Fundamental Studies of NOx Adsorber Materials

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Today's Discussion

- DOE/OFCVT-funded studies of BaO/Al_2O_3 Lean NOx Trap (LNT) materials
  - LNT catalyst material morphologies
    - Effects on desulfation. Also will discuss effects of sulfation levels.
    - New insights on LNT morphologies from FTIR, computations, and ultra-high field NMR.
    - Implications for LNT (and other) catalyst preparation processes.

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

EMSL
MATERIALS ANALYSIS USER CENTER
at the High Temperature Materials Laboratory (HTML)

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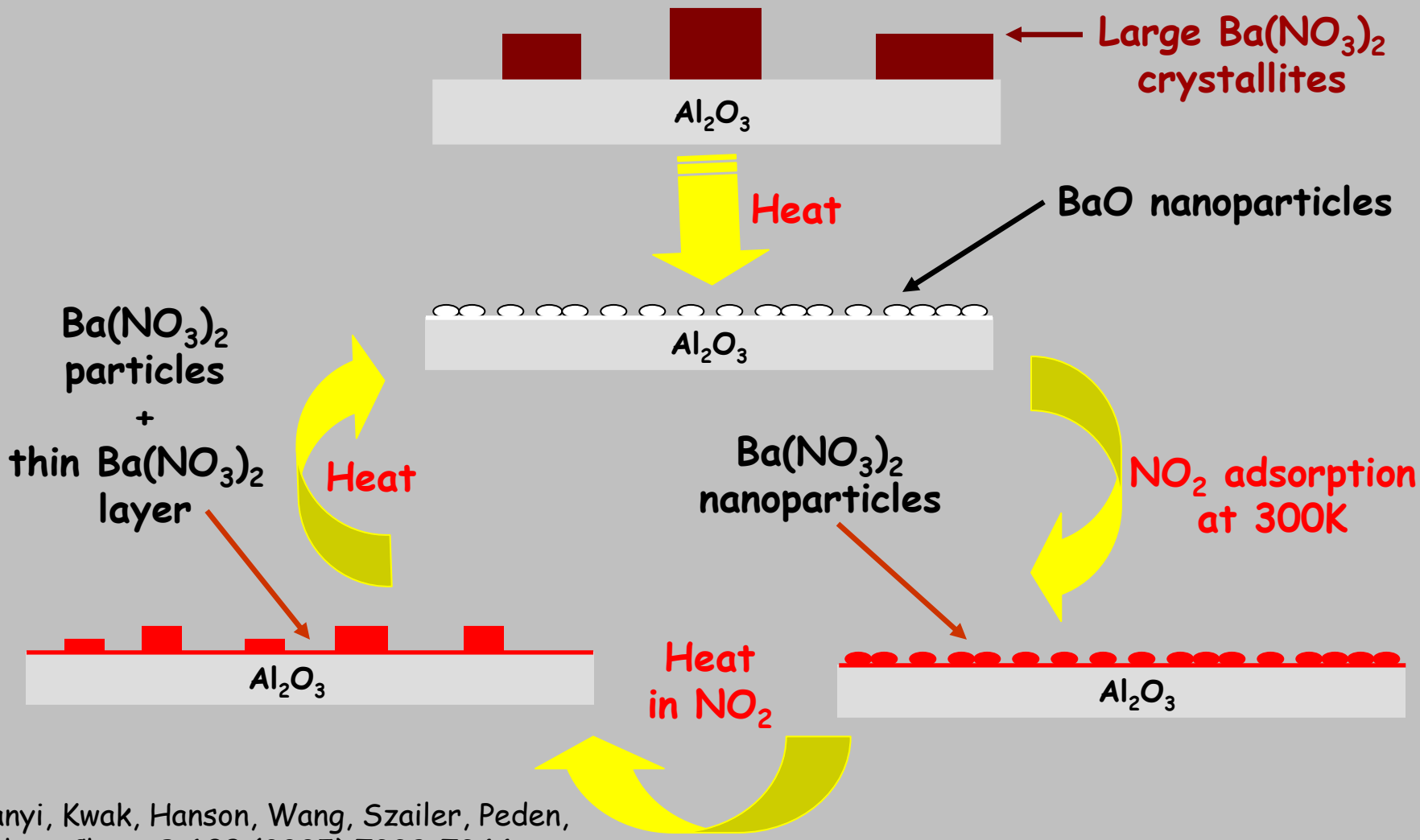
Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' $Ba(NO_3)_2$ morphologies present. These 'phases' can be distinguished spectroscopically.



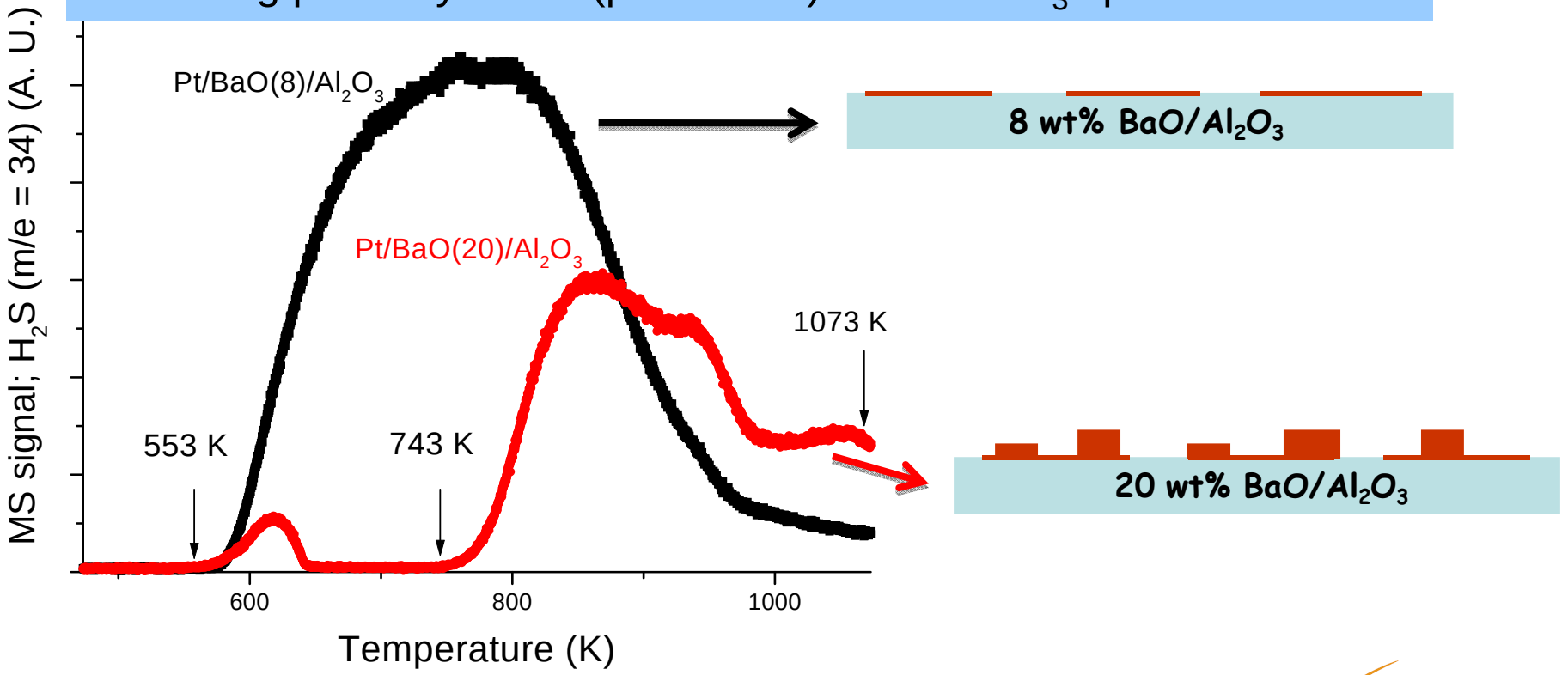
Szanyi, Kwak, Hanson, Wang, Szailer, Peden, J. Phys. Chem. B **109** (2005) 7339-7344.

