

# Fundamental Studies of NO<sub>x</sub> Adsorber Materials

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# Today's Discussion

- DOE/OFCVT-funded studies of BaO/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap (LNT) materials
  - LNT material morphology changes during preparation and use – implications for practical application.
  - High-field NMR studies of BaO impregnation to gamma alumina.
  - Synchrotron studies of sulfur speciation during sulfation and desulfation.

## 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 at PNNL



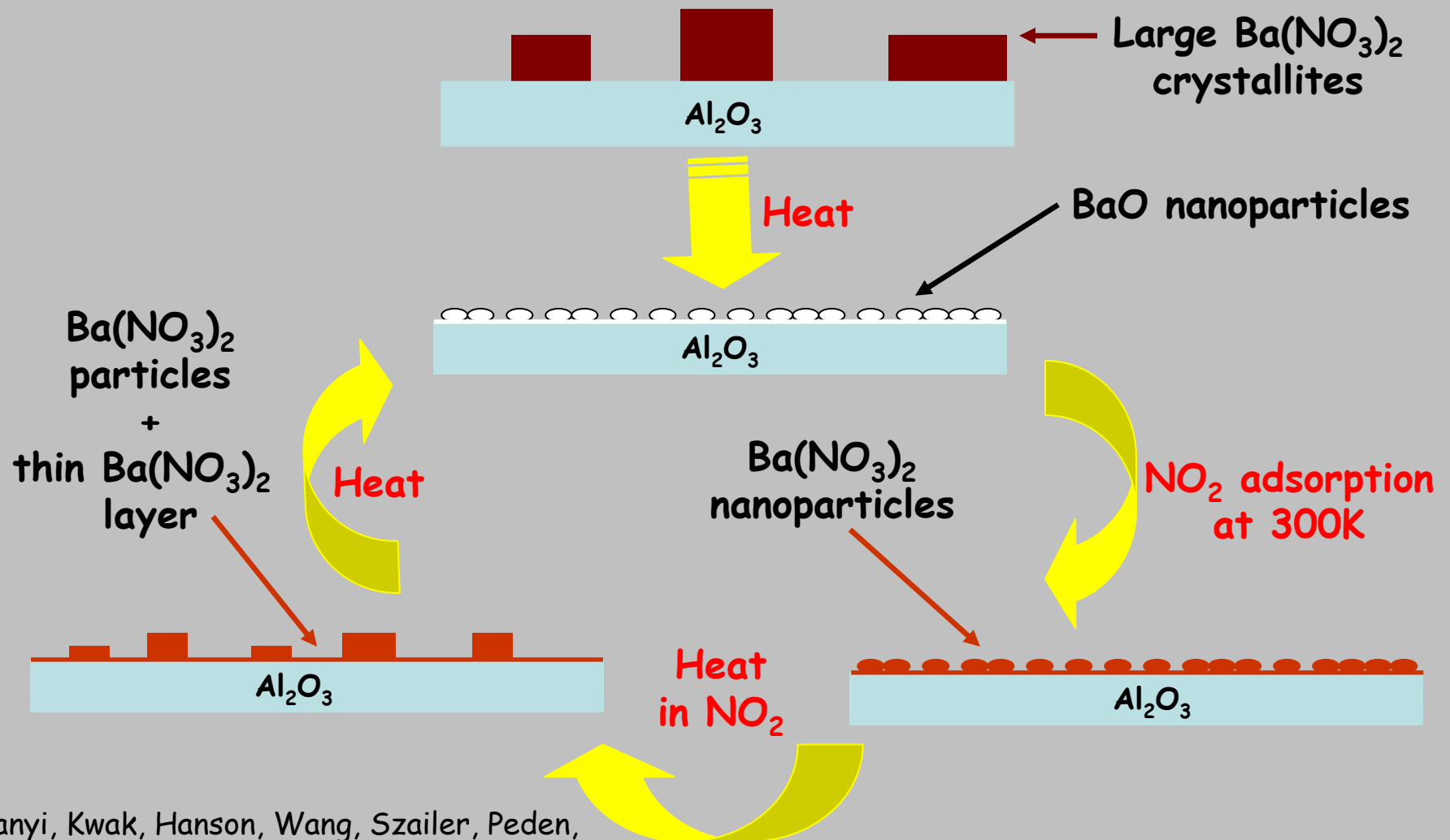
William R. Wiley

**EMSL**

Environmental Molecular Sciences Laboratory

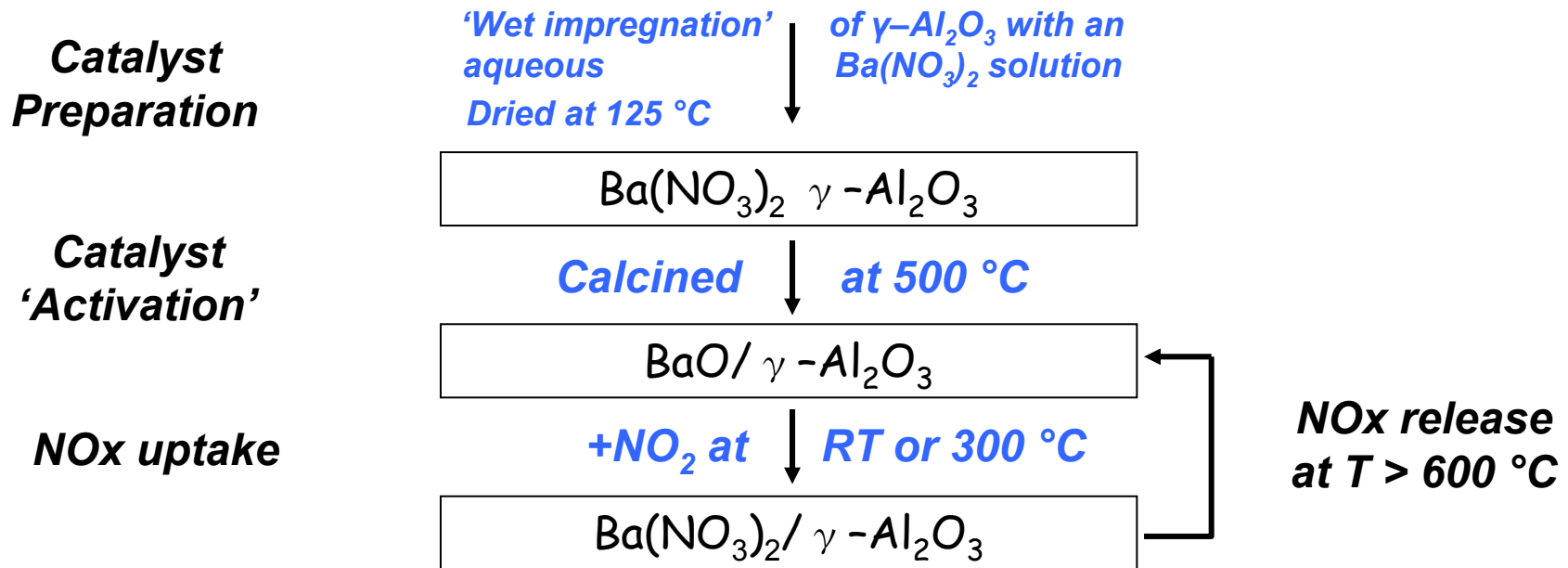


Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk'  $\text{Ba}(\text{NO}_3)_2$  morphologies present. These 'phases' can be distinguished spectroscopically.



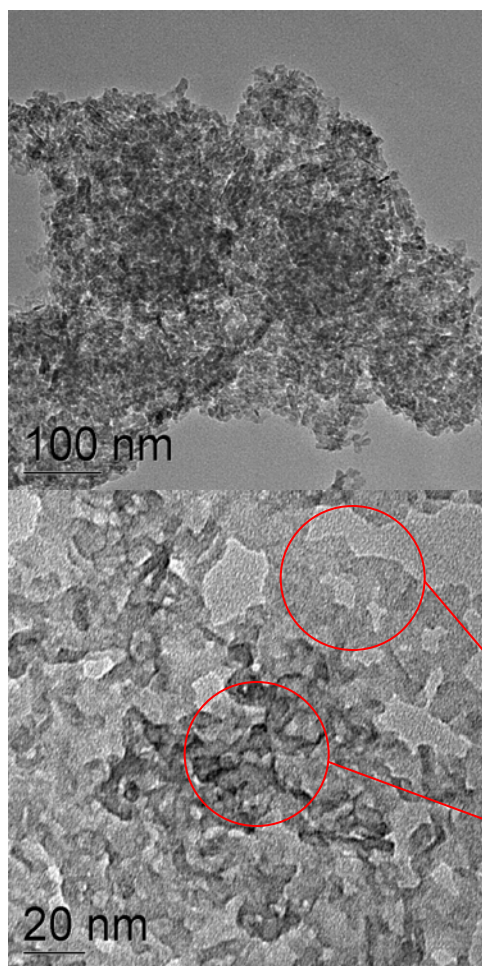
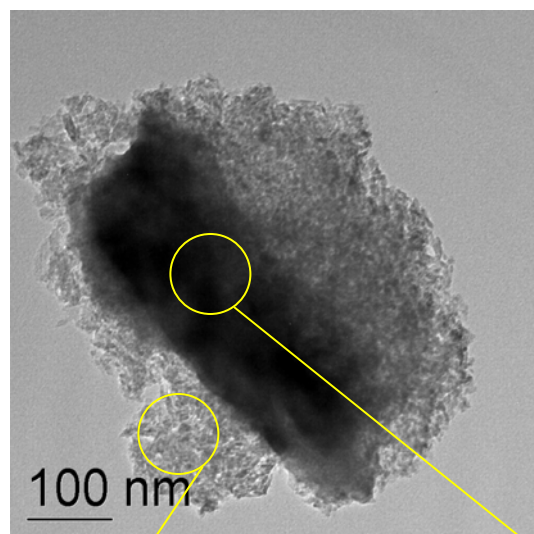
Szanyi, Kwak, Hanson, Wang, Szailer, Peden,  
J. Phys. Chem. B 109 (2005) 7339-7344.

# TEM/EDS and Temperature-Programmed X-Ray Diffraction (TP-XRD) Studies of Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

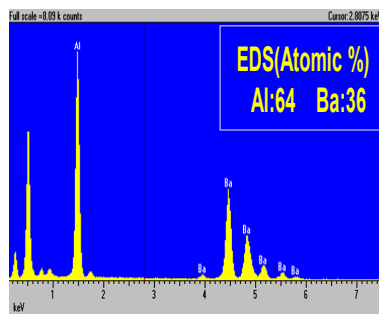
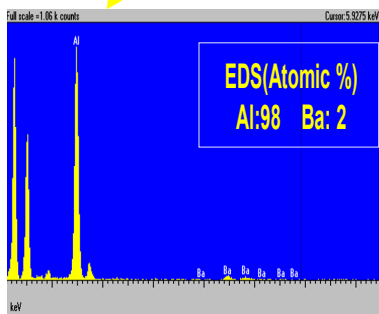


2%-, 8%-, and 20%-BaO on high surface area Al<sub>2</sub>O<sub>3</sub> materials by standard 'impregnation' techniques using aqueous Ba(NO<sub>3</sub>)<sub>2</sub> solutions.

