CLEERS: LNT Focus Area

NOx Adsorber (Lean NOx Trap) Fundamentals
(Agreement #10049 – PNNL Project #47120)

Chuck Peden

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

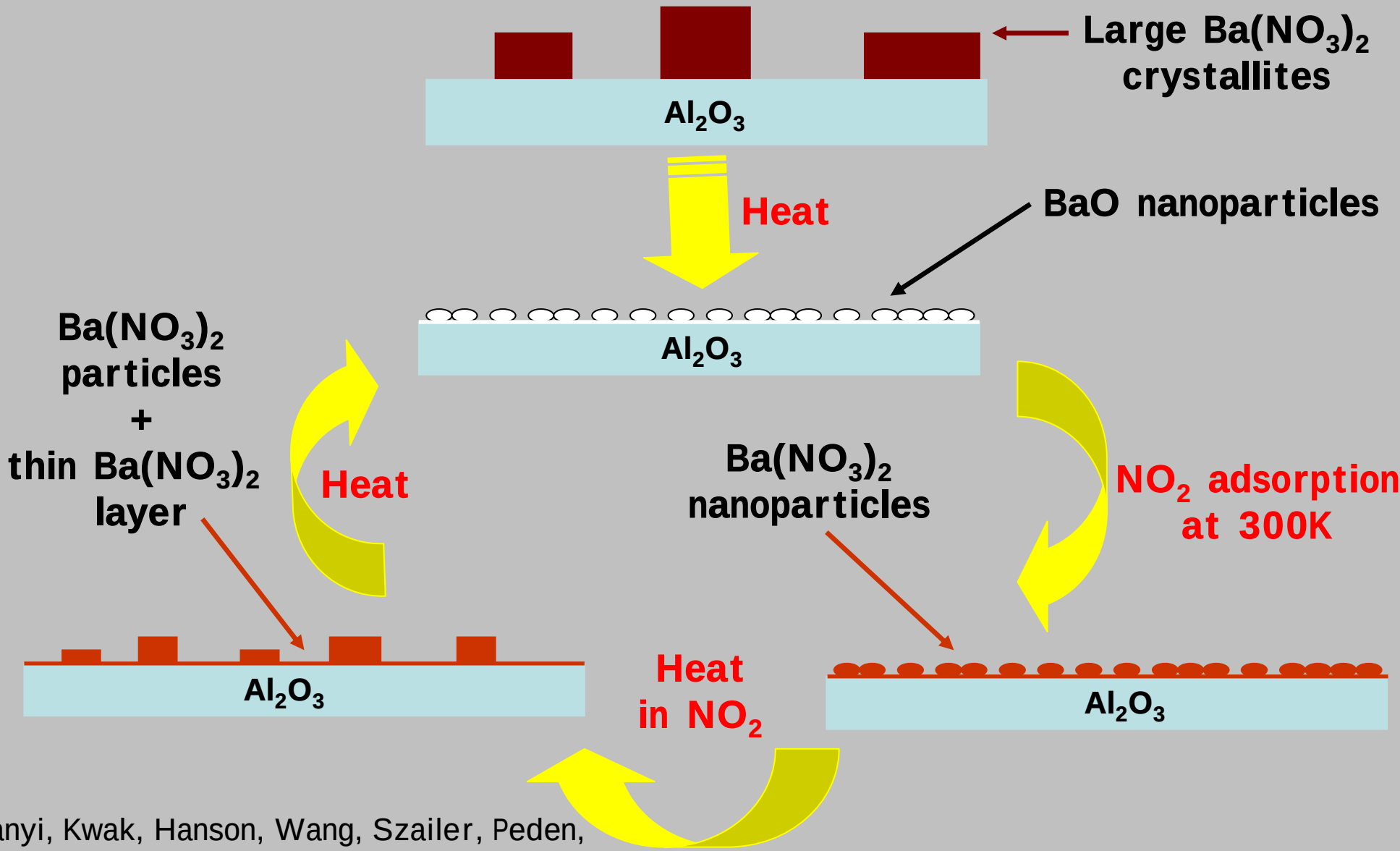
Dear Dr. Peden,

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.

Purpose of the Work - LNT

- This program element is aimed at developing a practically useful fundamental understanding of the NOx adsorber technology operation.
  - Chemical mechanisms of NOx adsorption, desorption, and reduction for inclusion in CLEERS models – emphasis this year: effect of CO_2 and H_2O on NOx adsorption, storage, and reduction.
  - Catalyst structure/function relationships – determine when catalyst structure changes are relevant for models.
    - Identify materials changes occurring during operation and chemical mechanisms of various operational processes (adsorption, desorption, catalytic reduction)
    - Effects of gas composition (CO_2, H_2O, reducing conditions) on catalyst structure changes
    - Roles of catalyst promoters (e.g., J.R. Theis, et al., "The effect of Ceria Content on the Performance of a NOx Trap", SAE 2003-01-1160)
  - On the basis of the *2007 CLEERS R&D Priorities Survey*, we have initiated some effort on lean-NOx trap materials for higher temperature operation as will be encountered in GDI applications.
- *No specific comments about this program element were received last year so there are no reviewer comments to address.*

Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' $Ba(NO_3)_2$ morphologies present. These 'phases' can be distinguished spectroscopically.



Szanyi, Kwak, Hanson, Wang, Szailer, Peden, J. Phys. Chem. B **109** (2005) 7339-7344.

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We've determined a number of practical implications of the observed Ba-phase morphologies.

- From TPD experiments, the "monolayer" morphology is found to decompose at lower temperature in vacuum and in a reducing atmosphere than "bulk" nitrates.
- "Monolayer" Ba-phase is also easier to 'de-sulfate'.
- Formation of a high-temperature (deactivating?) $BaAl_2O_4$ phase requires BaO coverages above 1 monolayer.
- Morphology model at least partially explains relatively small use of Ba species (often <20%) in storing NOx during typical lean-rich cycling.

