

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

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Ace026

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

Timeline

- Start – July 2009
- Finish – July 2012
- 20% complete

Budget

- Total project funding
 - DOE: ~\$1,000K
 - Matched 50/50 by Cummins as per CRADA agreement
- DOE funding received in FY09:
 - \$200K

Barriers

- Discussed on next slide

Partners

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



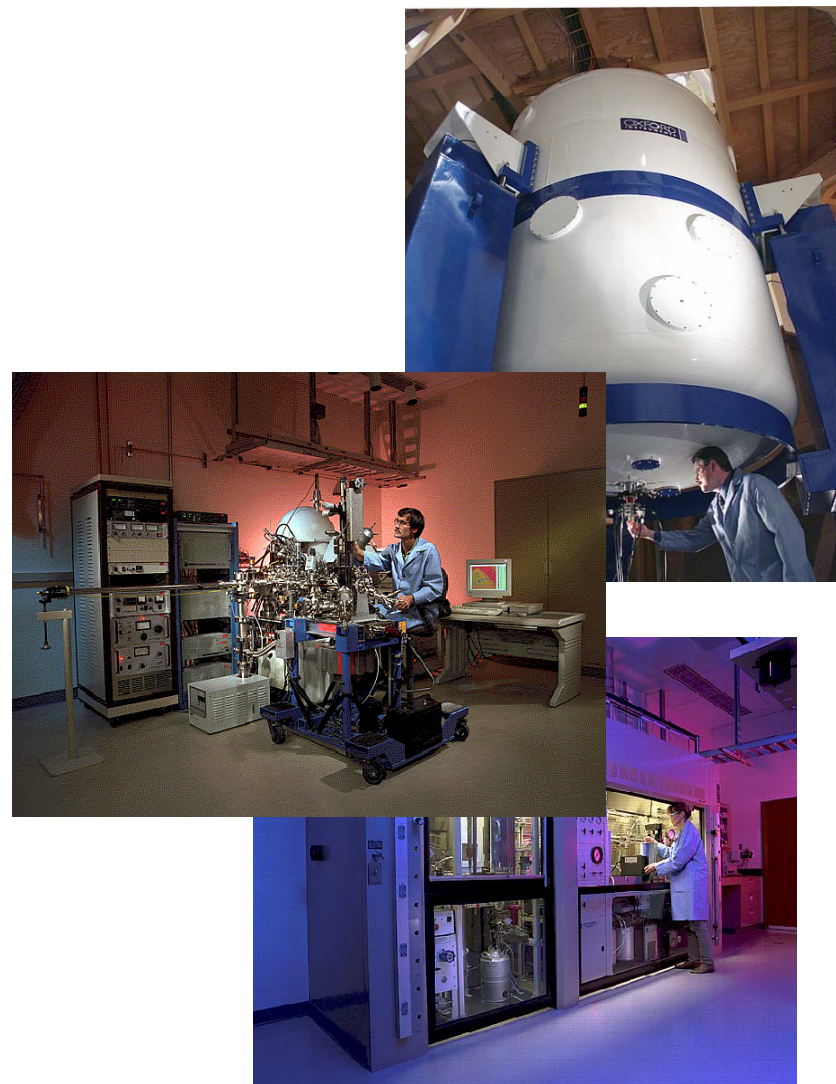
- In looking forward to 2012 and beyond with expected more stringent regulations, a critical need for future NSR systems will be significantly **improved higher temperature performance** and stability. For example, current NSR catalyst formulations are not effective for NO_x removal during high temperature system maintenance events including desulfation.
- It is important to reduce system costs by, for example, **minimizing the precious metal content** while maintaining, even improving, performance and long-term stability.

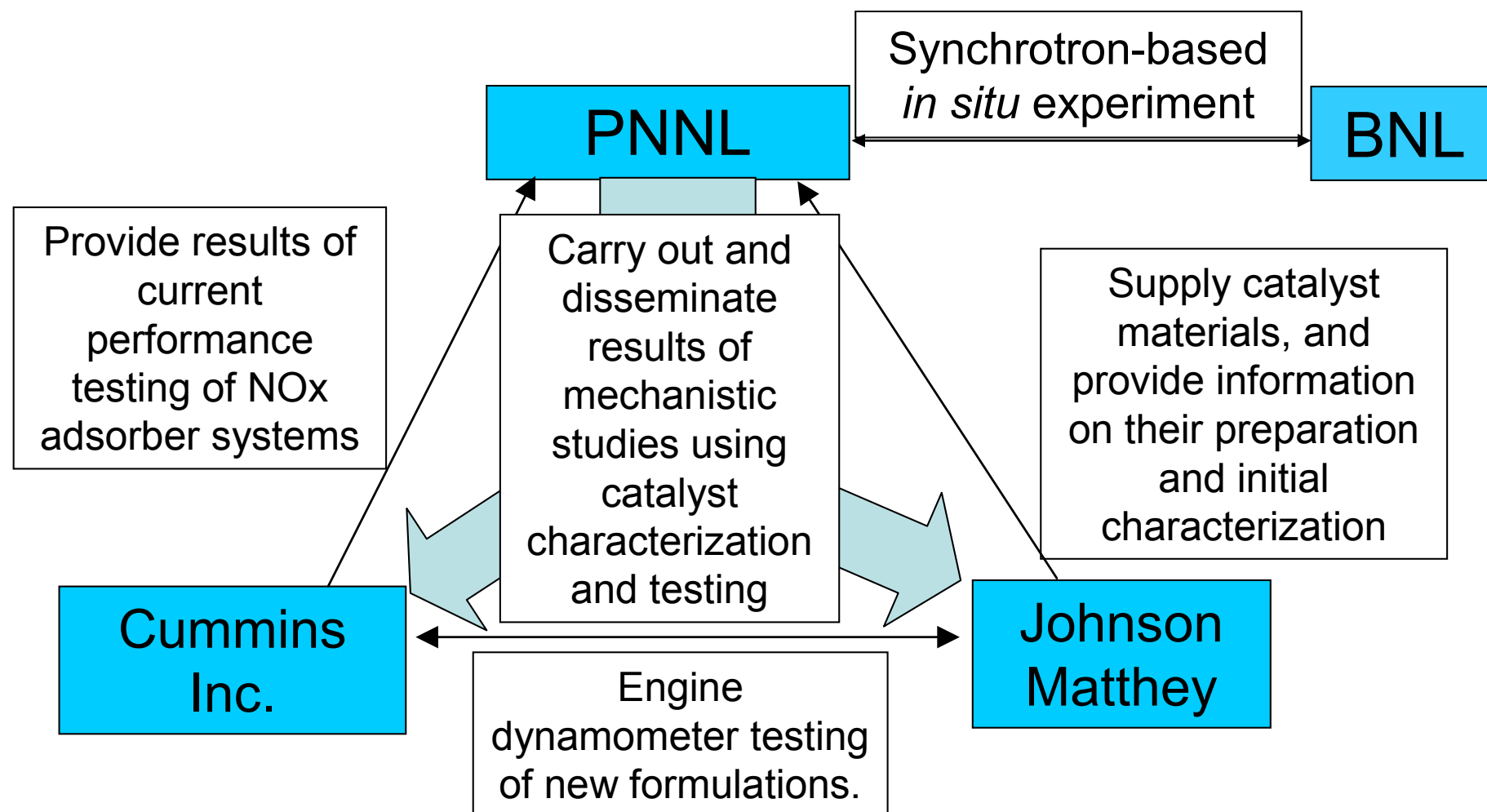
Higher Temperature Lean NO_x Performance:

