Fundamental Studies of NOx Adsorber Materials

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Chuck Peden, Janos Szanyi
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CLEERS Workshop #11
May 13, 2008

Today's Discussion

- DOE/OFCVT-funded studies of BaO/Al_2O_3 Lean NOx Trap (LNT) materials
  - LNT material morphologies – new insights from FTIR, computations, and ultra-high field NMR.
  - BaO on CeO_2 – performance and sulfur poisoning.
  - Other support and alkaline earth oxide storage materials.

Acknowledgments

U. S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy/FreedomCAR and Vehicle Technologies Program

Experiments performed in DOE/BER's Environmental Molecular Sciences Laboratory located at PNNL, and in DOE/EE/VT's High Temperature Materials Lab at ORNL

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Vehicle Technologies Program

William R. Wiley EMSL Environmental Molecular Sciences Laboratory

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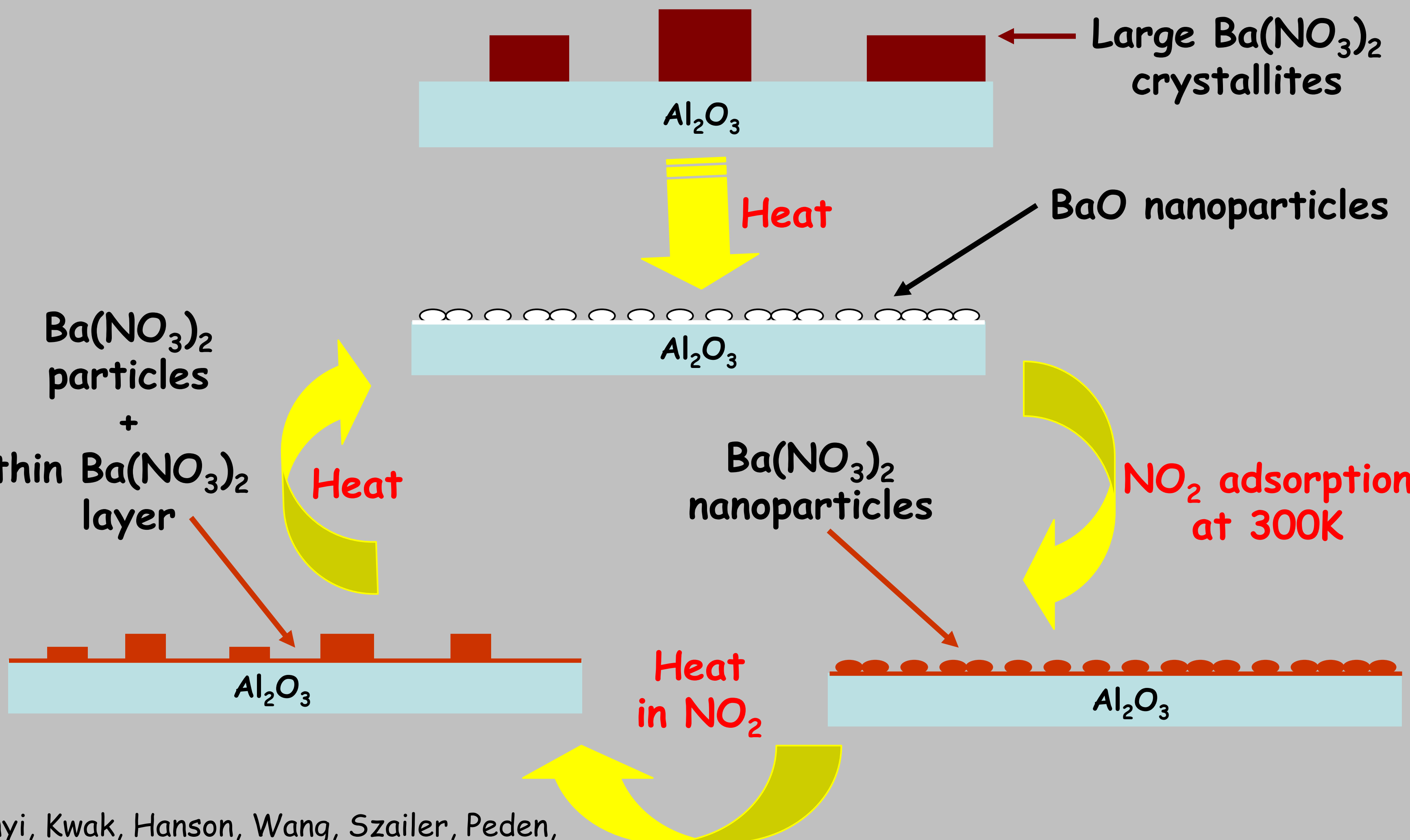
Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' $Ba(NO_3)_2$ morphologies present. These 'phases' can be distinguished spectroscopically.



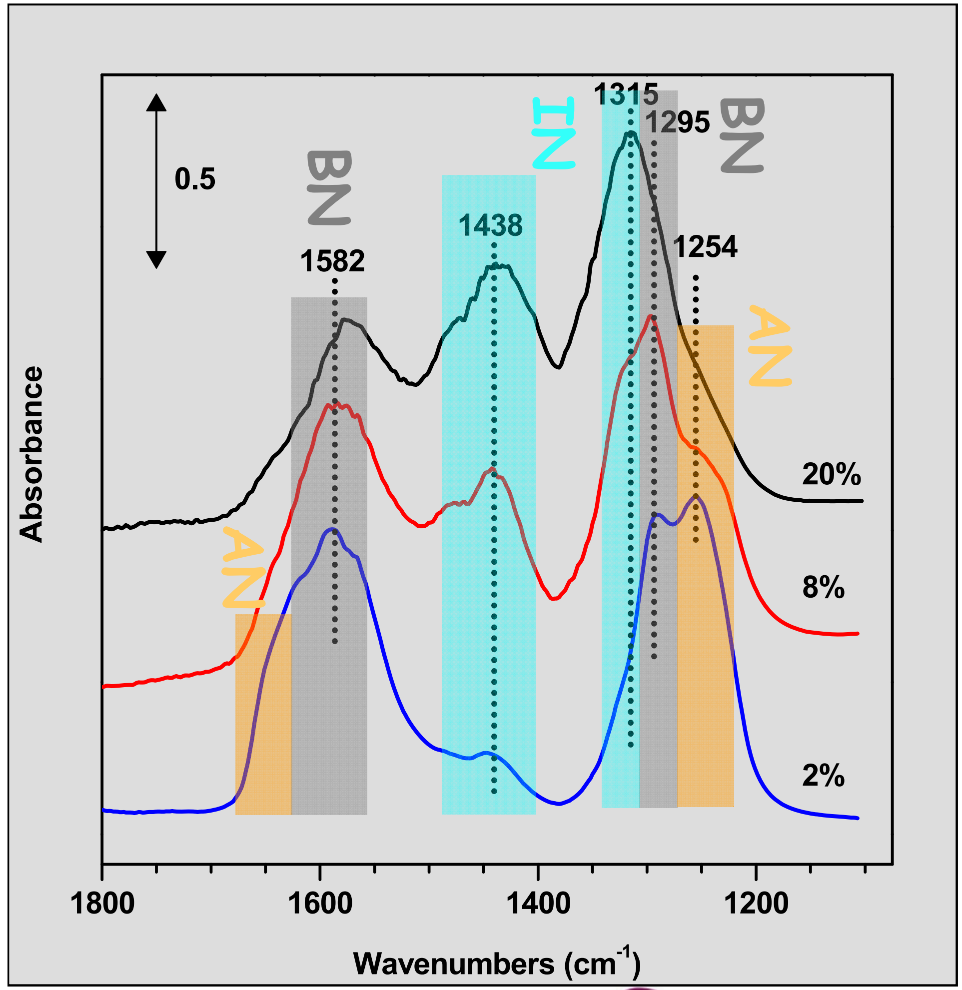
Szanyi, Kwak, Hanson, Wang, Szailer, Peden,
J. Phys. Chem. B **109** (2005) 7339-7344.

Observed practical implications of the Ba-phase morphology.

- 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.

FTIR after NO_2 adsorption on 2%, 8%-, and 20%-BaO/Al_2O_3 at 300K

- Al_2O_3-bound nitrates (AN) decrease continuously with Ba coverage.
- Surface ("bidentate" – BN) and bulk (ionic – IN) nitrates are observed on BaO/Al_2O_3 catalysts. Their ratio (BN/IN) also decreases with BaO loading.



