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

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ACE026

Project Overview

Timeline

- Start – March 2009
- Finish – Feb 2012
- 70% complete

Budget

- Matched 50/50 by Cummins as per CRADA agreement
- DOE funding in FY11 WAS:
  - $200K

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 NSR 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.
- It is important to reduce system costs by, for example, **minimizing the precious metal content** while maintaining, even improving, performance and long-term stability.

Barriers - Relevance

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

Vehicle Technologies Program

- 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.

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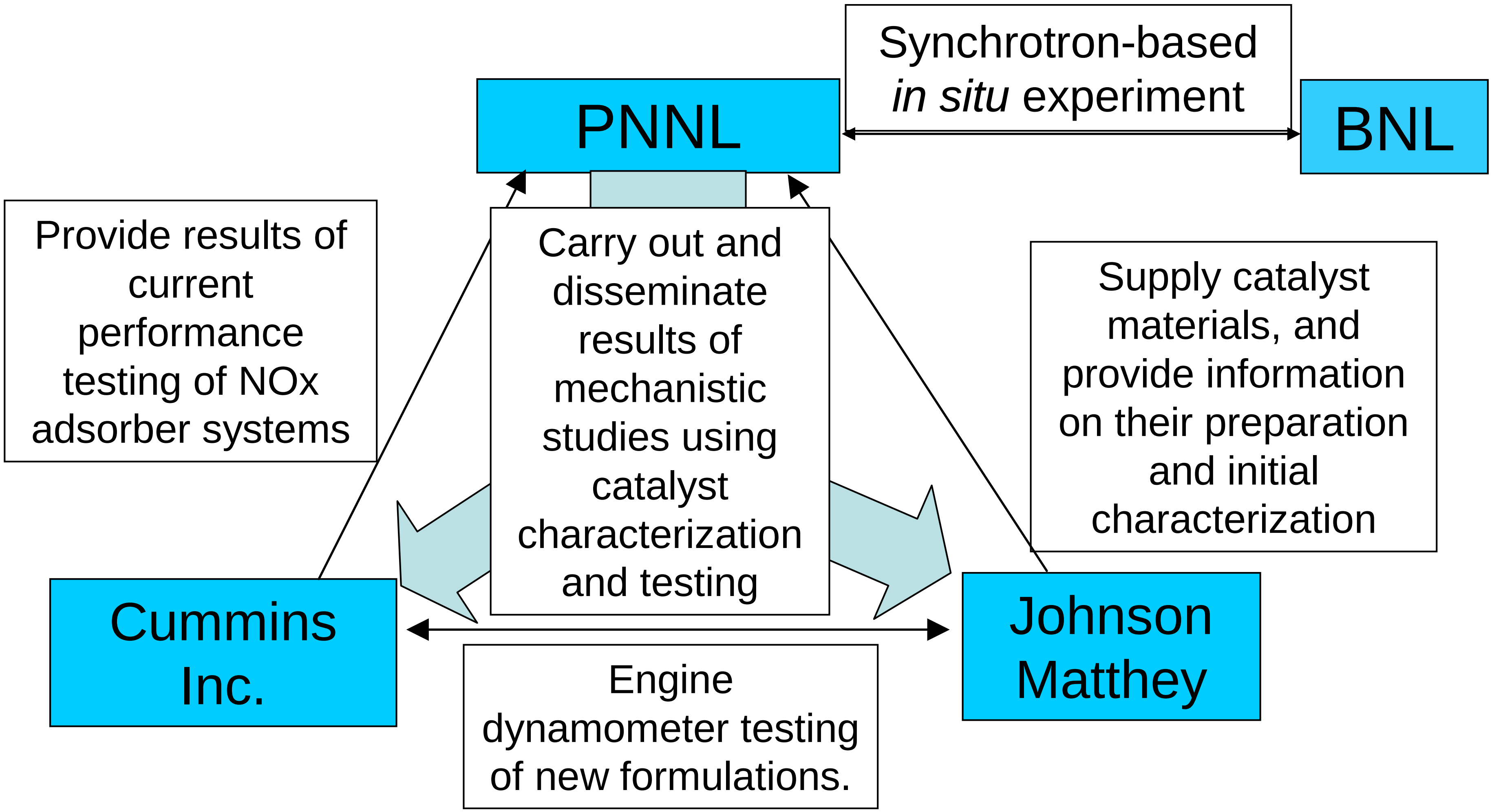
Approach

- 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
  - NO_2 TPD, H_2 TPRX
  - Synchrotron based techniques (*in situ* time-resolved XRD)
  - Lab reaction system

Collaborations/Interactions



- 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 Devon, PA (October, 2010).

Collaborations/Interactions

Synchrotron-based
in situ experiment

BNL

Provide
cu
perfo
testing
adsorbe

Cu

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

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Technical Accomplishments

- Fully formulated high temperature NSR catalysts supplied from JM – baseline studies for comparison with new materials
  - Explore the storage behavior of a fresh developmental catalyst sample as a function of temperature.
  - Investigate the effects of thermal aging and sulfation/desulfation on the NOx storage activity.

- 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.

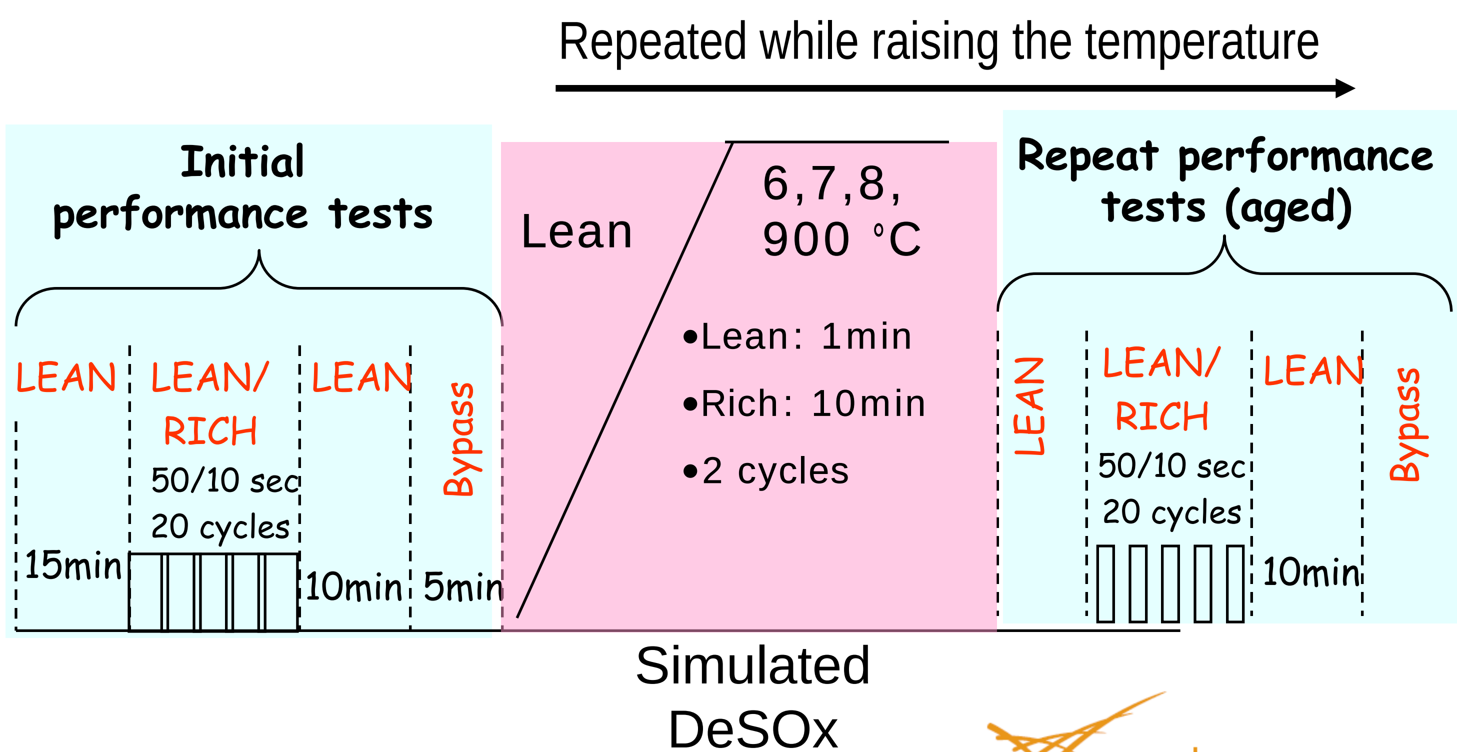
Reaction Protocol:

Fresh brick: 0.7906 g (4x4 cell), sealed around the sample with quartz wool

Gas flow:

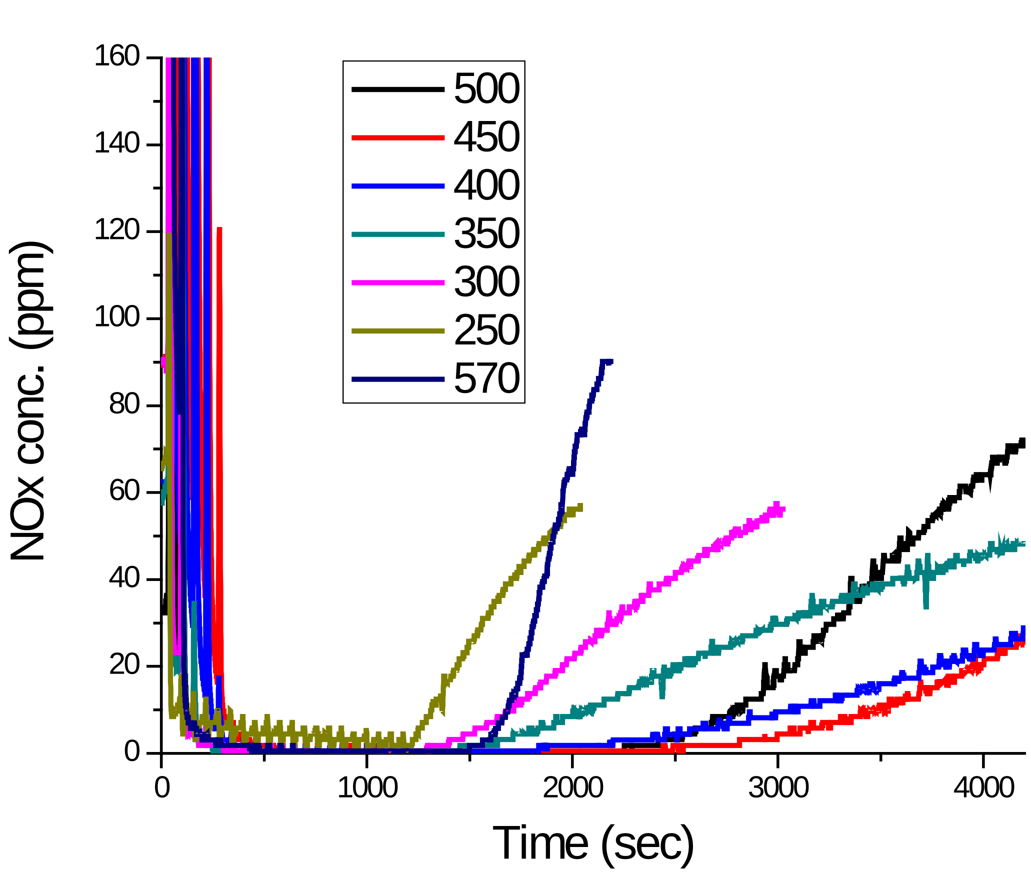
- Total gas flow: 400 sccm (~ 30k h^{-1} G.H.S.V)
- Lean: 5%O_2, 5%CO_2, 5%H_2O, 150 ppm NO,
- Rich: 0%O_2, 5%CO_2, 5%H_2O, 4.25%H_2

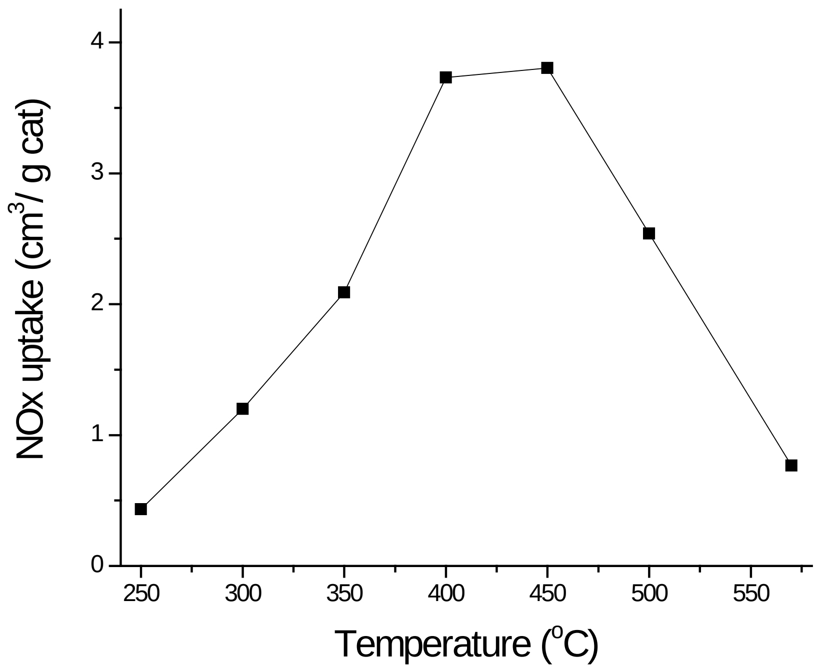
- **As received**
- **Initial performance tests measured at 500, 450, 400, 350, 300, 250 and then 570 °C**



Technical Accomplishments/ Progress/Results

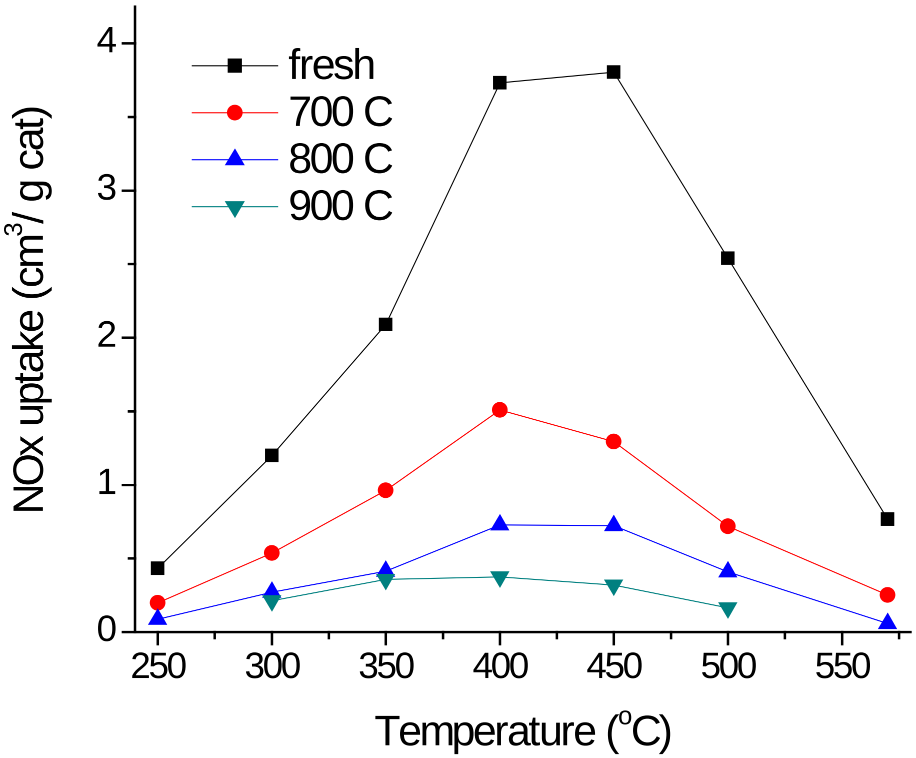
A fully formulated developmental H-T NSR catalyst system, supplied from JM, shows highest activities between 400 and 450 ºC. These catalysts were also tested after thermal aging at elevated temperature to understand the thermal stability.