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

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

- **Prepare and Process High Temperature NSR Materials**
 - **Fully formulated catalyst** has been provided by Johnson Matthey.
 - **PNNL is preparing model HT NSR catalysts**, including changes to the storage element and support material.
 - **These materials are studied:**
 - 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
 - NO₂ TPD, H₂ TPRX
 - Lab reaction systems
 - Synchrotron based techniques (XANES, EXAFS, and *in situ* time-resolved XRD)





- Conference calls are typically held once every month or two to discuss the results.
- Annual face to face CRADA review will be held in Detroit this September during the DEER meeting.

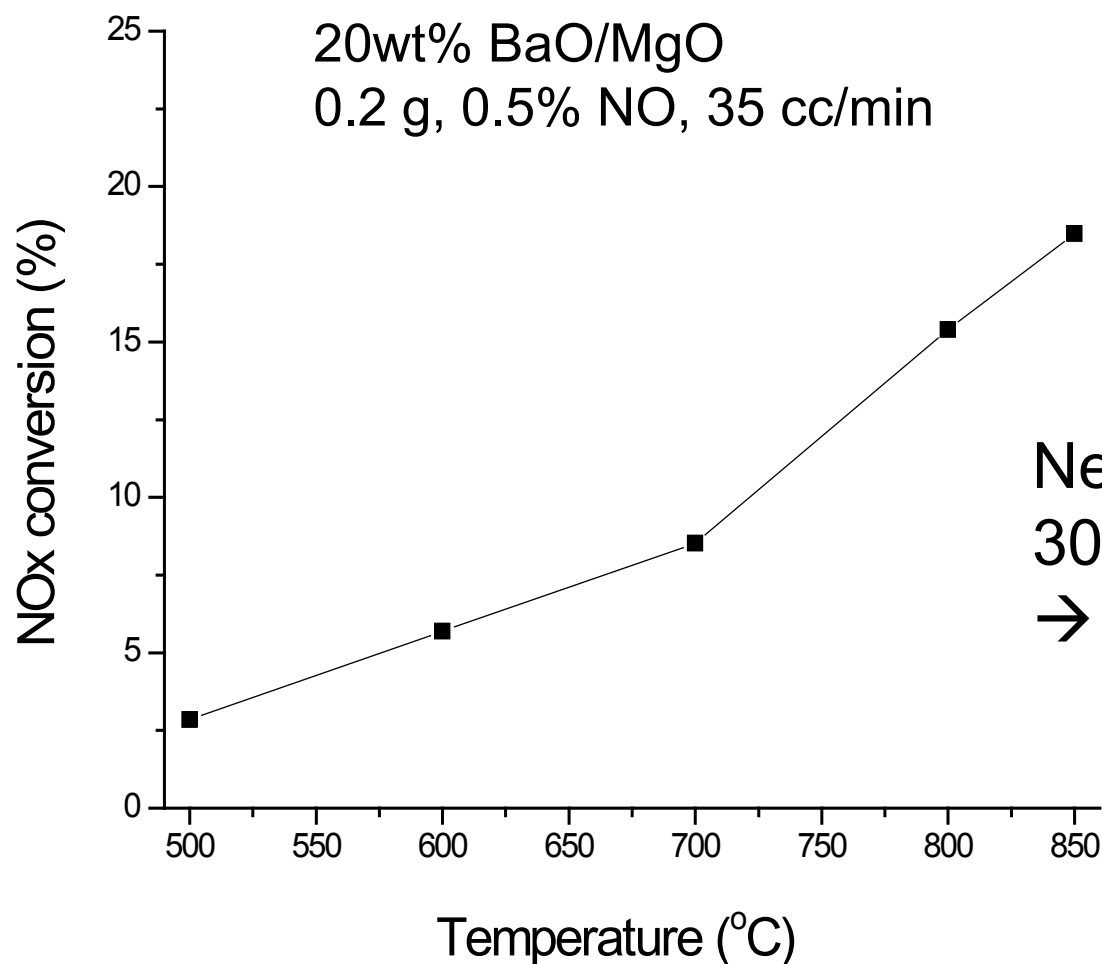
- **A quick survey of high temperature DeNOx catalysts**
 - Candidates and limitations
- **Fully formulated high temperature NSR catalysts supplied from Johnson Matthey.**
 - As a baseline for comparison with model catalysts, NSR performance of fresh samples as a function of temperature is measured.
 - The effects of thermal aging and sulfation/desulfation on the NOx storage activity of these materials is being determined.
- **High temperature NSR catalysts prepared by PNNL**
 - Examine the effects of storage elements and various supports on the NOx storage activity, while screening catalyst activity behavior.
 - Determine the mechanisms of NOx storage on the high temperature storage materials.