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.
- 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.
- "Monolayer" Ba-phase is also easier to 'de-sulfate'.

Temperature programmed desulfation of LNT catalysts in H_2

Sulfated Pt-BaO(8)/Al_2O_3, consisting of predominantly of "surface" (monolayer) BaO/$BaCO_3$ species, displays more facile desulfation by H_2 at lower temperature than sulfated Pt-BaO(20)/Al_2O_3, a material containing primarily "bulk" (particulate) BaO/$BaCO_3$ species.



D.H. Kim , J. Szanyi, J.H. Kwak, T. Sailer, J.C. Hanson, C.M. Wang, C.H.F. Peden, J. Phys. Chem. B **110** (2006) 10441.

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In situ Synchrotron EXAFS/XANES and XRD

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)

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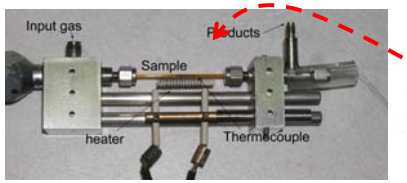
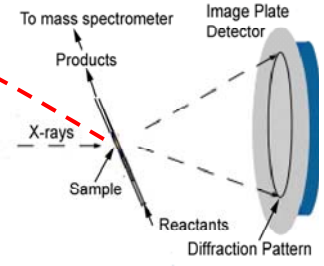
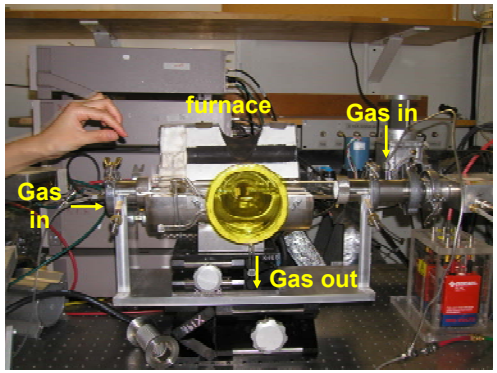
In-situ TR-XRD







In-situ *S* XANES & Pt EXAFS

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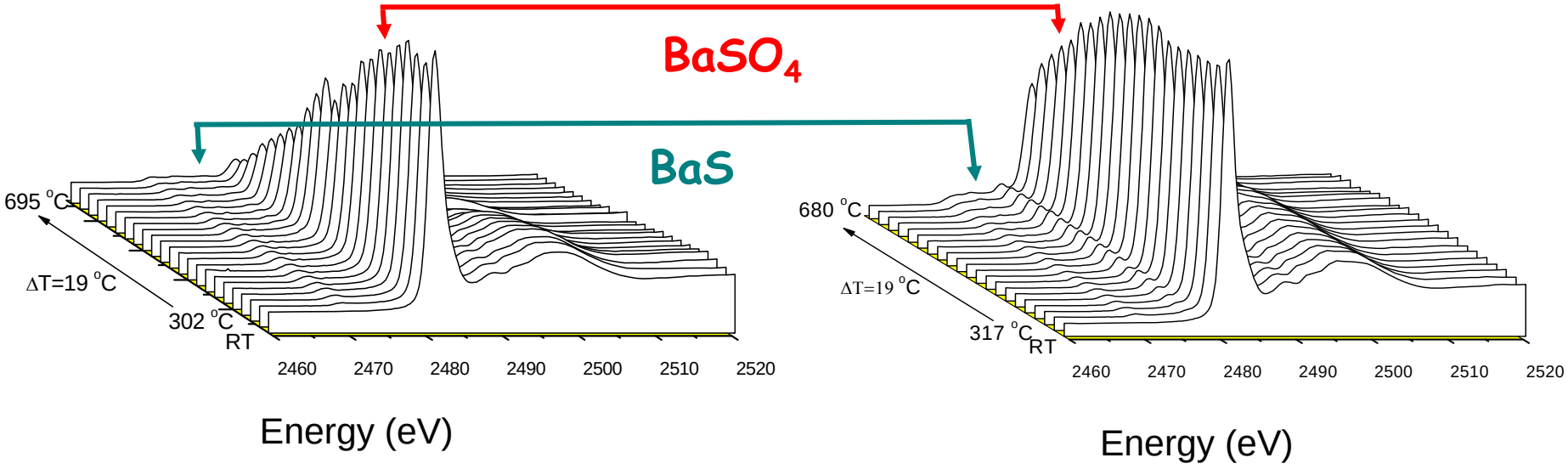
XANES results confirm that catalysts with lower Ba loading desulfate more readily

Catalysts with lower Ba loading desulfate at lower temperatures, desulfate more completely, and result in a much lower amount of a refractory BaS phase.

Pt-BaO(8)/Al_2O_3, 5 g/L, with H_2 only

Pt-BaO(20)/Al_2O_3, 5 g/L, with H_2 only



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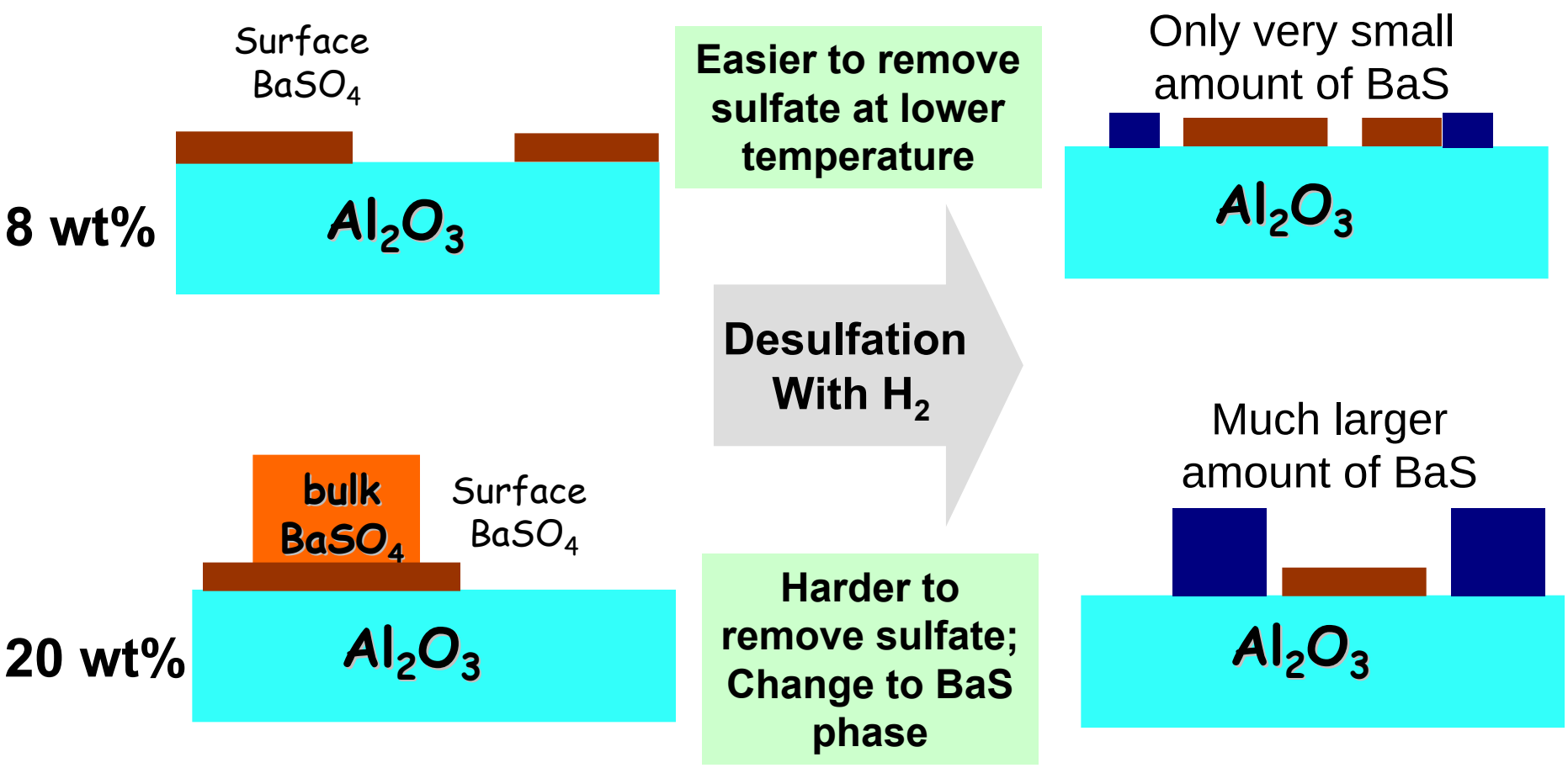
Schematic Model