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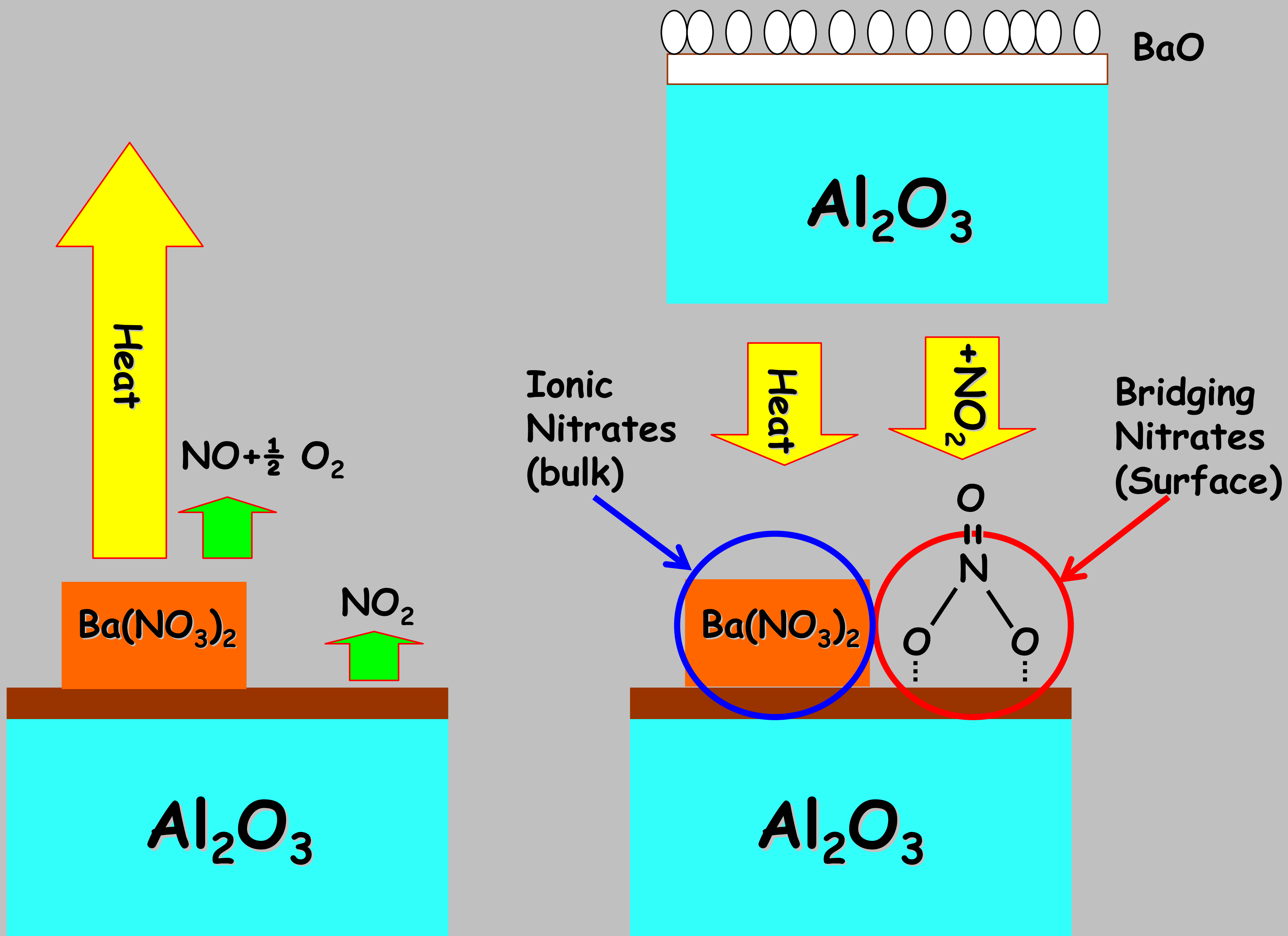
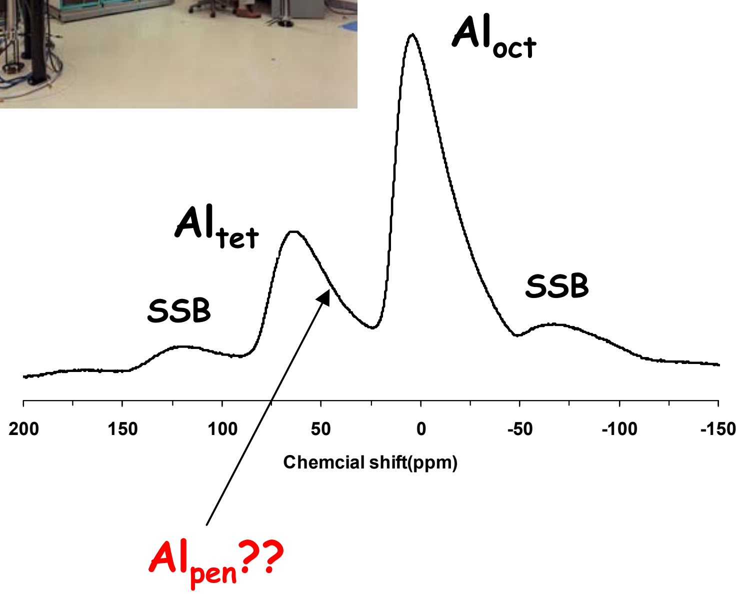
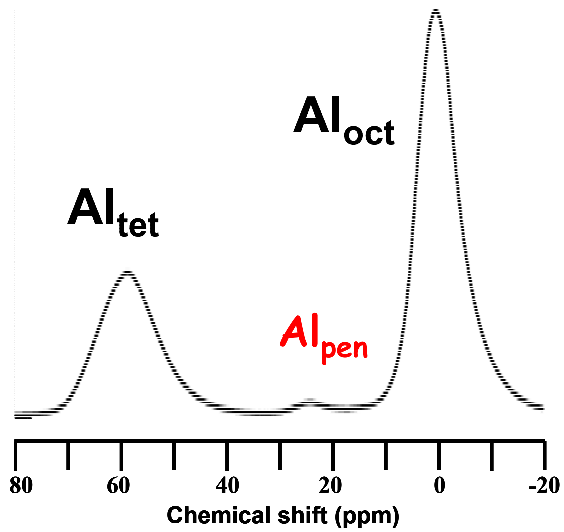


Use of a one-of-a kind Ultra-High Field NMR in the Environmental Molecular Science Lab at PNNL





- Penta-coordinate Al^{+3} ions readily observable in γ-Al_2O_3;
- Are these species are located at the alumina surface?

JH Kwak, JZ Hu, DH Kim, J Szanyi, CHF Peden, Journal of Catalysis, **251** (2007) 189-194.

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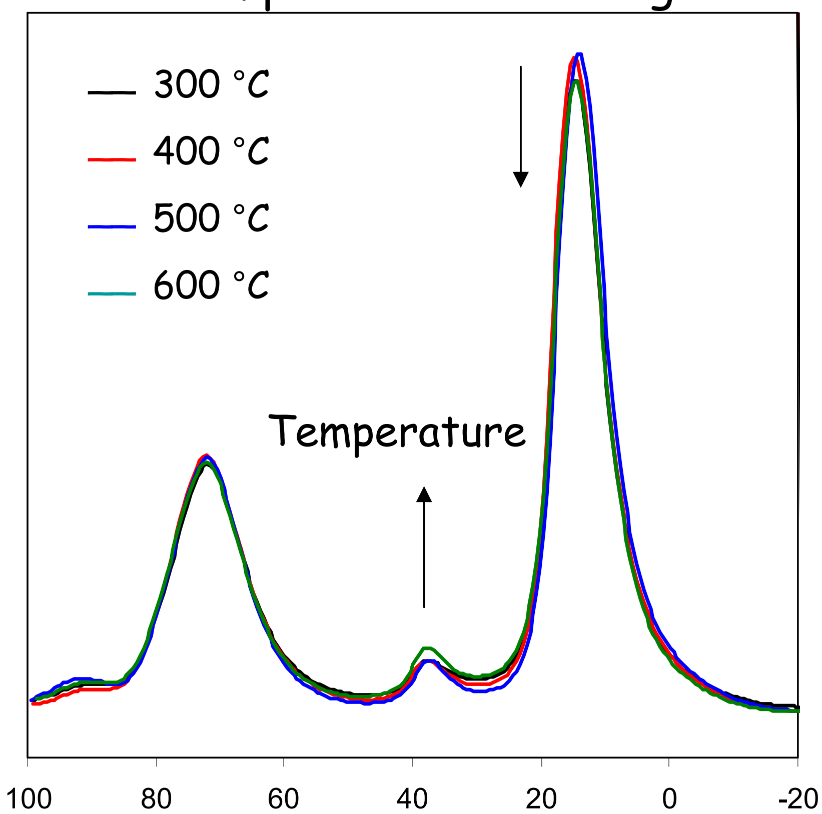
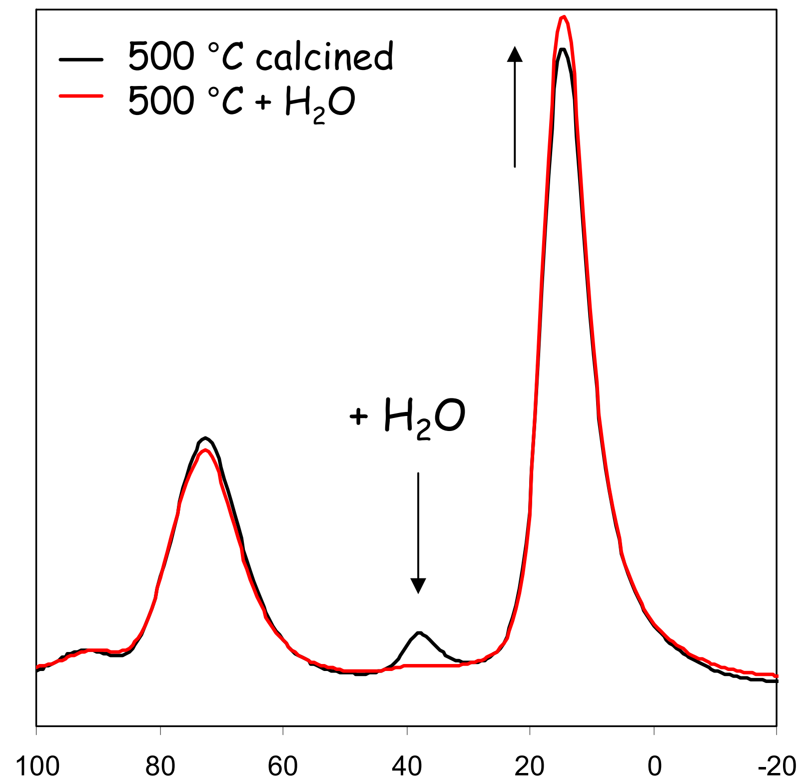
5-fold Al-atoms display 'chemical' characteristics of being surface cations

5-fold Al cations increase at the expense of 6-fold cations after high temperature annealing

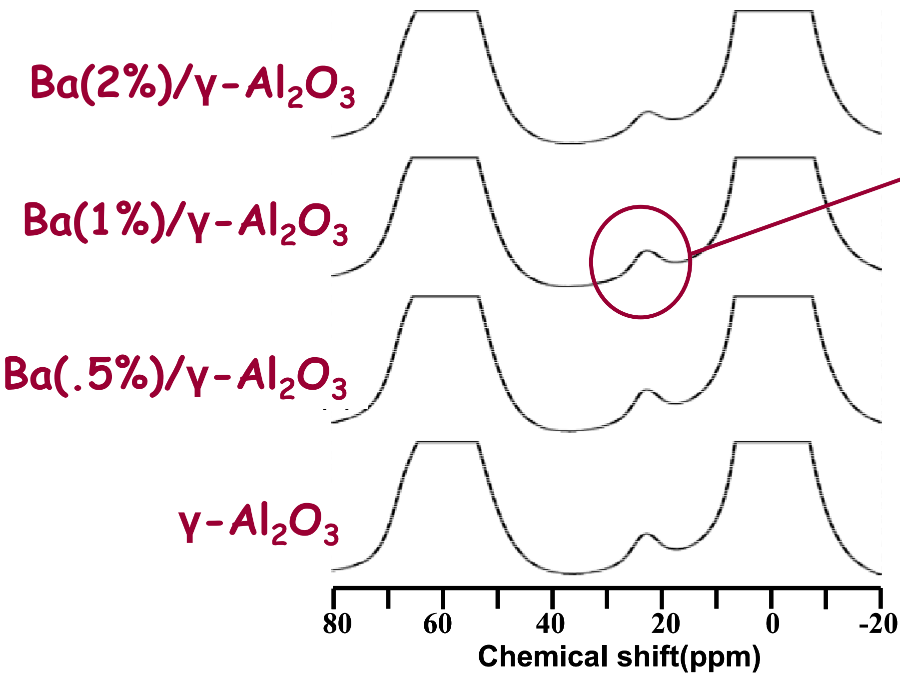


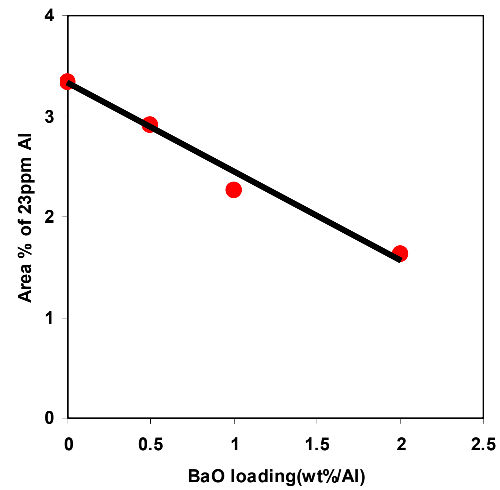
5-fold cations disappear and octahedral Al increases after exposure to H_2O



Lewis acidic 5-fold Al sites on γ-Al_2O_3 surfaces are nucleation sites for catalytic phases!

Addition of a catalytic phase, BaO, quantitatively 'titrates' 5-fold Al sites.