NO decomposition, perhaps the most ideal process for removing NO_x at high temperature, was surveyed. However, even recently reported materials were found to have impractically low activity.

catalyst	conditions	Author
BaO/MgO	1% NO, 0.2 g, 40 cc/min	Lunsford (Texas A&M)
$(\text{Gd}_{0.7}\text{Y}_{0.26}\text{Ba}_{0.04})_2\text{O}_{2.96}$	1% NO, 1g, 20 cc/min	Imanaka (Osaka)
$\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{0.8}\text{In}_{0.2}\text{O}_3$	1% NO, 1g, 20 cc/min	Ishihara (Kyushu)
$\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$	1% NO, 1g, 20 cc/min	Ishihara (Kyushu)
$\text{La}_{1.2}\text{Ba}_{0.8}\text{NiO}_4$	4%NO, 0.5g, 25 cc/min	Yuan (Heilongjiang)

- Impractical reaction condition: too low Space velocity
- Strong inhibition by O₂: not applicable for lean condition
- Quite low activity up to 700 °C
- low surface area of the mixed oxides (<10 m²/g)

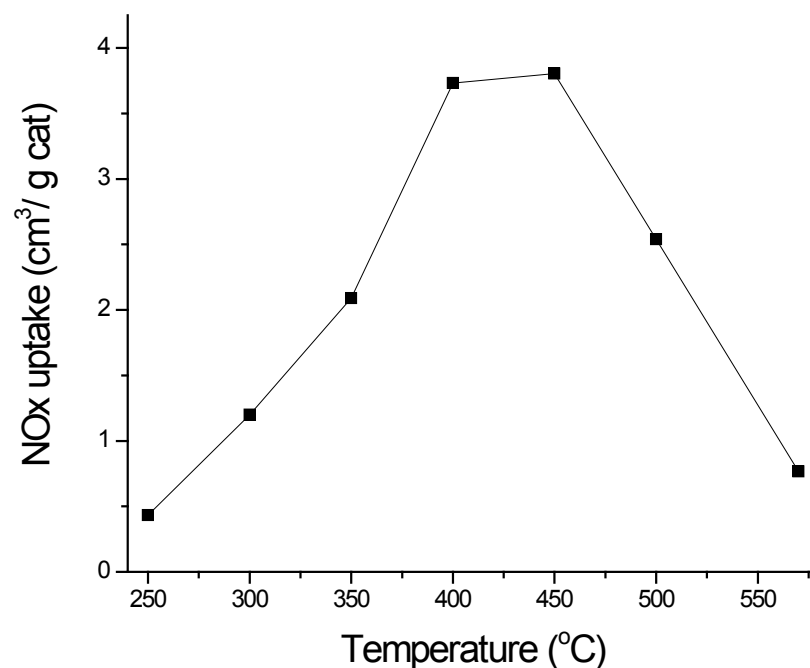
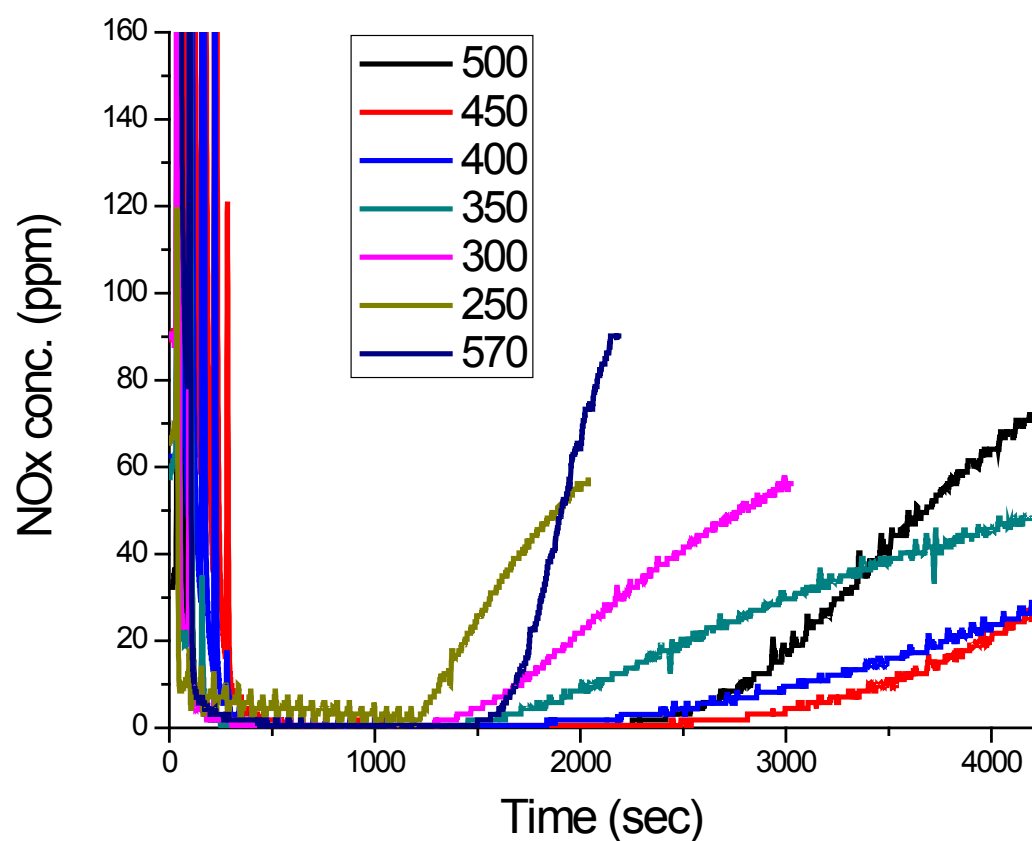
As a baseline study to compare more recently published formulations, BaO/MgO catalysts, known to have good NO decomposition activity, were studied. In fact, while these were the best materials in our hands, their performance seems too low for practical application.