# 20%-BaO/Al<sub>2</sub>O<sub>3</sub>, Calcined at 500 °C: TEM and EDS

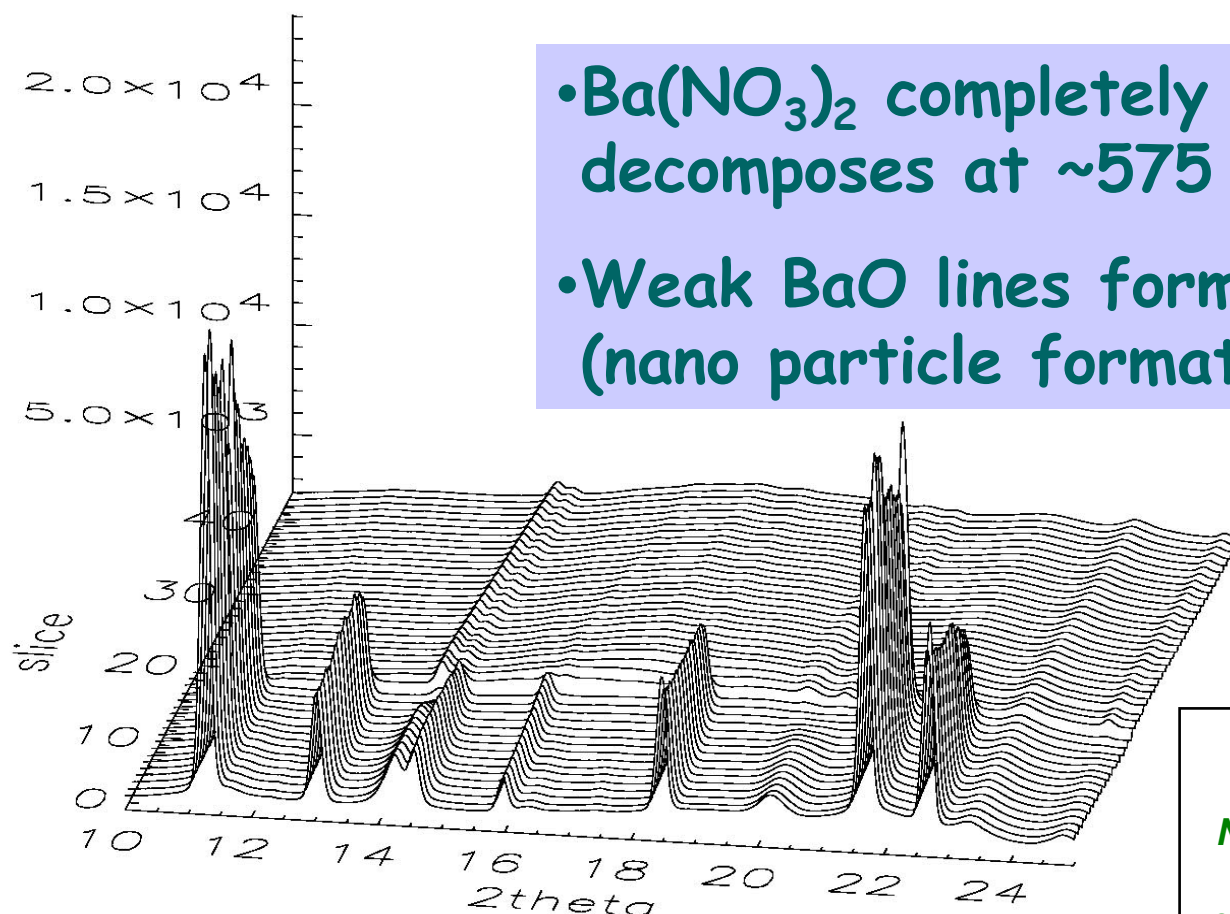


Well dispersed  
BaO particles  
all over the  
Al<sub>2</sub>O<sub>3</sub> support  
surface.



EDS (Atomic%)  
Al:83 Ba:17  
82 18

# Calcination of 20%-BaO/Al<sub>2</sub>O<sub>3</sub>: TP-XRD

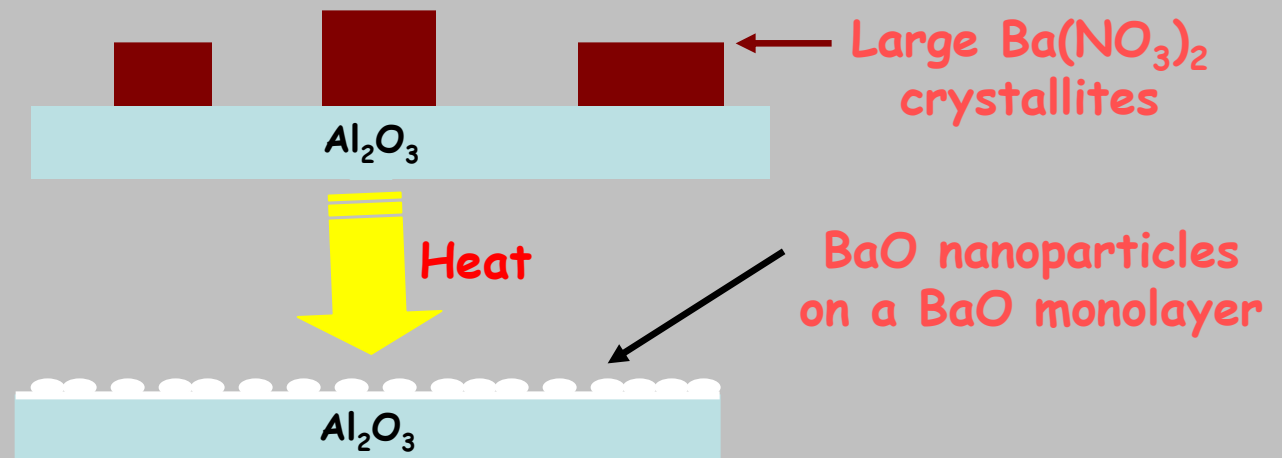


- Ba(NO<sub>3</sub>)<sub>2</sub> completely decomposes at ~575 °C
- Weak BaO lines form (nano particle formation)

Experiments performed at the National Synchrotron Light Source in collaboration with Jon Hanson, Brookhaven National Laboratory

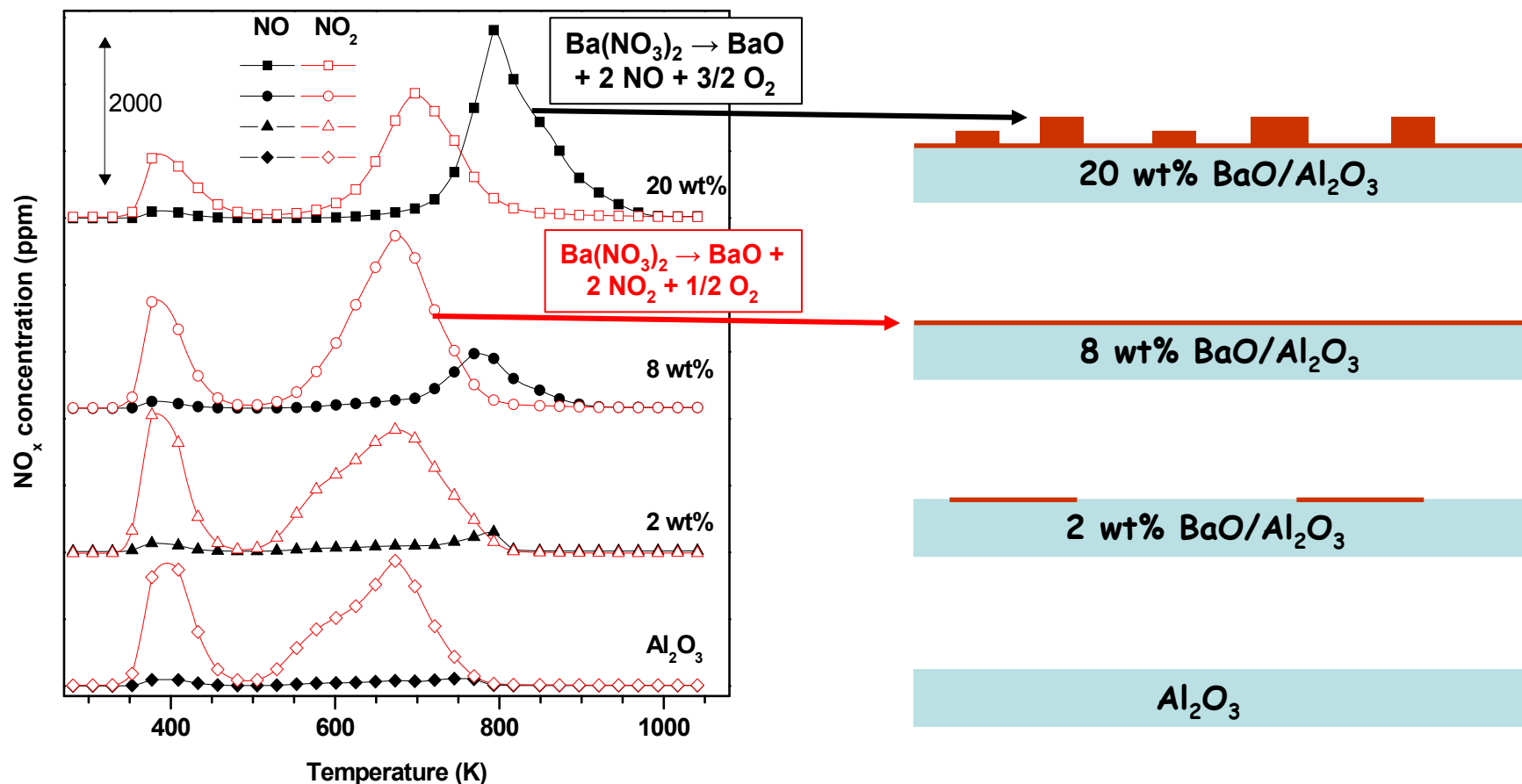
Szanyi, Kwak, Hanson, Wang, Szailer, Peden,  
J. Phys. Chem. B **109** (2005) 7339-7344.

# The morphology of BaO/ $\text{Al}_2\text{O}_3$ as synthesized



- TEM/EDS and synchrotron TR-XRD also used to determine morphology changes during  $\text{NO}_x$  uptake and release. Spectroscopic 'signatures' were identified for these two morphologies in TPD, FTIR and NMR data.

