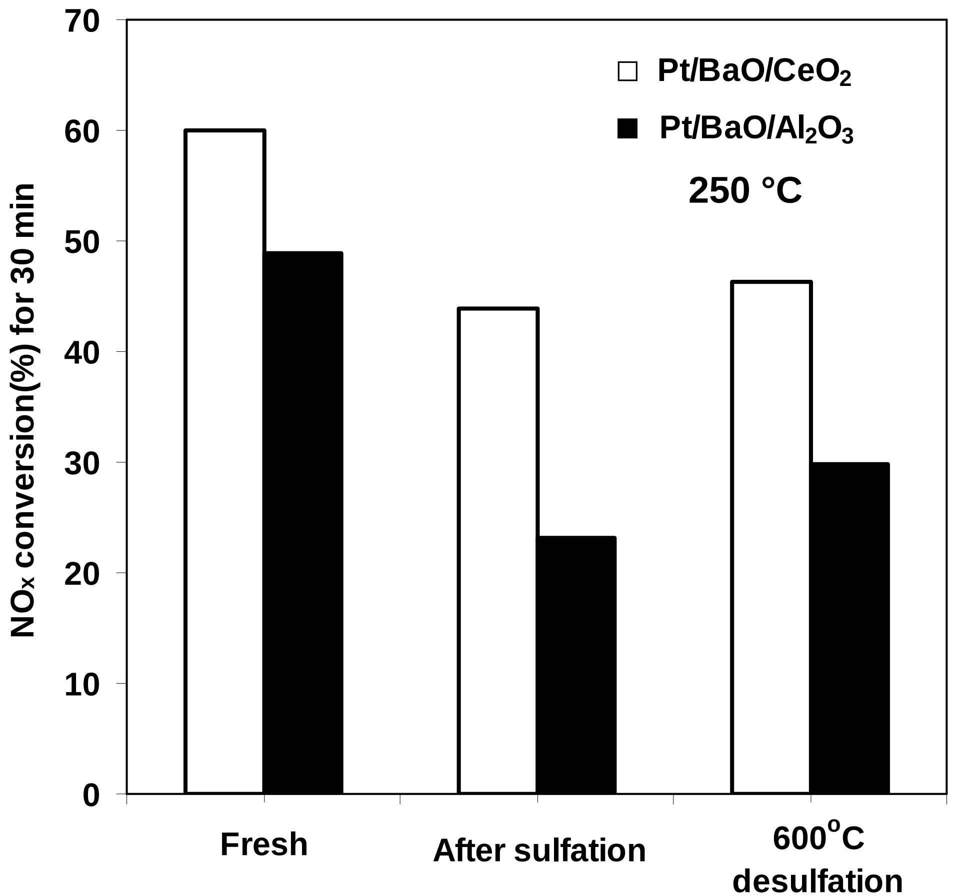
"Cooperatively" desulfated with H_2/H_2O up to 800 °C