Negligible activity (<2%) at high SV
300 ppm NO with 100 cc/min
→ Low intrinsic activity

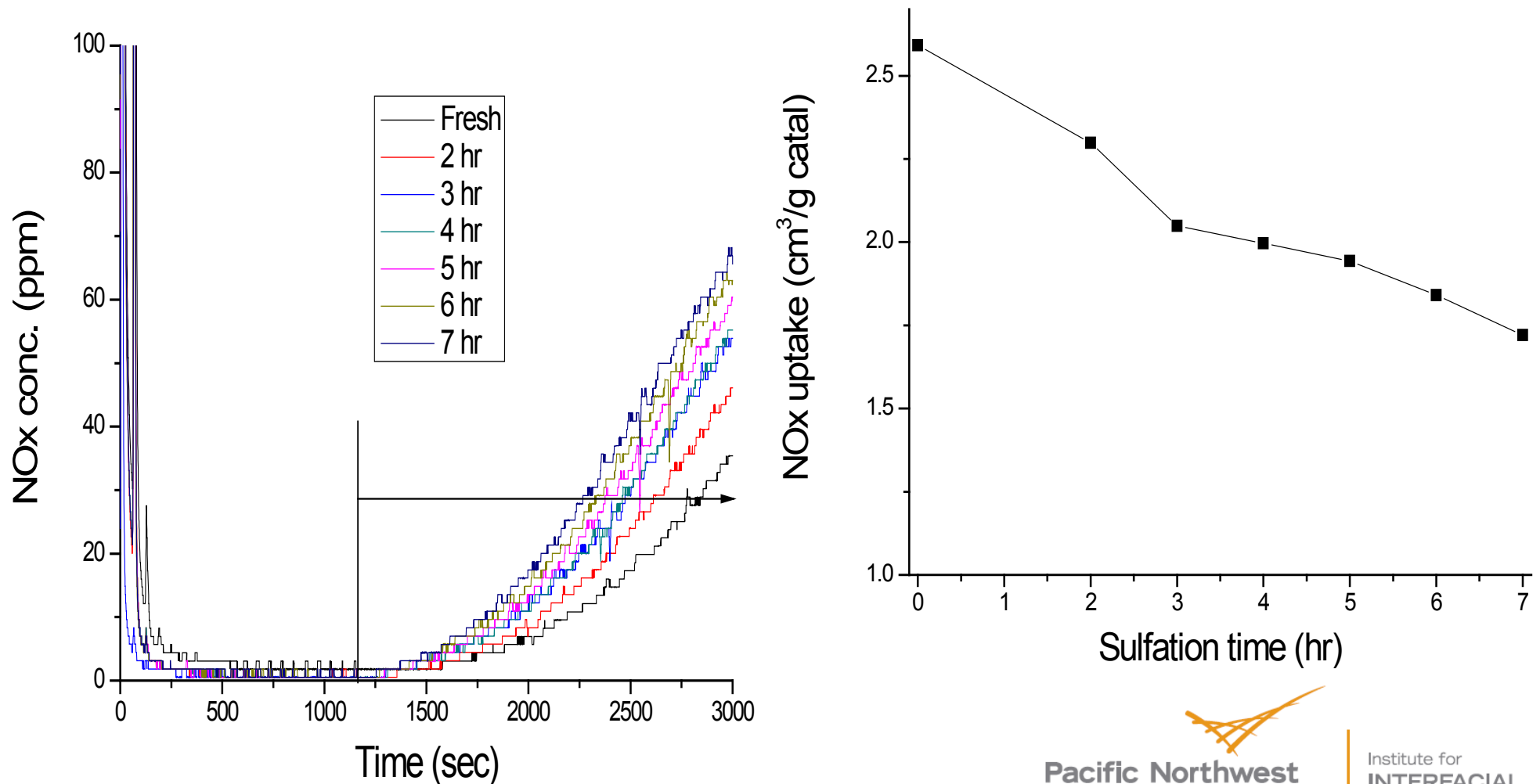
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The sample supplied from JM shows highest activities between 400 and 450 °C. The sample was also tested after aging at elevated temperatures to understand its thermal stability.