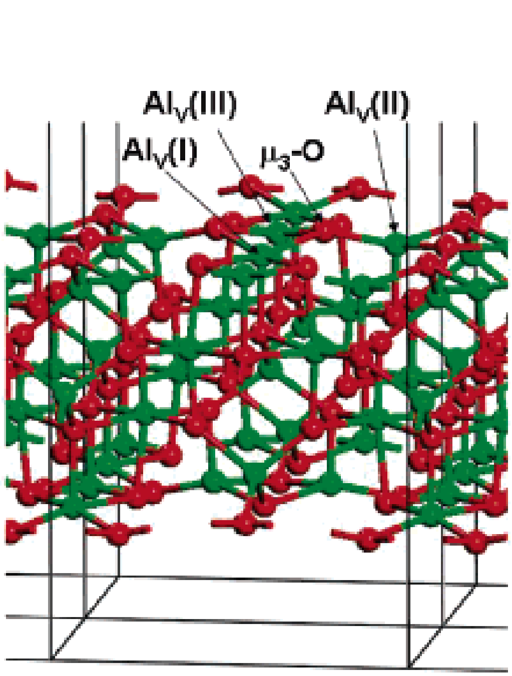
5-fold sites are fully titrated at ~4 weight % loading of BaO on 200 m^2/gm γ-Al_2O_3.

JH Kwak, JZ Hu, DH Kim, J Szanyi, CHF Peden, Journal of Catalysis **251** (2007) 189-194.

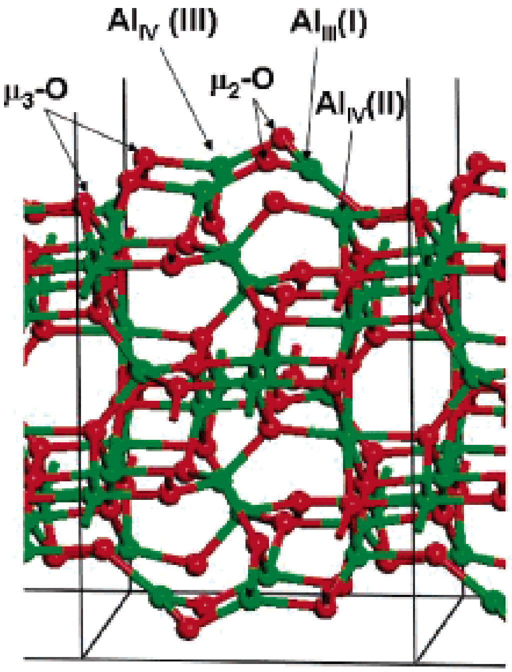
The titration results consistent with expected distribution of γ-Al_2O_3 surfaces

- 4 weight % loading of BaO sufficient to titrate all 5-fold Al^{+3} sites.
- Assuming that BaO forms perfect 2D clusters or domains on the 200 m^2/g γ–Al_2O_3 substrate, 1 ML of BaO will be reached at ~25% weight loading.
- Thus, ~16% of the alumina surface consists of 5-fold Al^{+3} sites.

γ-Al_2O_3(100) surfaces are estimated to be ~17% of the total surface area



γ-Al_2O_3(100)



γ-Al_2O_3(110)

γ-Al_2O_3(100) – ~17%

γ-Al_2O_3(110) – ~70-83%

γ-Al_2O_3(111) – stable?

Yates and coworkers, *J. Phys. Chem. B* **110** (2006) 4742, and Digne, *et al.*, *J. Catal.* **226** (2004) 54, and references therein.

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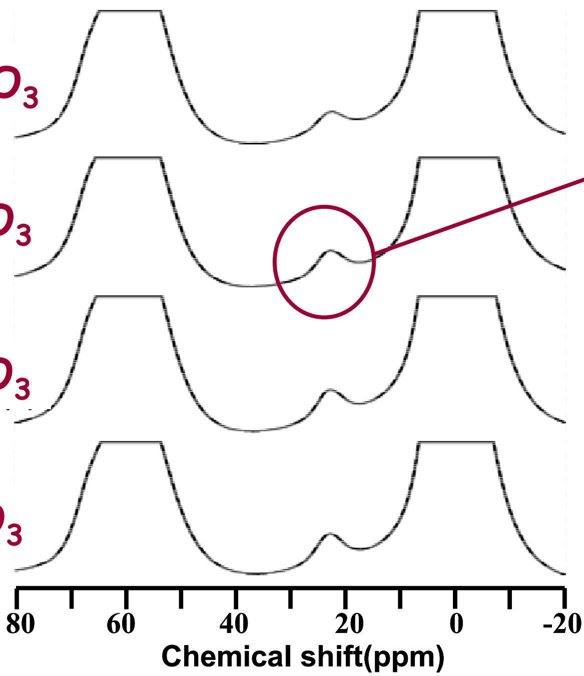

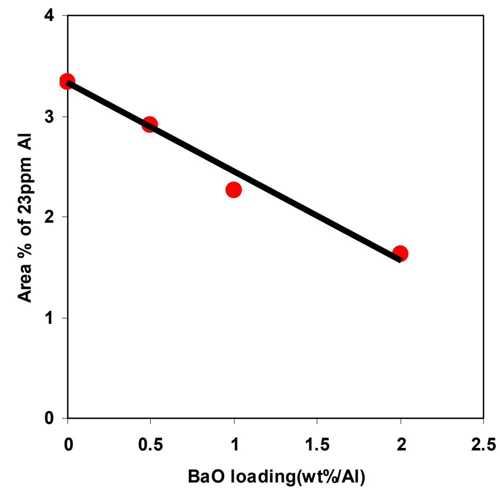

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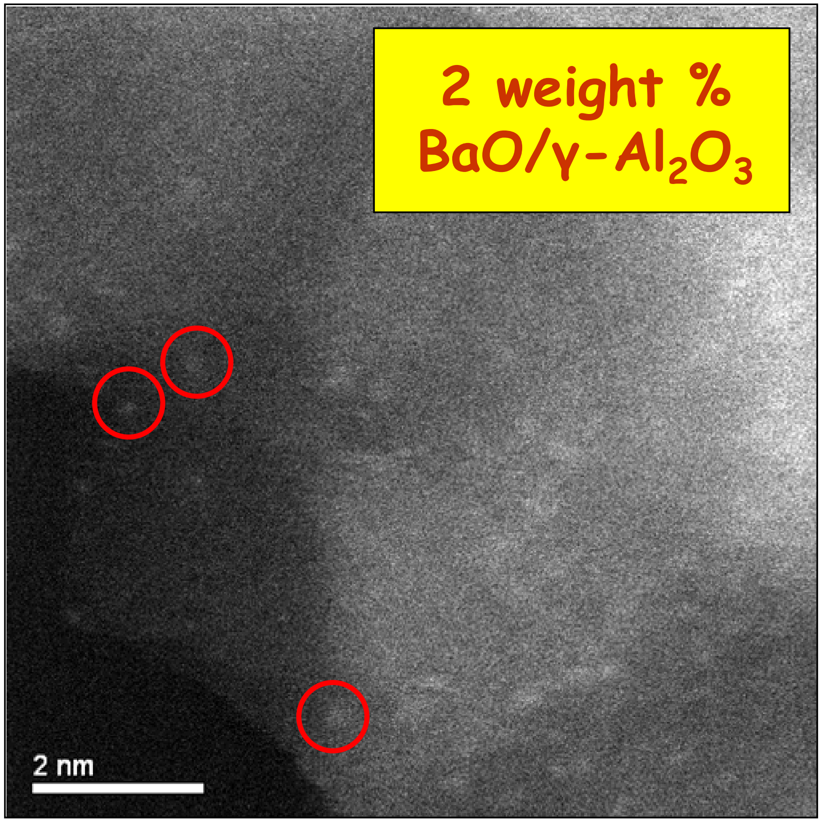
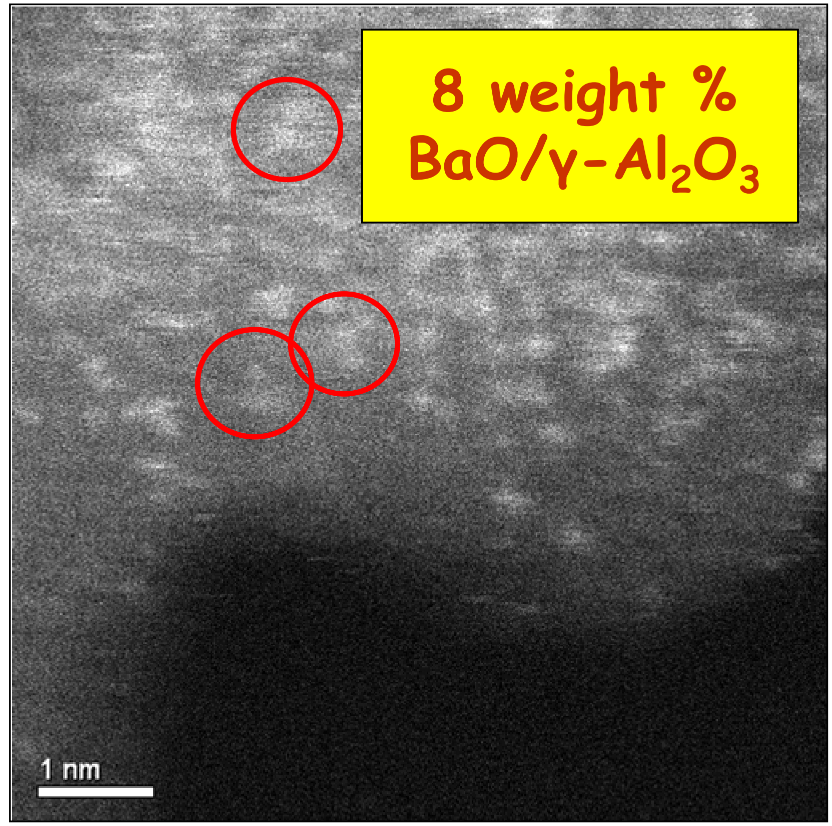
HR-TEM shows BaO monomers at low and dimers a higher loadings





JH Kwak, D Mei, C-W Yi DH Kim, CHF Peden, LF Allard, J Szanyi, Angew. Chemie, submitted.