Question: What about effects of sulfur loading?

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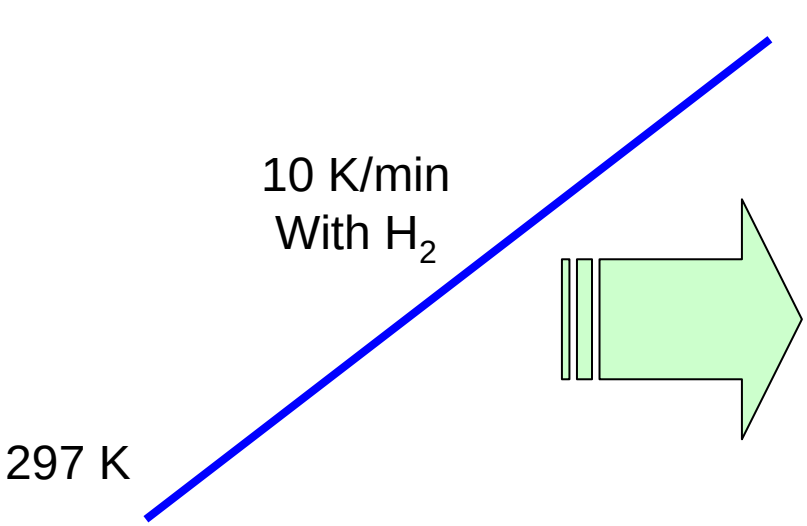
Approach

- Pre-sulfated with SO_2/O_2 at 573 K
  - 1g/L Pt-BaO(20)/Al_2O_3 (S uptake / Ba = 0.12)
  - 5 g/L Pt-BaO(20)/Al_2O_3 (S uptake / Ba = 0.62)
- Temperature programmed reaction with H_2

  → desulfation behavior of the sulfated samples with H_2 as a function of temp.



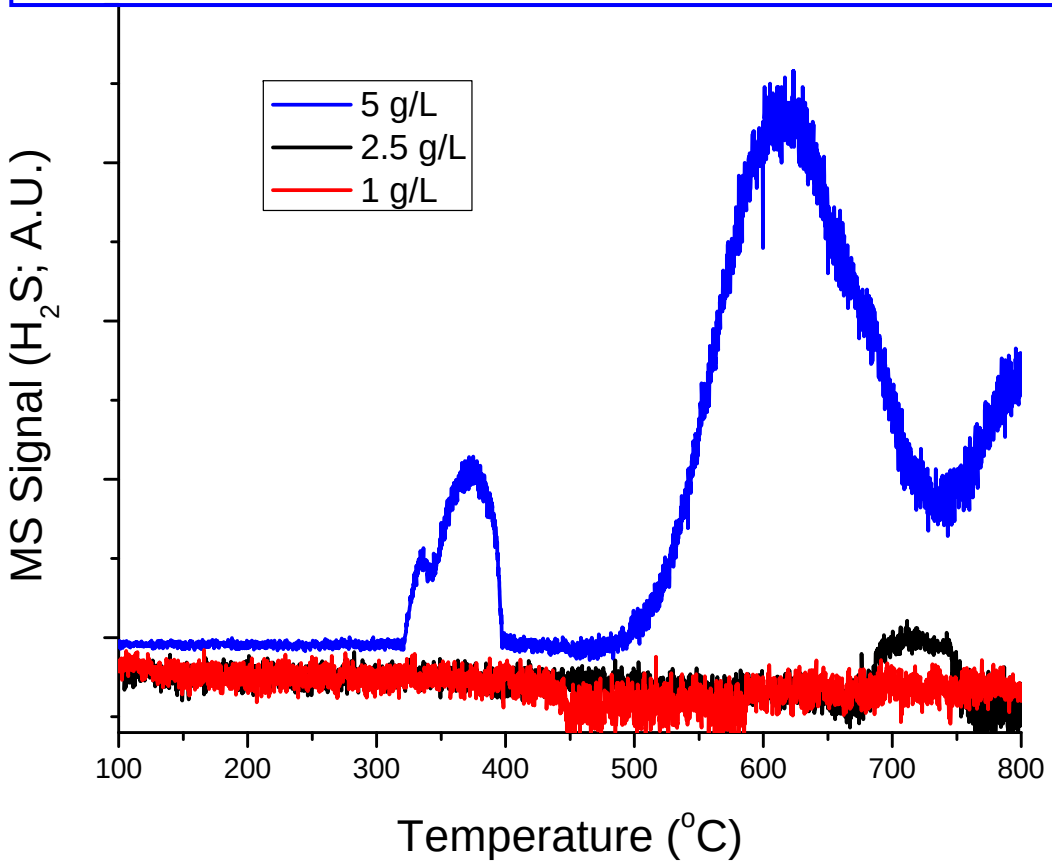
Desorption gas analysis (**H_2 TPRX**)

Residual sulfur analysis (***in situ* S XANES**)

Morphology analysis (**TR-XRD**)

H_2 TPRX: sulfur loading effect

$$BaSO_4 + H_2 \rightarrow H_2S \uparrow + ??$$



The amount of H_2S desorbed is not proportional to the sulfur loading. Sulfur species deposited at the early stage are much harder to remove.

D.H. Kim , J. Szanyi, J.H. Kwak, X. Wang, J.C. Hanson, M.H. Engelhard, C.H.F. Peden, J. Phys. Chem. C **113** (2009) 7336.