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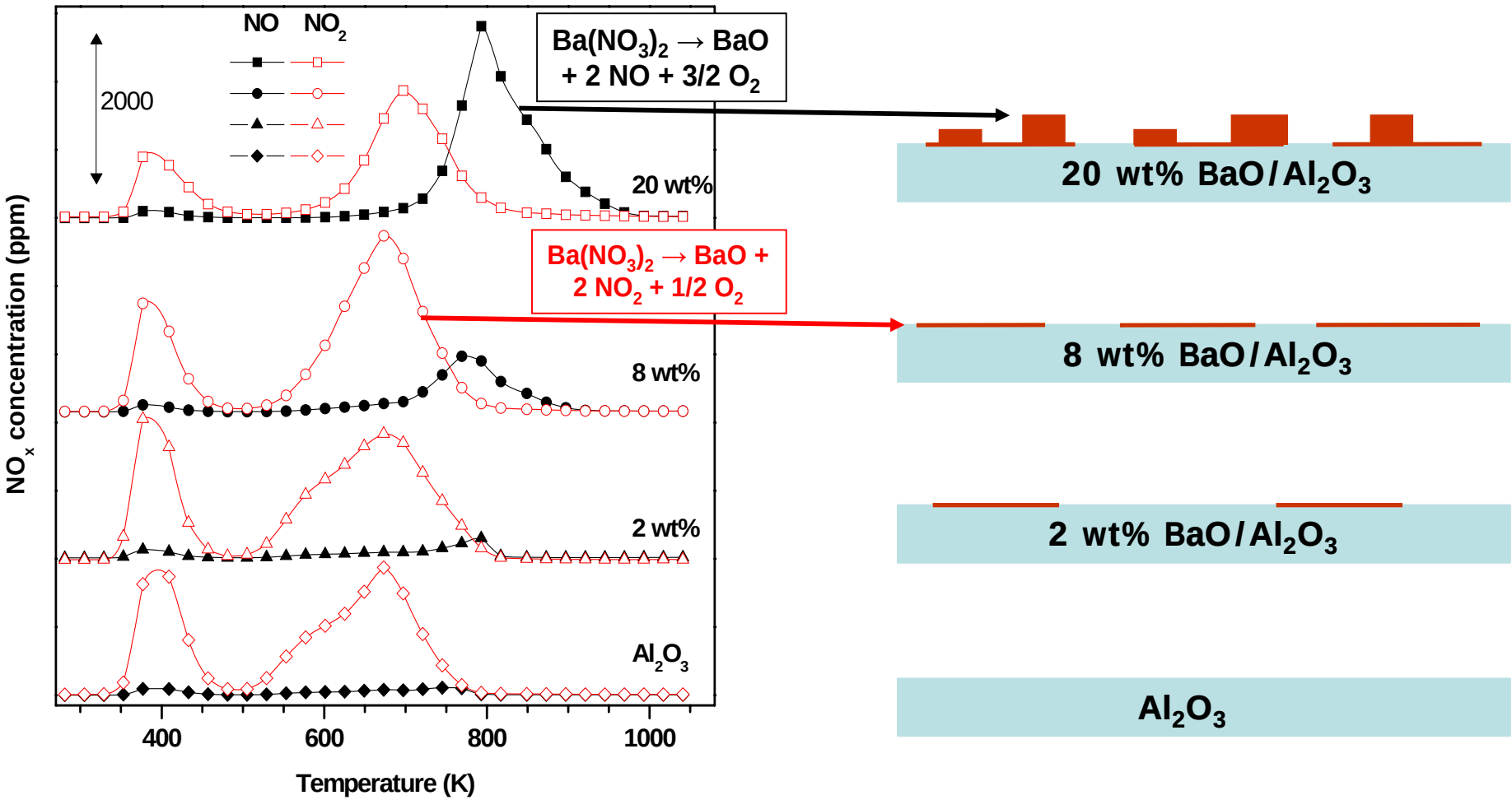
Distribution of NO and NO_2 Temperature Programmed Desorption Features are Very Sensitive to BaO Loading



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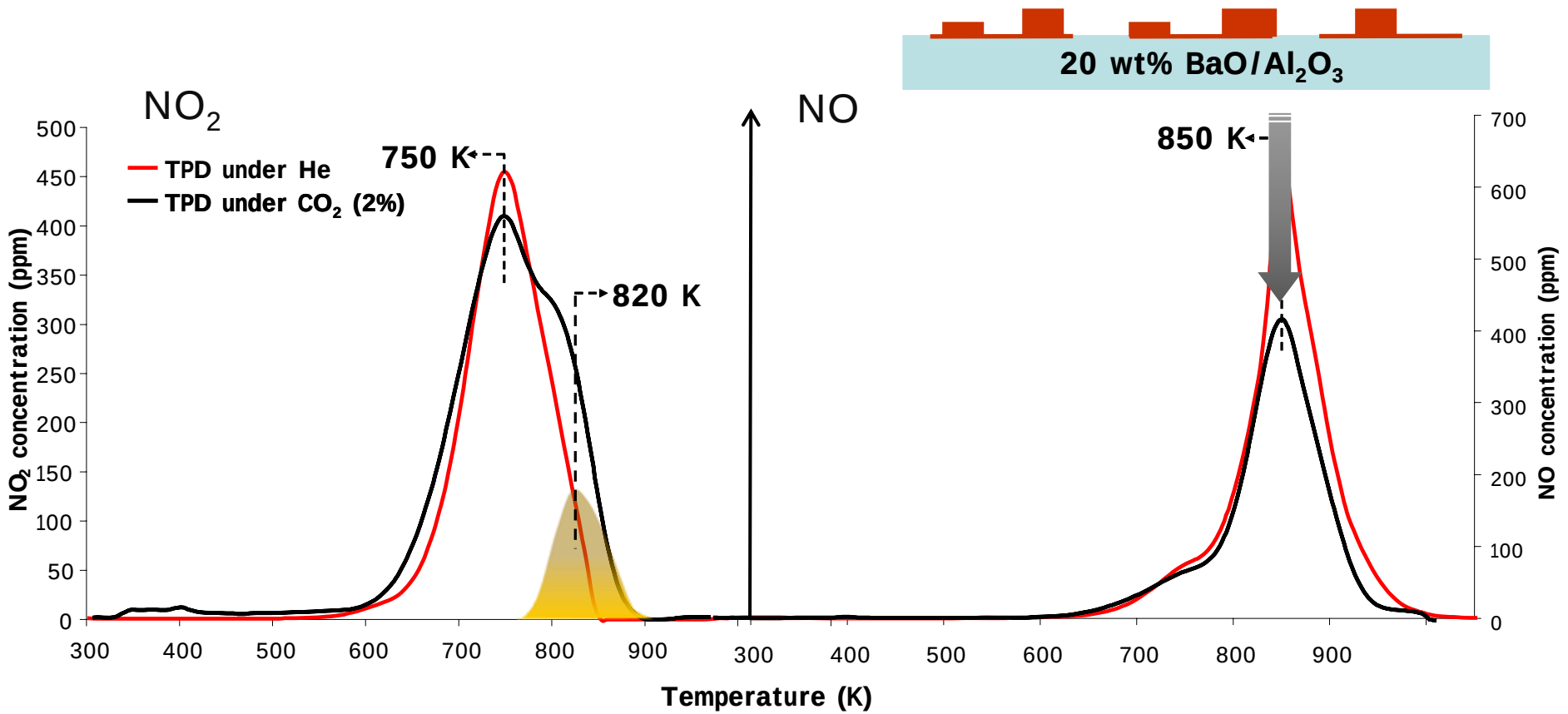
Effect of CO_2 on NOx release: TPD under CO_2 (5%) after NO_2 uptake at 300 K on $BaO(20\%)/Al_2O_3$



- Appearance of a second NO_2 desorption feature at higher temperature
- Decrease in the amount of NO release