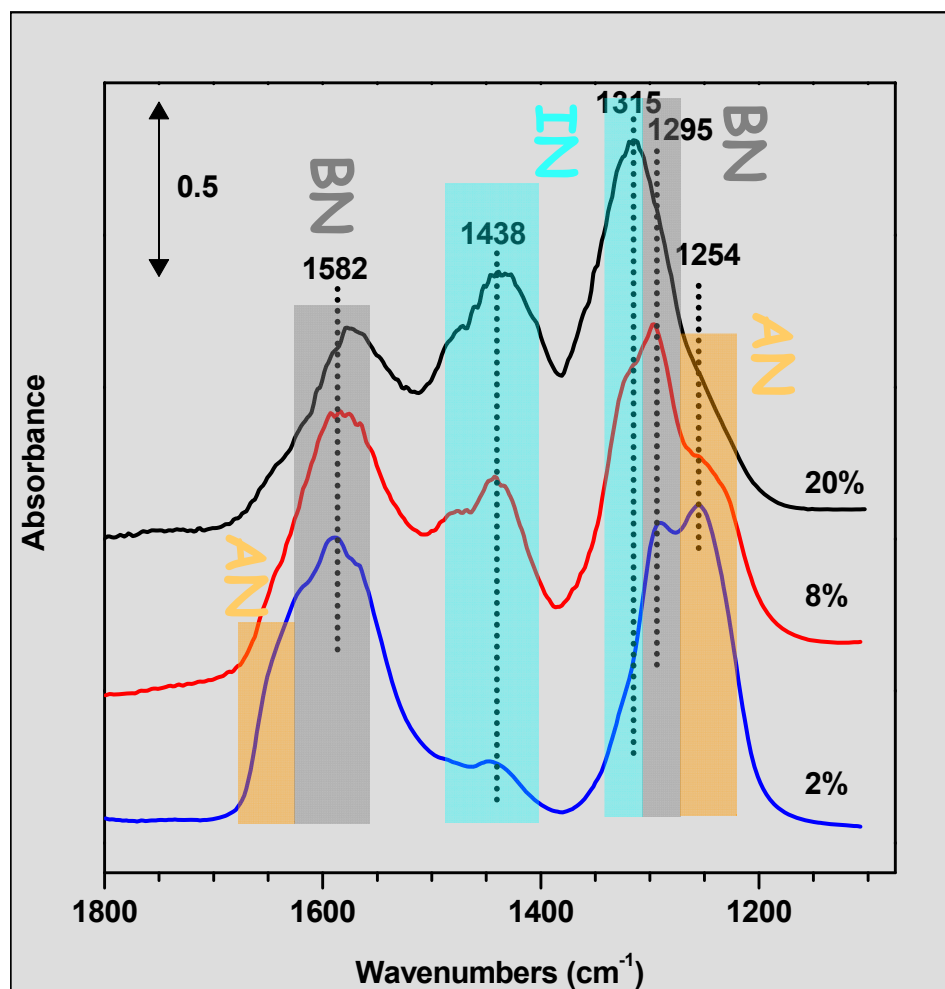
# Distribution of NO and NO<sub>2</sub> Desorption Features Very Sensitive to BaO Loading



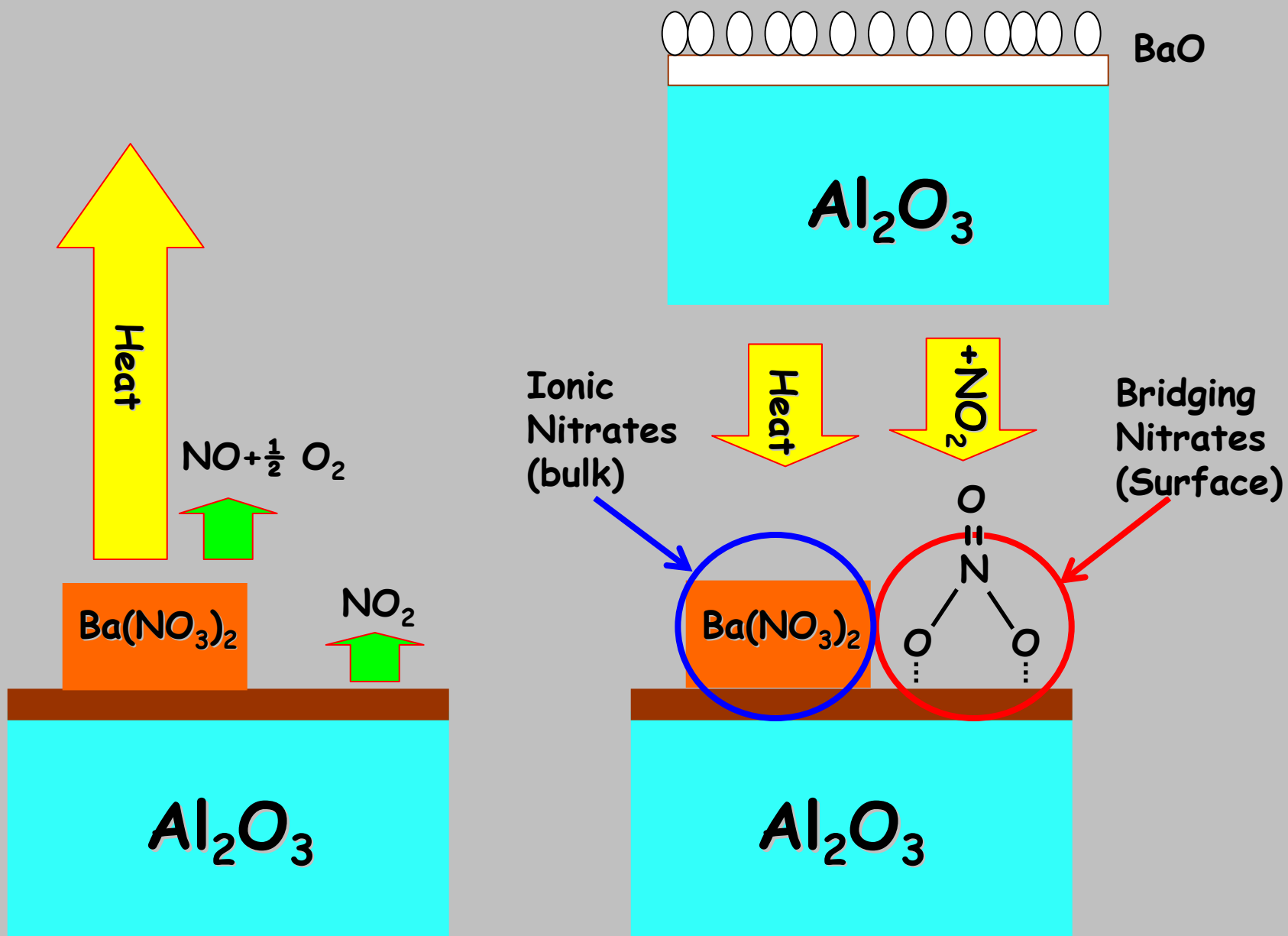


# FTIR after $\text{NO}_2$ adsorption on 2%, 8%-, and 20%-BaO/ $\text{Al}_2\text{O}_3$ at 300K

- $\text{Al}_2\text{O}_3$ -bound nitrates (AN) decrease continuously with Ba coverage.
- Surface ("bidentate" - BN) and bulk (ionic - IN) nitrates are observed on BaO/ $\text{Al}_2\text{O}_3$  catalysts. Their ratio (BN/IN) also decreases with BaO loading.



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?)  $\text{BaAl}_2\text{O}_4$  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.

# Potential problem with the morphology model



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Applied Catalysis B: Environmental 46 (2003) 393–413



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FTIR analysis of storage behavior and sulfur tolerance in barium-based NO<sub>x</sub> storage and reduction (NSR) catalysts

Paul T. Fanson<sup>a</sup>, Margaret R. Horton<sup>a</sup>, W. Nicholas Delgass<sup>a</sup>, Jochen Lauterbach<sup>b,\*</sup>

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<sup>b</sup> Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

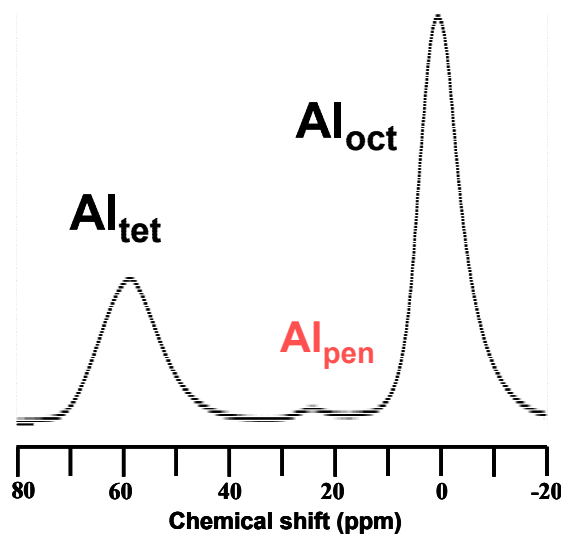
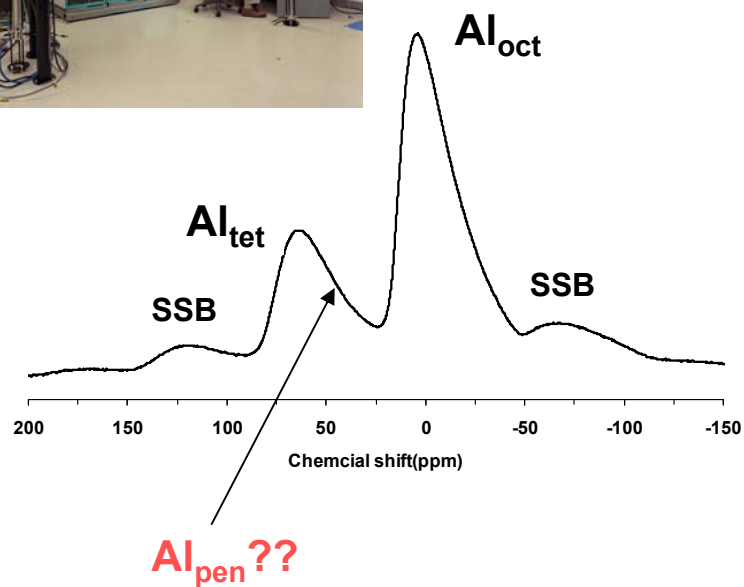
Received 12 August 2002; received in revised form 11 December 2002; accepted 16 June 2003

## 2. Experimental methods

...The low solubility of the barium nitrate salt and the pore volume of the support, limited the amount of barium that could be impregnated in a single step to **8–10 wt.%**. **Based on the unit cell of bulk BaO and the surface area of the support, this loading corresponds to approximately one monolayer.** Multiple impregnation steps were employed in the samples where the barium loading exceeds 10 wt.%...

- Assuming that BaO forms perfect 2D clusters or domains on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> substrate is 200 m<sup>2</sup>/g, 1 ML of BaO on 200 m<sup>2</sup>/gm alumina is more like 25% weight loading, not 8%.

# Use of one-of-a-kind Ultra-High Field NMR in EMSL for Catalysis Studies



- Penta-coordinate  $\text{Al}^{3+}$  ions readily observable in  $\gamma\text{-Al}_2\text{O}_3$ ;
- These species are located at the alumina surface.