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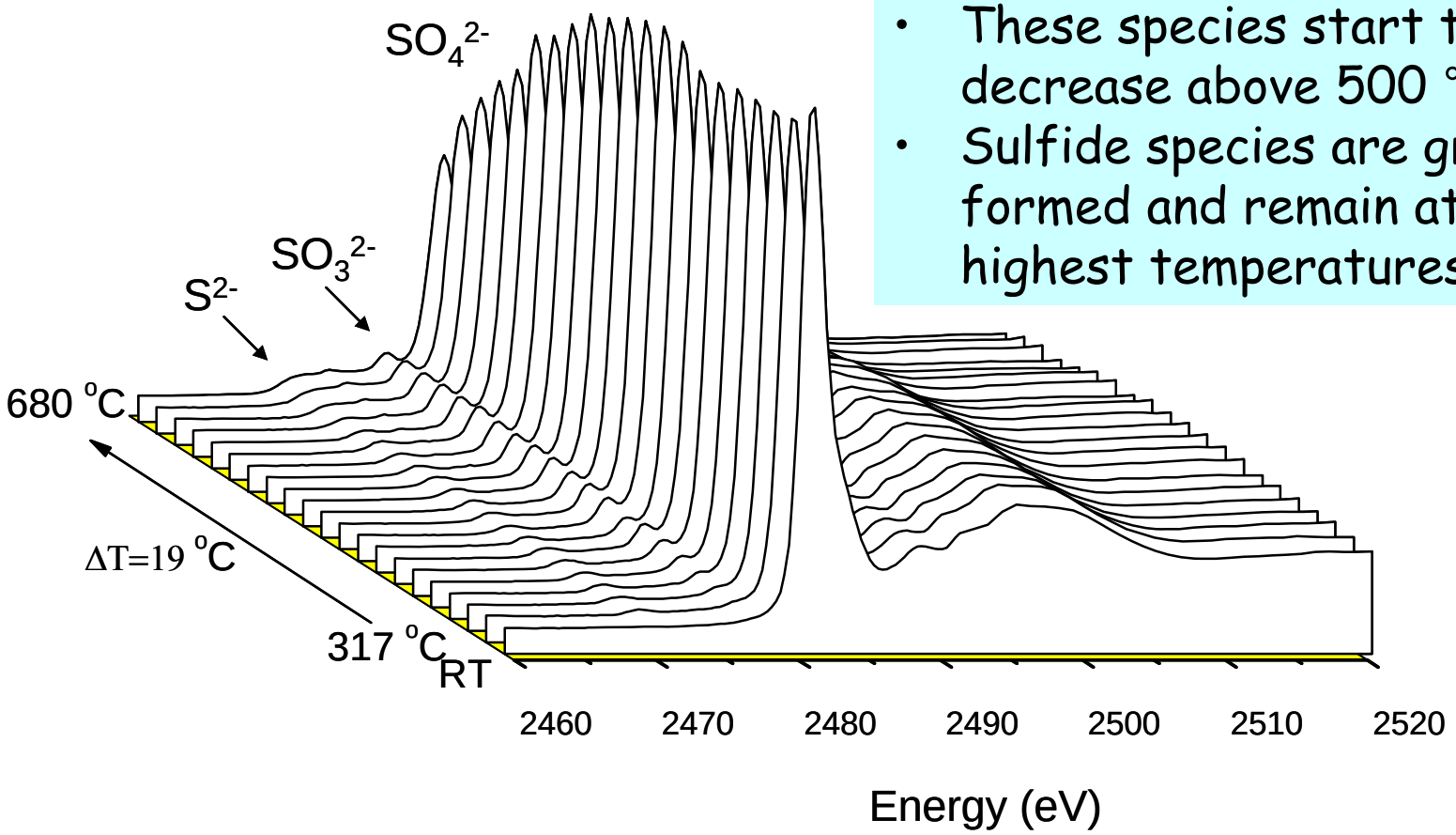
Pt-BaO(20)/Al_2O_3, 5 g/L, with H_2 only

- Initially, only sulfate species are present
- These species start to decrease above 500 °C
- Sulfide species are gradually formed and remain at the highest temperatures.



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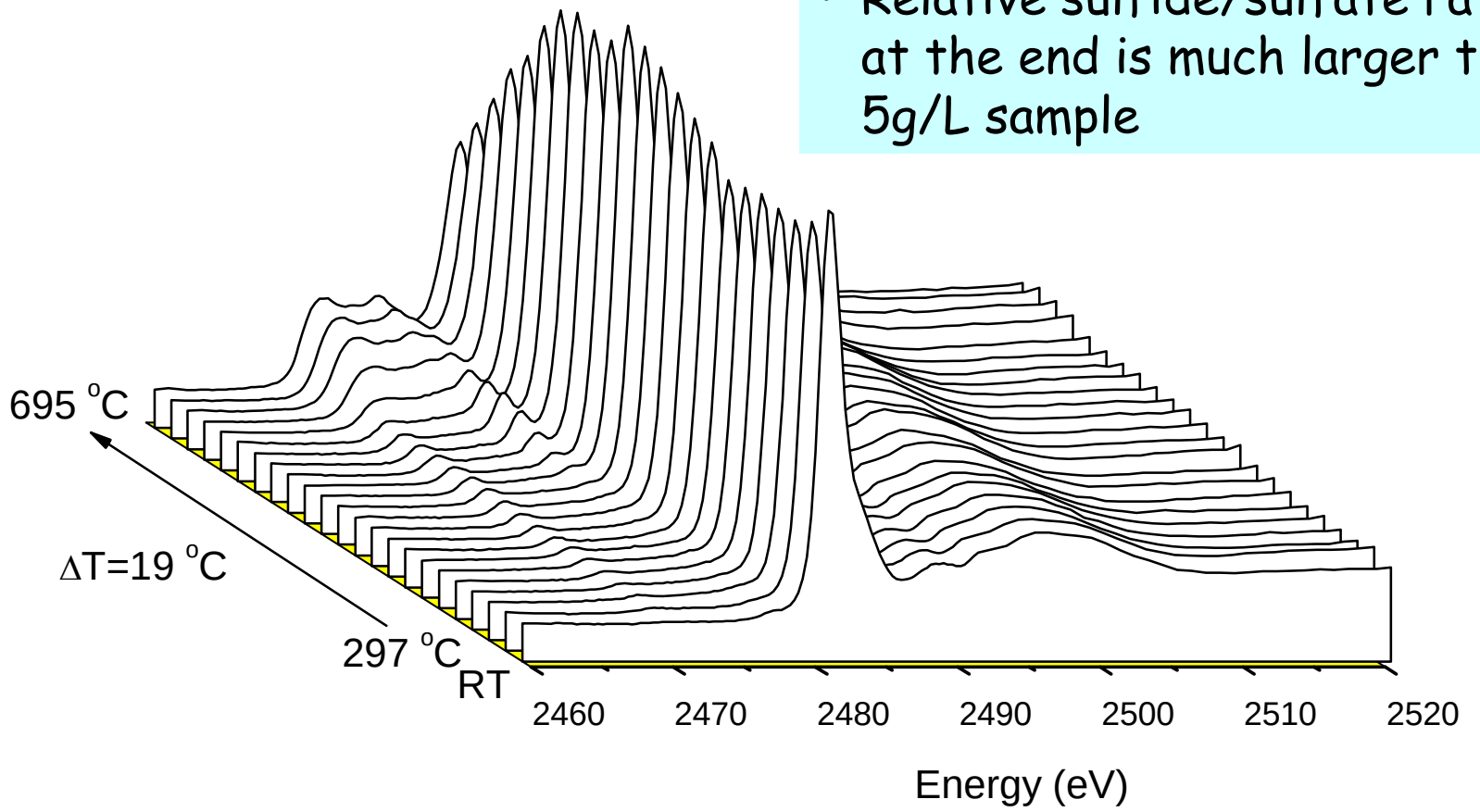
Pt-BaO(20)/Al_2O_3, 1 g/L, with H_2 only

- Little, if any loss of sulfur
- Relative sulfide/sulfate ratio at the end is much larger than 5g/L sample