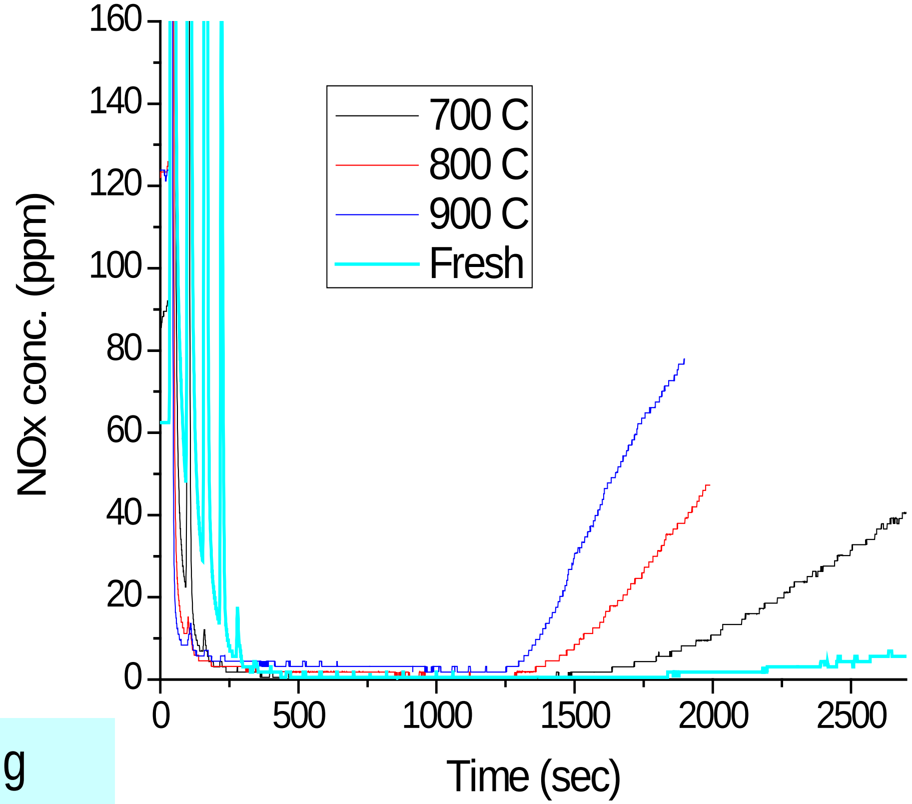




Note: NOx uptake = total NOx uptake up to 20% NOx 'breakthrough'

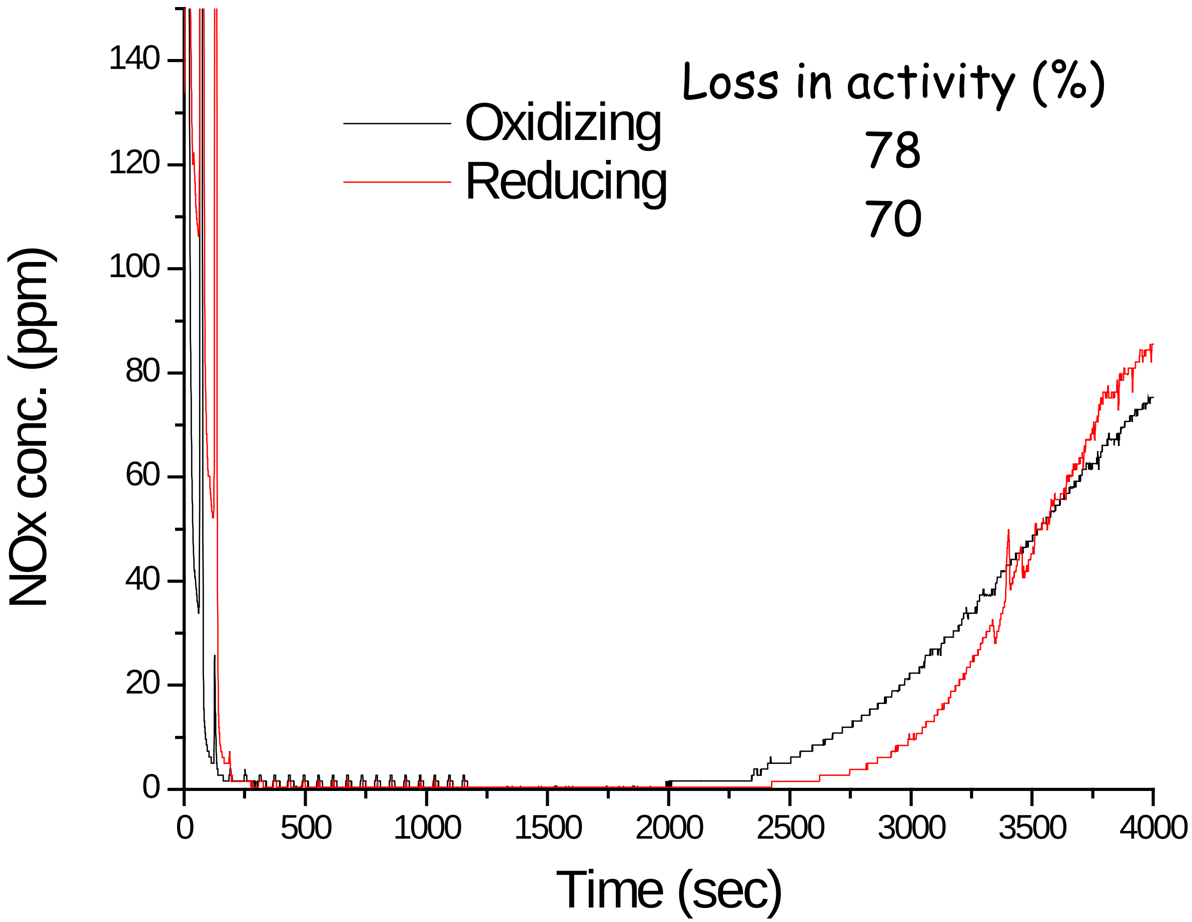
Thermal stability of the NSR sample from JM





- NOx uptakes decrease significantly with increasing aging temperatures.
- Thermal treatment over 700 °C deteriorates NOx uptakes in these samples.
- However, this is compared to fresh (NOT de-greened) catalyst.

Which treatment is more detrimental, oxidizing or reducing?



Oxidizing conditions gives rise to a somewhat greater loss in NOx uptake, compared with reducing conditions.

After treating the sample at 700 ºC under oxidizing or reducing conditions.

