Enhanced High Temperature Performance of NOx Storage/Reduction (NSR) Materials

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

Neal Currier, Junhui Li, 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 16, 2012
This presentation does not contain any proprietary, confidential, or otherwise restricted information.

ACE026
Project Overview

Timeline
• Start – March 2009
• Finish – Scheduled for September 2012

Budget
• Matched 50/50 by Cummins as per CRADA agreement
• DOE funding in FY12
  Work Authorization:
  • $225K

Barriers
• Discussed on next slide

Partners
• Pacific Northwest National Laboratory
• Cummins, Inc.
  • w/Johnson Matthey
Barriers - Relevance

• In looking forward to 2012 and beyond with expected more stringent regulations, a critical need for future NOx reduction systems will be significantly improved higher temperature performance and stability.
  – For example, current NSR catalyst formulations are not effective for NOx removal during high temperature system maintenance events, including desulfation. The possibility of using NSR systems for natural gas engines will also require higher temperature performance.
  – Similarly, high temperatures experienced during DPF regenerations can damage the high temperature performance of urea SCR catalysts.

• It is important to reduce system costs by, for example, minimizing the precious metal content while maintaining, even improving, performance and long-term stability.
Higher Temperature Lean NOx Performance:

- Better NOx storage at higher temperatures
  - Modify the NSR storage 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?
Goals and Objectives

- Develop a fundamental understanding of candidate next generation NSR materials operated at high temperatures for NOx after-treatment for light-duty lean-burn (including diesel) engines.
- Focus on characterizing and understanding the following specific issues:
  - mechanisms for deactivation in NOx storage performance in alternative LNT materials for high-temperature application;
  - the sulfur adsorption and regeneration mechanisms for modified and/or alternative storage materials;
  - the effects of high temperatures on the precious metal and storage elements in their various roles;
  - the various roles for the precious metals.
Approach

- Prepare and Process High Temperature NSR Materials
  - Fully formulated catalyst has been provided by Johnson Matthey (NOTE that the composition of this catalyst is proprietary and unknown to Cummins and PNNL).
  - Based on prior PNNL results and published literature, PNNL is preparing model HT NSR catalysts, including changes to the storage element and support material.
  - These materials are studied:
    - Fresh, as-received (AR) and degreened
    - Variably sulfated (thermally-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
  - NO₂ TPD, H₂ TPRX
  - Synchrotron based techniques (in situ time-resolved XRD)
  - Lab reaction system
Collaborations/Interactions

- Provide results of current performance testing of NOx adsorber systems (Cummins Inc.)
- Carry out and disseminate results of mechanistic studies using catalyst characterization and testing (PNNL)
- Supply catalyst materials, and provide information on their preparation and initial characterization (Johnson Matthey)
- Carry out and disseminate results of engine dynamometer testing of new formulations (PNNL)
- Synchrotron-based in situ experiment (BNL)

- Conference calls were held typically once every month or two to discuss the results.
- The most recent annual face-to-face CRADA Review was held in Columbus, IN (March, 2012).
Collaborations/Interactions

Results obtained on similar model catalyst formulations in more fundamental CLEERS-funded studies are essential for this program’s success.

- Conference calls were held typically once every month or two to discuss the results.
- The most recent annual face-to-face CRADA Review was held in Columbus, IN (March, 2012).
Specific Technical Focus

• Fully formulated high temperature NSR catalysts supplied from JM – baseline studies for comparison with new materials
  – Storage behavior of a degreened developmental catalyst sample as a function of temperature.
  – Effects of thermal aging and sulfation/desulfation on the NOx storage activity. Especially focus on how sulfur loading and degrees of desulfation effect performance loss and regeneration.

• High temperature NSR catalysts prepared by PNNL
  – Studies of the effects of storage elements and various supports on the NOx storage activity, are being carried out as part of PNNL’s CLEERS activities.
  – Detailed studies of the deactivation mechanisms in these high temperature NOx storage materials. These studies involve activity testing, thermal treatments, variable desulfation processing, and extensive catalyst characterization.
K/Pt/Al₂O₃ (2%, 5%, 10%, 15%, 20%, weight):

- **Pt/Al₂O₃ (1%)**: Impregnation of Al₂O₃ (150 m²/g) with Pt(NH₃)₄(NO₃)₂, 500°C calcination for 4hrs

- **K loading**: Impregnation of Pt/Al₂O₃ with K₂CO₃ of different K loadings, 600°C calcination for 4hrs

K/Pt/MgAlOₓ (2%, 5%, 10%, 15%, 20%, weight):

- **MgAlOₓ Supports** (Pural MG30: Mg/Al=0.6; MG50: Mg/Al=1.4; MG70: Mg/Al=3.0): Calcination of MG30, MG50 and MG70 600°C for 4hrs

- **K and Pt loading**: as with the alumina-supported catalysts

Baseline performance and characterization studies – CLEERS program.