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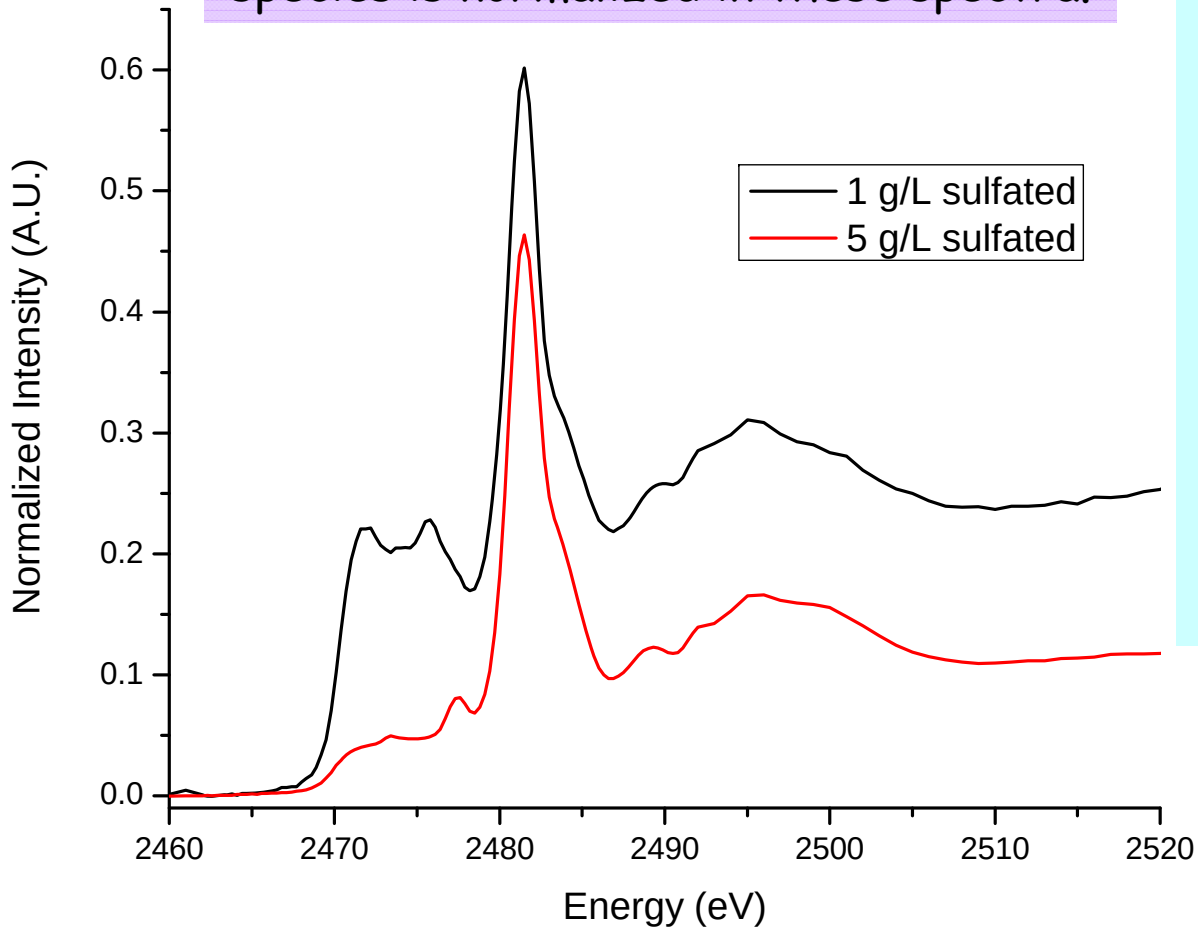
Different sulfur species distribution after desulfation up to 700 °C for two different sulfur loading

The peak intensity of the sulfate species is normalized in these spectra.



- Relative amounts of residual sulfur species after the same desulfation process are larger at lower loading → more difficult to remove the sulfur species at lower loading
- Greater tendency to form sulfide at low loading of sulfur.

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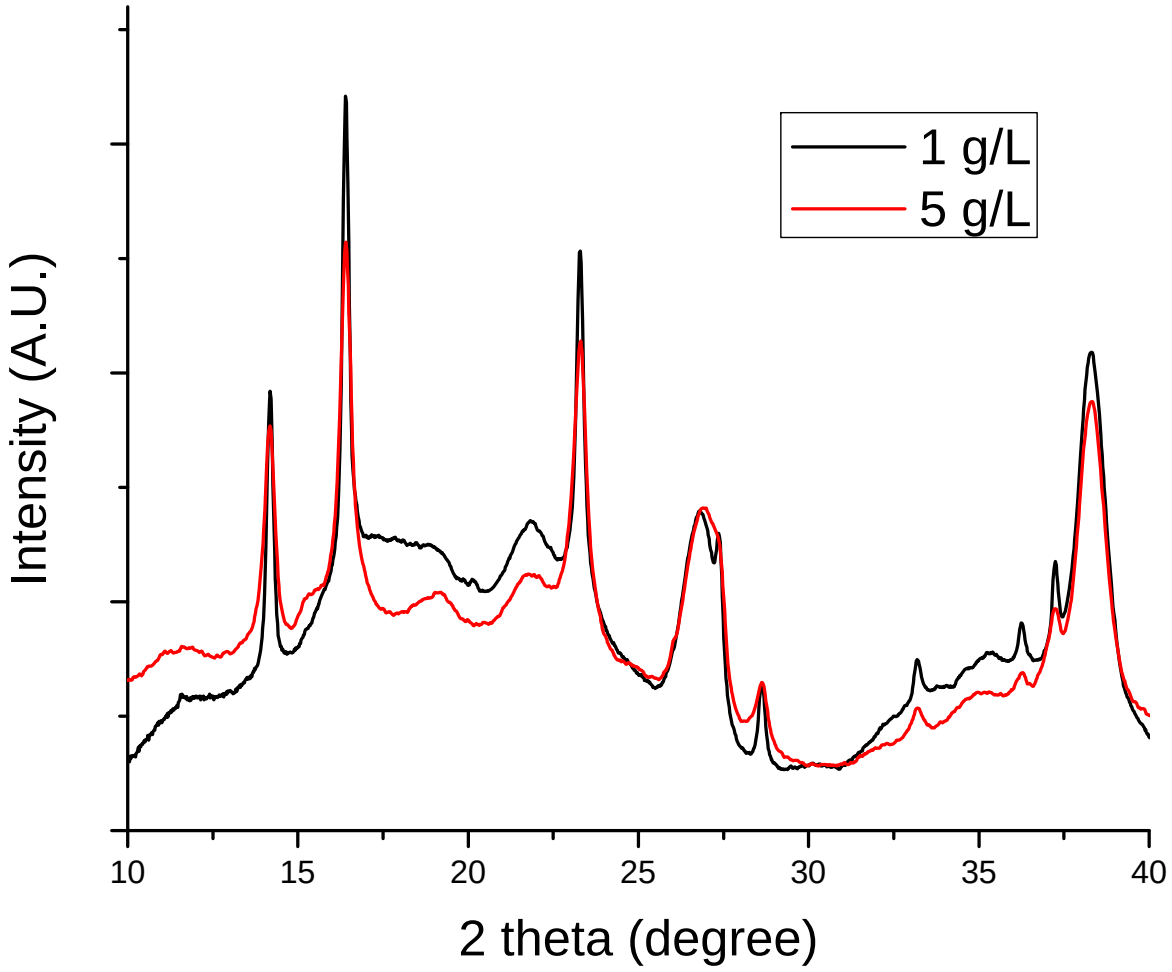
Comparison: after desulfation at 800 °C



BaS XRD peak intensities (normalized to Al_2O_3 peaks) are similar for both sulfur loadings, indicating that the first sulfur deposited will predominantly form the BaS phase.

D.H. Kim , J. Szanyi, J.H. Kwak, X. Wang, J.C. Hanson, M.H. Engelhard, C.H.F. Peden, J. Phys. Chem. C **113** (2009) 7336.