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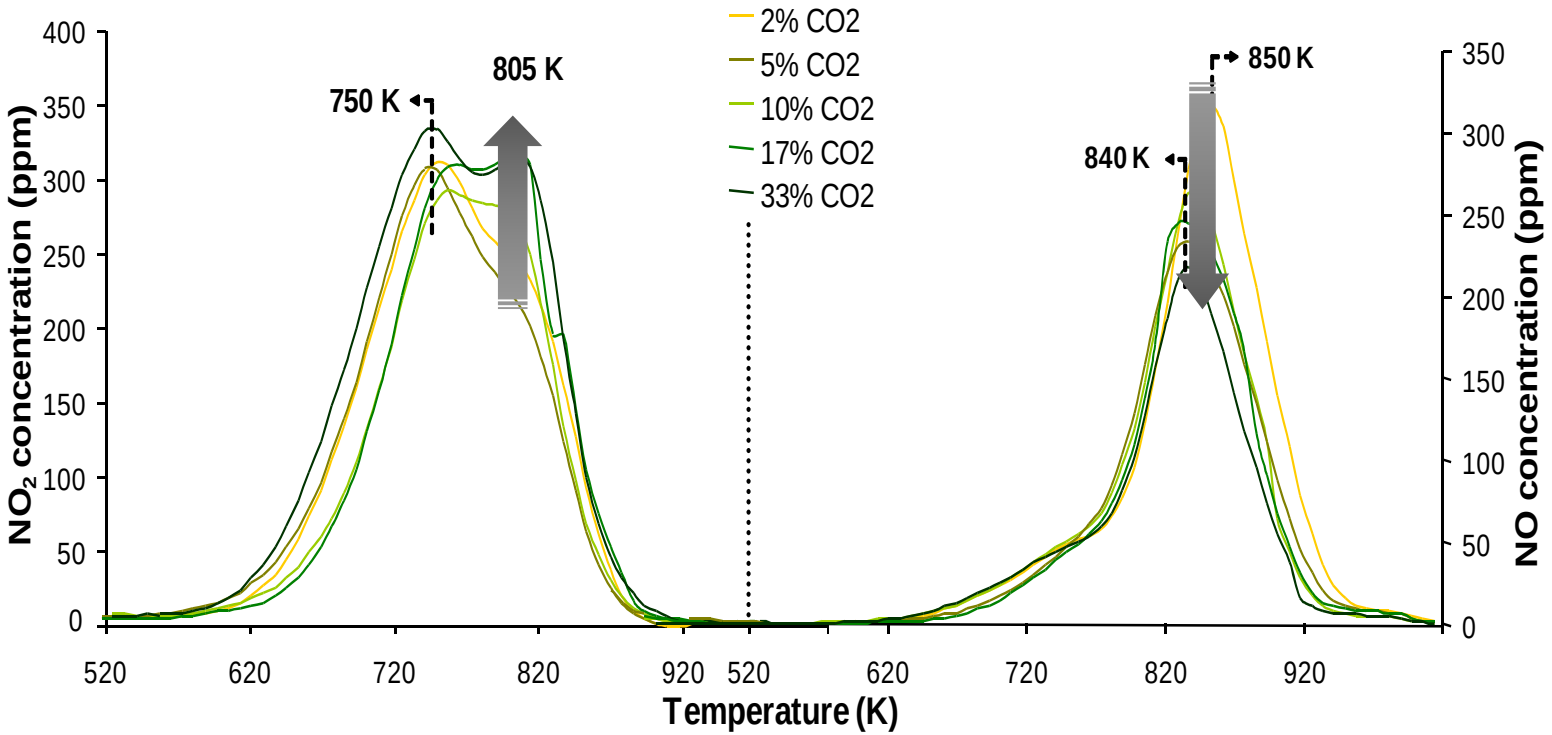
Effect of CO_2 on NOx release: TPD under CO_2 flow (2-33%) after NO_2 uptake at 300 K on (20%) BaO/Al_2O_3



CO_2 ⇗ NO ⇘

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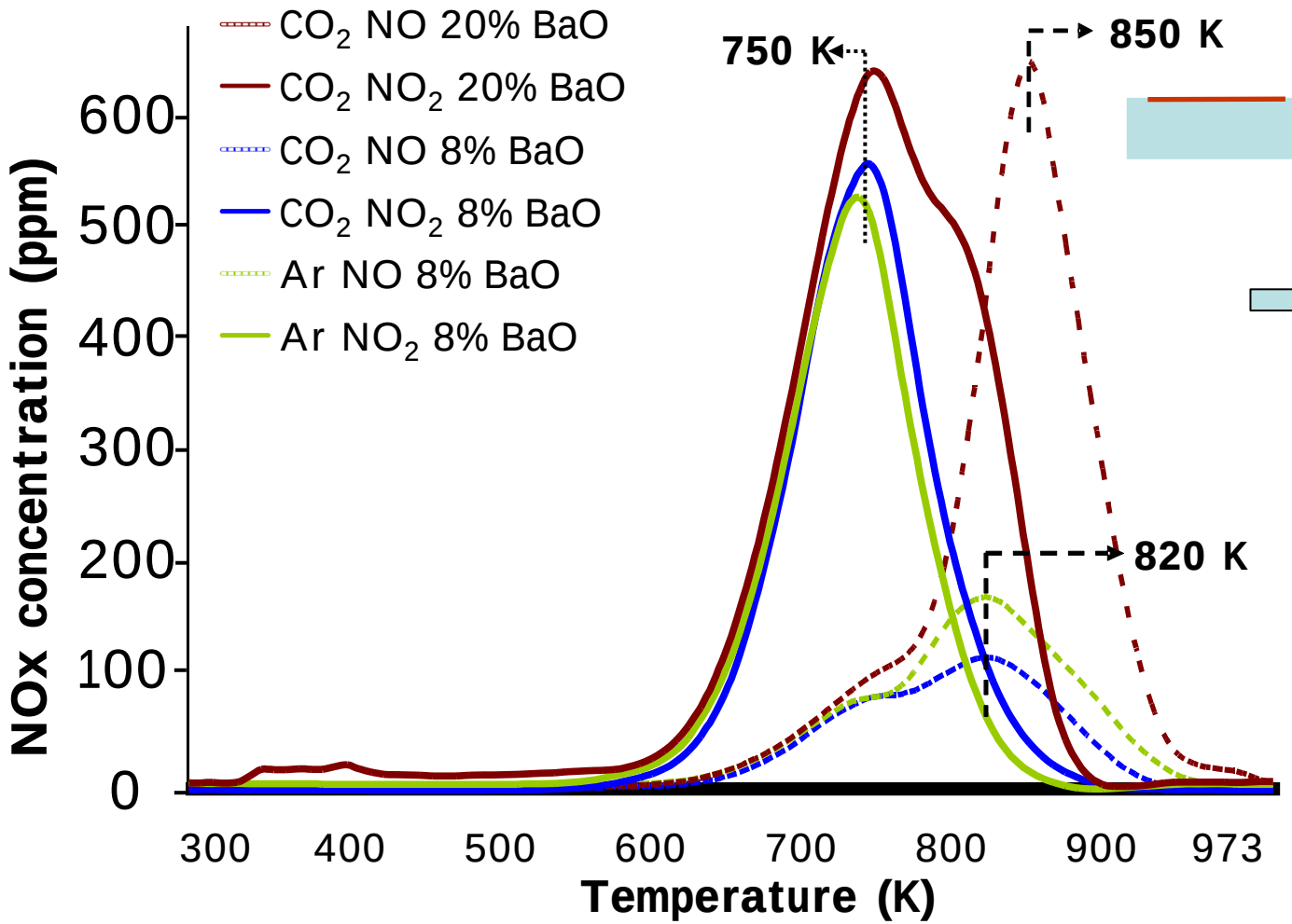
Effect of CO_2 on NOx release: TPD under CO_2 (5%) after NO_2 uptake at 300 K on $BaO(8\%)/Al_2O_3$