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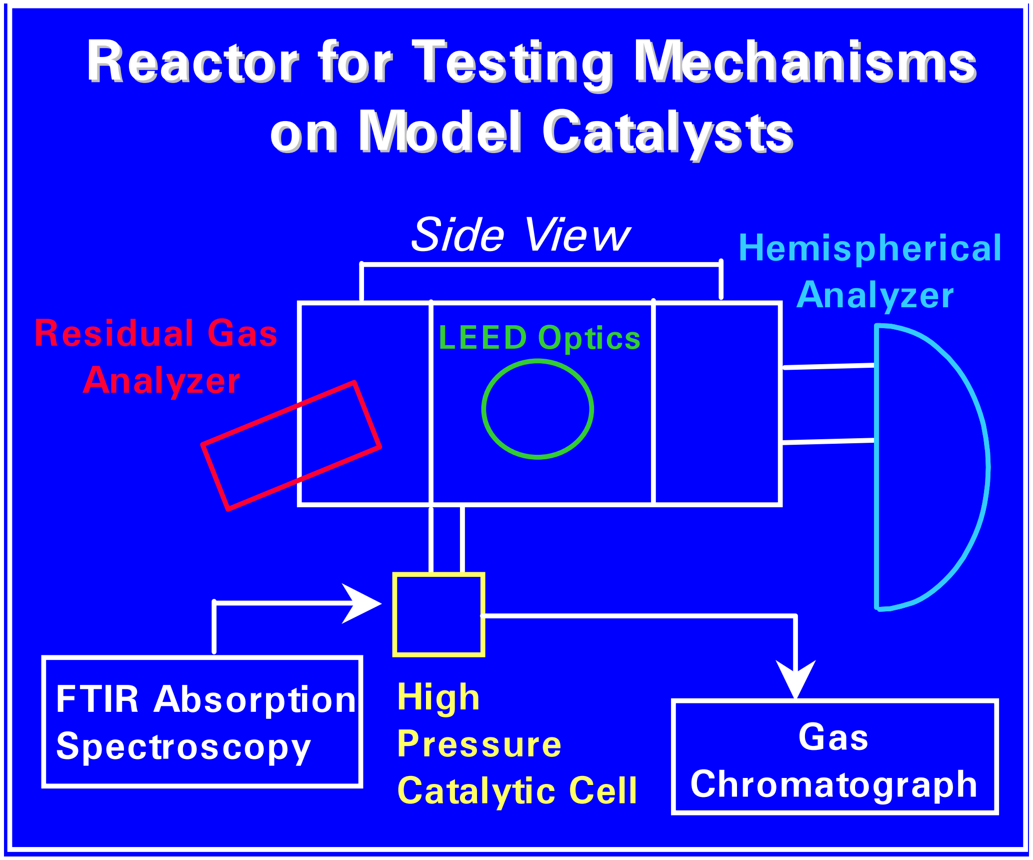
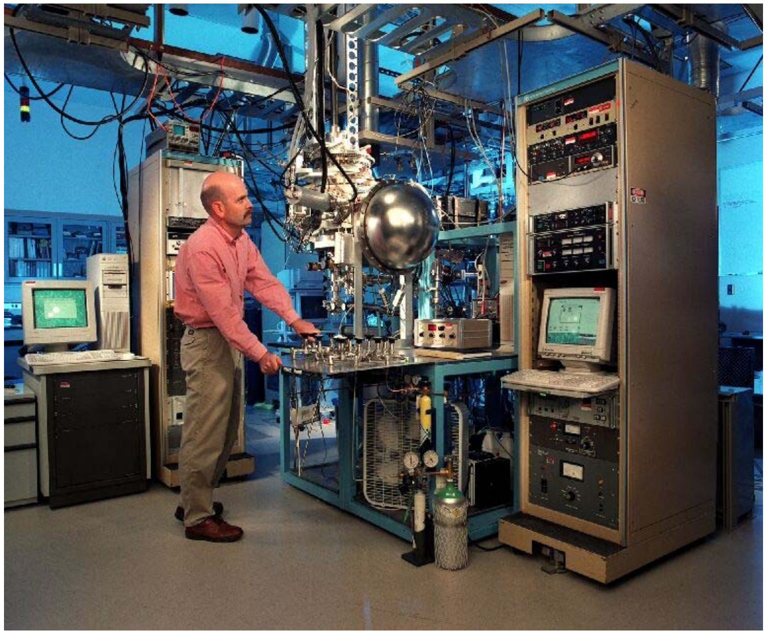
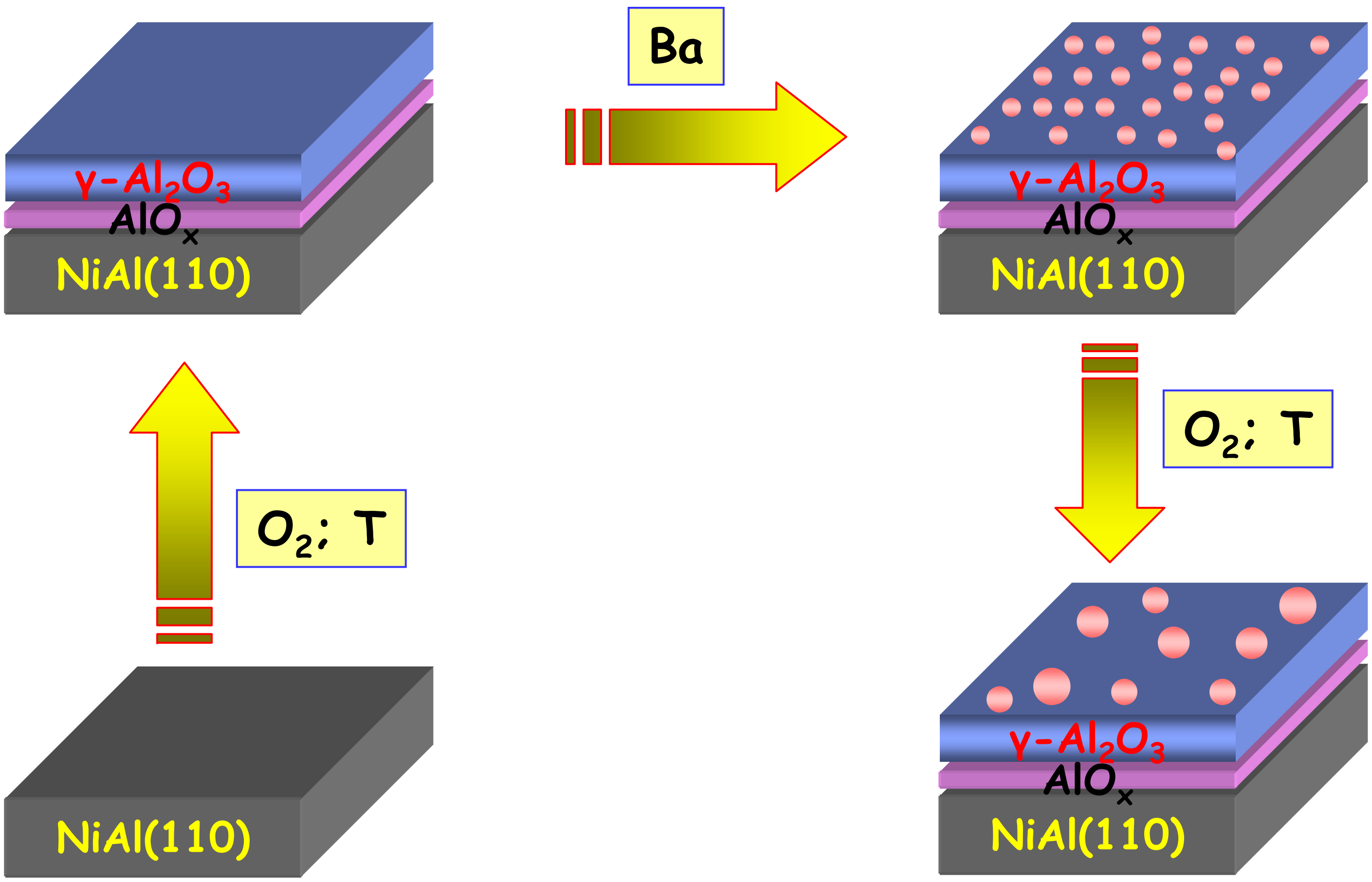
Catalytic Reactor/UHV Surface Science Apparatus for Model Catalyst Studies



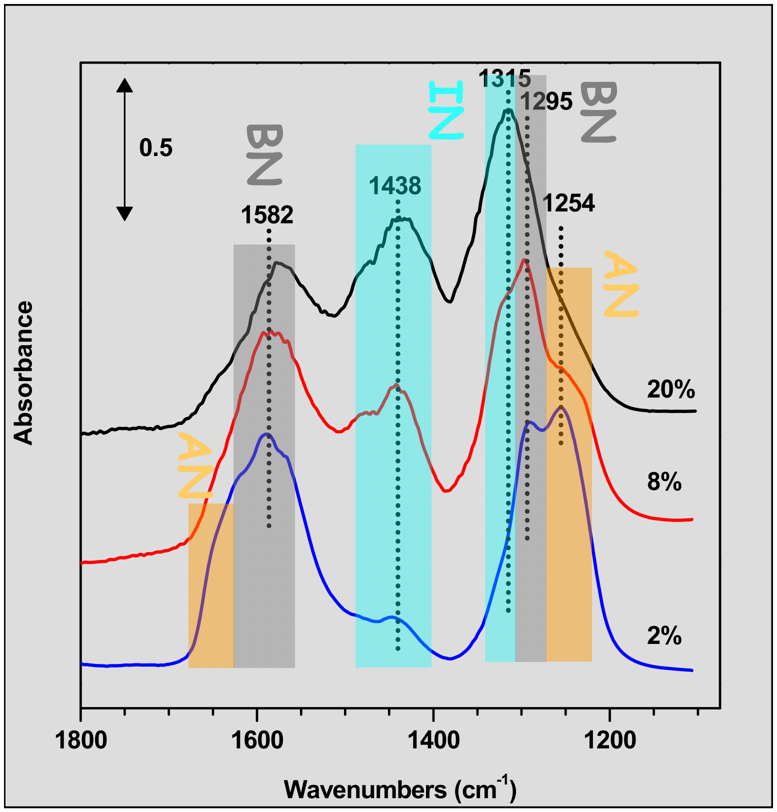


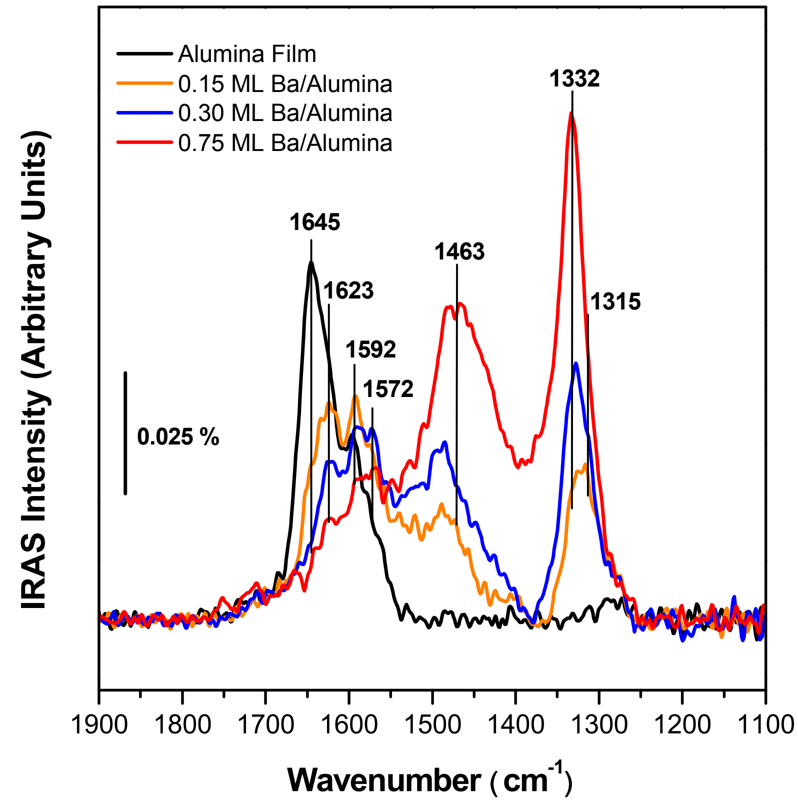
Model Catalyst Synthesis Strategy



Ozensoy, E.; Szanyi, J.; Peden, C.H.F. J. Phys. Chem. B **109** (2005) 3431-3436; 15977-15984.
Ozensoy, E.; Peden, C.H.F.; Szanyi, J. J. Phys. Chem. B **110** (2006) 17001-17008; 17009-17014.

