CLEERS: Aftertreatment Modeling and Analysis

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Pacific Northwest National Laboratory

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ACE023

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Overview

- **Timeline**
  - Status: On-going core R&D
  - Originated FY03 with DPF
- **Budget**
  - FY09 funding - $750K
  - FY10 funding allocation $750K
    - Split between LNT, SCR and DPF focus areas

- **Barriers**
  - Limitations on:
    - available modeling tools
    - chemistry fundamentals
    - knowledge of material behavior
  - Effective dissemination of information
  - Technical “Valley of Death”
- **Partner**
  - Diesel Crosscut Team
  - 21CT partners
  - USCAR partners
  - Oak Ridge National Lab

Goal and Relevance

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…

…provide the practical scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- **VT program goals are achieved through these project objectives:**
  - **interact with technical community to indentify relevant technological gaps**
  - **understand fundamental underlying mechanisms and material behavior**
  - **develop analytical and modeling tools, methodologies, and best practices**
  - **apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency**
- **Specific work tasks in support of the objectives are arrived at through:**
  - **focus group industrial monthly teleconferences, diesel x-cut meetings**
  - **yearly workshops and surveys**
  - **submission of SOW to the VT office**

Technical Milestones & Approach

- Approach - “Science to Solutions”
- The overall performance measure of the project is inextricably linked to the interests of industry
  - PNNL CLEERS activities have resulted in the formation of new CRADAs
  - Tremendous success of the annual workshops
  - Strong participation in the monthly teleconferences
- Specific performance measures are developed with the industrial/academic partners and captured in SOW
  - Specific technical targets and major milestones are described in our AOPs and annual reports to VT

PNNL FY10 Portfolio

CLEERS activity

Integrated Systems - Herling

- **DPF subtasks* – Mark Stewart**
- **SCR subtasks* – John Lee**
- **LNT subtasks – Chuck Peden**

CRADA activities

DPF – DOW Automotive (Stewart)

SCR/DPF – PACCAR (Rappe)

SCR – Ford Motor Company (Peden)

SCR – General Motors (Peden, Lee)

LNT – Cummins Inc. (Peden)

Oxidation (HCCI) – Caterpillar (Rappe)

***PNNL led subteam**

FY2009/2010 Scope Objectives

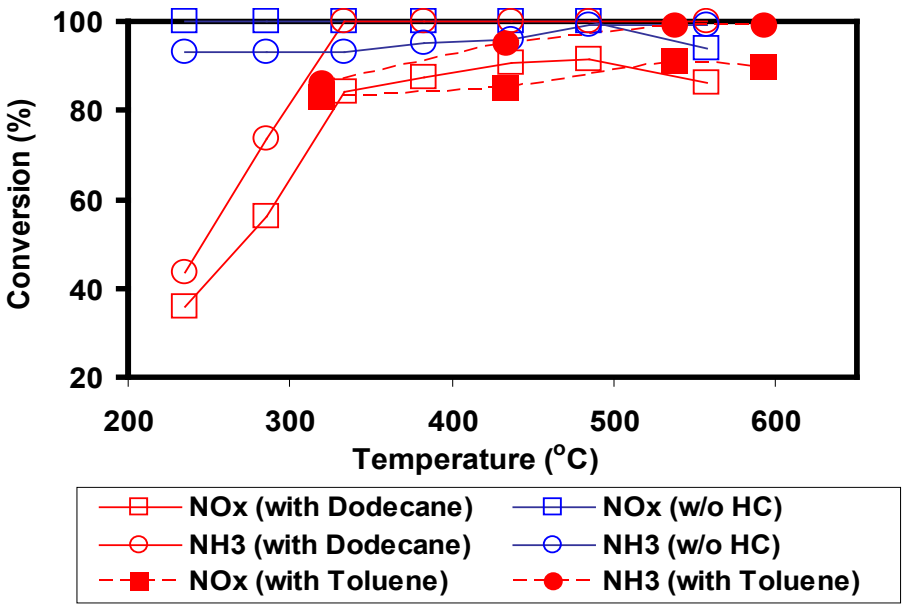
- SCR
  - Investigate the competitive adsorption effects on NH3 storage under controlled lab reactor conditions
  - Develop kinetic models to characterize competitive adsorption and inhibition, and to describe the impact on SCR performance quantitatively
- LNT
  - Optimization of catalyst morphology via controlled synthesis.
  - Mechanisms of CO2 and H2O promotion of desulfation
  - Characteristics (performance and poisoning) of ceria-supported LNT materials