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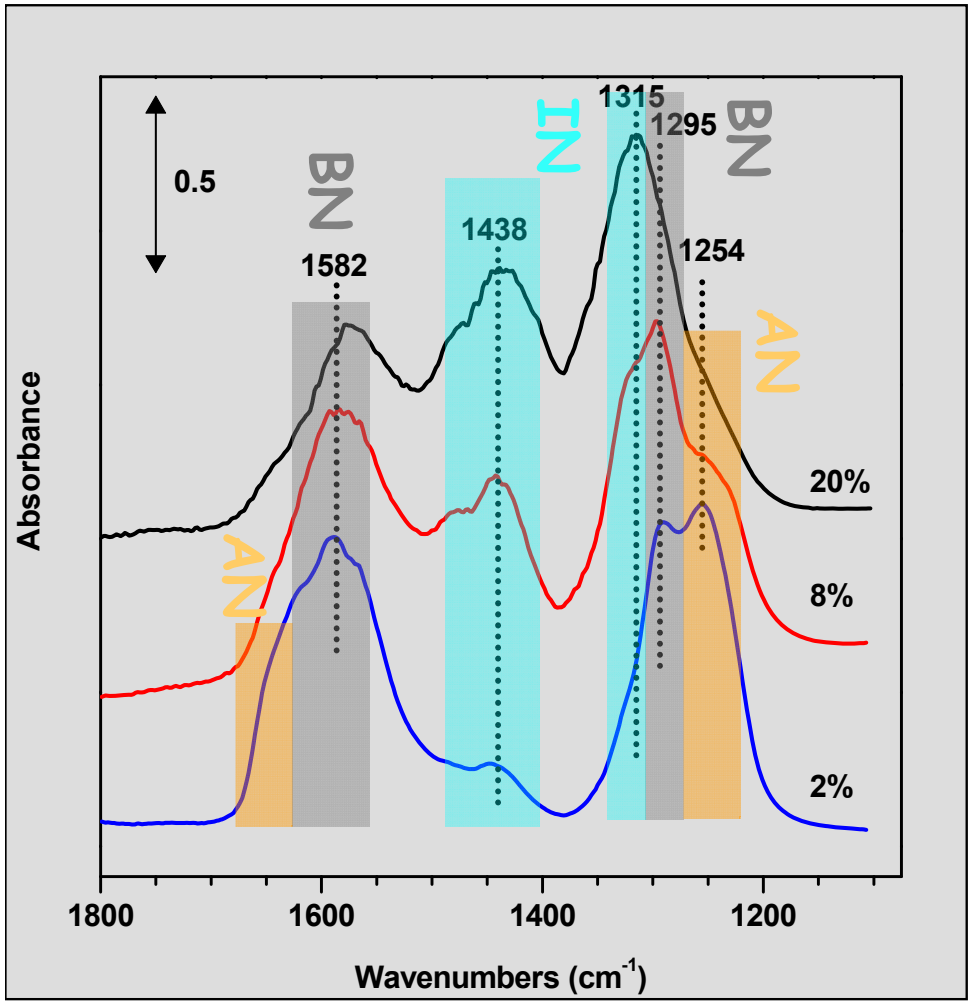
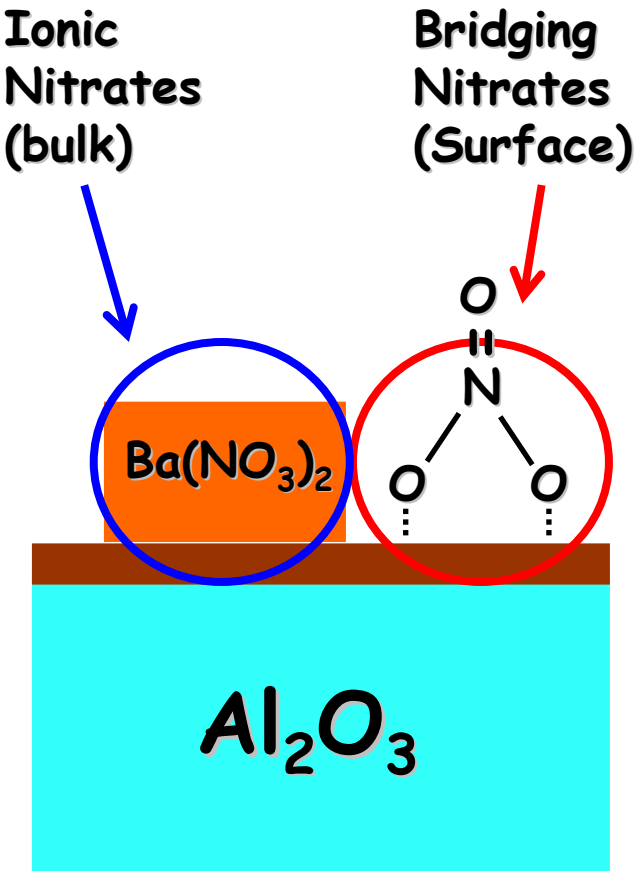
    - Implications for LNT (and other) catalyst preparation processes.

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





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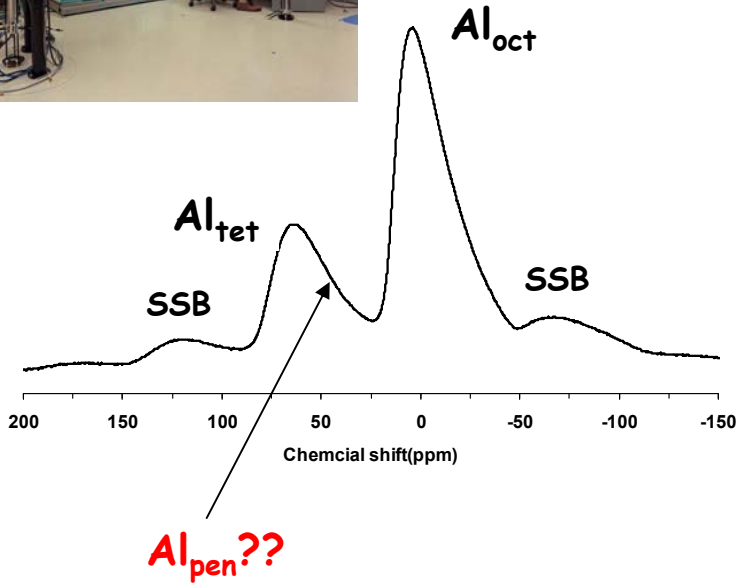
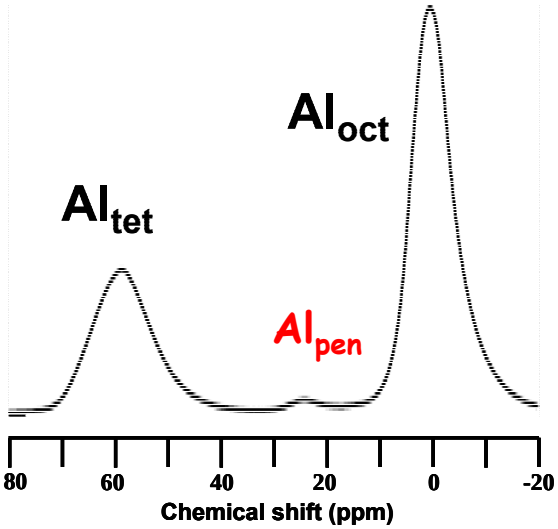
Unique Ultra-High Field NMR at PNNL offers special advantages for probing alumina surface chemistry