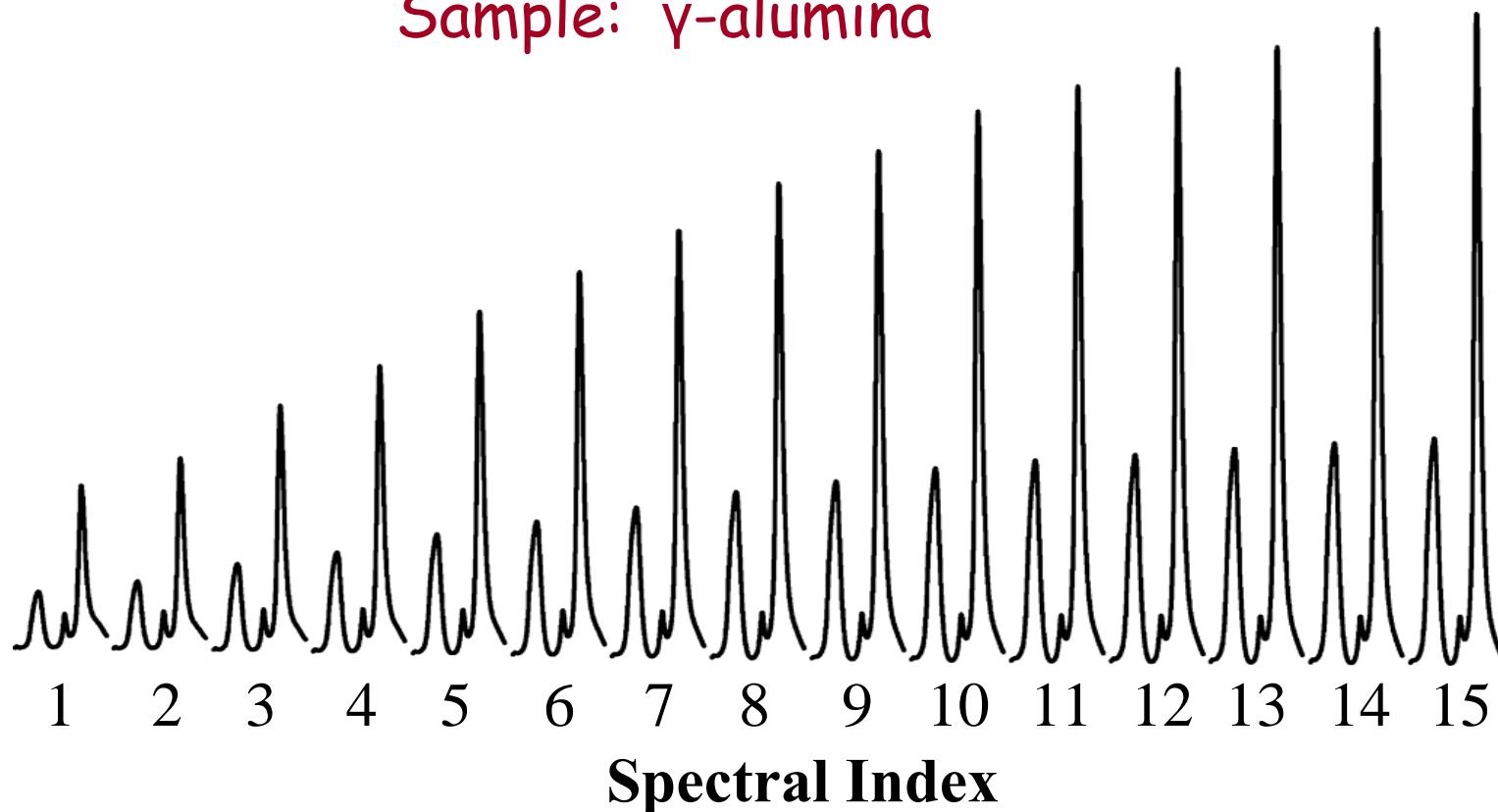
JH Kwak, JZ Hu, DH Kim, J Szanyi, CHF Peden, Journal of Catalysis, submitted.

# The Spin-Lattice $^{27}\text{Al}$ Relaxation Time ( $T_1$ ) Measurement

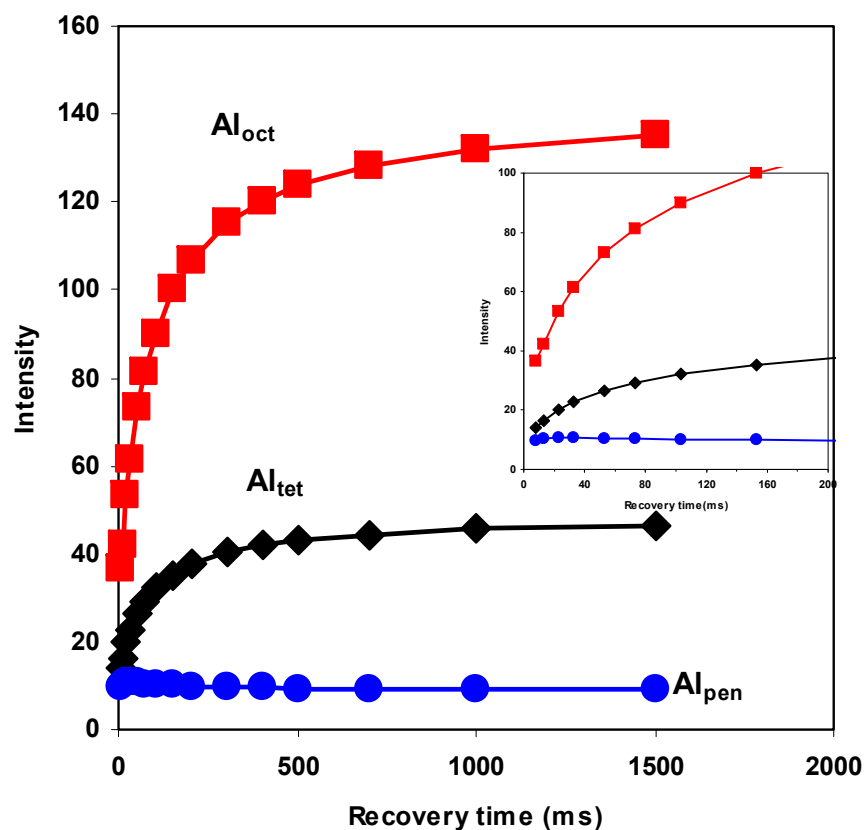
## Recovery Time

- 1: 8m
- 2: 13m
- 3: 23m
- 4: 33m
- 5: 53m
- 6: 73m
- 7: 0.103s
- 8: 0.153s
- 9: 0.203s
- 10: 0.303s
- 11: 0.403s
- 12: 0.503s
- 13: 0.703s
- 14: 1.003s
- 15: 1.503s

Sample:  $\gamma$ -alumina



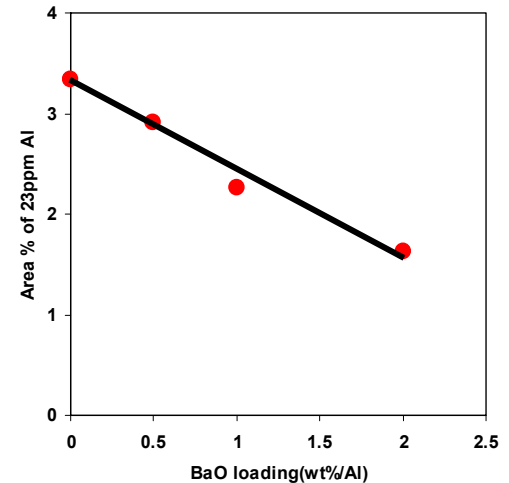
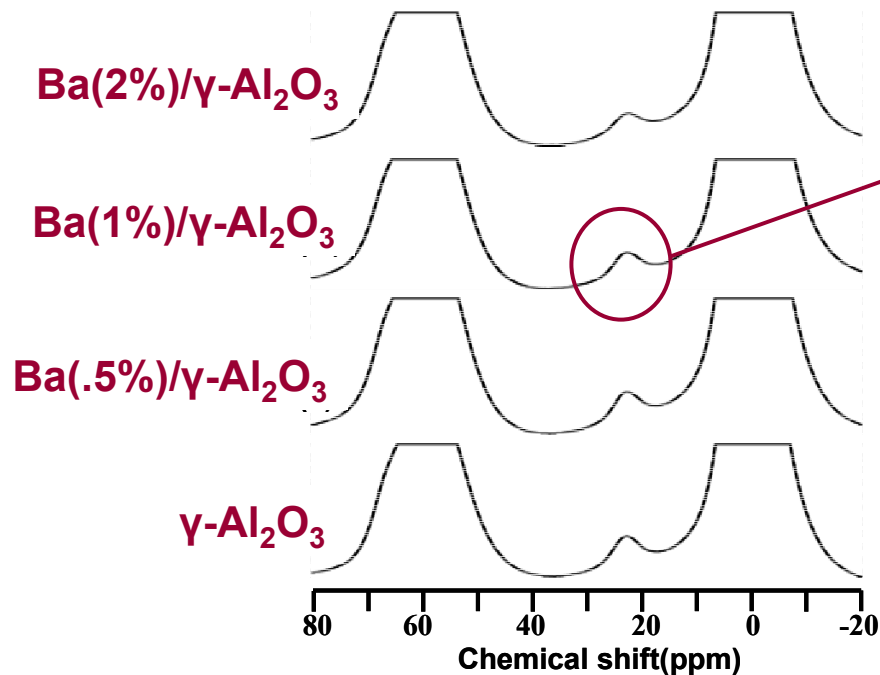
JH Kwak, JZ Hu, DH Kim, J Szanyi, CHF Peden, Journal of Catalysis, submitted.



**Conclusion:** The 23ppm peak relaxes extremely fast with the value of the  $^{27}Al$   $T_1$  much less than 8ms, indicating that this species is located at the surface.

# Lewis acidic 5-fold Al sites on $\gamma$ - $\text{Al}_2\text{O}_3$ surfaces are nucleation sites for catalytic phases!

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



Impregnation with aqueous  $\text{Ba}(\text{NO}_3)_2$  followed by calcination in dry air at 500 °C.

JH Kwak, JZ Hu, DH Kim, J Szanyi, CHF Peden, Journal of Catalysis, submitted.