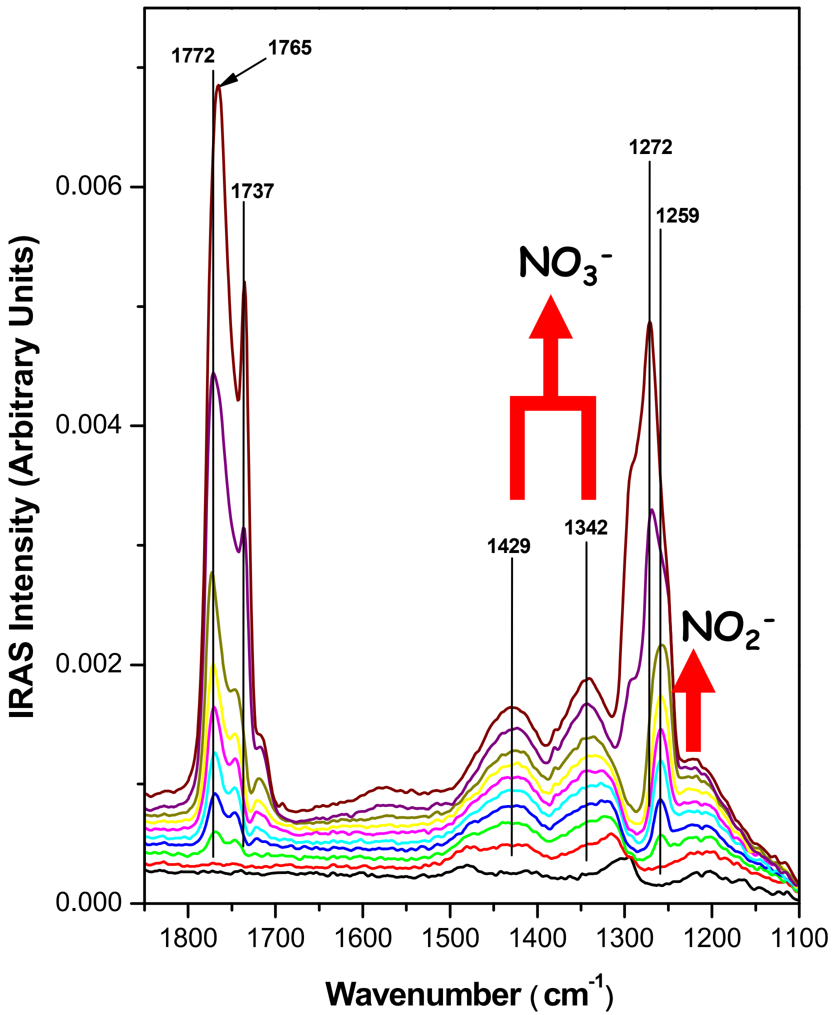
Identical FTIR features observed for 300K NO_2 adsorption on model BaO/Al_2O_3





Szailer, T.; Kwak, J.H.; Kim, D.H.; Szanyi, J.; Wang, C.M.; Peden, C.H.F., Catal. Today **114** (2005) 86.
Yi, C.W.; Kwak, J.H.; Peden, C.H.F.; Wang, C.M.; Szanyi, J., J. Phys. Chem. C **111** (2007) 14942.

UHV IRAS Studies: NO_2 adsorption on Model BaO Surface at 90 K



At the lowest NO_2 exposure:

- * both NO_2^- & NO_3^- are present
- * no adsorbed NO_2/N_2O_4

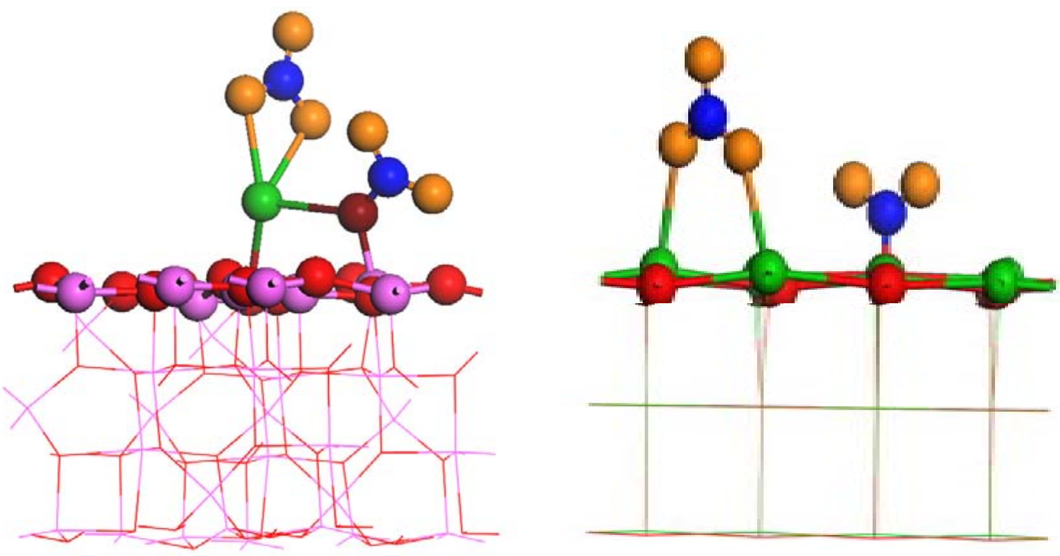
At high NO_2 exposures:

- * NO_x^- intensities saturate
- • N_2O_4 ice grows

DFT Calculations of Stable NOx Species on Dispersed BaO and Bulk BaO Surfaces

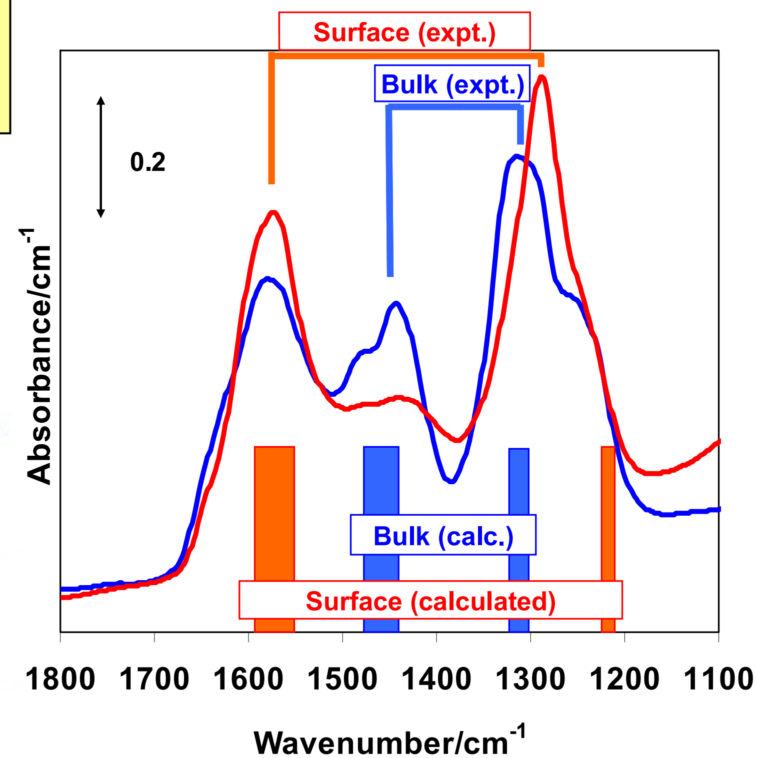
NO_2 Adsorption On:

$(BaO)_1/Al_2O_3(100)$ BaO(100)



1540-1600 cm^{-1}
1200-1230 cm^{-1}

1430-1475 cm^{-1}
1280-1310 cm^{-1}



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Szanyi, Kwak, Hanson, Wang, Szailer, Peden,
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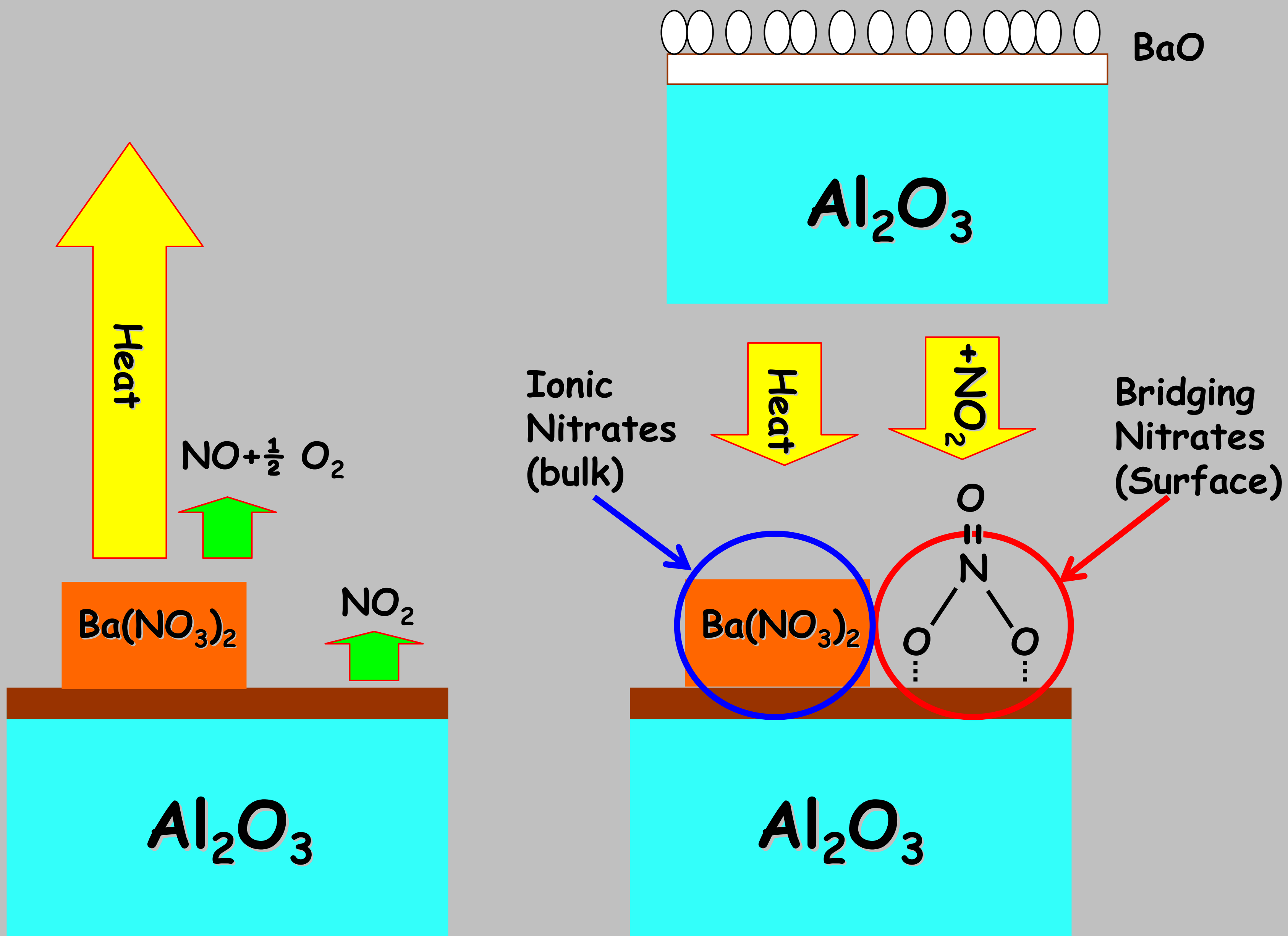
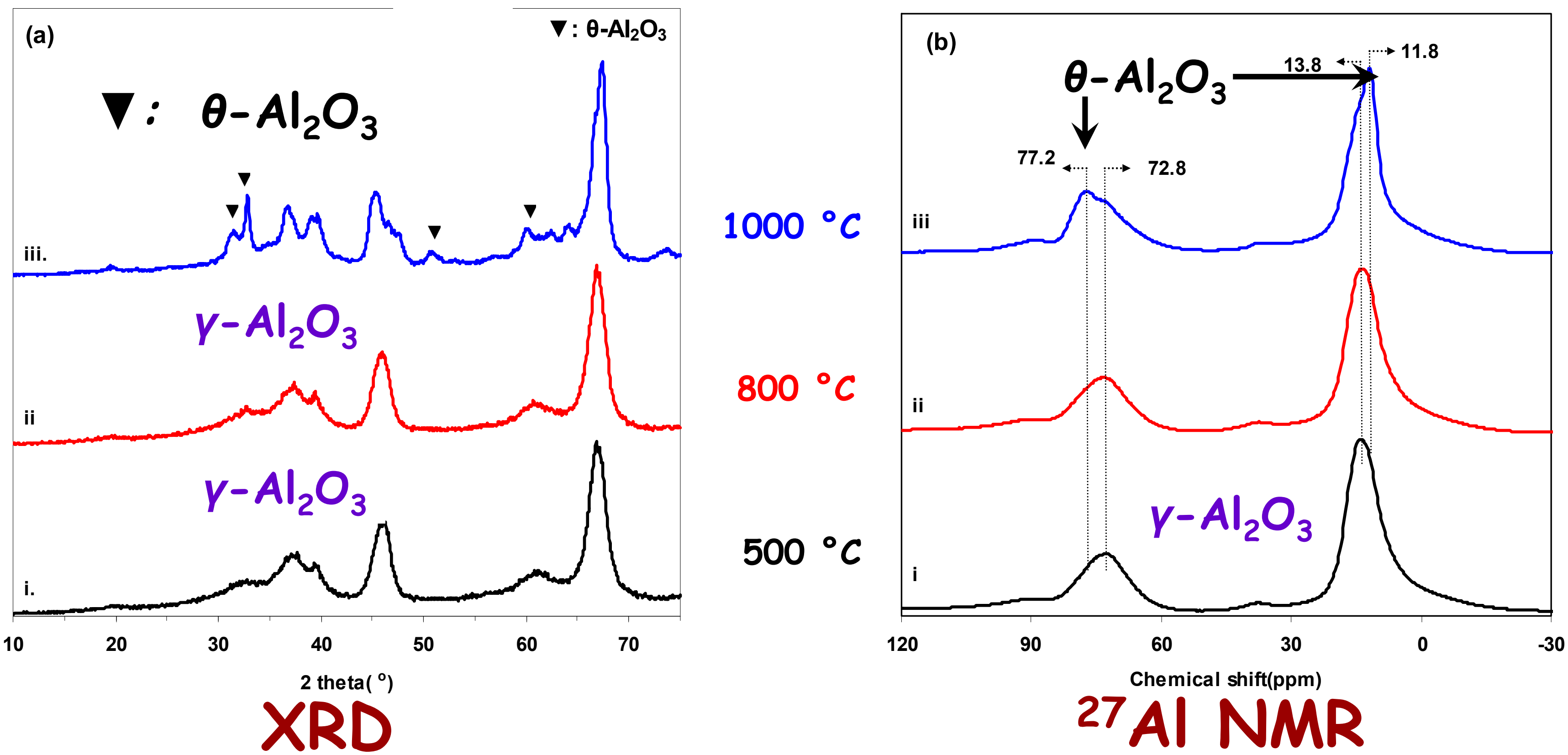