Only "bulk" Ba nitrates are effected by the presence of CO_2

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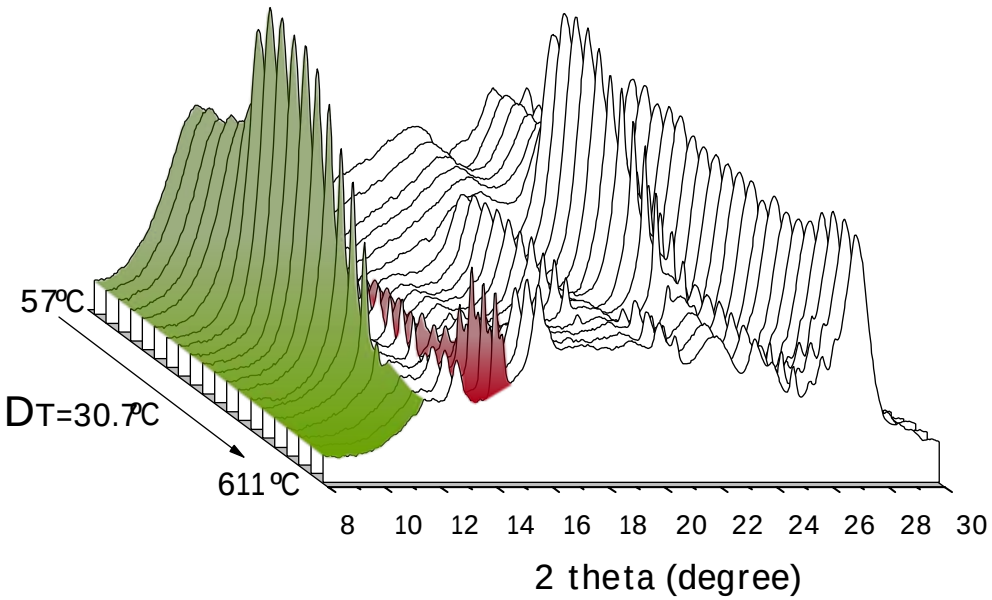
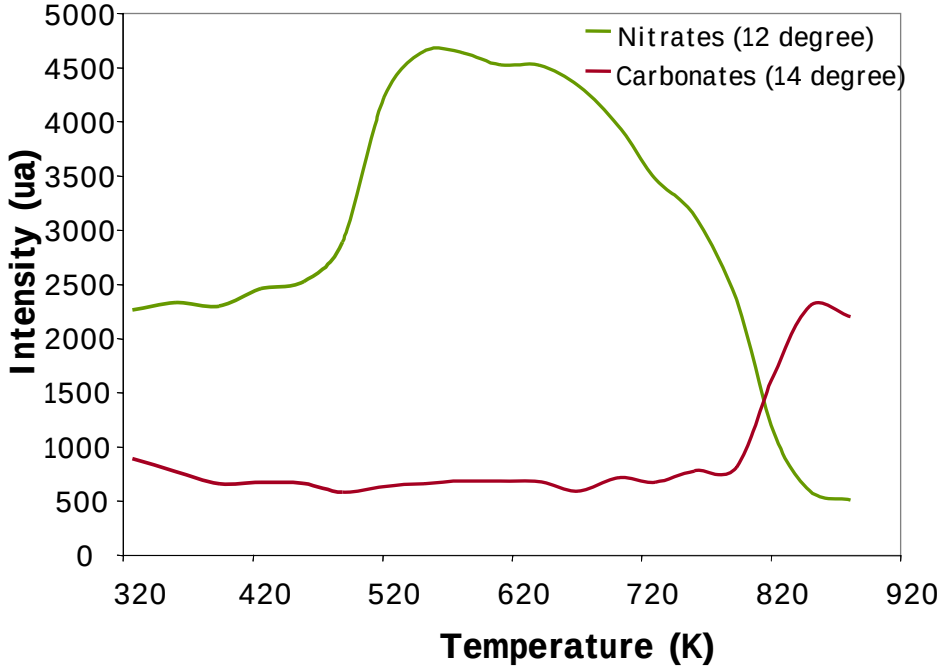
XRD Analysis: TPD under CO_2 (5% in Ar) after NO_2 uptake at 300 K on $BaO(20\%)/Al_2O_3$





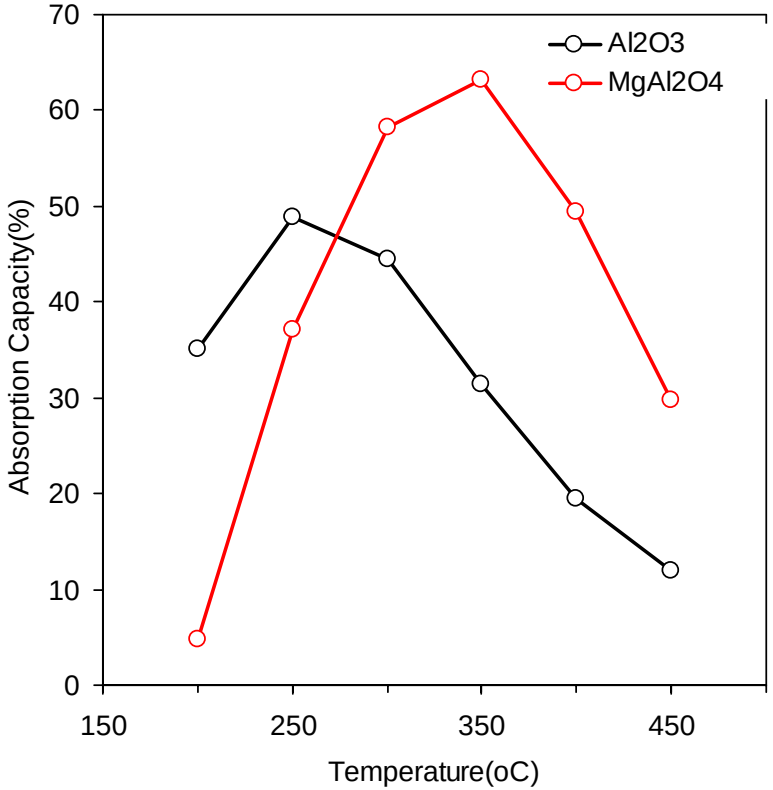
Decrease of the intensity of nitrate peak

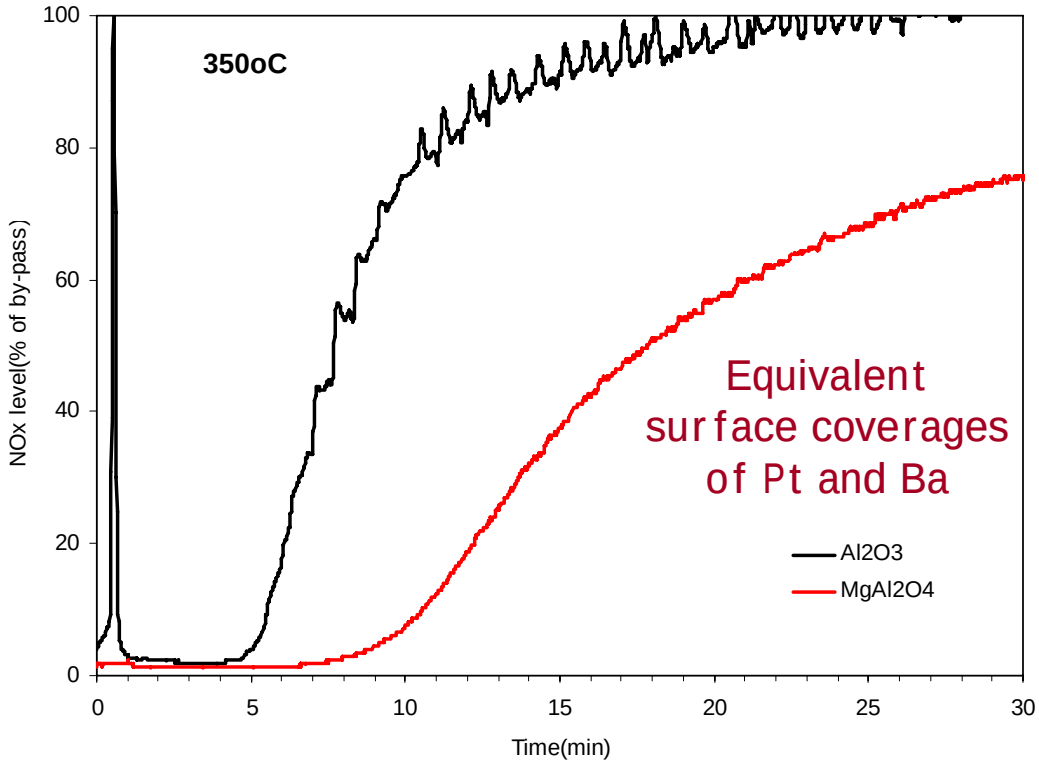
Increase of the intensity of carbonate peak