# Ultra-High Resolution Electron Microscopy for Characterization of Catalyst Microstructures and Deactivation Mechanisms

*L. F. Allard, D. A. Blom, C. K. Narula, and S. A. Bradley\**

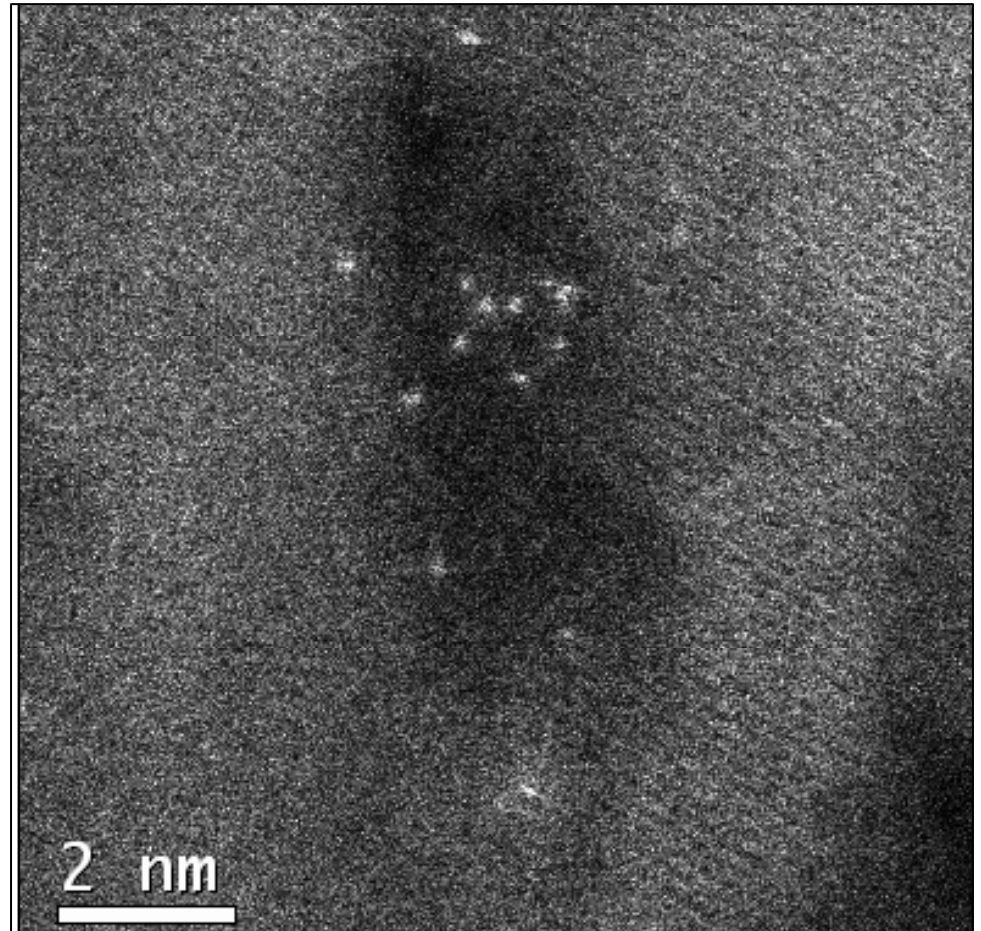
*Oak Ridge National Laboratory*

*P.O. Box 2008, MS-6064*

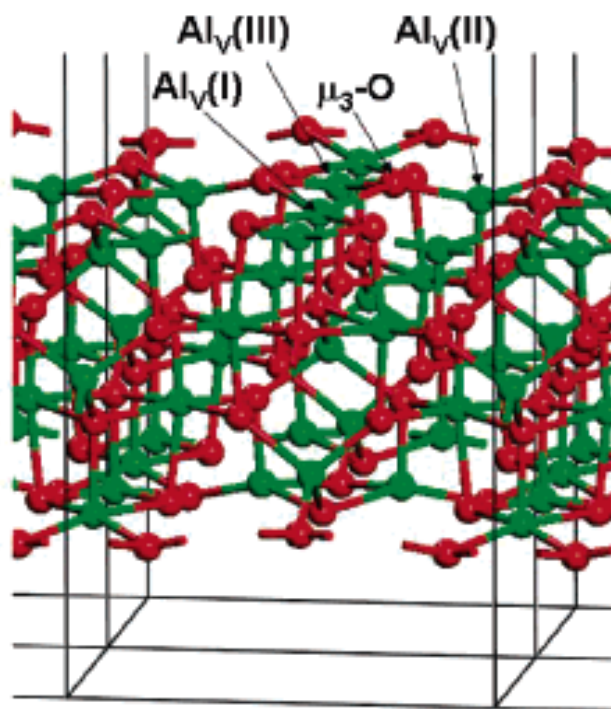
*Oak Ridge, TN 37831-6064*

*\*UOP LLC, Des Plaines, IL 60017*

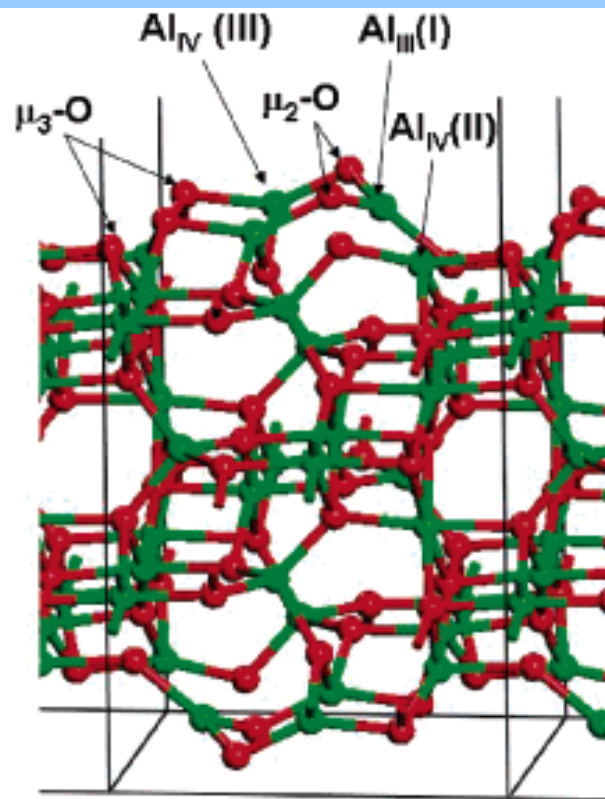
Oxidized platinum species on  $\gamma\text{-Al}_2\text{O}_3$  after impregnation and calcination; very high-resolution micrograph shows Pt dispersed as only single atoms or dimers.



# Stable $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Surfaces Expose 5- and 3-fold Al-atoms



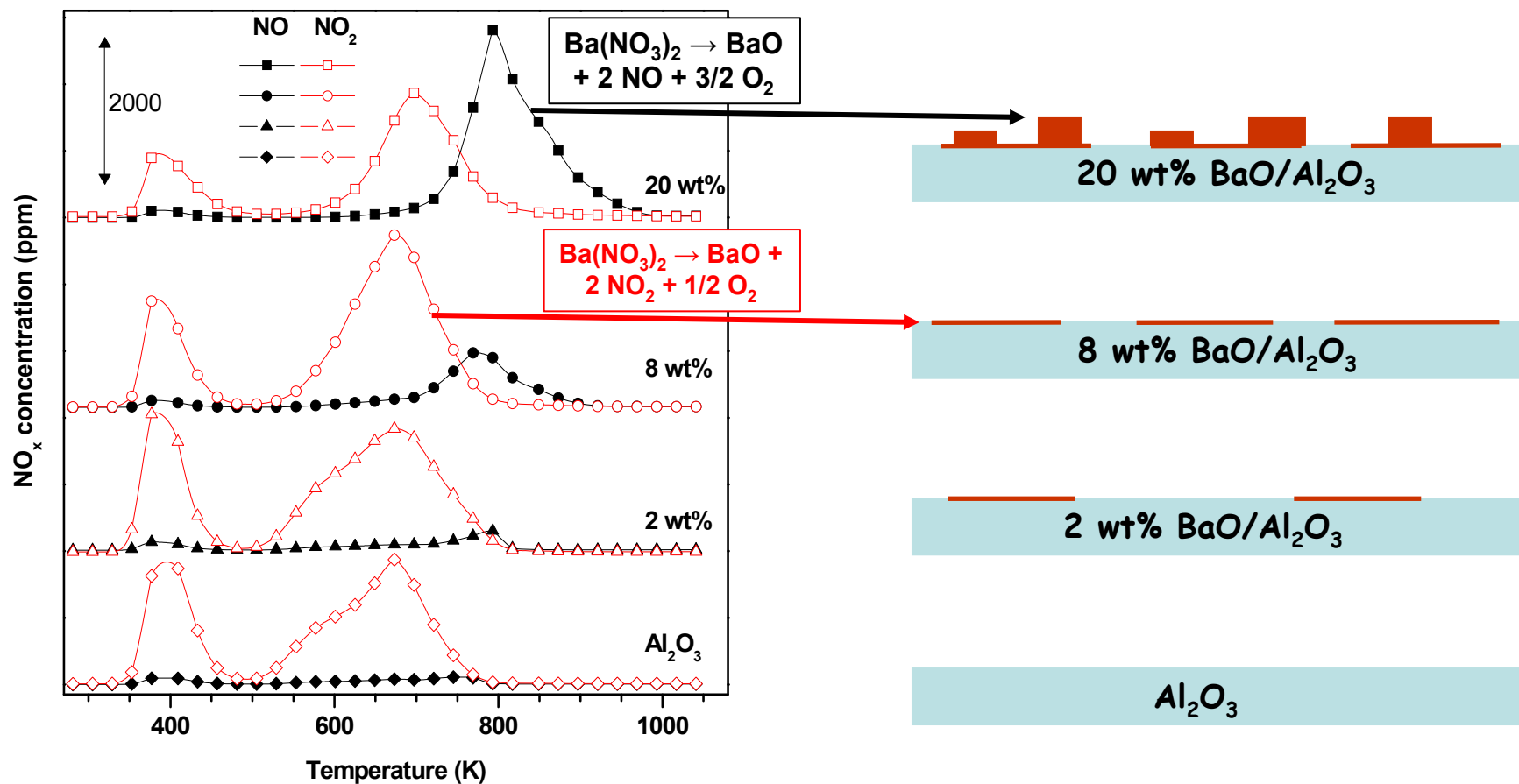
$\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100)



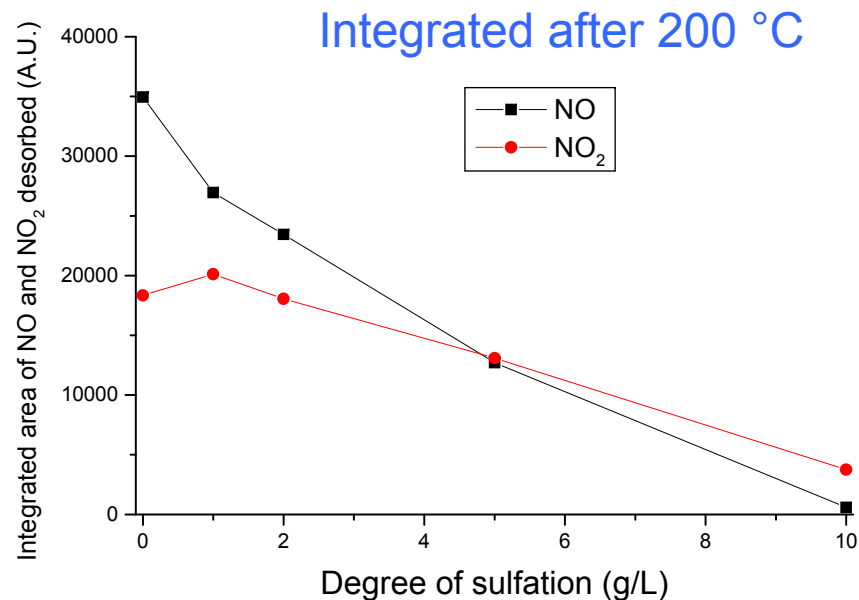
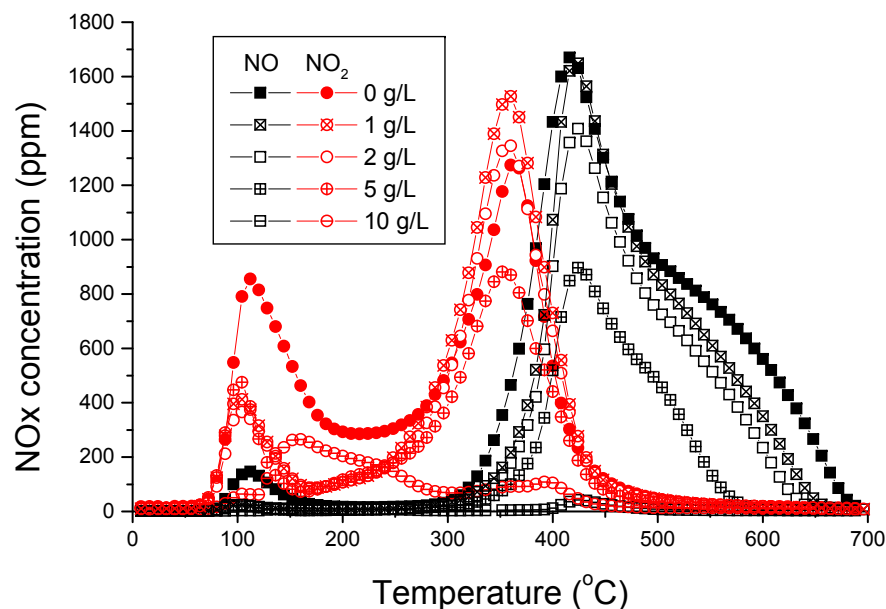
$\gamma$ -Al<sub>2</sub>O<sub>3</sub>(110)

S.H. Kim, D.C. Sorescu, O. Byl, and J.T. Yates, Jr., *J. Phys. Chem. B* 2006, 110, 4742.