Reaction protocol: sulfation-desulfation

1) Degreening: at 700 °C, Lean/Rich (1 min/10min) cycling for ~16hrs

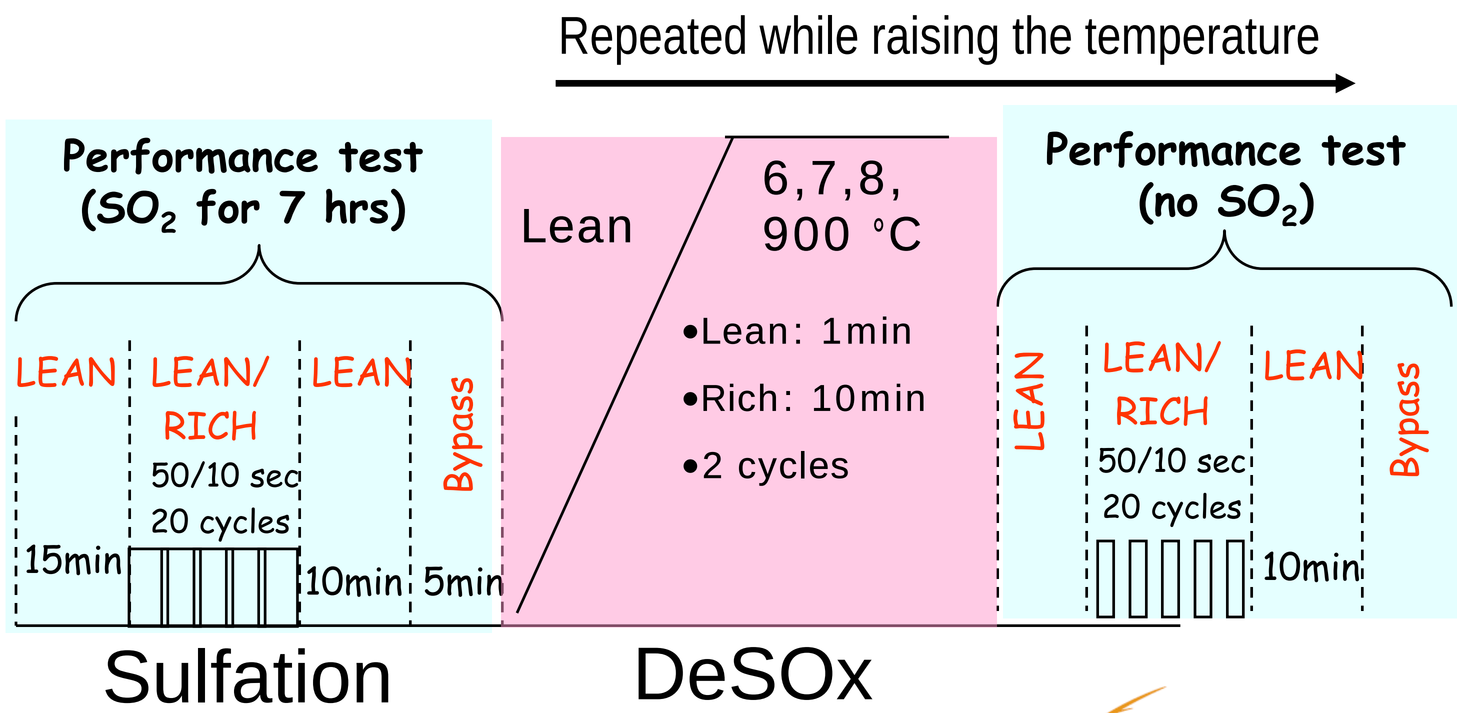
2) Sulfation: SO_2 exposure at 400 ^oC for 7 hrs (7.5 ppm)

→ 1.08 cm^3 of SO_2 in total

→ Periodic activity measurements during sulfation

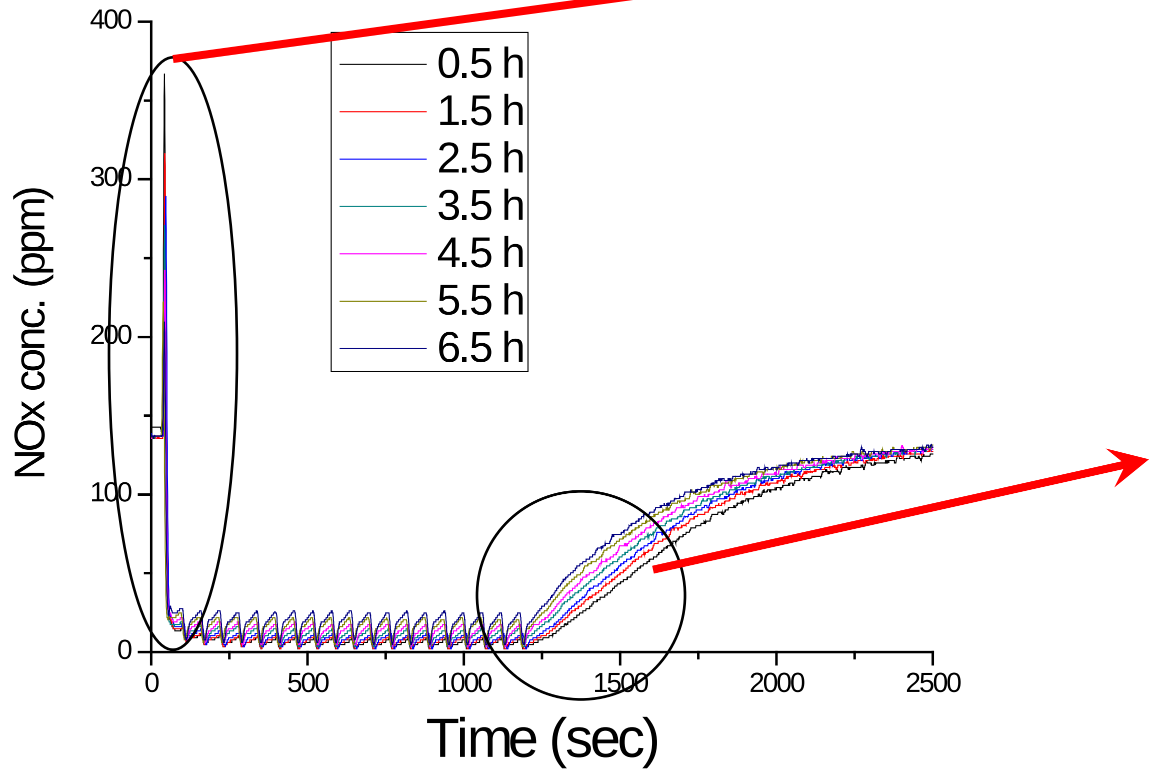
3) Desulfation: see below

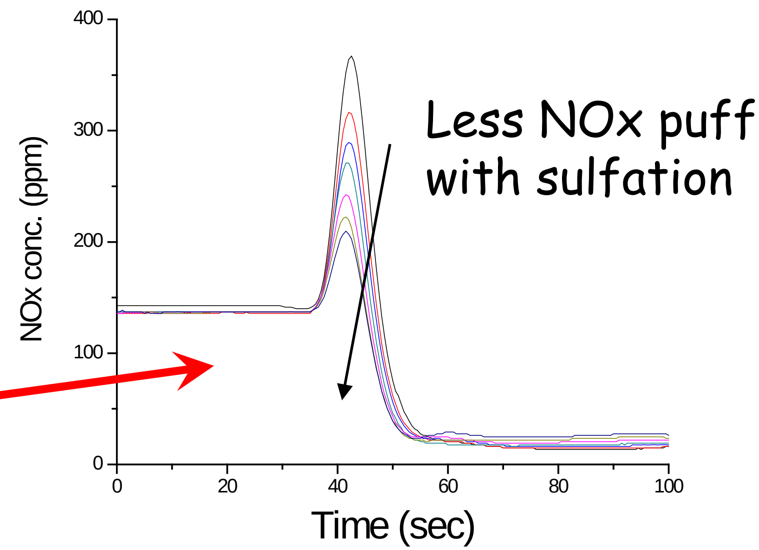
- **Activity at 400 ^oC**
- **De-greening at 700 ^oC**
- **86 pulses (10 min rich/1min lean)**