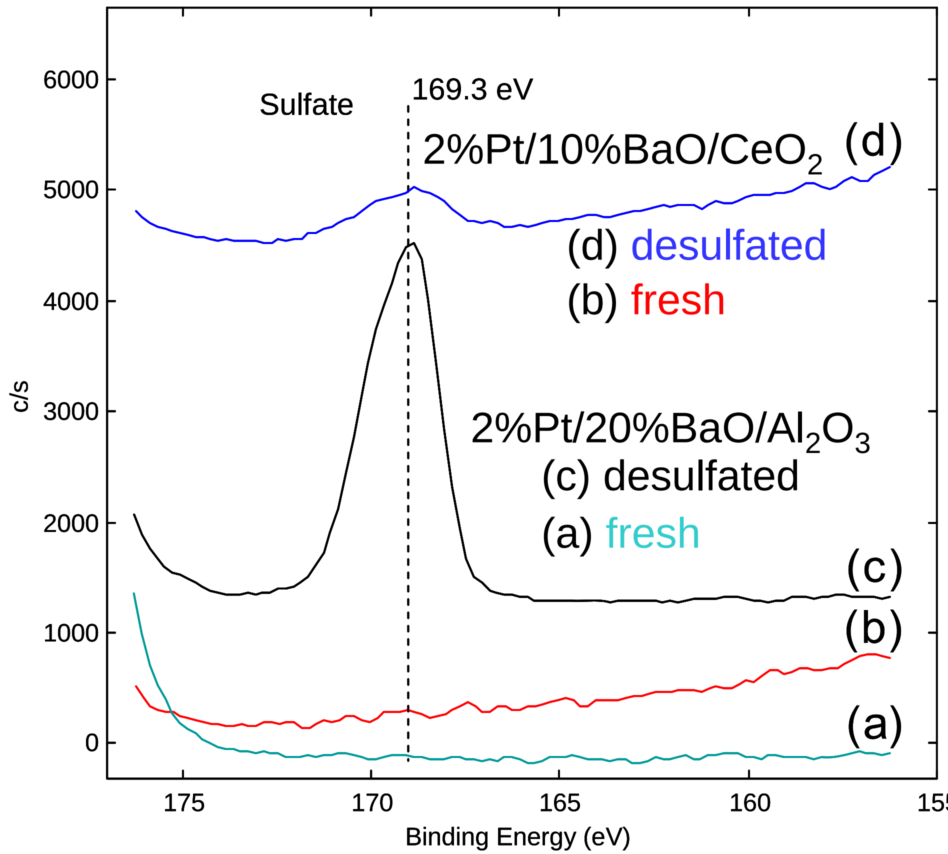


Sequentially desulfated with H_2 up to 800 °C, followed by H_2O at 300 °C

The TEM data show that Pt sintering was significantly inhibited due to the absence of H_2O during the desulfation at high temperatures, while sulfur removal was essentially equivalent for both processes.

A ceria-supported catalyst is much more active per amount of Ba, and much more readily desulfated than an alumina-supported Pt-BaO LNT.





J.H. Kwak, D.H. Kim, J. Szanyi and C.H.F. Peden, Appl. Catal. B, submitted for publication.

Technical Accomplishments/ Progress/Results

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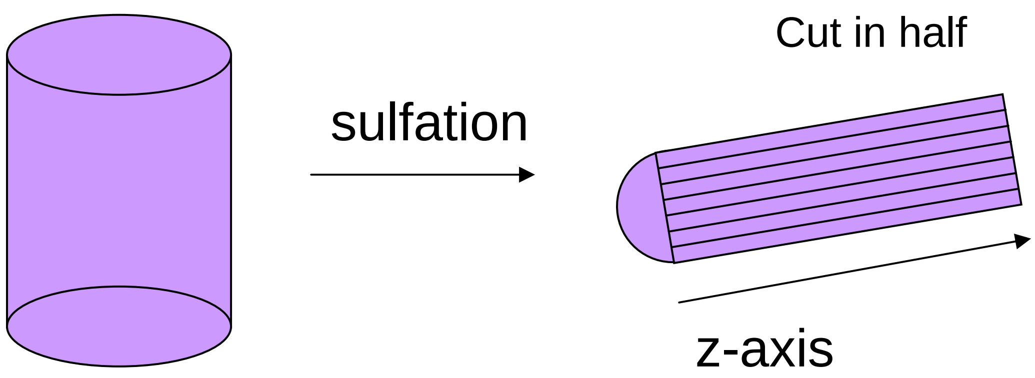
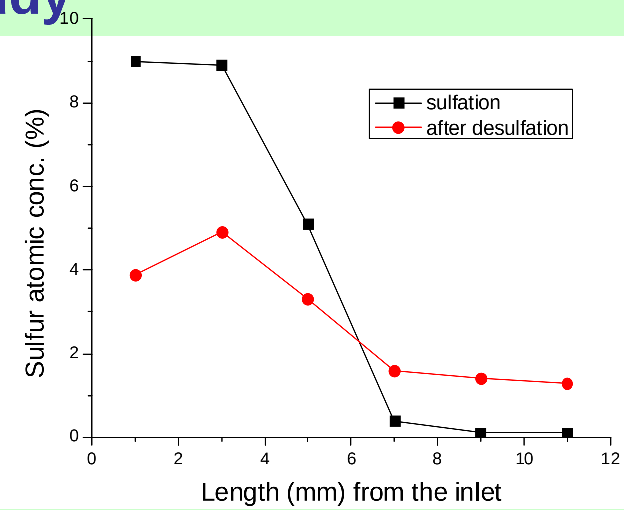
Spatial analysis of sulfur species during sulfation/desulfation along the z-axis of field tested monolith samples: XPS study

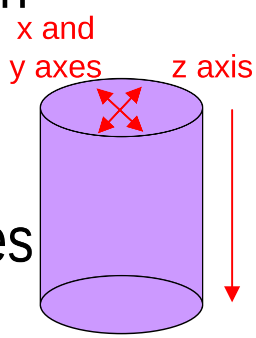




Cross-sectional analysis of sulfur species during sulfation along the x-y axis of field tested monolith samples: SEM/EDS study