# Distribution of NO and NO<sub>2</sub> Desorption Features Very Sensitive to BaO Loading

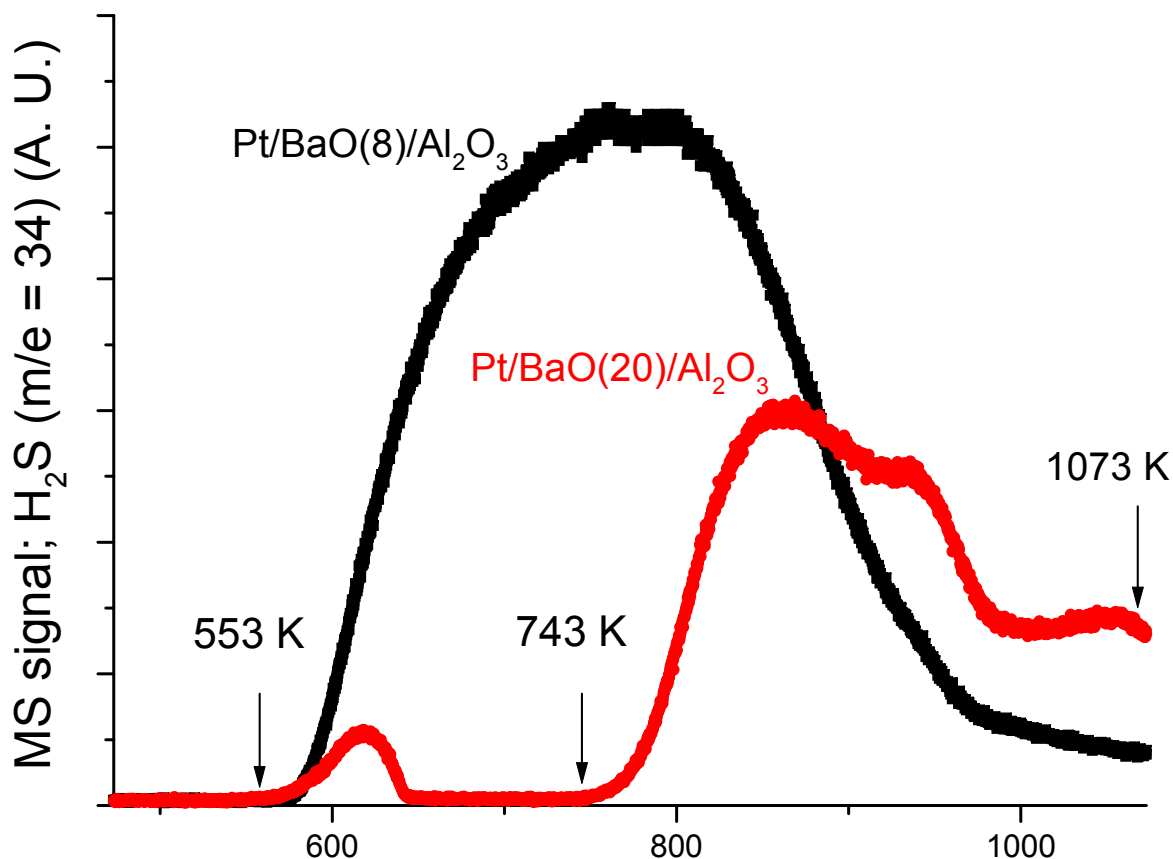


# Sulfation of a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> LNT followed by *in situ* NO<sub>2</sub> TPD



In other studies, we have assigned the desorption of NO<sub>2</sub> and NO, around 350 °C and 450 °C, to decomposition of 'monolayer' and 'bulk' nitrates, respectively. While SO<sub>2</sub> monotonically decreased the desorption from 'bulk' nitrates, NO<sub>2</sub> adsorption on 'monolayer' nitrates is unaffected at low sulfur levels.

Sulfur is removed much more readily from sulfated Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub> than from Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub>.



H<sub>2</sub> TPRX spectra for 5g/L sulfated Pt/BaO(8)/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO(20)/Al<sub>2</sub>O<sub>3</sub> samples.

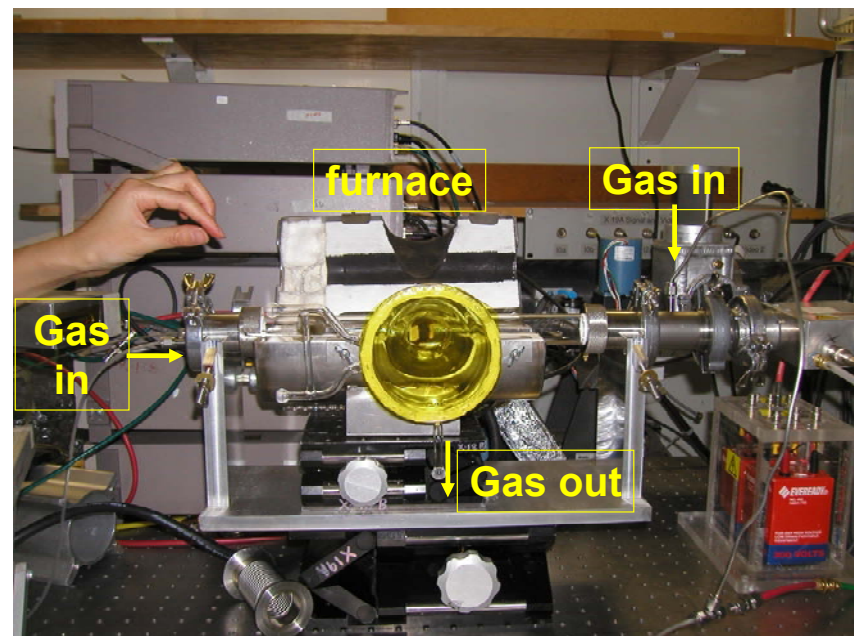
Kim, Szanyi, Kwak, Szailer, Hanson, Wang, Peden, *J. Phys. Chem. B* **110** (2006) 10441.

# Mechanistic Studies of Sulfation and Desulfation Chemistry at the National Synchrotron Light Source (Brookhaven National Laboratory)

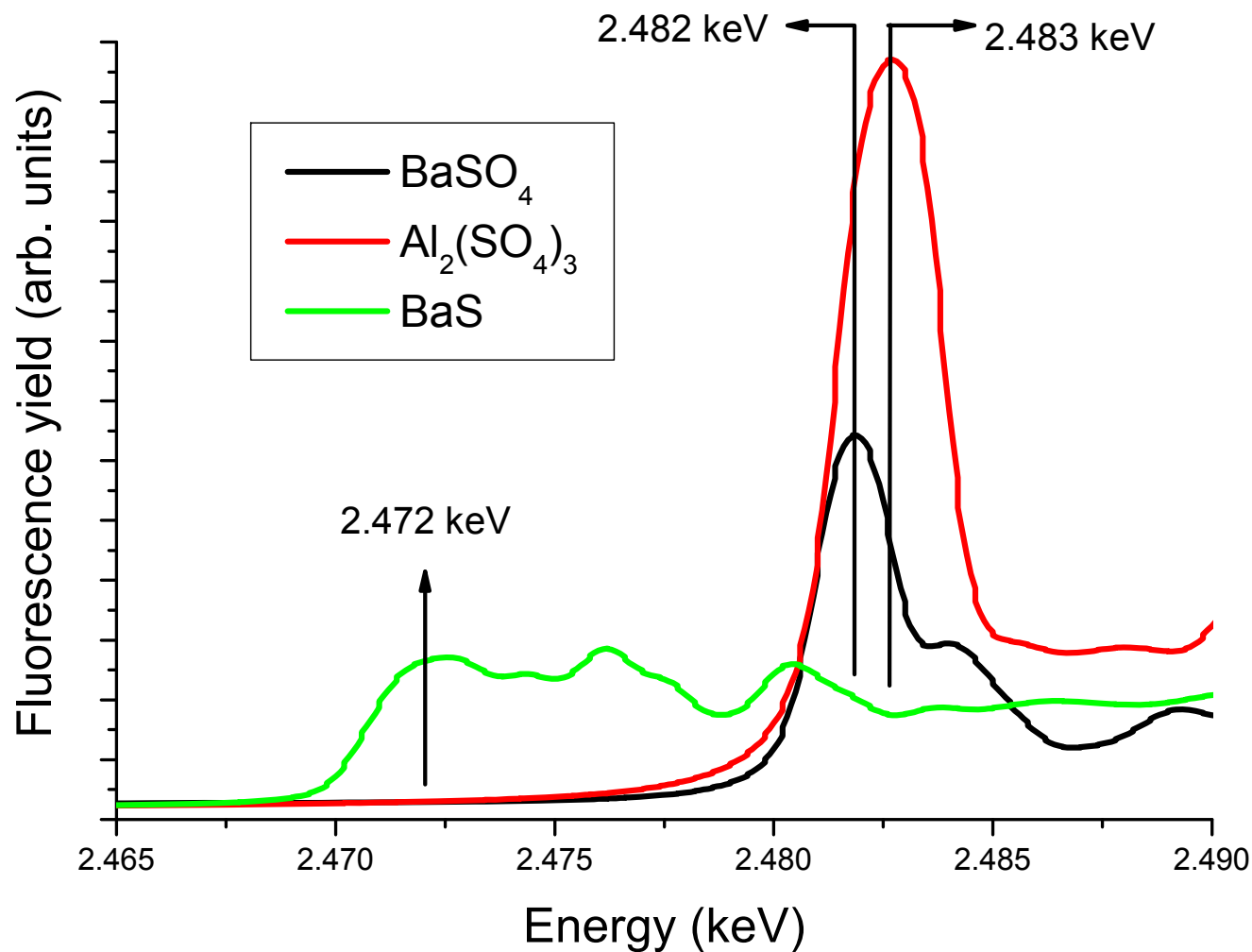
Do Heui Kim, Janos Szanyi, Xianqin Wang, Chuck Peden  
Pacific Northwest National Laboratory