The γ- to θ-Al_2O_3 phase transition, between 900-1000 °C, can be followed by XRD and ^{27}Al NMR



JH Kwak, JZ Hu, AC Lukaski, DH Kim, J Szanyi, CHF Peden, J. Phys. Chem. C (2008) in press.

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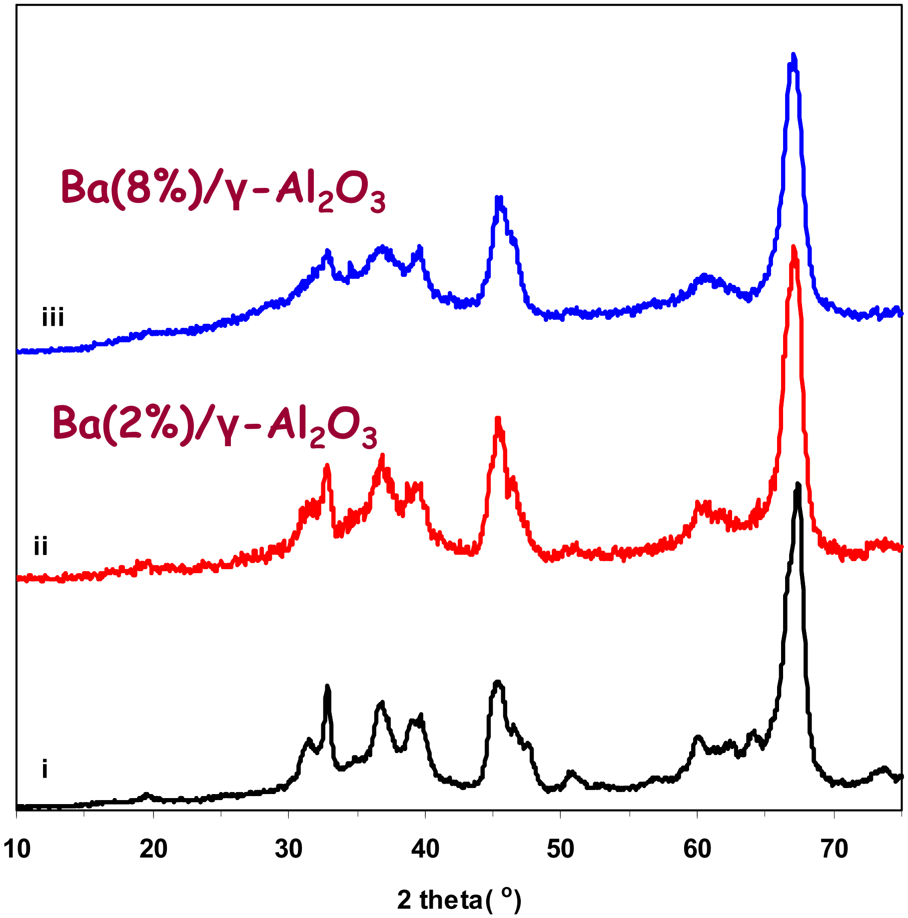
Addition of barium oxide stabilizes γ-Al_2O_3 to a high temperature phase transition at 1000 °C

Could this stabilization be related to occupation of surface 5-coordinate Al sites?



JH Kwak, JZ Hu, AC Lukaski, DH Kim, J Szanyi, CHF Peden, J. Phys. Chem. C (2008) in press.

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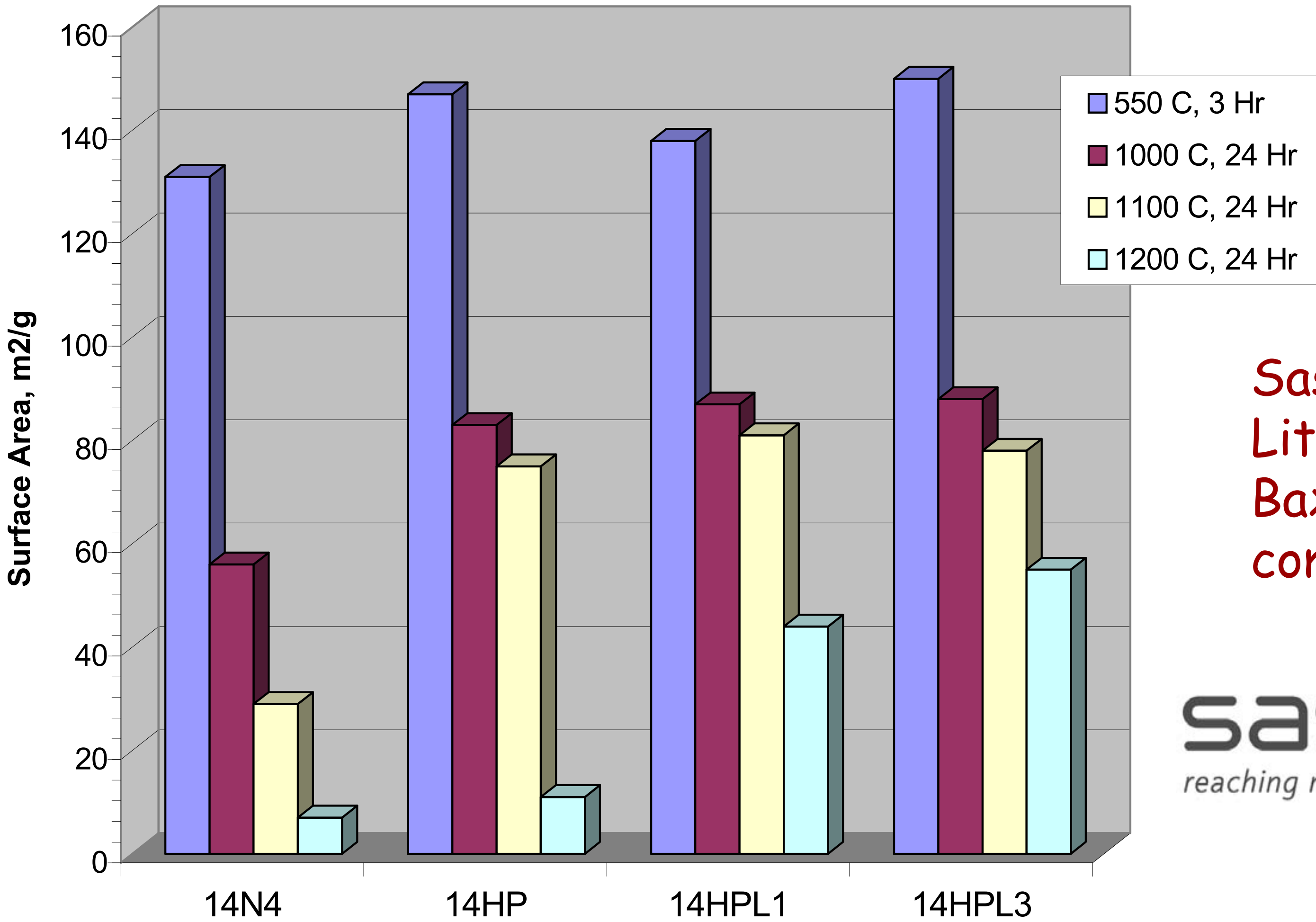
γ-Al_2O_3 Thermal Stability As A Function Of Crystallite Structure And Lanthanum Oxide Content



Sasol Promotional Literature, S.L. Baxter, private communication.