➡ Formation of bulk carbonates once all nitrate species are removed from the surface

Technical Accomplishments/ Progress/Results

We have initiated studies of LNTs that operate at higher temperatures for GDI applications.





We discovered that supporting BaO on $MgAl_2O_4$ produced much more active materials at higher temperatures.

Technical Accomplishments/ Progress/Results

Recently published work from Toyota demonstrate that $MgAl_2O_4$ is also an improved support material for K-based LNTs.

Takahashi, et al., Toyota, Appl. Cat. B **77** (2007) 73-78.

New approach to enhance the NO*x* storage performance at high temperature using basic $MgAl_2O_4$ spinel support

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

TOYOTA Central Research & Development Labs., Inc., Nagakute, Aichi 480-1192, Japan

Received 12 July 2006; received in revised form 7 July 2007; accepted 9 July 2007
Available online 13 July 2007

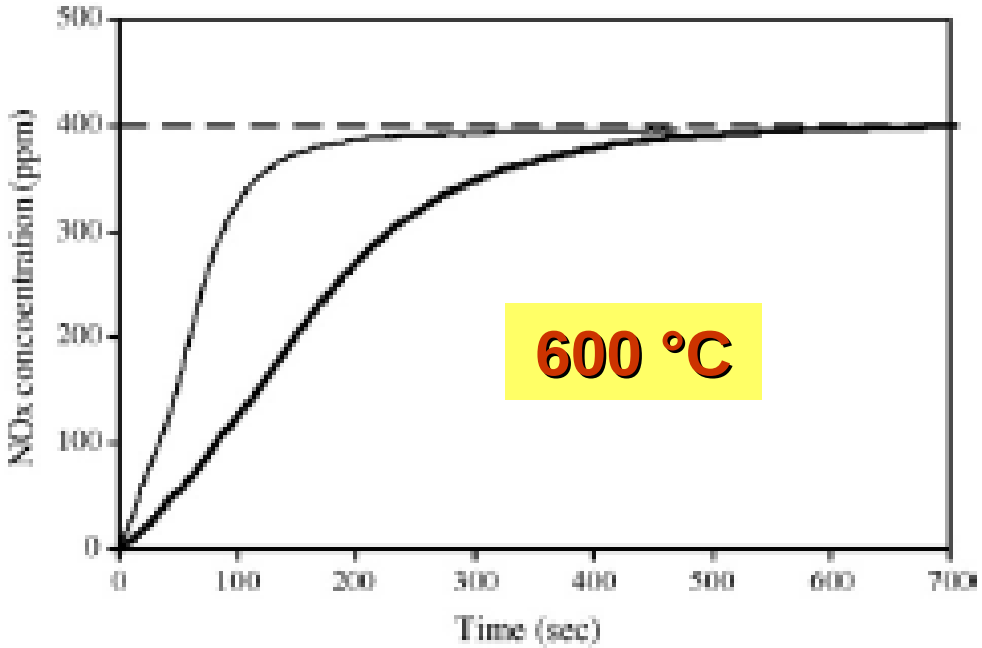


Fig. 2. NOx concentrations in the outlet and inlet gases of the catalysts. Outlet NOx concentration of the $K/Pt/MgAl_2O_4$ catalyst (——). Outlet NOx concentration of the $K/Pt/Al_2O_3$ catalyst (—). Inlet NOx concentration (— —).

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

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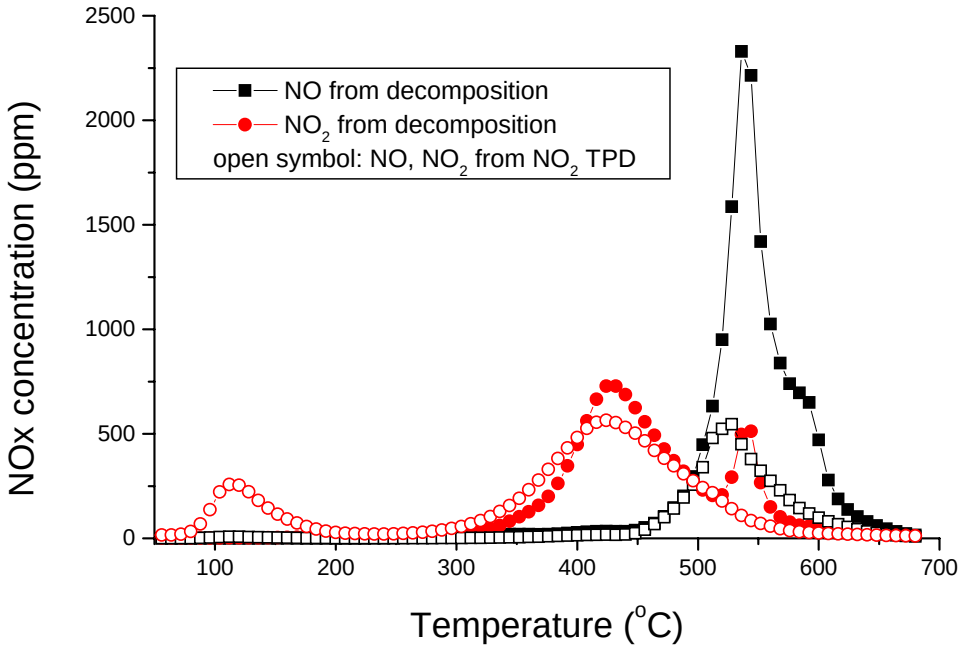
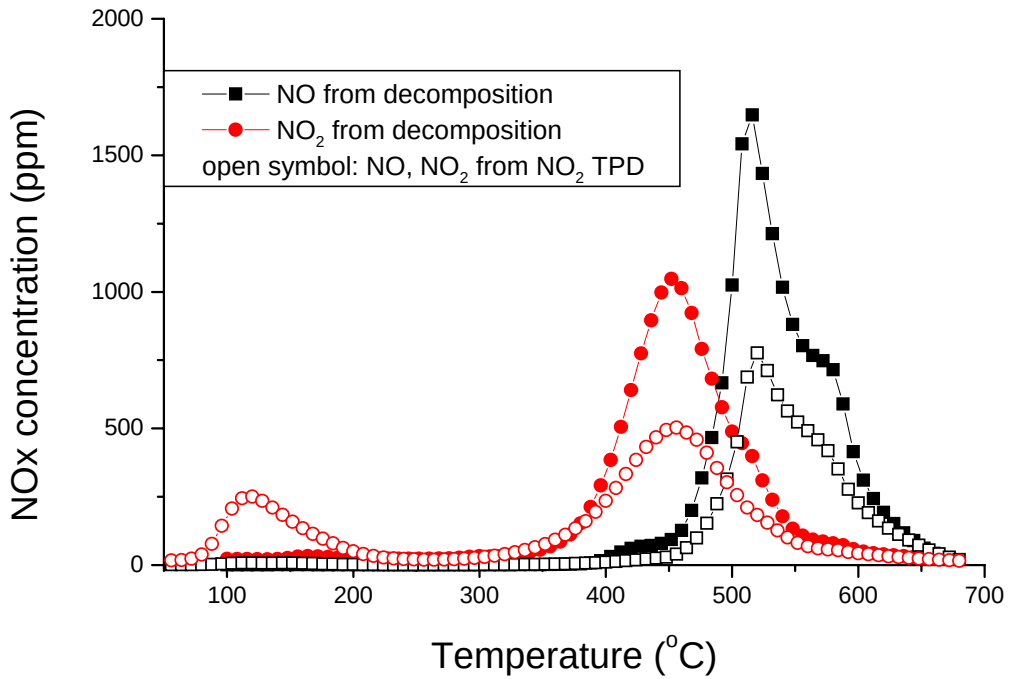
Technical Accomplishments/ Progress/Results