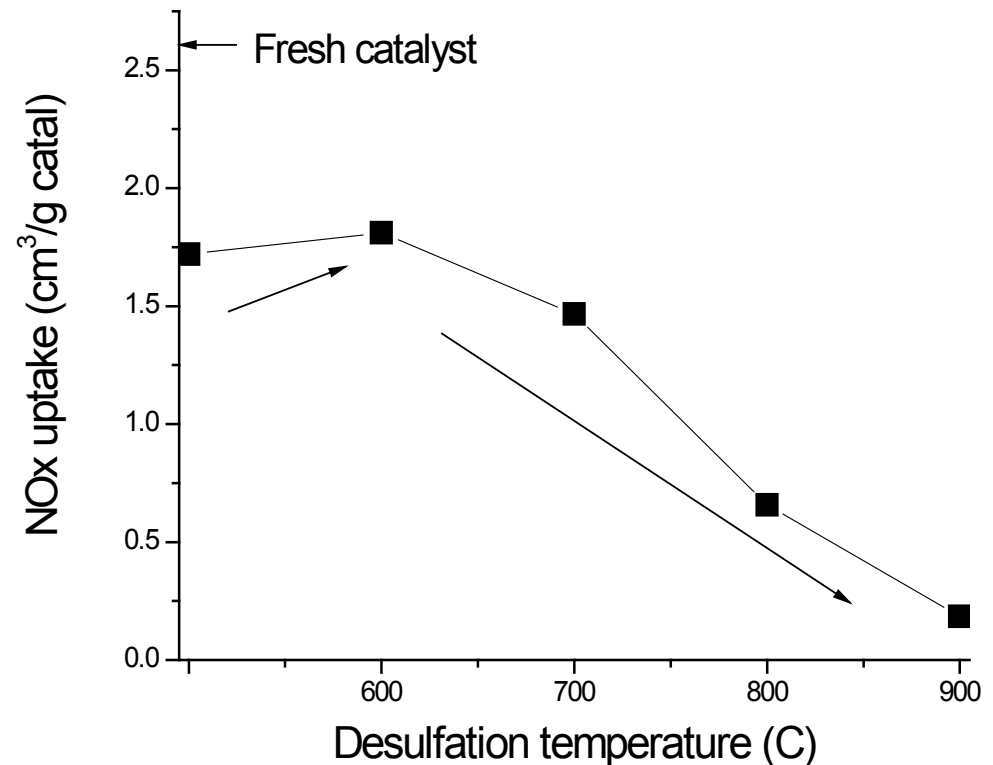
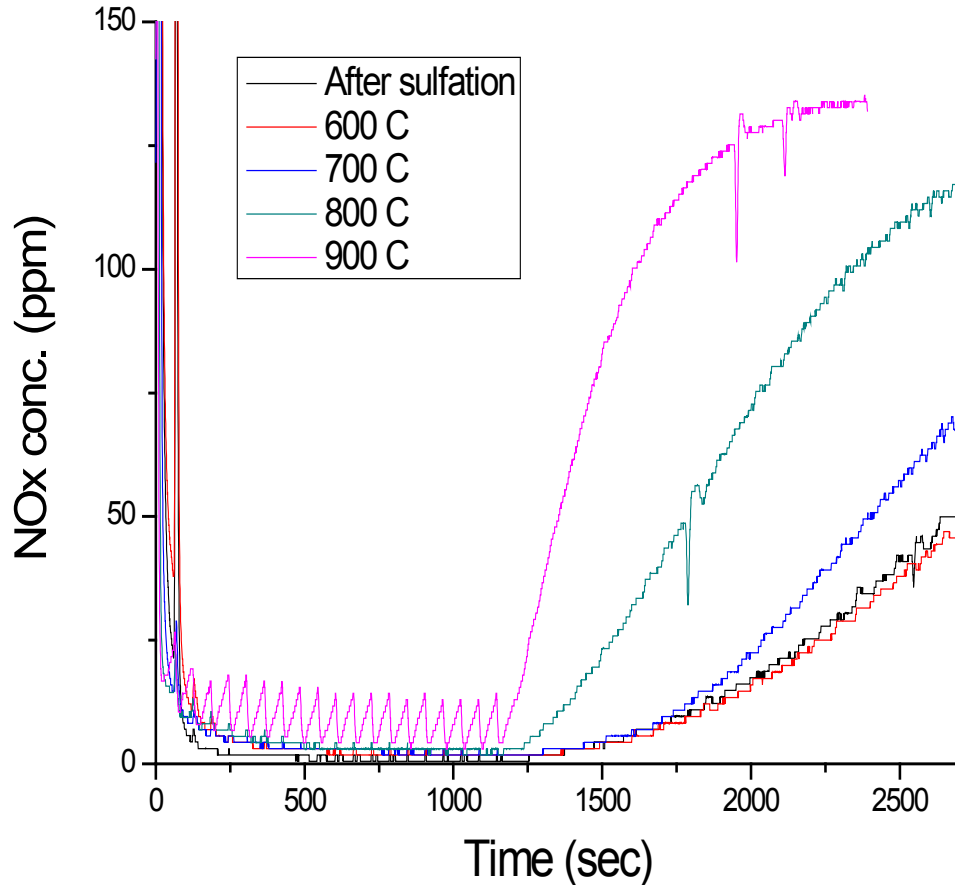


Note: NOx uptake = total NOx uptake up to the 20% of NOx conc.

The NO_x storage performance of the JM sample monotonically decreased with increasing exposure to SO₂.