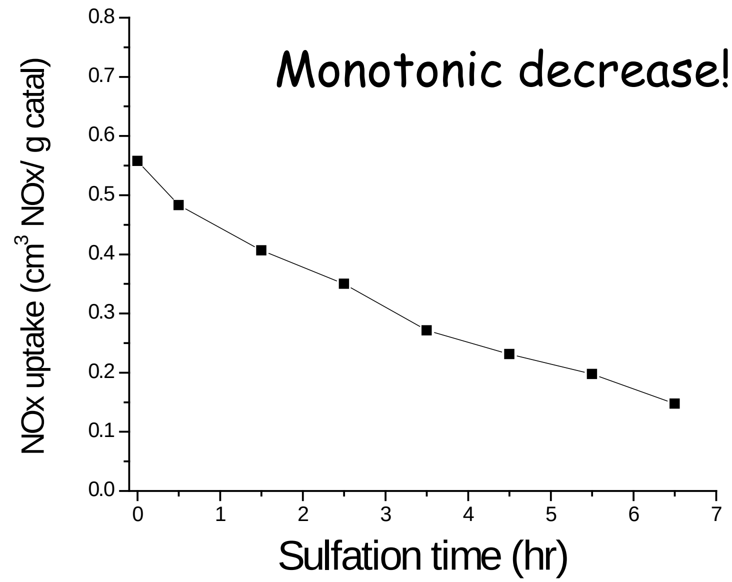


Technical Accomplishments/ Progress/Results

NOx storage in a **degreened JM catalyst sample** monotonically decreases with incremental increases in SO_2 exposure; even relatively small amounts of SO_2 can deteriorate NOx storage performance.