Aging and sulfur tolerance issues are being addressed as part of this CRADA.

- **Focus today will be on recent studies of thermal aging.**
Sample: 0.12g sample loaded in fixed bed quartz reactor (I.D.=3/8 in.)

Aging conditions:
- Calcination in laboratory air (“lean aging”) at 800 °C for 4 hours
- Reduction in 4% H₂/He at 800 °C for 1 hours

Reactant gas mixtures:
- Total gas flow: 400 sccm (~ 30k h⁻¹ G.H.S.V)
- Lean: 10%O₂, 5%CO₂, 5%H₂O, 150 ppm NO, balance He
- Rich: 0%O₂, 5%CO₂, 5%H₂O, 5%H₂, balance He

• 20 cycles first to reach a steady cycle-to-cycle performance.
• NOx Uptakes: Total amount of adsorbed NOₓ in final long lean cycle until outlet NOₓ reached 30 ppm.)
Unlike Ba-based NSRs, the temperature for optimum performance of Al₂O₃-supported K NSR catalysts show a large and unexpected dependence on loading.

MgAl₂O₄ support materials provide for even higher temperature performance of K-based NSRs, and also show the unusual dependence on K loading.
Effects of aging on performance

- Aging at 800°C under oxidizing conditions significantly decreases the overall performance.
- The MG30 sample shows the highest performance after aging.

K Loading was 10% in all of these samples
Re-reduction restores performance, especially for the MG30 catalyst.

- A reduction at 800 °C after lean aging restores performance especially for the MgAl₂O₄-supported catalysts.
- The temperature for maximum performance ($T_{max}$) was reduced somewhat for all catalysts.

K Loading was 10% in all of these samples.
Compared with the fresh catalyst, aging followed by re-reduction decreases the maximum NOx uptake for Al$_2$O$_3$ to half, as well as lowering $T_{\text{max}}$.

For the MgAl$_2$O$_4$-supported catalyst, aging and reduction at 800ºC, the performance at high temperature is restored, while at the low temperature actually increases as compared with the fresh sample.

The drop in $T_{\text{max}}$ is also evident in NOx TPD carried out after these aging treatments (data not shown).
By XRD, Pt particle size is MUCH more stable on MgAl$_2$O$_4$-Supported NSRs.

- After aging at 800°C in air, sharp and intense Pt peaks are observed for the Al$_2$O$_3$ sample but, interestingly, **no Pt-related peaks** are detected in the MgAlO$_x$ samples after lean aging.

- MgAlO$_x$-supported catalysts contain two phases; MgAl$_2$O$_4$ spinel and MgO.

- After high temperature reduction, much smaller particles of Pt are observed for the MgAlO$_x$-supported catalysts.
Two types of Pt present in the Pt-K(10%)/Al₂O₃: catalyst after lean aging

- Large Pt particles (XRD visible)
- Oxidized Pt, perhaps strongly interacting with K species (XRD and TEM invisible)

After high temperature reduction, increased numbers of large (>10 nm) Pt particles are observed.
Unlike the Al$_2$O$_3$-supported catalyst, no Pt particles can be seen in the TEM from aged the MG30 catalyst.

After reduction, small (<5 nm) Pt particles are visible, smaller than the Al$_2$O$_3$ sample - no large change between fresh and aged MG30-supported catalysts.
Planned Future Work

1. Model K-based MgAl$_2$O$_4$- and Al$_2$O$_3$-supported catalysts:
   - Studies of the stability of the K-storage phase:
     - Microdiffraction and aberration-corrected TEM measurements.
     - At the suggestion of one of last year’s reviewer, will explore mixed K-Ba NSR materials as possible route to stabilize K.
   - Understanding of sulfation/desulfation behavior at various sulfur loadings, as a function of support material and K loading.

2. High temperature NSR materials supplied from JM:
   - Continued characterization, especially with respect to performance regeneration as a function of sulfur loading and sulfur removal levels for comparison with model catalysts.
Summary

• A critical need for future NOx emission control technologies will be significantly **improved higher temperature performance** and stability, since current systems are not effective during high temperature system maintenance events (for example, soot filter regenerations).

• PNNL’s role has been to prepare and characterize model NSR catalysts known for enhanced performance at higher temperatures, and provide fundamental insights into specific issues concerning HT-NSR catalyst deactivation due to sulfur poisoning and/or thermal degradation.

• Technical highlights from this project included:
  – PNNL prepared and evaluated a number of candidate materials, which led to a choice of a HT-NSR catalyst, Pt-K/MgAl$_2$O$_4$, as a promising model system. In addition, comparative behavior of Pt-K/Al$_2$O$_3$ is being studied. Unusual dependence of K loading and high temperature oxidizing and reducing treatments on performance have been observed and are being characterized.
  – We are also evaluating proprietary HT-NSR materials supplied from JM regarding the durability issues of thermal aging and sulfation/desulfation.