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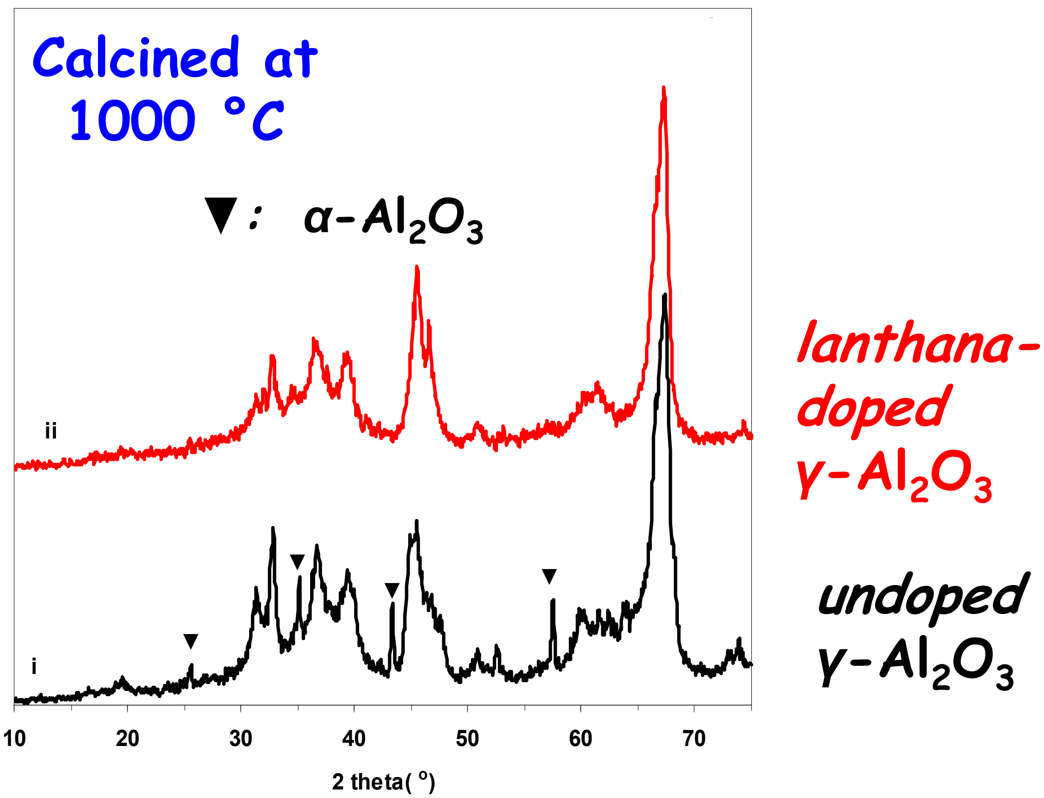
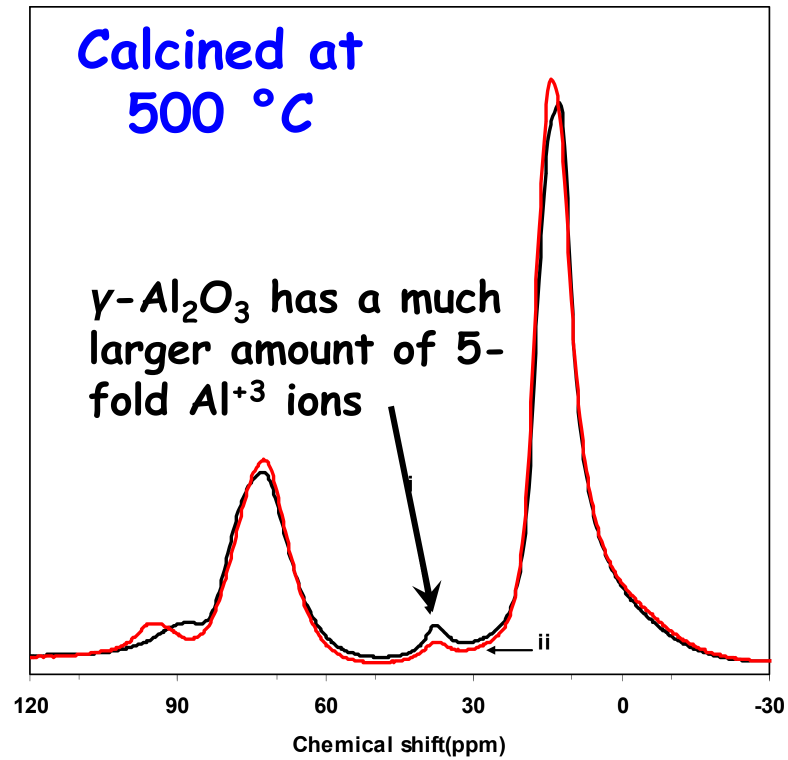
Addition of lanthana stabilizes γ-Al_2O_3 to a high temperature phase transition at 1000 °C



XRD



^{27}Al NMR

JH Kwak, JZ Hu, AC Lukaski, DH Kim, J Szanyi, CHF Peden, J. Phys. Chem. C (2008) in press.

Today's Discussion

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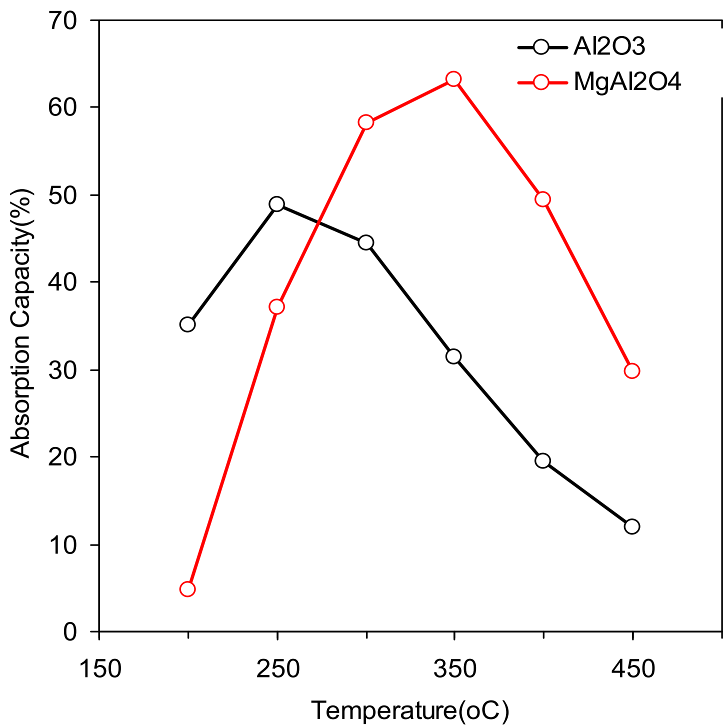
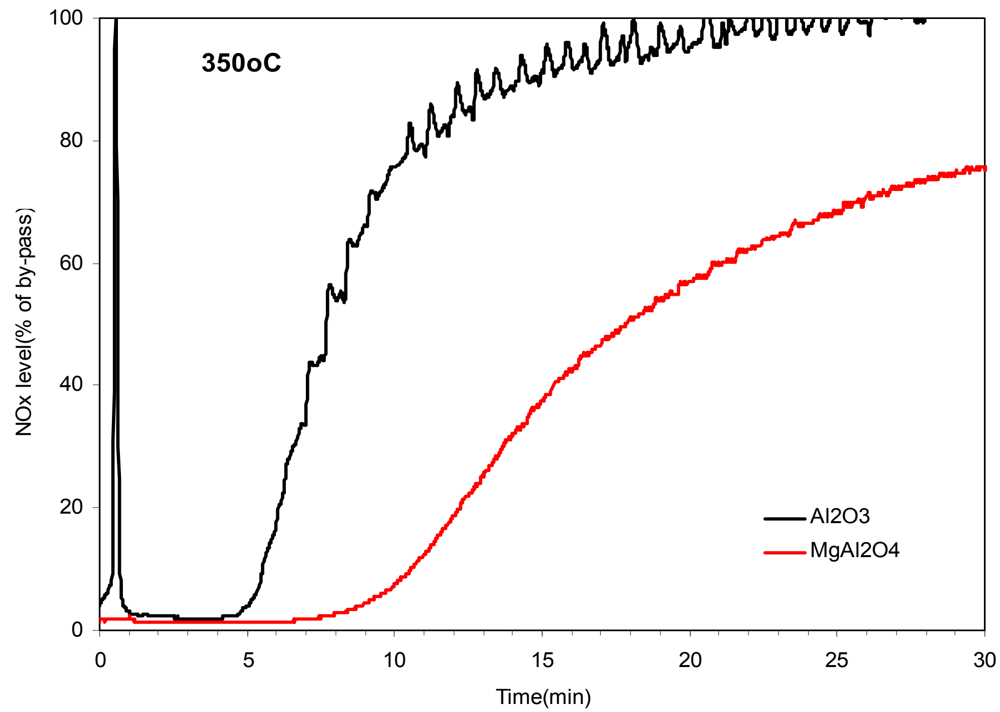
  - LNT material morphologies – new results from FTIR, computations, and ultra-high field NMR.
  - BaO on CeO_2 – performance and sulfur poisoning.
  - Other support and alkaline earth oxide storage materials.

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





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

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 NOx 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

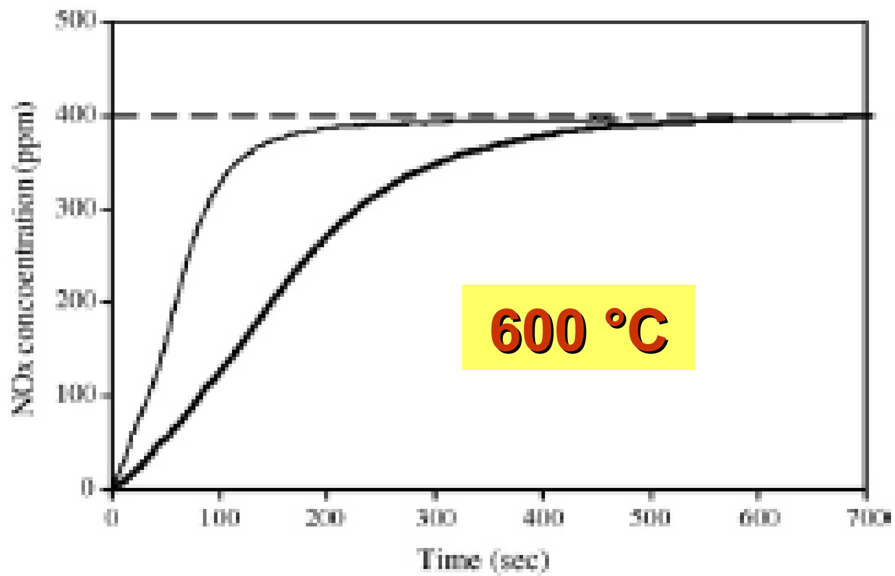


Fig. 2. NOx concentrations in the outlet and inlet gases of the catalysts. Outlet NOx concentration of the K/Pt/$MgAl_2O_4$ catalyst (——). Outlet NOx concentration of the K/Pt/Al_2O_3 catalyst (—). Inlet NOx concentration (– –).