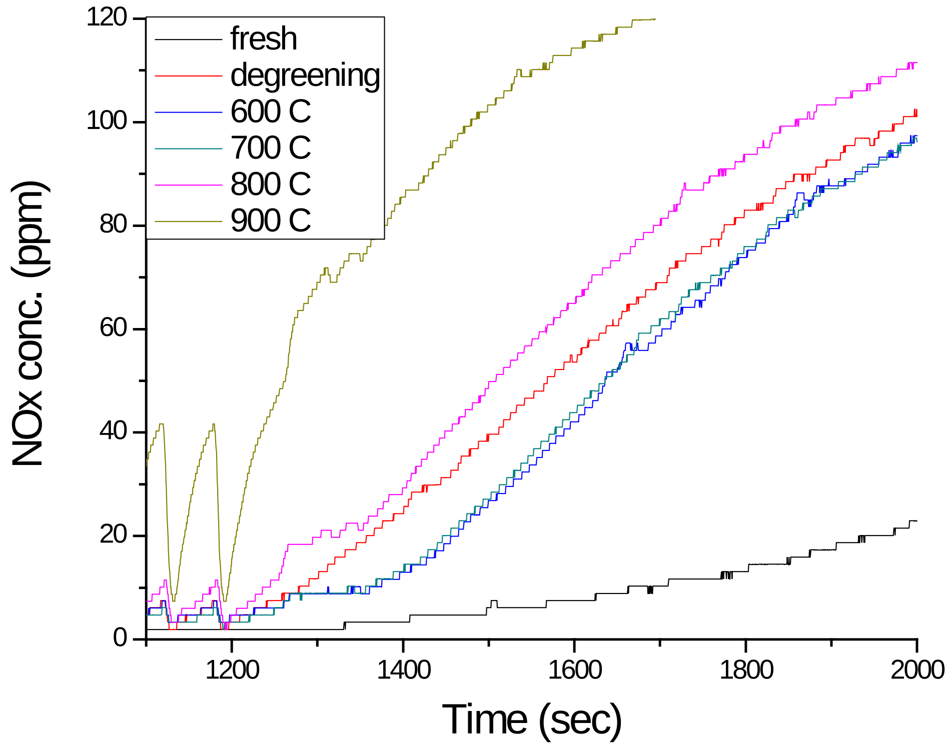


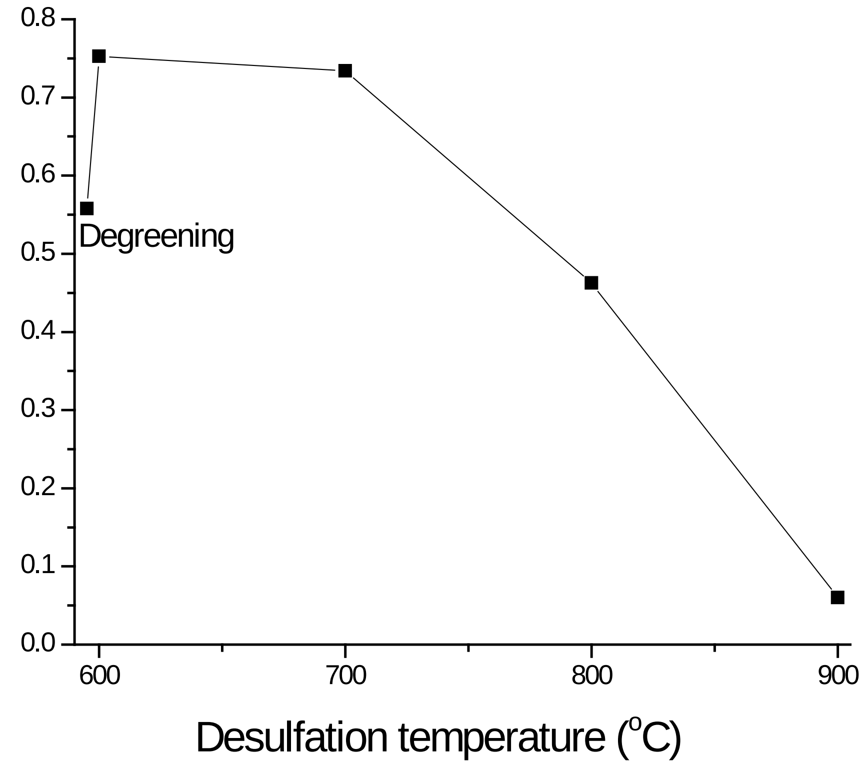




Technical Accomplishments/ Progress/Results

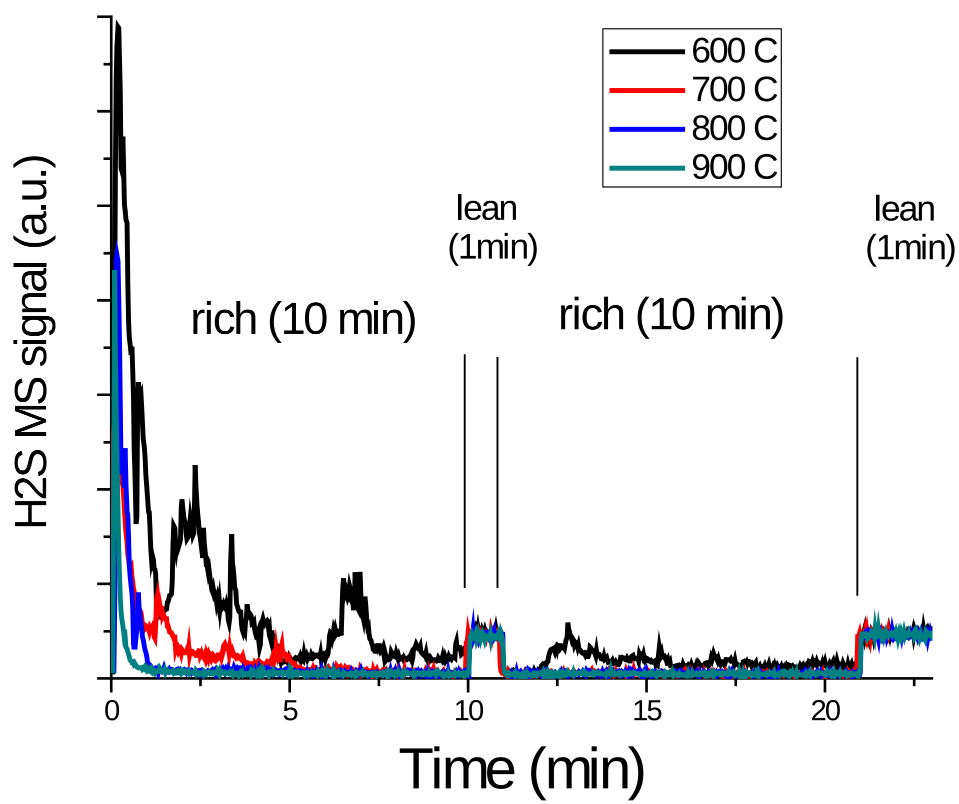
The activities after sulfation followed by desulfation at 600 and 700 ºC are slightly higher than a degreened one before any sulfation. Activities after desulfation above 800 ºC are significantly lower due to detrimental thermal aging effects.

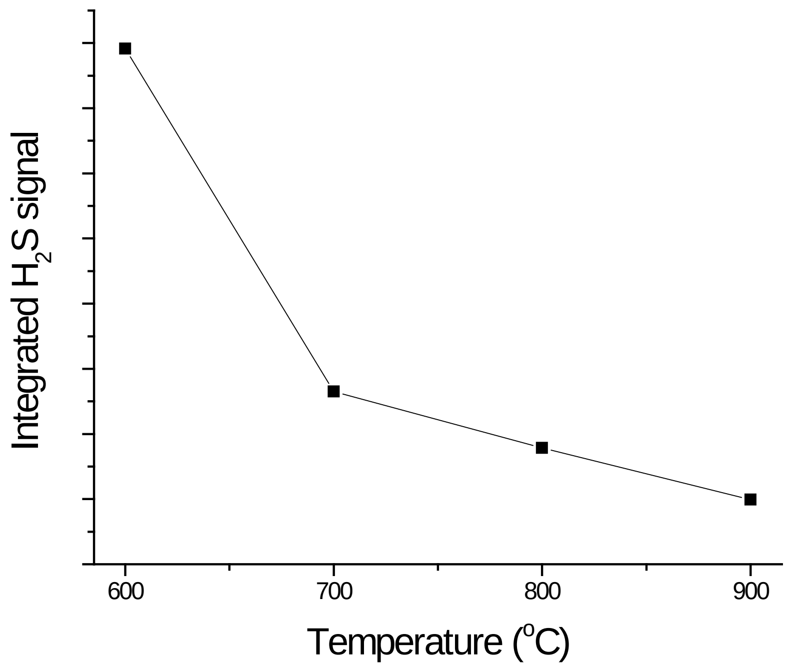




Desulfation as a function of temperature

During isothermal desulfation, the primary sulfur-containing product, H_2S, is emitted early during desulfation at 600 ºC, and this sulfur removal results in regenerated activity. Lower amounts of H_2S evolve at higher desulfation temperatures. However, removal of sulfur above 700 ºC is harmful rather than helpful.





Technical Accomplishments

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  - Explore the storage behavior of a fresh developmental catalyst sample as a function of temperature.
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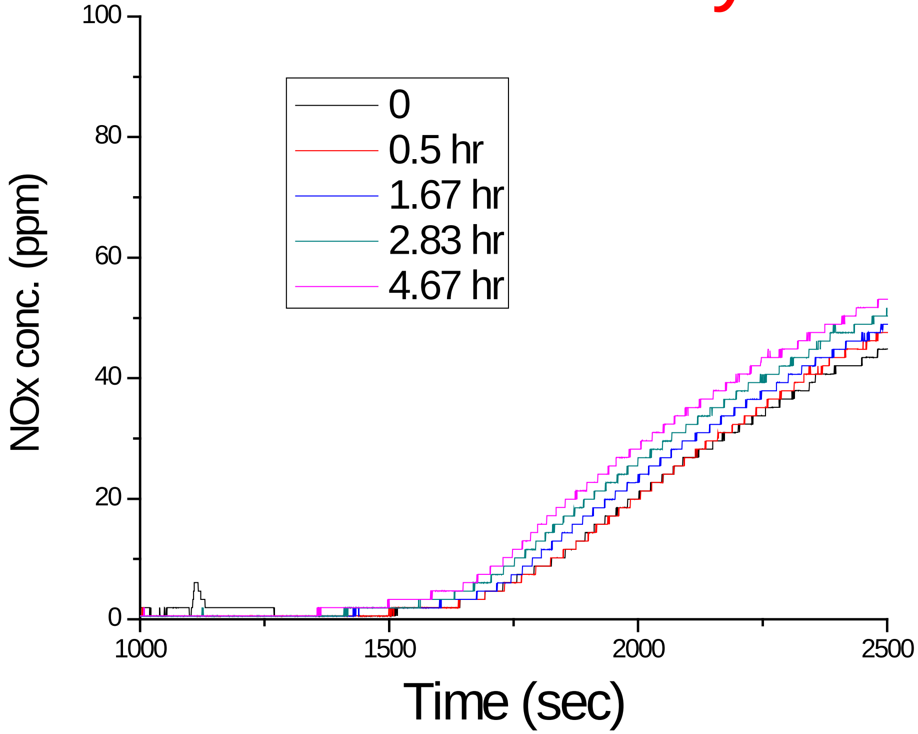
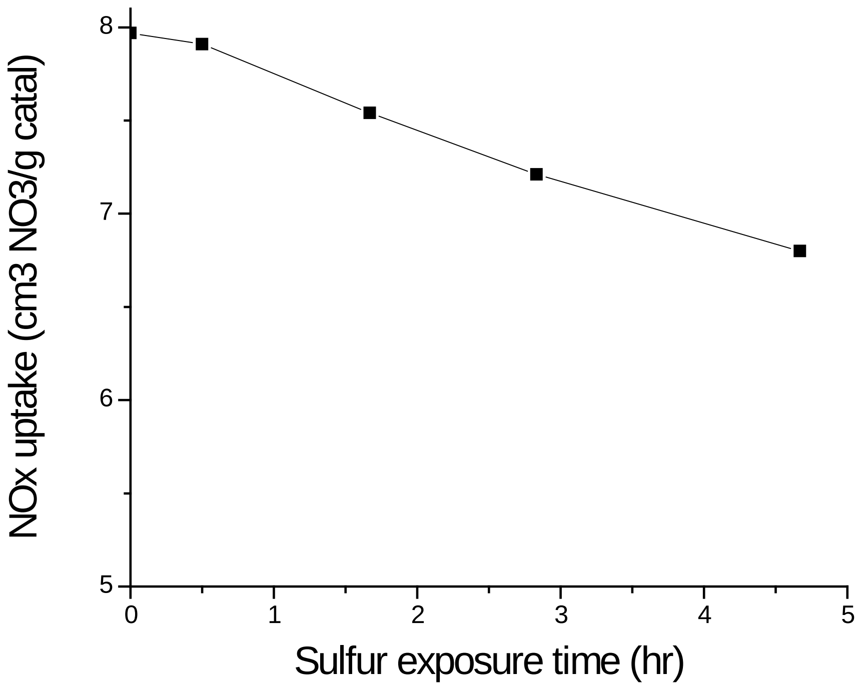
- High temperature NSR catalysts prepared by PNNL (Pt-K(10)/$MgAl_2O_4$)
  - Studies of the effects of storage elements and various supports on the NOx storage activity, are being carried out as part of PNNL's CLEERS activities.
  - Detailed studies of the deactivation mechanisms in these PNNL-prepared model high temperature NOx storage materials. These studies involve activity testing, thermal treatments, variable desulfation processing, and extensive catalyst characterization