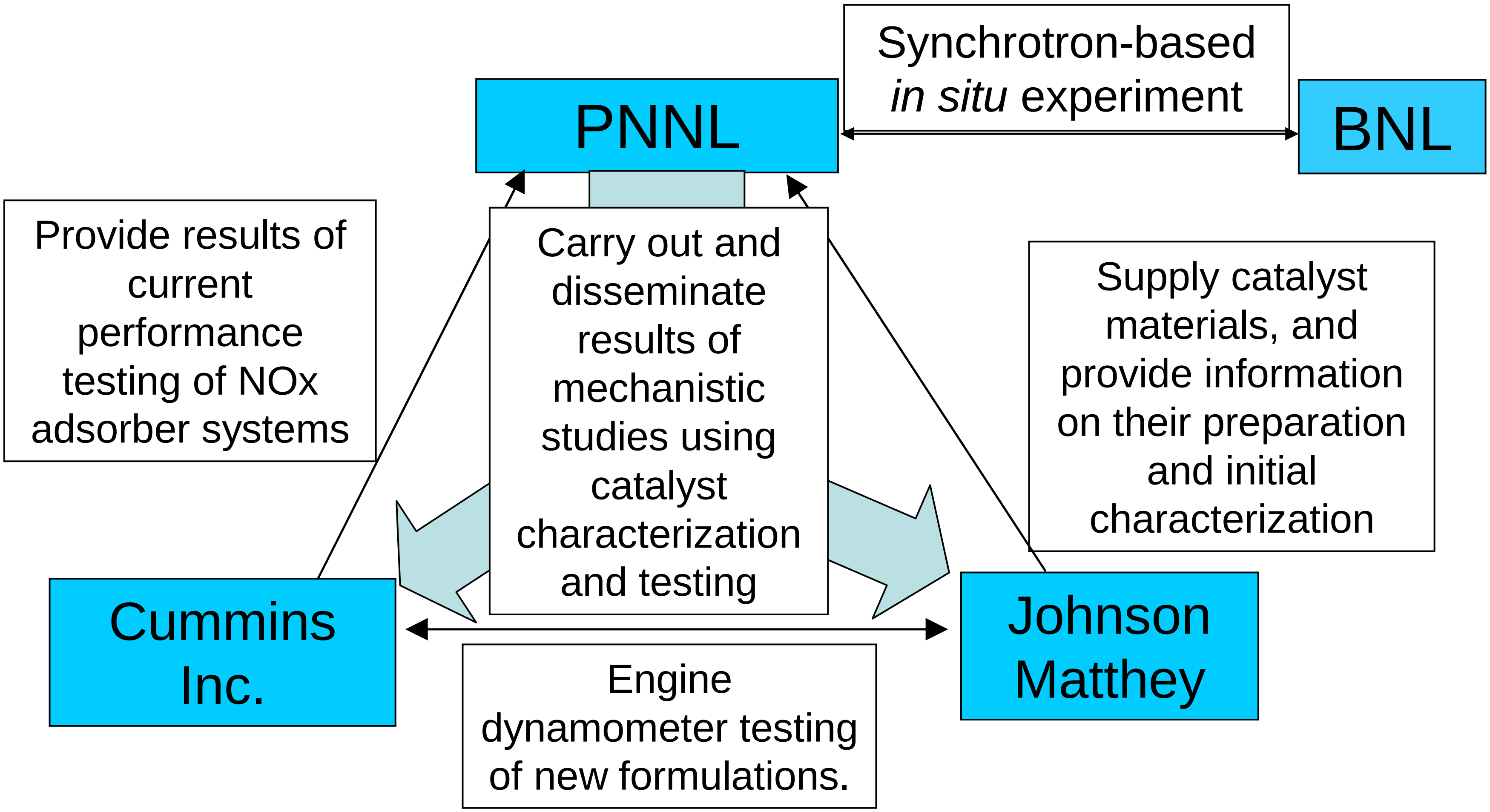
Principal conclusions of these studies to date:

- Several state-of-the-art characterization tools, including XPS and SEM/EDX, were applied to investigate the sulfur distribution of fresh and field-tested monolith catalysts.
  - XPS: spatial distribution of sulfur along the z axis
  - SEM/EDX: cross-sectional distribution of sulfur along the x and y axes



- We found both positive and negative roles for water in desulfation processes
  - Positive role of water: BaS conversion to BaO and H_2S by reaction with H_2O.
  - Negative role of water: promoting 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.
- The various physicochemical effects of Pt-Ba/Al_2O_3 model lean NOx trap catalyst during sulfation and desulfation steps have been identified, and were found to include:
  - The chemical form of stored sulfur as a function of gas composition (e.g., reducing or oxidizing) has been identified – of note is that PtS is formed under reducing conditions leading to significantly higher performance loss;
  - Ba-containing phases out-compete the alumina support material for sulfur; and
  - The form of the barium phase affects the sulfation/desulfation significantly.