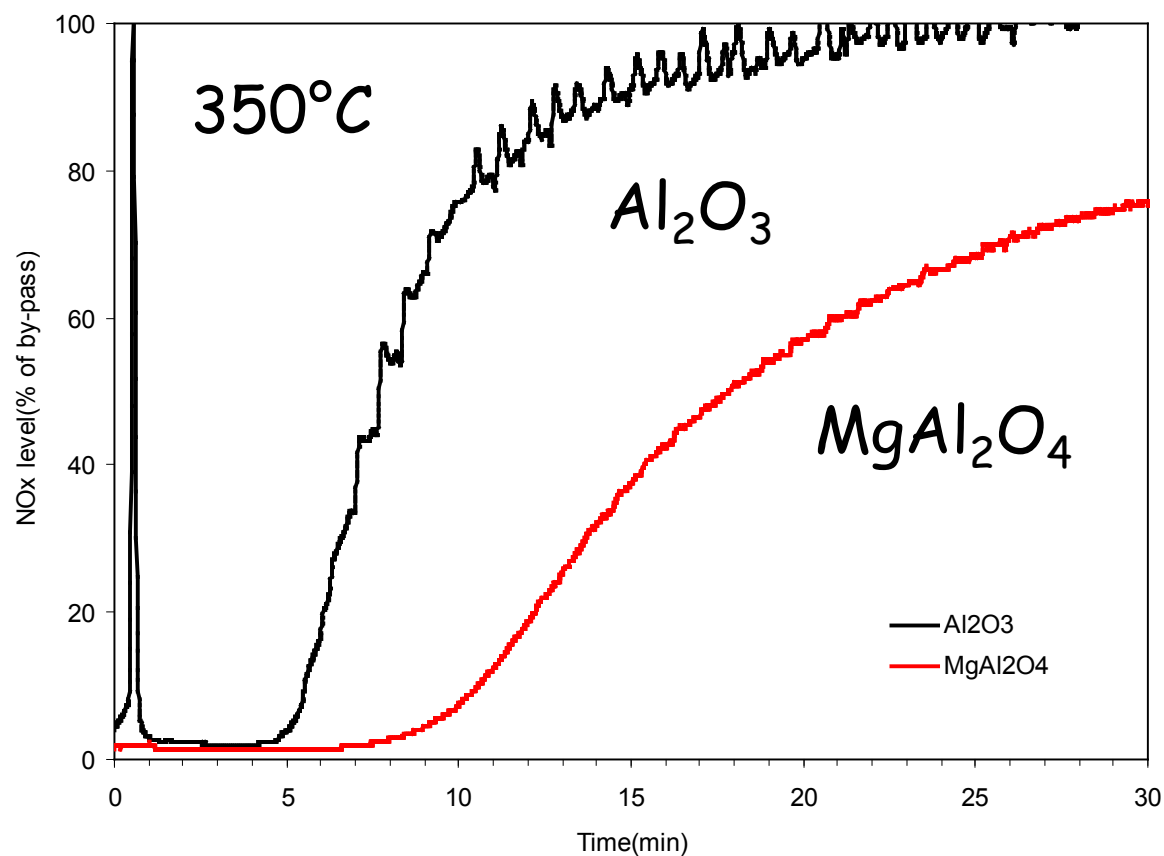
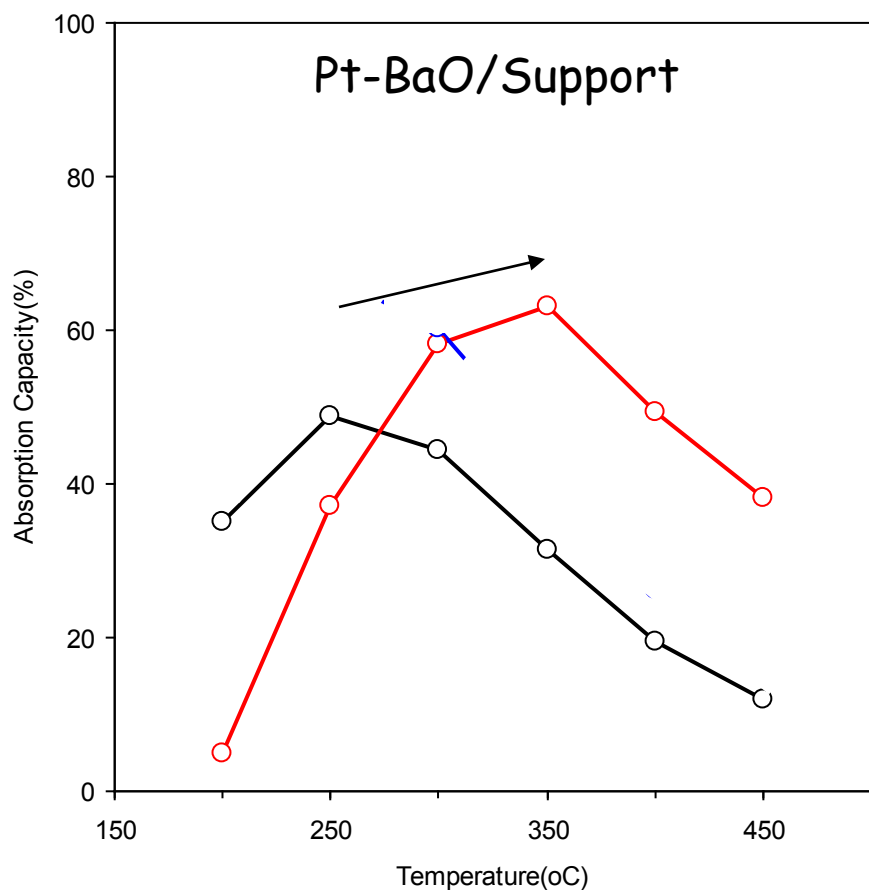


NO_x uptake increased after desulfation at 600 °C due to sulfur removal. However, performance monotonically decreased for desulfations above 700 °C due to dominant thermal aging effects. Further studies will address optimum regeneration conditions.



- **A quick survey of high temperature DeNOx catalysts**
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 - The effects of thermal aging and sulfation/desulfation on the NOx storage activity of these materials is being determined.
- **High temperature NSR catalysts prepared by PNNL (including model materials relevant to JM formulation – won't discuss these).**
 - Examine the effects of storage elements and various supports on the NOx storage activity, while screening catalyst activity behavior.
 - Determine the mechanisms of NOx storage on the high temperature storage materials.

NSR catalysts with varied storage element (K) and supports giving HT storage ability have been reported. For example, our results, shown below, indicate that NO storage ability can be improved by changing the support material from Al_2O_3 to MgAl_2O_4 .