SO_2 effects on NOx uptake for PNNL-prepared model HT-NSR catalyst material (Pt-K(10)/$MgAl_2O_4$)

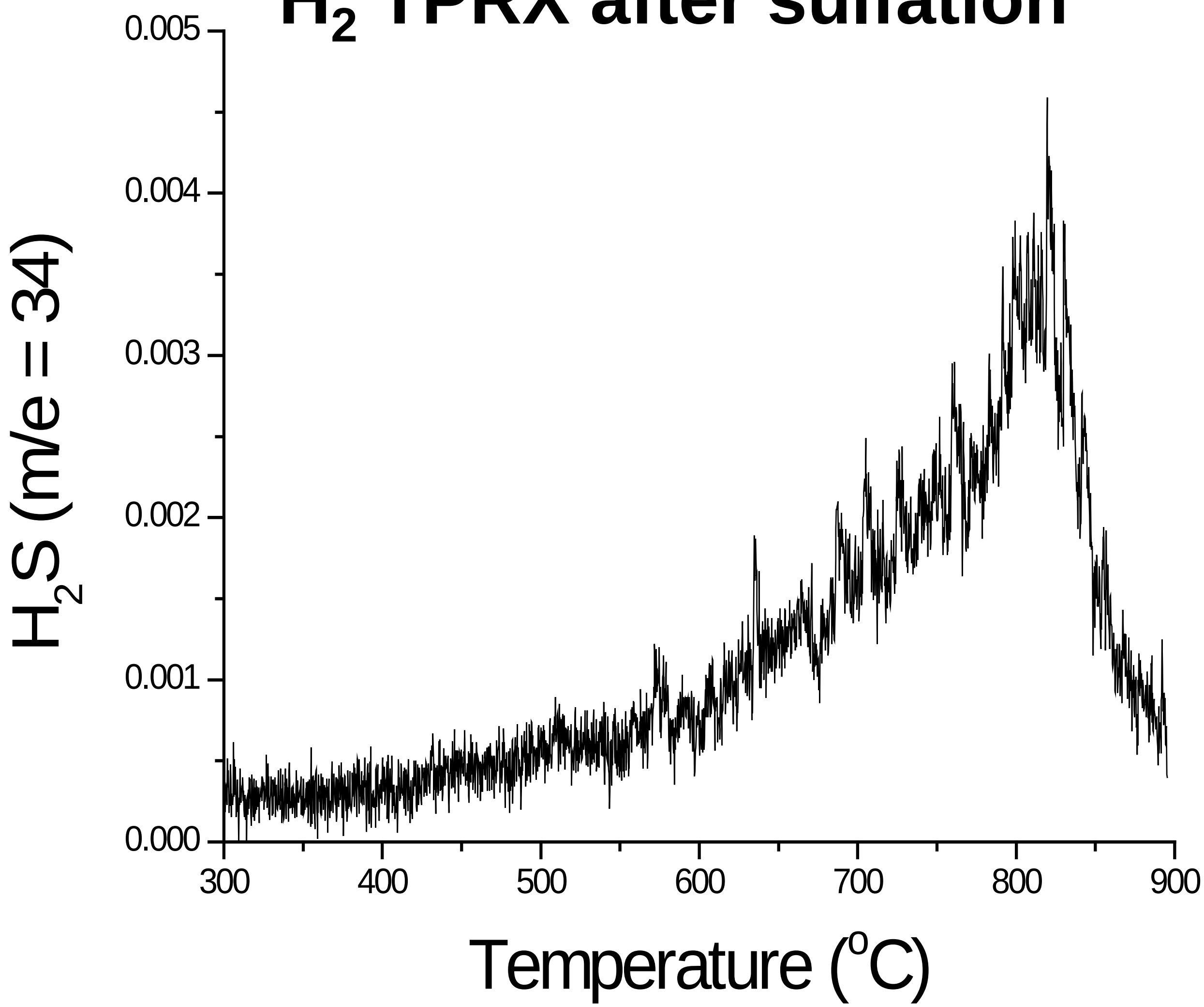




Like the sample from JM, even small exposures of SO_2 gives rise to a decrease in NOx uptake.

Desulfation Behavior:

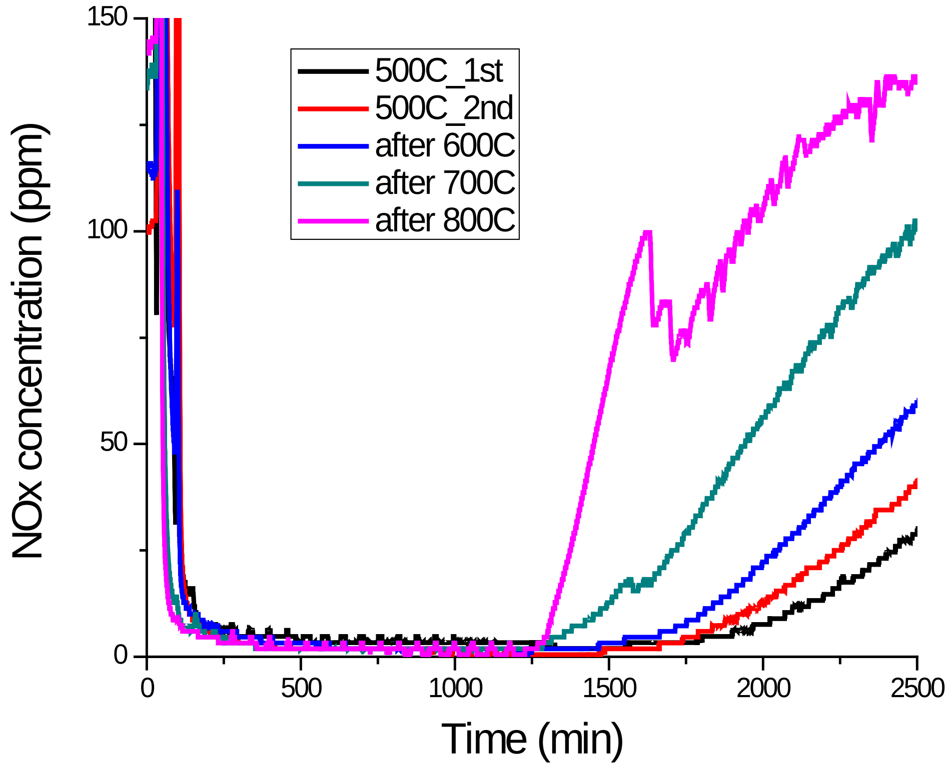
H_2 TPRX after sulfation

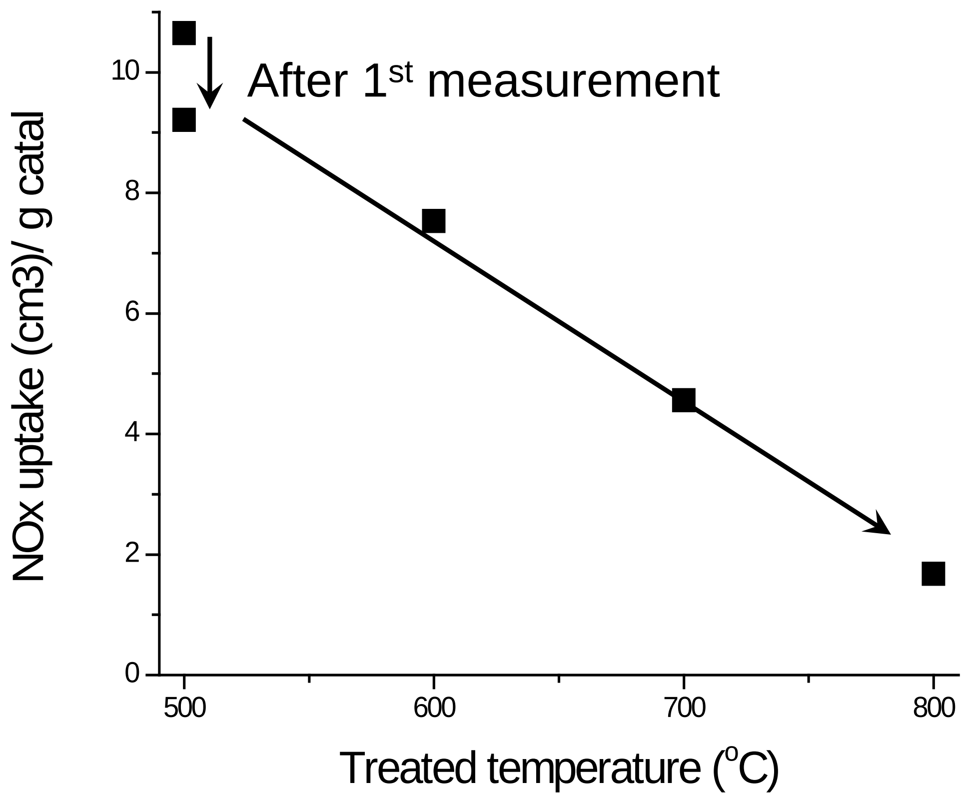


PNNL-prepared model HT-NSR catalyst material ($Pt-K(10)/MgAl_2O_4$)

H_2S begins to be formed around 500 ºC and has a maximum peak around 800 ºC, which is higher than Ba-based LNTs.

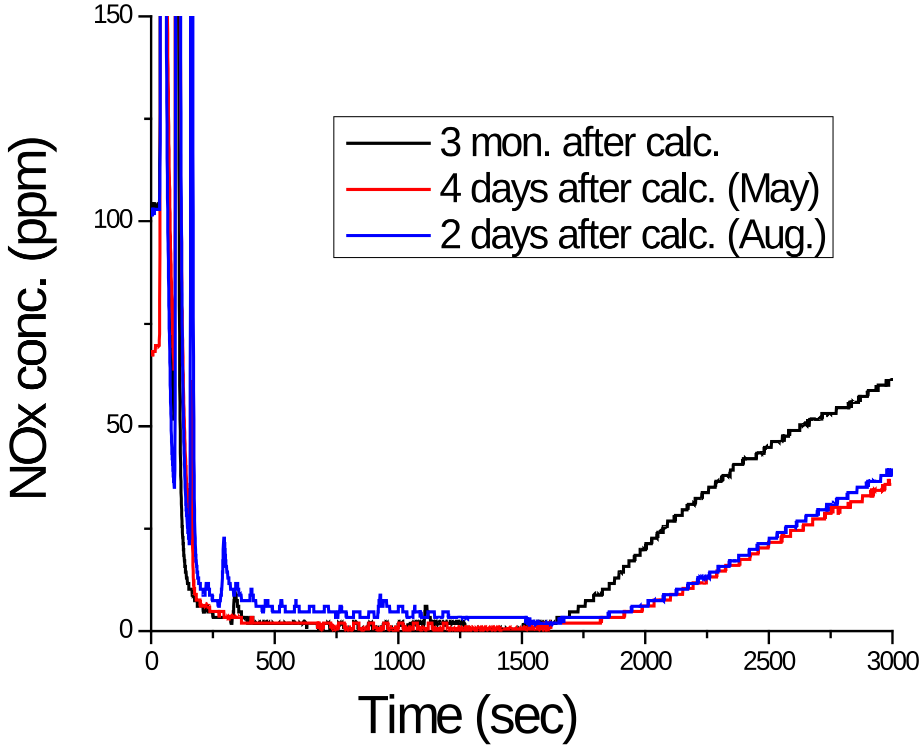
Thermal stability of model HT NSR catalyst: Activity at 500 ºC after thermal treatment at each T for 1 hr (lean)

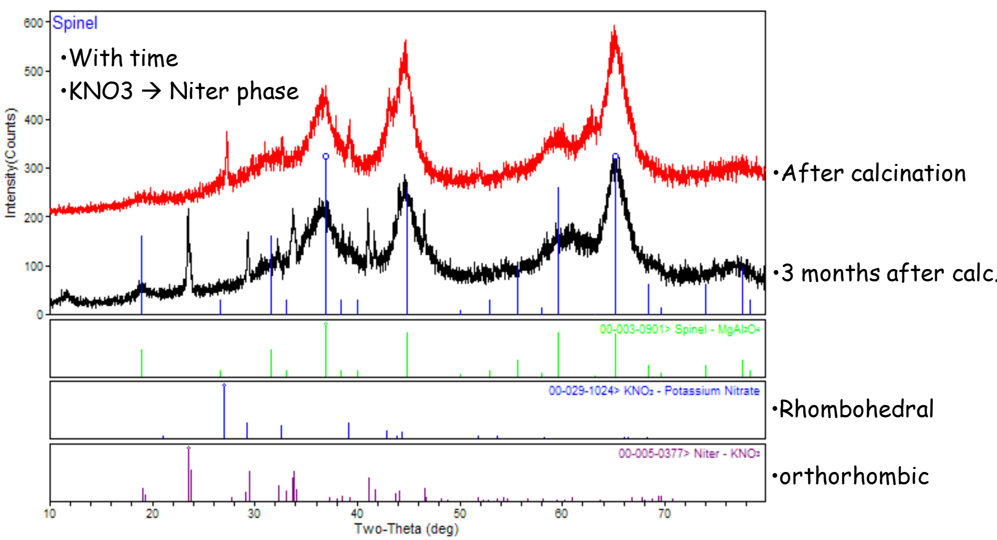




- NOx uptake begins to decrease gradually after treatment above 600 ºC.
- After treatment at 800 ºC, about 80% loss in activity.

NOx uptake change: PNNL HT-NSR Pt-K(10)/$MgAl_2O_4$ after calcination





- Sample just after calcination has higher NOx uptake.
- This result suggests that the sample is changing with time, which has a negative effect on NOx uptake.
- Some changes observed in XRD data.
- More characterization studies underway.

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Planned Future Work

1. Preparation and characterization of High temperature NSR materials at PNNL
   - Detailed comparative characterization of $K/MgAl_2O_4$ and K/Al_2O_3 catalysts after high temperature thermal treatments and sulfation/desulfation experiments.
   - Investigate support and K-loading effects with respect to nitrate and sulfate adsorption/desorption behavior at high temperatures.

2. Characterization of high temperature NSR materials supplied from JM
   - Understanding of sulfation/desulfation behavior at various sulfur loadings, and relationship of sulfur loading with thermal stability
   - Determination of optimum conditions for regeneration (sulfur removal) with minimized thermal deactivation.

Summary

- A critical need for future NSR systems will be significantly **improved higher temperature performance** and stability, since current NSR systems are not effective during high temperature system maintenance events (desulfations and/or upstream 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/$MgAl_2O_4$, as a promising model system. In addition, comparative behavior of Pt-K/Al_2O_3 is being studied. Some sulfur and high temperature aging has been observed and these are now being characterized in detail.
  - We are also evaluating proprietary HT-NSR materials supplied from JM regarding the durability issues of thermal aging and sulfation/desulfation.