# *In situ* Sulfur XANES Experiments

- All of the sulfated samples were prepared in advance and measured *in situ* while flowing gas mixtures of varying composition.
- Beamline at X19A of NSLS at Brookhaven Natl. Lab.
- Spectra were recorded in fluorescence mode using a Lytle detector.
- Specially designed fluorescence reactor cell

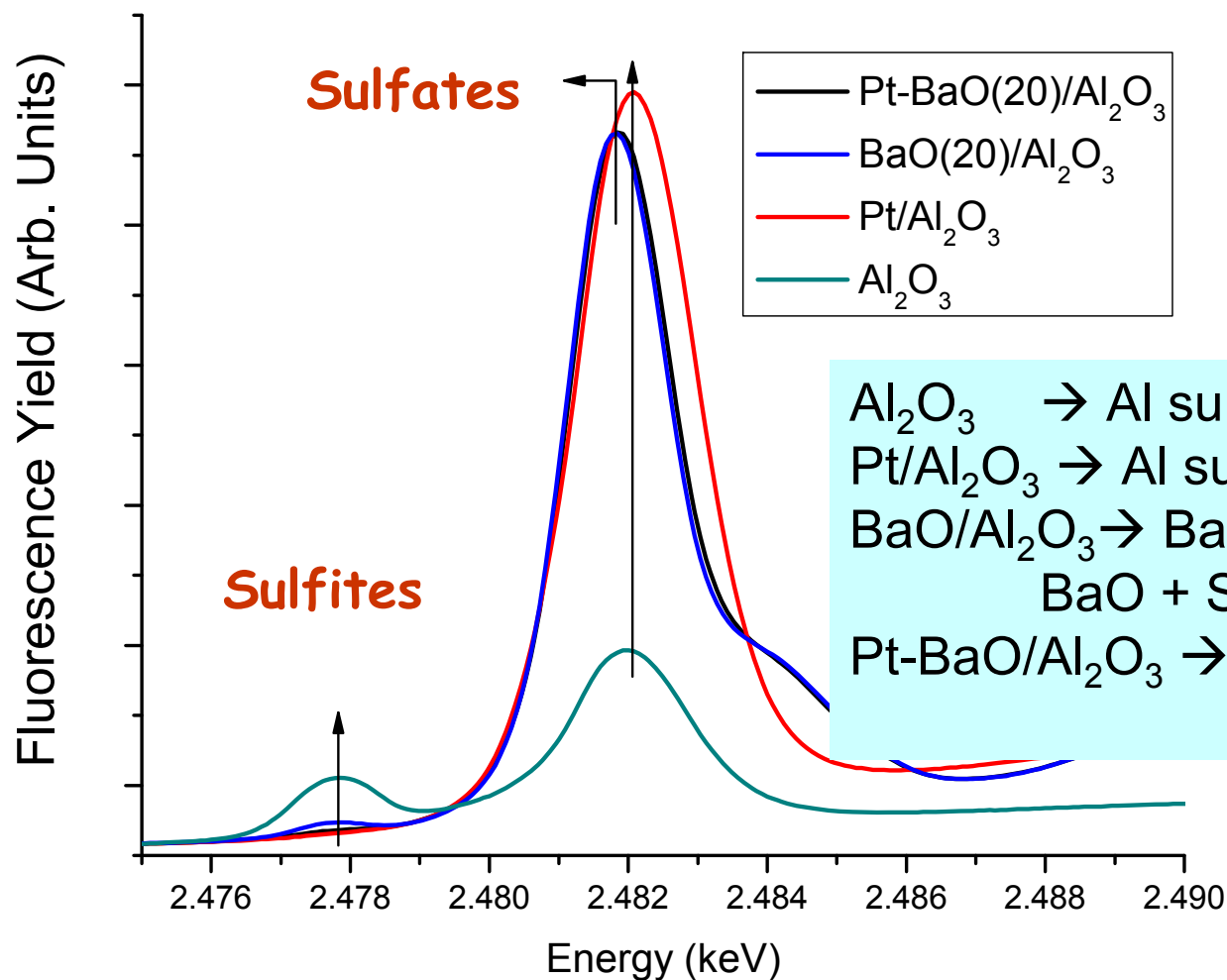


# S XANES Reference Spectra

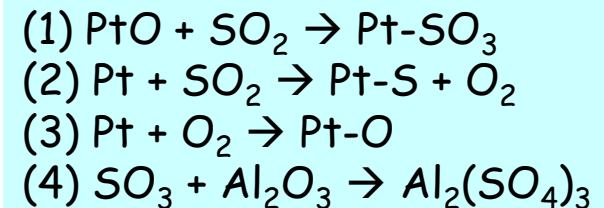
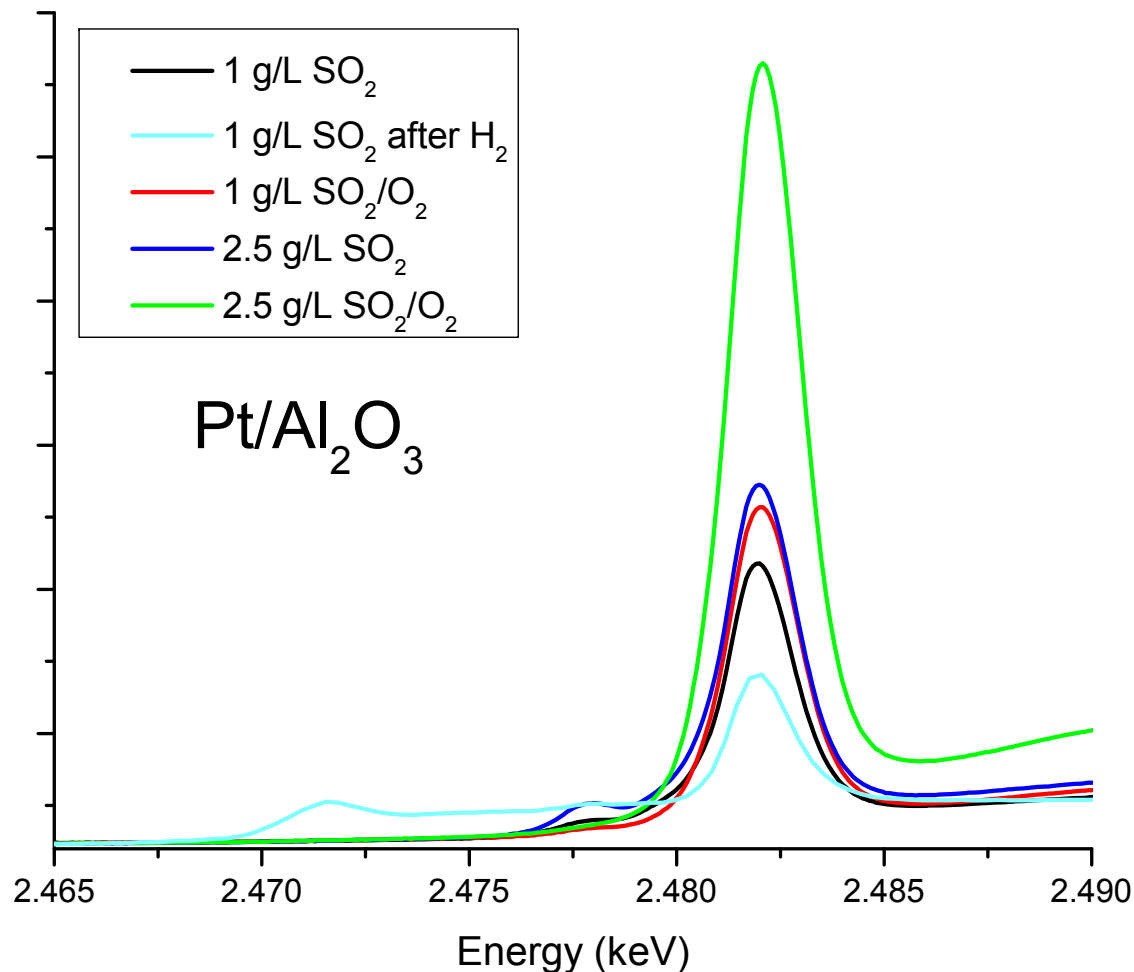




# Sulfation ( $\text{SO}_2/\text{O}_2$ , 2.5 g/L) of different materials

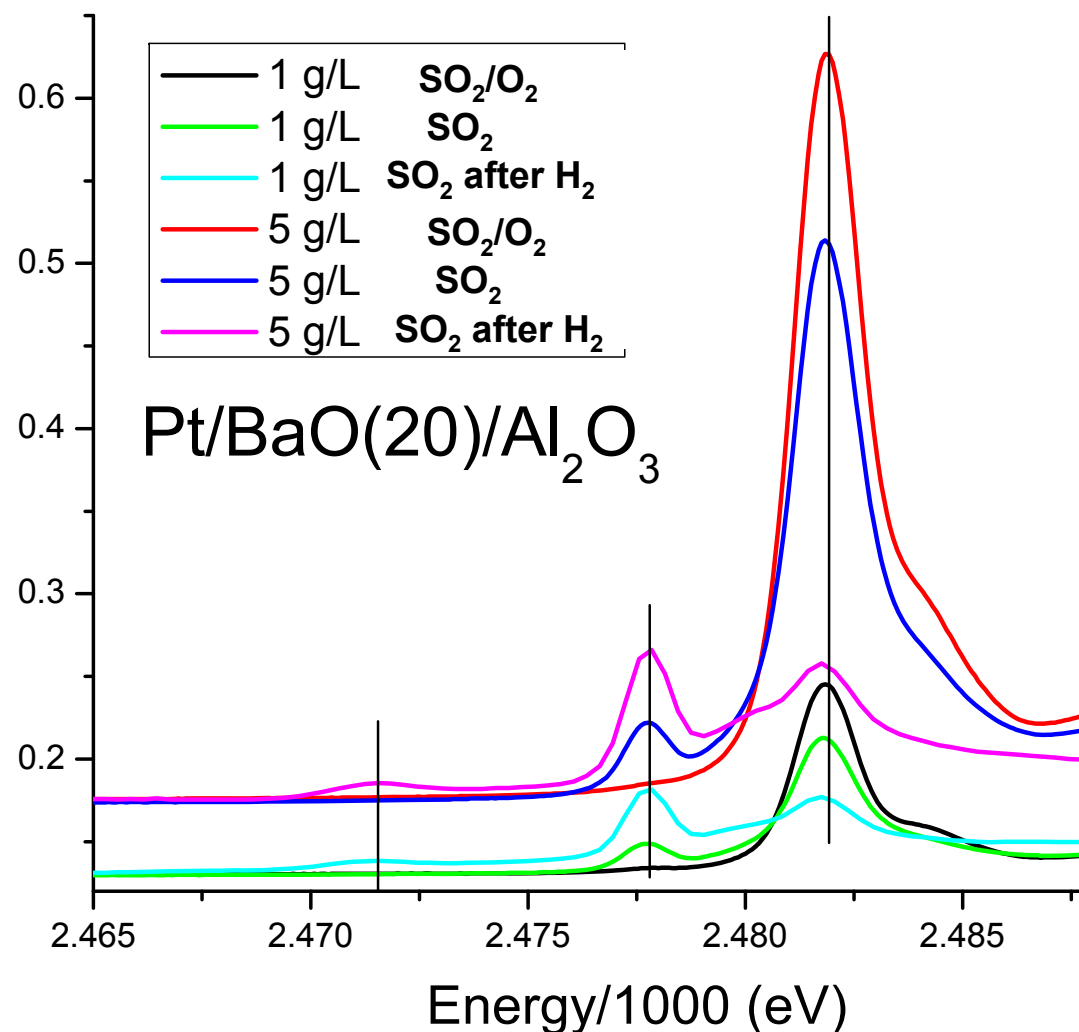


# Sulfation over Pt/Al<sub>2</sub>O<sub>3</sub> with various methods



- Even in the absence of gas-phase O<sub>2</sub>, SO<sub>3</sub> can form from Rxn (1), and then spill over to the neighboring alumina to form aluminum sulfates (via rxn (4)).
- In the presence of gas-phase O<sub>2</sub>, rxn (3) proceeds insuring that rxn (1) can continue.
- Rxn (2) is dominant when the Pt is reduced.