Toyota-published high temperature NSR catalyst

Vehicle Technologies Program

Applied Catalysis B: Environmental 77 (2007) 73–78

New approach to enhance the NO_x storage performance at high temperature using basic MgAl₂O₄ spinel support

Naoki Takahashi*, Shin'ichi Matsunaga, Toshiyuki Tanaka,
Hideo Sobukawa, Hirofumi Shinjoh

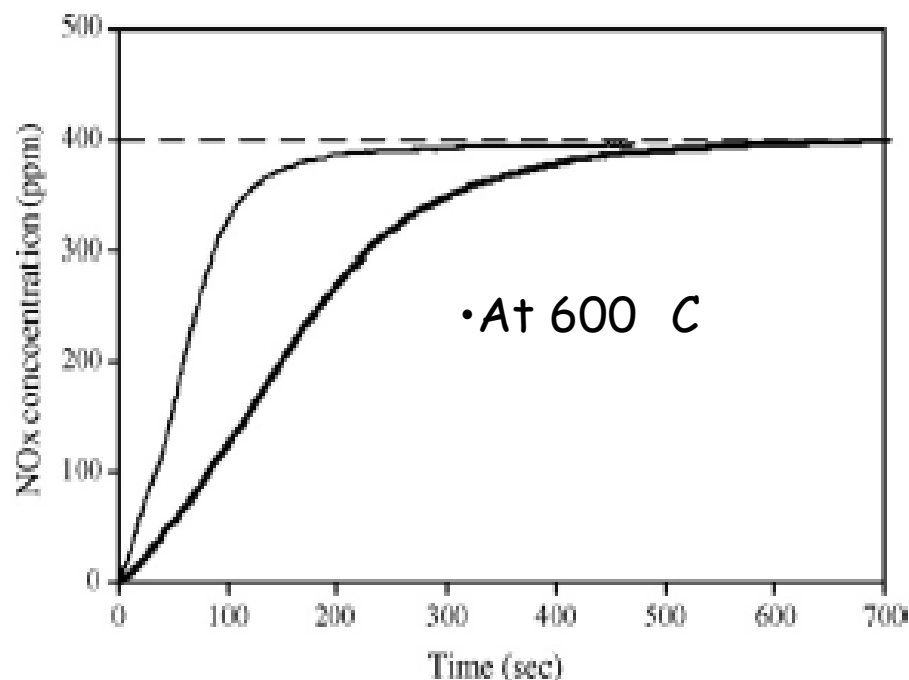


Fig. 2. NO_x concentrations in the outlet and inlet gases of the catalysts. Outlet NO_x concentration of the K/Pt/MgAl₂O₄ catalyst (—). Outlet NO_x concentration of the K/Pt/Al₂O₃ catalyst (---). Inlet NO_x concentration (— —).