- Penta-coordinate Al^{+3} ions readily observable in γ-Al_2O_3;
- 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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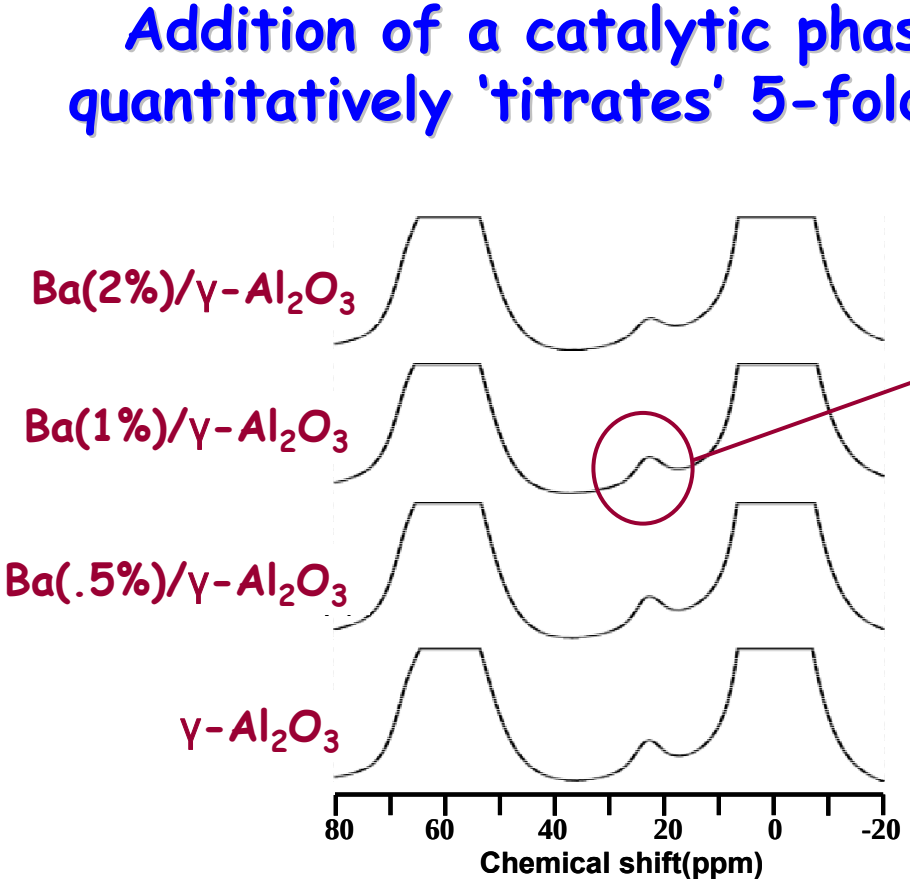
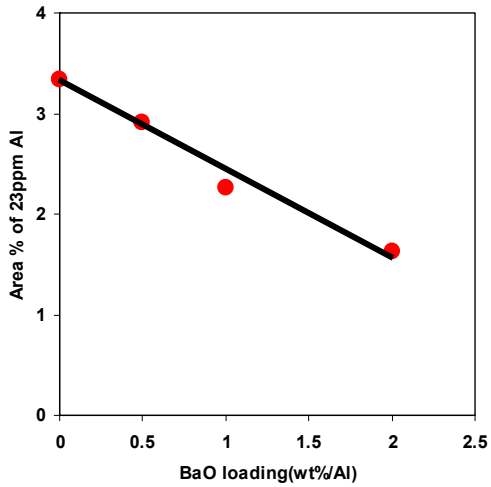
Lewis acidic 5-fold Al sites on γ-Al_2O_3 surfaces are nucleation sites for catalytic phases!

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.

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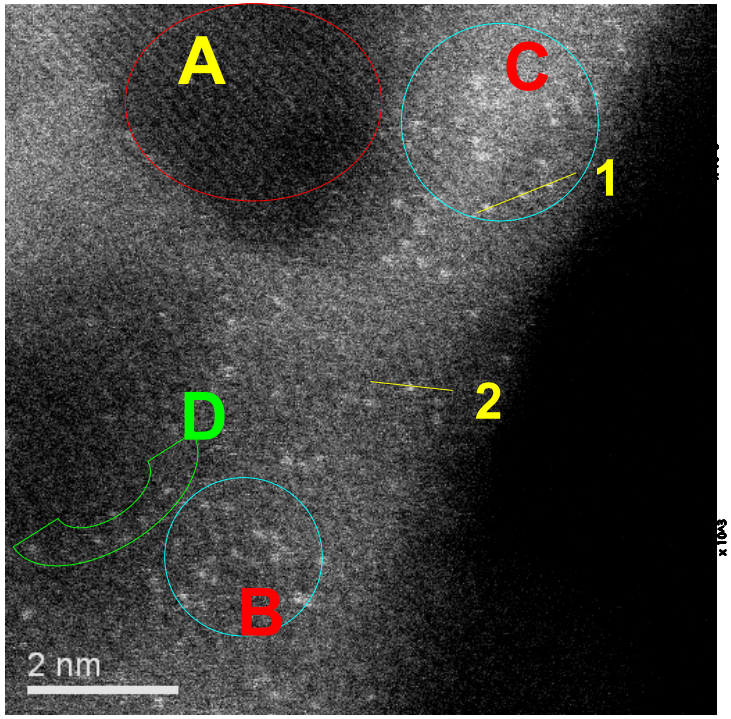
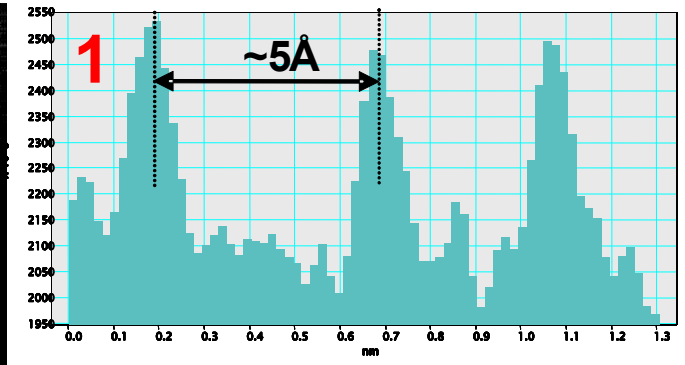
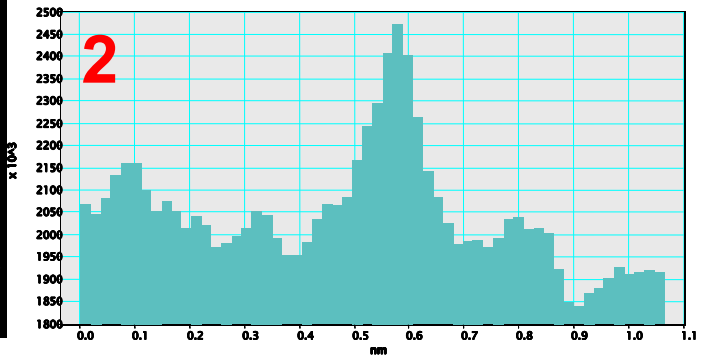
Ultra-high resolution STEM (aberration-corrected) shows BaO monomers at low loading







B,C: fairly uniform dispersion of BaO

Line scans 1,2: confirms the single BaO

A: no BaO

D: BaO monomer decorate the facet boundary

2%BaO/γ-Al_2O_3

JH Kwak, D Mei, C-W Yi DH Kim, CHF Peden, LF Allard, J Szanyi, J. Catal. **261** (2009) 17-22