Collaborations/Interactions



- ***Conference Call is held approximately once a month to discuss the results.***
- ***Letter from Cummins VP acknowledges this program's contributions to Dodge Ram emissions system developments and commercialization***

Activities for the remainder of this Fiscal Year

- Complete identification of LNT thermal history diagnostics techniques
- Continue to improve mechanistic understanding of sulfur removal processes
  - Identify important desulfation intermediates
  - Effects of sulfur concentration on Pt accessibility and barium phase changes
- Complete statement of work (SOW) and CRADA documents for a new CRADA proposed for end of FY08 start
  - SOW draft developed at Annual CRADA Review Meeting held late last week.

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!"

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 continues to be to provide fundamental insights into specific issues concerning LNT deactivation identified from Cummins' and J/M's field experience.
- Technical highlights this year included:
  - Studies of engine dynamometer and field aged samples are now seeking to understand an observed but unexpected deactivation mode.
  - Fundamental studies of sulfur-removal mechanisms are yielding insights important for optimizing desulfation strategies.
  - We identified a sequential desulfation method, which can minimize Pt sintering via limiting the presence of H_2O during high temperature desulfation.
- This has been a highly interactive program with a recent focus driven by specific field experience with the LNT technology.

Publications, Presentations, Patents

Publications

- D.H. Kim, J.H. Kwak, X.Q. Wang, J. Szanyi and C.H.F. Peden, "Sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated lean NOx trap catalysts", Catalysis Today, in press (2008).
- D.H. Kim, J.H. Kwak, J. Szanyi, S.J. Cho, C.H.F. Peden, "The Roles of Pt and BaO in the Sulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Materials: Sulfur K-Edge XANES and Pt L_{III} EXAFS Studies". Journal of Physical Chemistry C, In press (2008).
- D.H. Kim, X.Q. Wang, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, N. Currier, H.Y. Chen and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2007 Annual Progress Report* (2008) in press.
- J.H. Kwak, D.H. Kim, J. Szanyi and C.H.F. Peden, "Excellent sulfur resistance of a Pt-BaO/CeO_2 lean NOx trap catalyst", Appl. Catal. B, submitted for publication.

Presentations

- D. H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE SMMI Review, Washington, DC, June, 2007.
- D.H. Kim, J.H. Kwak, J. Szanyi, X. Wang, J.C. Hanson, and C.H.F. Peden, "Barium loading effects on the Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts: an *in situ* Sulfur XANES and TR-XRD Study", presentation at the 20th Meeting of the North American Catalysis Society, Houston, TX, June, 2007.
- D.H. Kim, J.H. Kwak, J. Szanyi, Xianqin Wang, J. Hanson, William Epling, C.H.F. Peden, "The use of in situ synchrotron techniques to study desulfation processes of Pt/BaO/Al_2O_3 lean NOx trap catalysts", 2007 AIChE annual meeting, Salt Lake City, UT, November, 2007.
- D.H. Kim, "Fundamental understanding of sulfation/desulfation mechanisms over Pt-BaO/Al_2O_3 lean NOx trap catalysts" CLEERS (Cross-cut lean exhaust emission reduction simulation) conference call, December, 2007.

Cummins acknowledges contributions of these studies to their Dodge Ram emission control system development

Cummins Reveals Best-In-Class 2007 Turbo Diesel Engine

Strongest. Cleanest. Quietest.

WASHINGTON--(BUSINESS WIRE)--Jan. 23, 2007--Cummins Inc. (NYSE:CMI) today unveiled the strongest, cleanest, quietest best-in-class 2007 Cummins Turbo Diesel. Leapfrogging the competition, the Cummins 6.7-liter Turbo Diesel engine, used exclusively in Dodge Ram 2500 and 3500 Heavy Duty pickup trucks, has increased displacement providing increased horsepower and torque while achieving the world's lowest 2010 Environmental Protection Agency (EPA) NOx standard a full three years ahead of the requirements.

Letter received from John Wall, Vice President and Chief Technical Officer, Cummins, dated February 15, 2007, recognizing and thanking PNNL for their technical contributions.

Dr. Charles H.F. Peden,
Associate Director, Institute for Interfacial Catalysis
Pacific Northwest National Laboratory
P.O. Box 999 / K8-93
Richland, WA 99352

Dear Dr. Peden,

With the recent announcement of the Dodge Ram heavy duty pickup truck employing a NOx-adsorber based aftertreatment system, I thought it would be timely to recognize the contribution of you and your colleagues at IIC/PNNL through our CRADA.