# Sulfation over Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub> with various methods



- Even without gaseous oxygen, sulfation proceeds over barium loaded samples, unlike Pt/Al<sub>2</sub>O<sub>3</sub> ones.
- After reduction, Pt-S is formed as Pt/Al<sub>2</sub>O<sub>3</sub>, but the main species are sulfite, attributed to the less metallic Pt due to the interaction neighboring barium species.
- After reduction, direction interaction between barium species and SO<sub>2</sub> to form sulfate is also affected, attributed to the change of barium species after reduction.

# Effect of SO<sub>2</sub> exposure conditions: SO<sub>2</sub> vs. SO<sub>2</sub> + O<sub>2</sub> vs. SO<sub>2</sub> + H<sub>2</sub>

For Pt/BaO/Al<sub>2</sub>O<sub>3</sub>:

Loss of NO<sub>x</sub> storage capacity upon sulfation decreases in the following order:

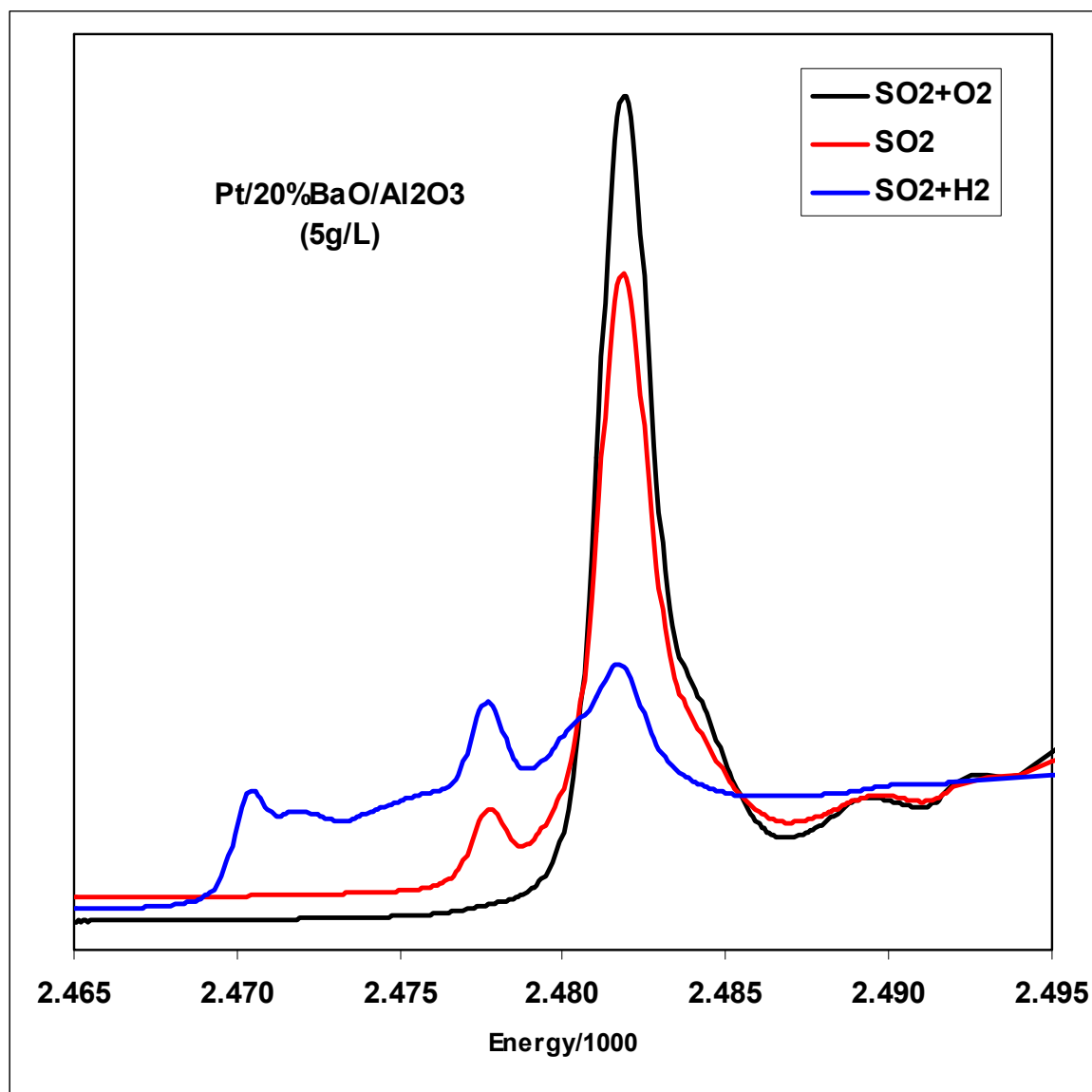


Sulfur deactivation of Pt/SiO<sub>2</sub>, Pt/BaO/Al<sub>2</sub>O<sub>3</sub>, and BaO/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage catalysts: Influence of SO<sub>2</sub> exposure conditions

Jazaer Dawody<sup>a,b,\*</sup>, Magnus Skoglundh<sup>a,c</sup>, Louise Olsson<sup>a,c</sup>, Erik Fridell<sup>a,b</sup>

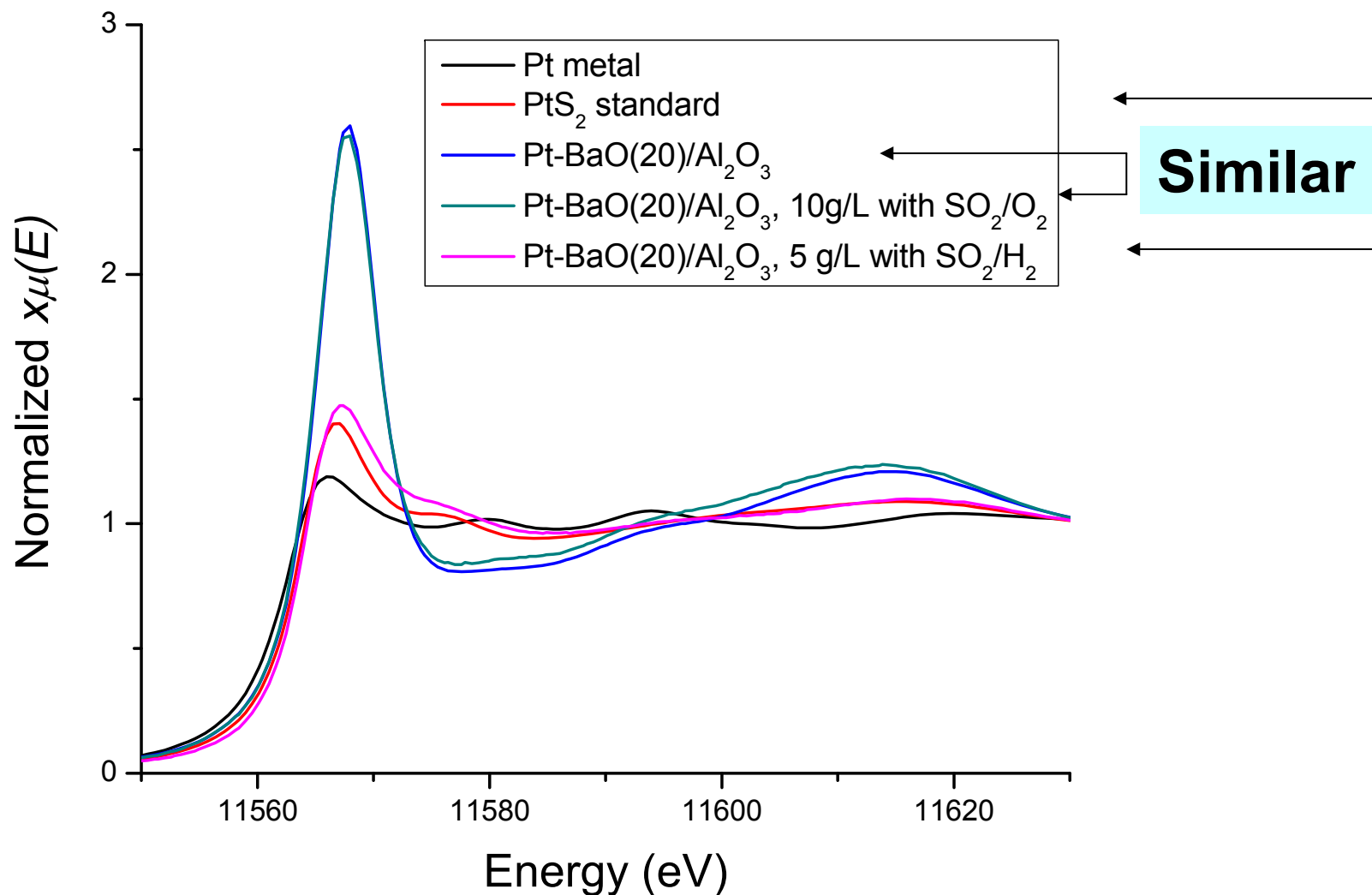
Journal of Catalysis 234 (2005) 206–218

# Effect of gas conditions during sulfation



- Nature of the species formed during sulfation depends on the gas composition. In oxidizing conditions, only sulfates form. However, for reducing conditions lead to the formation of sulfur species with various oxidation states.
- Higher sulfide peak compared with sulfation after reduction of the catalyst.

# Pt XANES: standard and sulfated samples



# Summary and Conclusions

- The morphology of BaO/Al<sub>2</sub>O<sub>3</sub> LNT materials is remarkably dynamic during NO<sub>x</sub> storage and reduction. A “monolayer” of Ba(NO<sub>3</sub>)<sub>2</sub> forms on the alumina surface in addition to large “bulk” Ba(NO<sub>3</sub>)<sub>2</sub> particles. *Effects of H<sub>2</sub>O and CO<sub>2</sub> on these morphology changes subject of just completed studies.*
- These different morphologies display dramatically different behavior with respect to NO<sub>x</sub> removal temperature, formation of a deactivating high-temperature BaAl<sub>2</sub>O<sub>4</sub> phase, and temperature requirements of desulfation.
- Synchrotron studies of sulfation and desulfation are being used to determine sulfur speciation during these processes. The results are aiding the understanding of the effects of gas composition during sulfur deposition and removal on the loss and recovery of NO<sub>x</sub> storage capacity.