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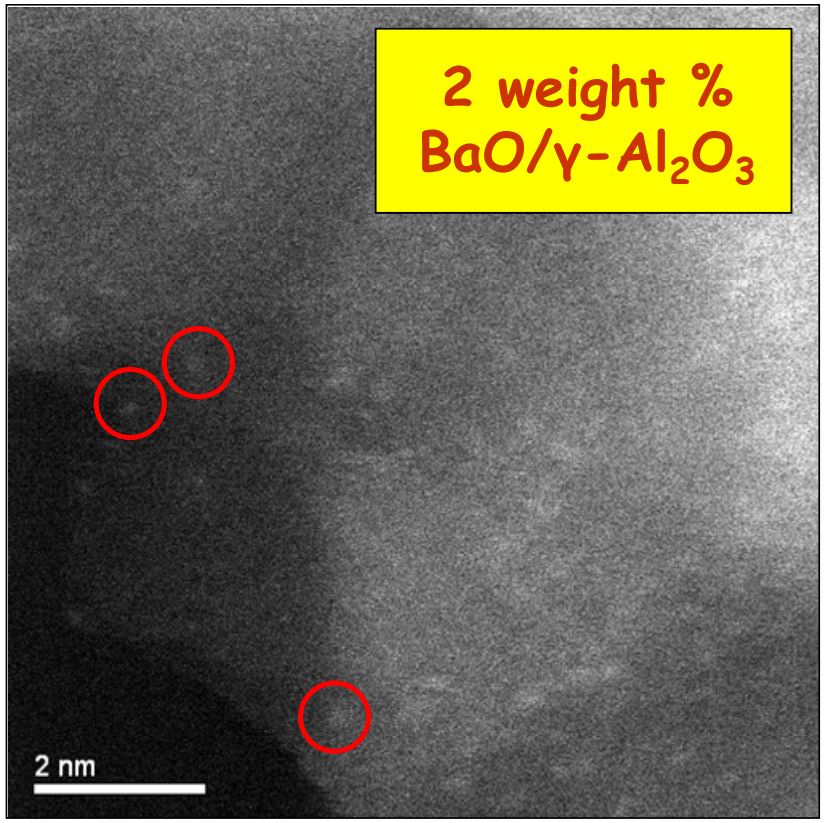
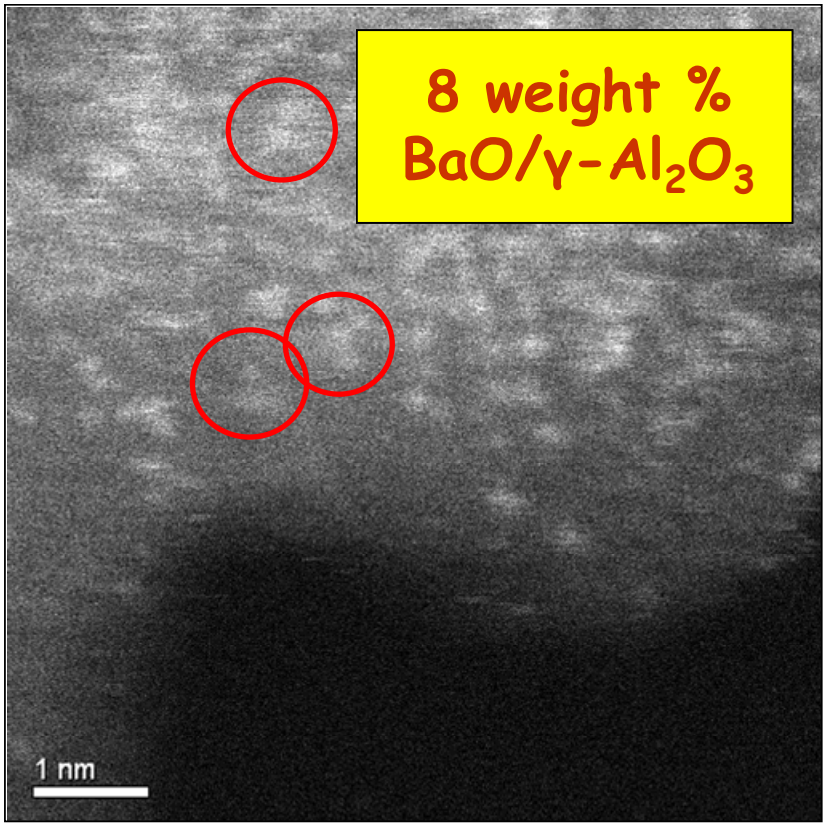
HR-TEM shows BaO monomers at low and dimers a higher loadings





JH Kwak, D Mei, C-W Yi DH Kim, CHF Peden, LF Allard, J Szanyi, J. Catal. **261** (2009) 17-22

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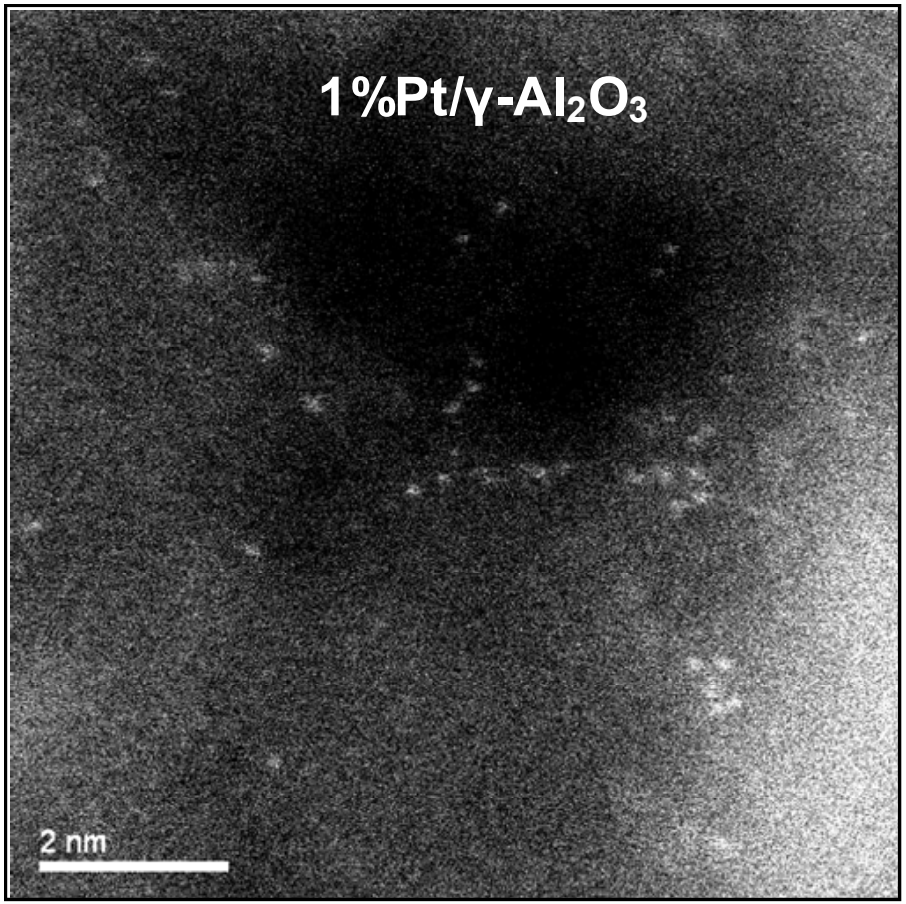
Ultra-high resolution STEM also shows that Pt can be monatomically dispersed at low loading



However, Pt 'clusters' on Al_2O_3 at a loading where the Pt/5-fold Al site ratio is much less than 1. Why??

JH Kwak, J Hu, D Mei, C-W Yi, DH Kim, CHF Peden, LF Allard, J Szanyi, Science (2009) submitted.

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Summary and Conclusions

- The morphology of BaO/Al_2O_3 LNT materials is remarkably dynamic during NOx storage and reduction. Both a supported "monolayer'" of $Ba(NO_3)_2$ and large "bulk" $Ba(NO_3)_2$ particles form on the alumina surface. *"Monolayer" phase is more readily and much more completely desulfated than "bulk" Ba phase.*
- Sulfur deposited initially on the "bulk" phase completely converts to BaS so is more difficult to remove.
- Because Ba phase morphology is so dynamic, it is important to understand the interaction with the alumina washcoat surface. 5-fold Al^{+3} surface structures identified in ^{27}Al NMR spectra are identified as 'anchoring' sites for both Ba and Pt.
- These new results provide additional considerations for LNT synthesis. (Recall that loading Pt first before Ba results in improved catalysts – Olsson and coworkers in this morning's presentation).