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

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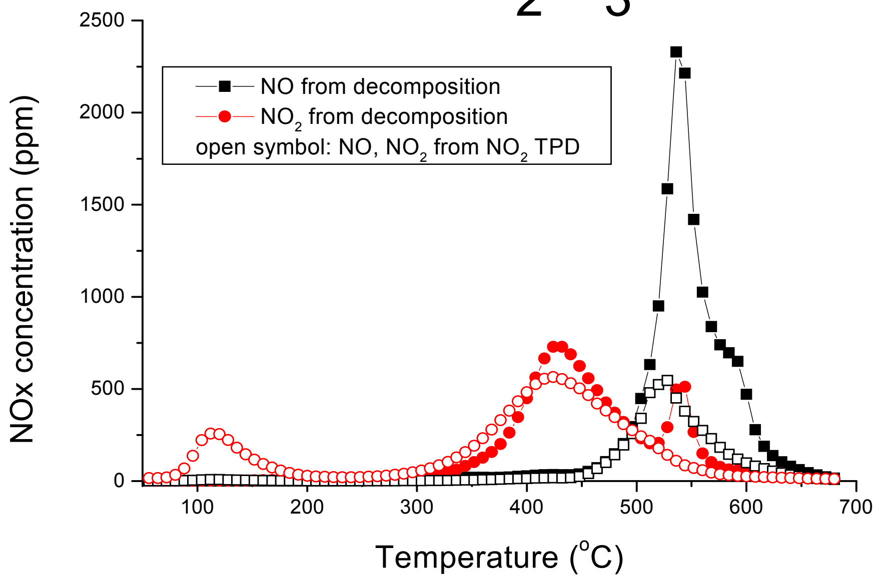
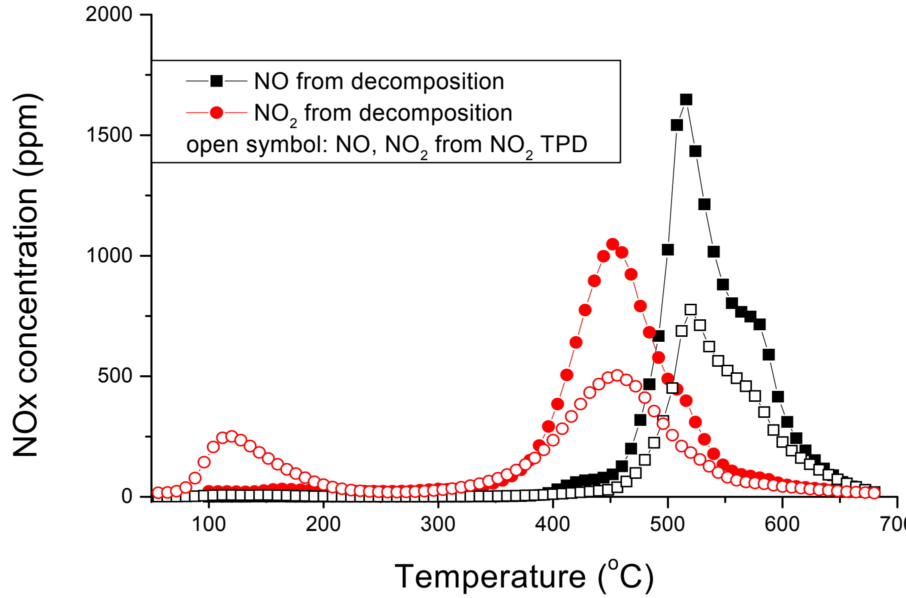
NO_2 TPD indicates enhanced performance may be related to better dispersion of BaO on the $MgAl_2O_4$ surface.

BaO/Al_2O_3



BaO/$MgAl_2O_4$



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

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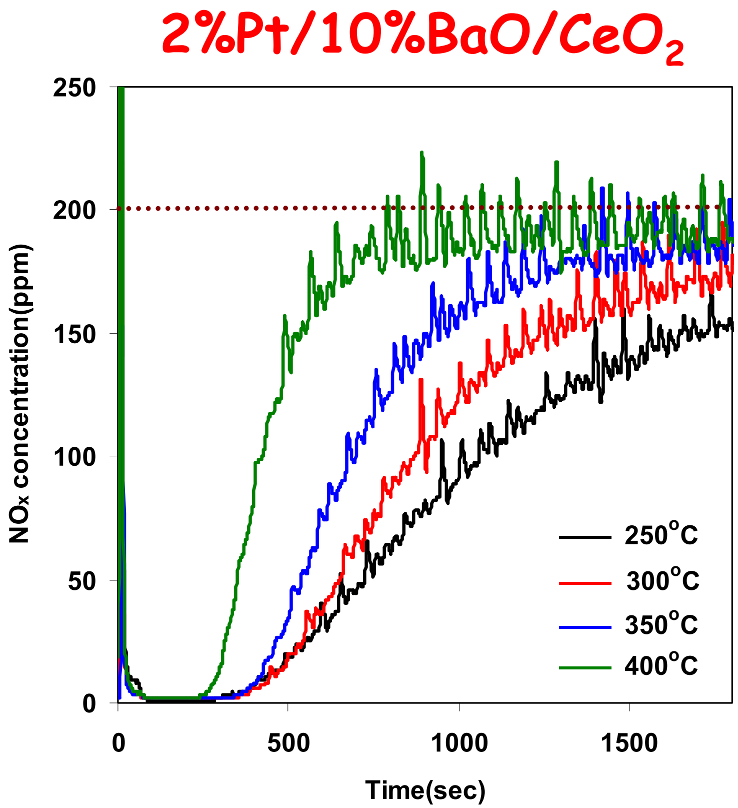
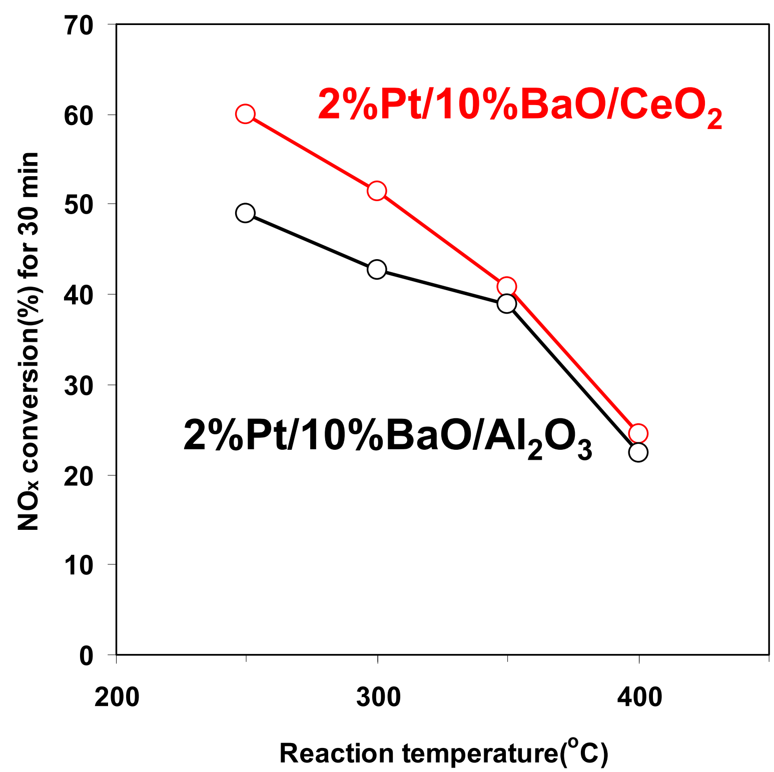
A ceria-supported catalyst is much more active per amount of Ba, and much more readily desulfated than an alumina-supported Pt-BaO LNT.





J.H. Kwak, D.H. Kim, J. Szanyi, and C.H.F. Peden, Appl. Catal. B (2008) in press.

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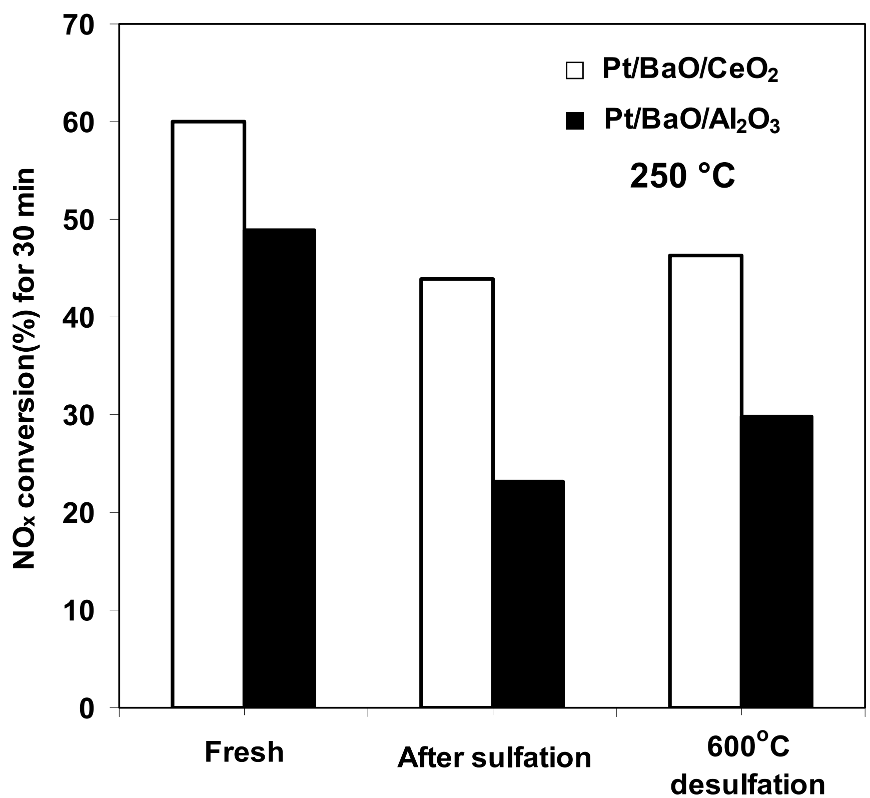

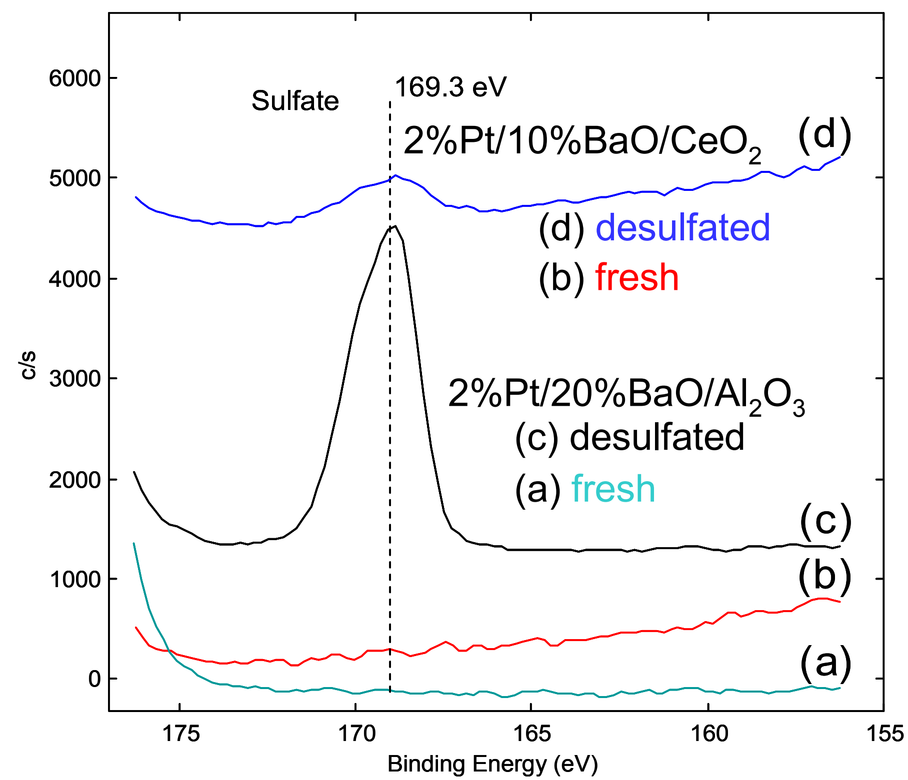

J.H. Kwak, D.H. Kim, J. Szanyi and C.H.F. Peden, Appl. Catal. B (2008) in press.

Summary and Conclusions

- 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. *Recent results provide clear evidence that "monolayer" BaO is chemically distinct from "bulk" BaO; i.e., the **surface** chemistry of* BaO/Al_2O_3 is quite different than "bulk" BaO.
- 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.
- 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 are included in this new work.