NO_2 TPD indicates enhanced performance may be related to better dispersion of BaO on the $MgAl_2O_4$ surface.

BaO/Al_2O_3



$BaO/MgAl_2O_4$



Transmission electron microscopy (TEM) micrographs also indicate better Pt dispersion on $MgAl_2O_4$-supported LNT.

Technical Accomplishments – Summary

- The morphology of BaO/Al_2O_3 LNT materials is remarkably dynamic during NOx storage and reduction. A "monolayer'" of $Ba(NO_3)_2$ forms on the alumina surface in addition to large "bulk" $Ba(NO_3)_2$ particles.
- These different morphologies display dramatically different behavior with respect to NOx removal temperature, formation of a deactivating high-temperature $BaAl_2O_4$ phase, and temperature requirements of desulfation.
- Effects of H_2O and CO_2 on the uptake and release of NOx was emphasized in studies performed this year. A notable conclusion from this work is that the presence of CO_2 only effects the decomposition of "bulk" Ba-nitrates with little, if any change is the properties of "monolayer" nitrates.
- On the basis of a recent CLEERS priorities poll, we have initiated studies of LNT materials that operate at higher temperatures than the baseline Pt/BaO/alumina. Both novel supports ($MgAl_2O_4$, CeO_2, etc.) and alternative storage materials (e.g., alkali metals) are included in this new work.
- Other highlights include:
  - Detailed comparative studies of the performance of all alumina-supported alkaline earth oxide (MgO, CaO, BaO, and SrO) storage materials.
  - Role of surface sites in the phase change and sintering of the common LNT support material, γ-Al_2O_3.
  - Ultra-high field NMR and aberration-corrected TEM studies of the anchoring and sintering of Pt on the γ-Al_2O_3 surface. TEM work done in collaboration with Larry Allard, ORNL/HTML.

Activities for Next Fiscal Year

- Complete studies of effects of CO_2 and H_2O on morphology and NO_x storage properties of baseline Ba-based materials.
- Higher temperature LNT operation: the anchoring, structure and mobility of alkali and alkaline earth NOx storage oxides on alumina and other supports.
- Roles of promoter species such as ceria.
  - Effects on Ba-phase morphology changes
  - Roles in minimizing deactivation processes
- Effects of other emission control systems on LNT performance. For example:
  - If soot filters are located downstream of LNTs as seems likely, the effects of soot accumulation on LNT catalyst morphology and NO_x reduction performance should be understood.
  - How to optimize LNT regeneration for NH_3 production if downstream urea SCR catalyst system present? Assess by fundamental understanding of the regeneration chemistry.

Acknowledgements

- PNNL CLEERS Program Team:
  Shelley Carlson, Jim Coleman, Heather Dillon, Tom Gallant, Darrell Herling, Do Heui Kim, Ja Hun Kwak, Jonathan Male, George Muntean, Gary Maupin, Chuck Peden, Tim Peters, Ken Rappe, Nat Saenz, Janos Szanyi, Russ Tonkyn, Diana Tran, Christelle Verrier
- Gurpreet Singh – Dept. of Energy/FCVT
- Ken Howden – Dept. of Energy/FCVT
- Stuart Daw, Dick Blint, Joe Bonadies
- Diesel Crosscut Team

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Publications since January 2007

1. Disselkamp, R.; Kim, D.-H.; Kwak, J.-H.; Szanyi, J.; Tonkyn, R.; Wang, X.; Peden, C.; Howden, K. 2007. "Fundamental Studies of NOx Adsorber Materials." Combustion and Emission Control for Advanced CIDI Engines, FY2006 Progress Report, pp. 135-141.
2. Kim D, J Kwak, J Szanyi, SD Burton, and CHF Peden. 2007. "Water-induced Bulk $Ba(NO_3)_2$ Formation From NO_2 Exposed Thermally Aged BaO/Al_2O_3." *Applied Catalysis. B, Environmental* **72**(3-4):233-239.
3. Kwak J, J Hu, D Kim, J Szanyi, and CHF Peden. 2007. "Penta-coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ-Al_2O_3: an Ultra-high Magnetic Field ^{27}Al MAS NMR Study." *Journal of Catalysis* **251**(2):189-194.
4. Szanyi J, J Kwak, RJ Chimentao, and CHF Peden. 2007. "The effect of H_2O on the adsorption of NO_2 on γ-Al_2O_3: an in situ FTIR/MS study." *Journal of Physical Chemistry C* **111**(6):2661-2669.
5. Szanyi J, J Kwak, D Kim, X Wang, J Hanson, RJ Chimentao, and CHF Peden. 2007. "Water-induced morphology changes in BaO/γ-Al_2O_3 NOx storage materials." *Chemical Communications* **2007**(9):984-986.
6. Szanyi J, J Kwak, D Kim, X Wang, RJ Chimentao, J Hanson, WS Epling, and CHF Peden. 2007. "Water-induced morphology changes in BaO/γ-Al_2O_3 NOx storage materials: an FTIR, TPD, and time-resolved synchrotron XRD study." *Journal of Physical Chemistry C* **111**(12):4678-4687.
7. Verrier C, J Kwak, D Kim, CHF Peden, and J Szanyi. 2008. "NOx uptake on alkaline earth oxides (BaO, MgO, CaO and SrO) supported on γ-Al_2O_3." *Catalysis Today*, in press.
8. Kim, D.-H.; Kwak, J.-H.; Szanyi, J.; Wang, X.; Peden, C.; Howden, K. 2008. "Fundamental Studies of NOx Adsorber Materials." Combustion and Emission Control for Advanced CIDI Engines, FY2007 Progress Report, in press.
9. Epling, W.S.; Peden, C.H.F.; Szanyi, J. 2008. "Carbonate Formation and Stability on a $Pt/BaO/Al_2O_3$ NOx Storage/Reduction Catalyst." *Journal of Physical Chemistry C*, submitted for publication.