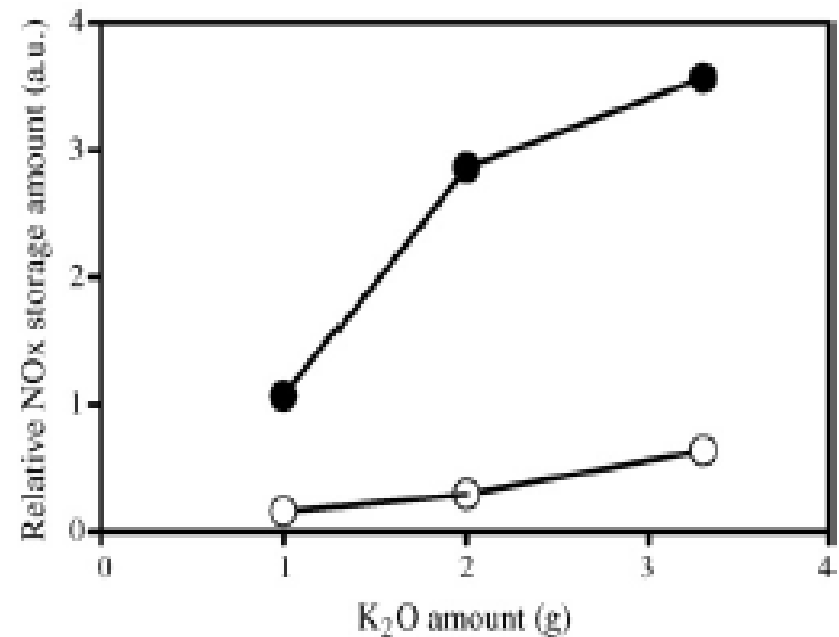
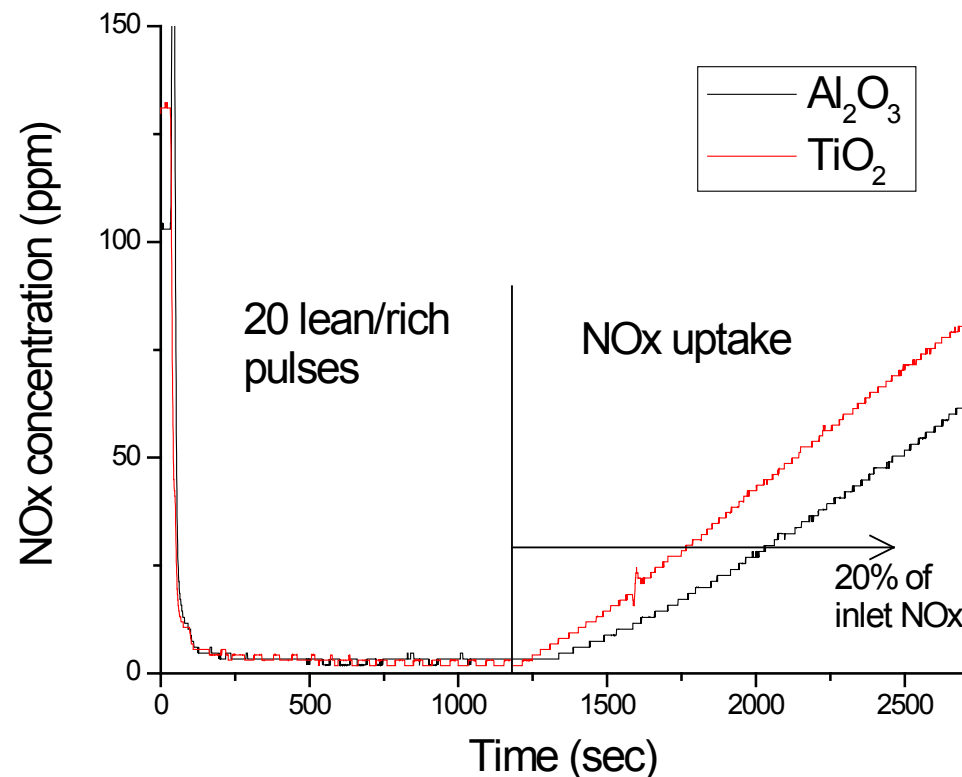
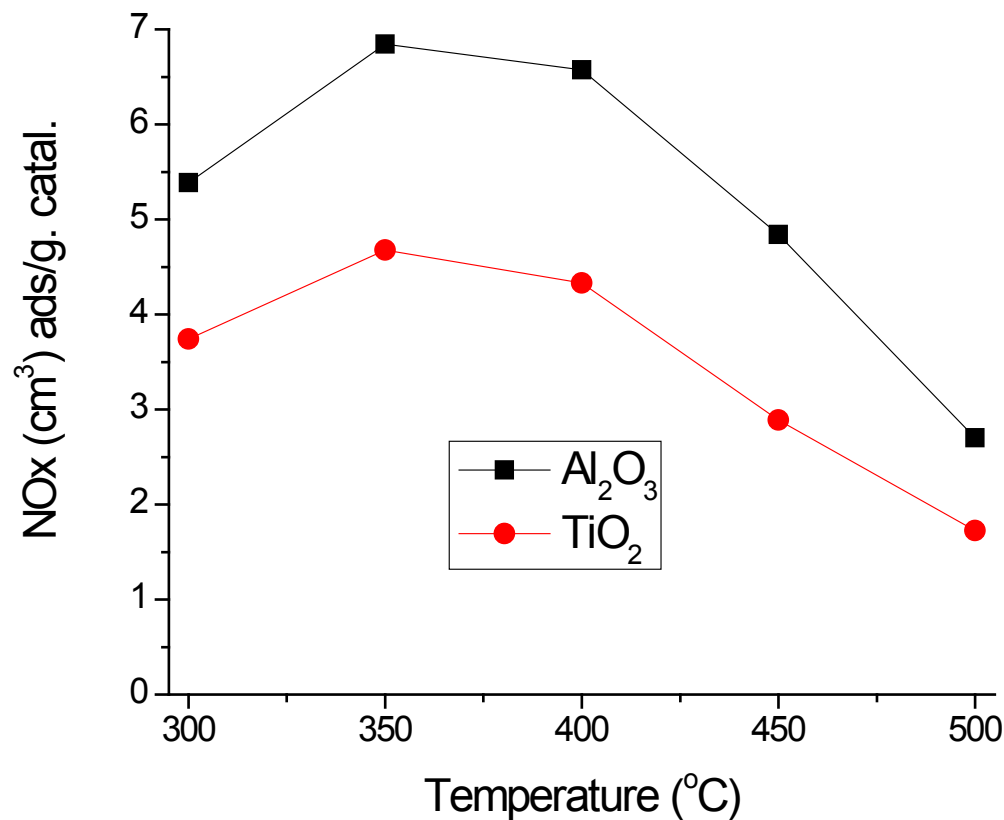


Fig. 7. NO_x storage performances of the thermally-aged K/Pt/MgAl₂O₄ and K/Pt/Al₂O₃ catalysts at 873 K vs. K₂O amount K/Pt/MgAl₂O₄ catalyst (●), K/Pt/Al₂O₃ catalyst (○).

- K/Pt/MgAl₂O₄ catalyst
- Durability (SO₂) not addressed in the paper

• Technical Accomplishments/ Progress/Results

• When K is used as a storage element, the temperature where NOx uptake is maximized shifted to 350 - 400 °C. The following graph clearly shows the importance of support material for higher NOx uptake.



• Further studies (K loading, other support, sulfur effect) are in progress.

1. Preparation and characterization of High temperature NSR materials at PNNL

- Activity measurement screening of candidate samples.
- Fundamental understanding of the behavior of K as a NO_x storage element, especially related to its mobility at high temperatures.
- Investigating NSR support effects, especially with respect to the chemistry of nitrates and sulfates at high temperature.

2. Characterization of high temperature NSR materials supplied from JM

- Providing information about thermal stability of the catalyst.
- Understanding sulfation/desulfation behavior.
- Determining optimum conditions for effective regeneration with minimized degradation.

- 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.
- PNNL's role is to prepare and characterize model NSR materials that show promise for higher temperature performance, and to provide fundamental insights into specific issues concerning HT NSR catalysts identified from Cummins' and JM's experiences during system development.
- Technical highlights from this project this year include:
 - Preparation and evaluation of candidate materials for HT DeNO_x, with a specific focus now on HT NSR catalysts.
 - Initial evaluations of HT NSR materials supplied from JM were obtained as a baseline, and durability issues of thermal aging and sulfation/desulfation are now being addressed.