Invited Presentations

1. Peden, C.H.F. "Fundamental Studies of Catalytic NOx Vehicle Emission Control." Invited Presentations made by Chuck Peden at the following locations:
   - Texas A&M University, College Station, TX, January 29, 2007.
   - Korea Institute for Energy Research (KIER), Daejon, Korea, November 9, 2007.
   - Argonne National Laboratory, Argonne, IL, December 10, 2007.
   - Northwestern University, Evanston, IL, January 11, 2008.

2. Peden, C.H.F; Ozensoy, E.; Yi, C.-W.; Szanyi, J. "Model Studies of BaO/Al_2O_3 NOx Storage Materials." Invited Presentation made by Chuck Peden at the 233rd American Chemical Society National Meeting, Chicago, IL on April 3, 2007.

3. Disselkamp, R.; Kim, D.-H.; Kwak, J.-H.; Szanyi, J.; Tonkyn, R.; Wang, X.; Peden, C.; Howden, K. "Fundamental Studies of NOx Adsorber Materials." Invited Presentation made by Chuck Peden at the 2007 Advanced Combustion Engine Peer Review Meeting, Washington, DC on June 18, 2007.

Chuck Peden co-organized diesel emission sessions at 20th NACS Meeting, 6/07.

Other Presentations

1. Peden CHF. "Fundamental Studies of NOx Adsorber Materials at PNNL." Presented by Chuck Peden at the 10th DOE CLEERS Workshop, Dearborn, MI on May 2, 2007.
2. Kwak J, D Kim, J Szanyi, and CHF Peden. "Solid State ^{27}Al NMR Study of BaO/Al_2O_3 Catalysts: $BaAl_2O_4$ Formation and Decomposition." Presented by Ja Hun Kwak at the 20th North American Meeting of the Catalysis Society, Houston, TX on June 18, 2007.
3. Verrier C, J Kwak, D Kim, CHF Peden, and J Szanyi. "NOx Storage over Alkaline Earth Oxides Supported on γ-Al_2O_3." Presented by Christelle Verrier at the 20th North American Meeting of the Catalysis Society, Houston, TX on June 18, 2007.
4. Szanyi J, J Kwak, D Kim, J Hanson, and CHF Peden. "The Effect of Water on the Adsorbed NOx species over BaO/Al_2O_3 NOx Storage Materials: A Combined FTIR and *In-Situ* Time-Resolved XRD study." Presented by Janos Szanyi at 20th North American Meeting of the Catalysis Society, Houston, TX on June 21, 2007.
5. Szanyi J, J Kwak, D Kim, J Hanson, and CHF Peden. "The Effect of Water on the Adsorbed NOx species over BaO/Al_2O_3 NOx Storage Materials: A Combined FTIR and *In-Situ* Time-Resolved XRD study." Presented by Janos Szanyi at EUROPACAT 8, Turku, Finland on August 27, 2007.
6. Peden CHF, J Kwak, D Kim, and J Szanyi. "The Use of Ultra-high Field NMR Spectroscopy to Study the Structure of γ-Al_2O_3 Surfaces." Presented by Chuck Peden at the 54th International Meeting, Seattle, WA on October 17, 2007.
7. Kim, D, J Szanyi, J Kwak, CM Wang, CHF Peden, X Wang, and J Hanson. "Fundamental Understanding of Sulfation/Desulfation Mechanisms over Pt-BaO/Al_2O_3 Lean NOx Trap Catalysts." Presented by Do Heui Kim for the CLEERS Monthly Teleconference on December 13, 2007.

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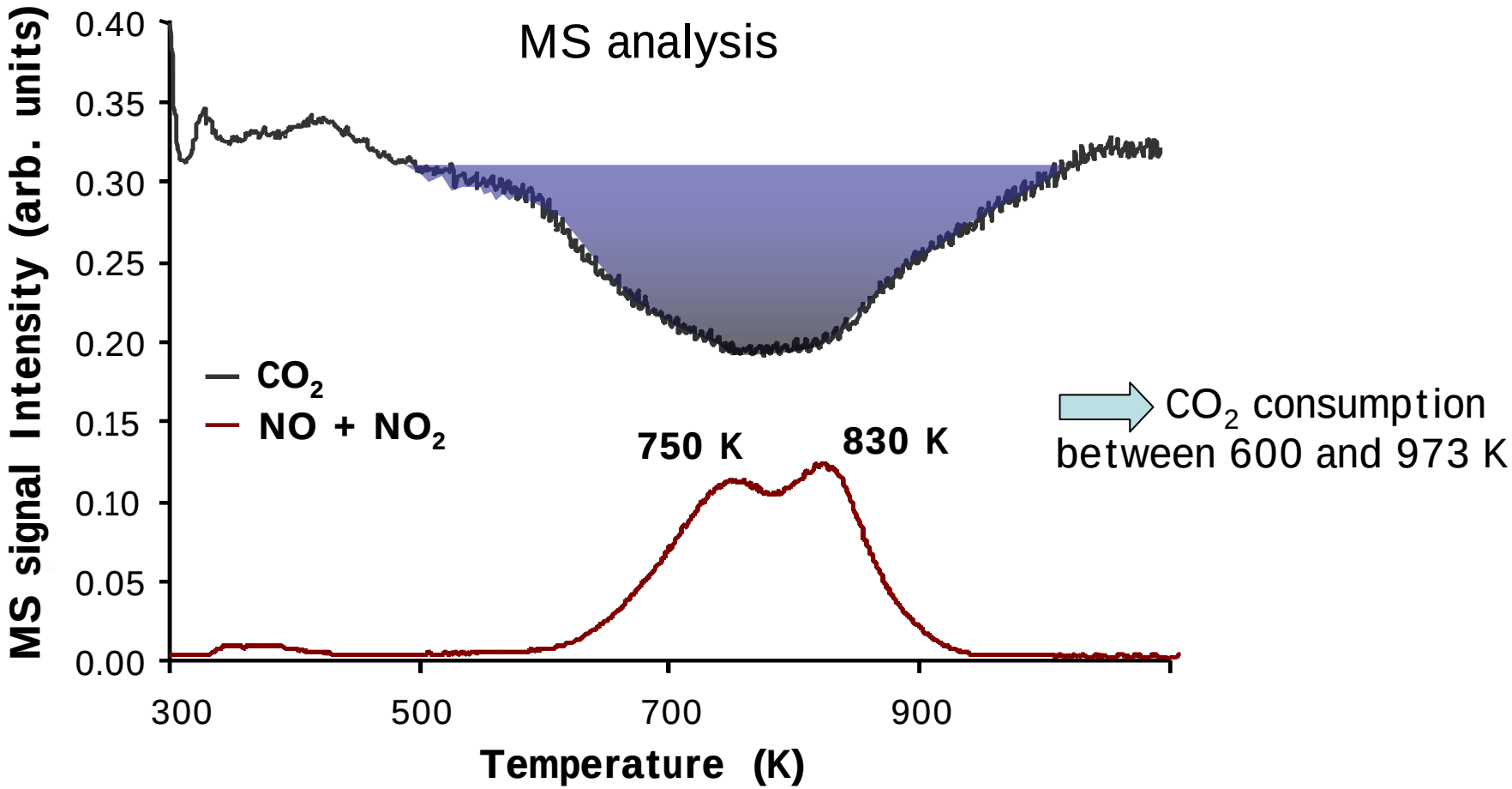
Effect of CO_2 on NOx release: CO_2 Consumption

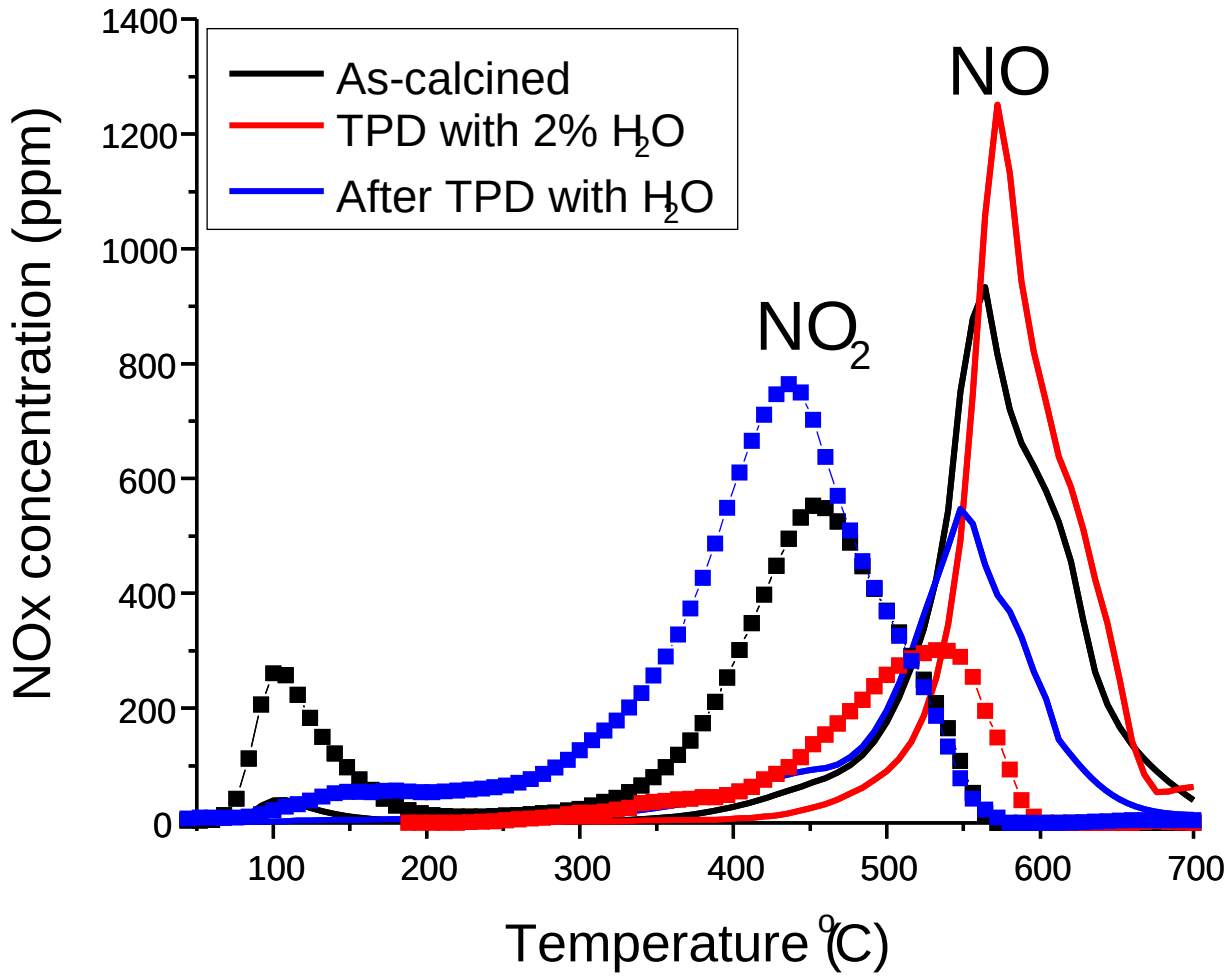


Technical Accomplishments/ Progress/Results

The presence of H_2O leads to stabilization of large crystallites of $Ba(NO_3)_2$ as evidenced by Temperature Programmed Desorption (TPD) experiments.

Desorption of NOx during TPD in the presence of 2% H_2O (red curves) occurs at higher temperature indicating the formation of bulk barium nitrates.

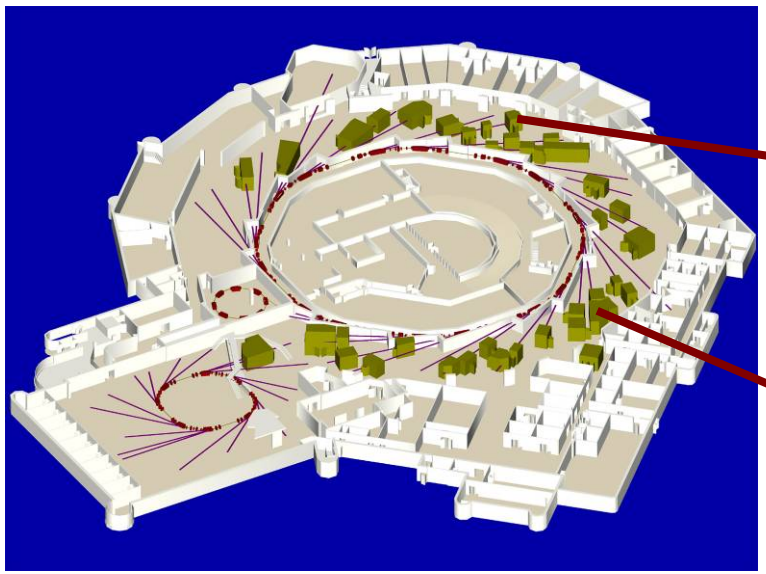
TPD results in a subsequent experiment without H_2O indicate significant changes to the Ba-based storage material.



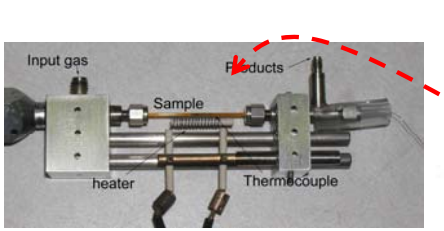
Technical Accomplishments/ Progress/Results

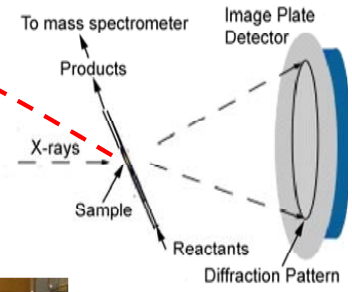
State-of-the-art *in-situ* synchrotron experiments performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Specific techniques used include:

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

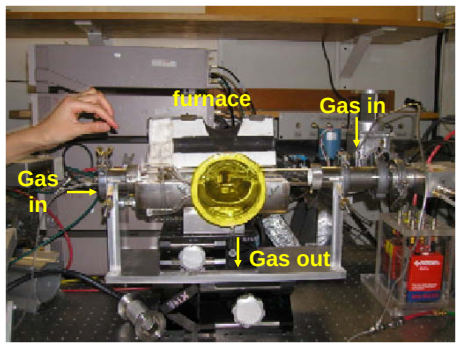


In-situ TR-XRD





In-situ XANES & EXAFS



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