Technical Accomplishments Outline

- Selective Catalytic Reduction
  - Characterized the effects of H2O and HC on SCR reaction
  - Develop and validate models for H2O and toluene storage
  - Developed single site kinetic models to describe the inhibition effects on NH3 sorption and NOx reduction
- Lean NOx Trap Fundamentals
  - Prior conclusions concerning morphology changes in LNT materials during operation
  - Ultra-high field NMR spectroscopy and ultra-high resolution TEM studies of the binding of Ba and Pt to washcoat alumina surfaces
- Conclusions & Future Work

Selective Catalytic Reduction

Effect of Hydrocarbon on NOx Reduction



Feed Conditions

175 ppm NO

175 ppm NO_2

350 ppm NH_3

14% O_2

2% H_2O

50 ppm toluene (350 C1)

29 ppm dodecane (350 C1)

29k h^{-1}

- No effect of ethylene, propane
- Detrimental effects of toluene, dodecane
- More pronounced effect on NO-SCR
- No effect on NO_2-SCR

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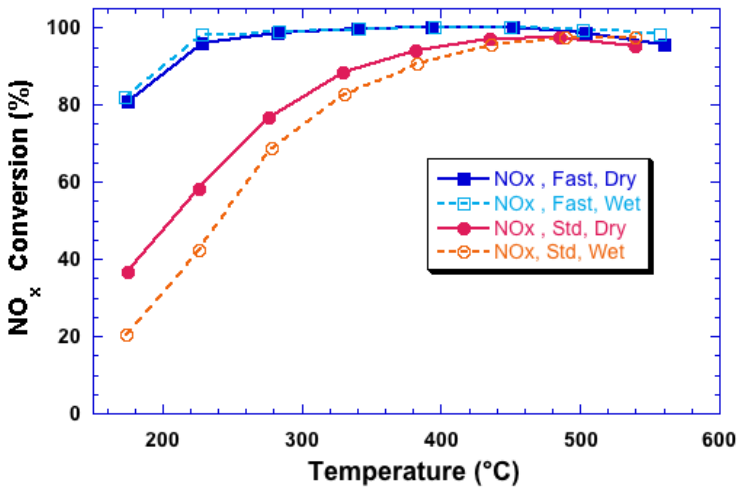
Overview of PNNL 1-D SCR Model

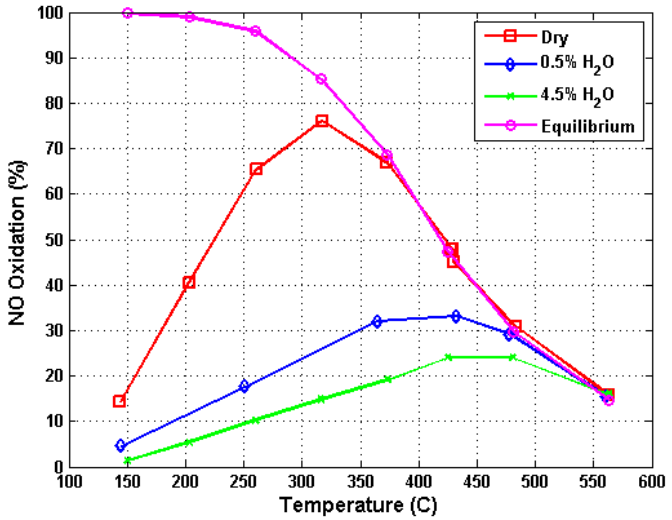
- Gas phase, surface phase concentrations and NH_3 storage as states
- Coded as 'C' S-functions and developed in Matlab/Simulink
- Optimized and validated using steady state and thermal transient reactor data

No	Reaction Name	Reaction	Reaction Rate
1	NH_3 Adsorption	$NH_3 + S \rightarrow NH_3^*$	$R_1 = k_1 C_{s,NH3}(1-\theta)\,\Omega$
2	NH_3 Desorption	$NH_3^* \rightarrow NH_3 + S$	$R_2 = k_2\,\theta\,\Omega$
3	Fast SCR	$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$	$R_3 = k_3 C_{NO} C_{NO2}\,\theta\,\Omega$
4	Standard SCR	$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$	$R_4 = k_4 C_{NO}\,\theta\,\Omega$
5	NO_2-SCR	$4NH_3+3NO_2 \rightarrow 3.5N_2+6H_2O$	$R_5 = k_5 C_{NO2}\,\theta\,\Omega$
6	NH_3 Oxidation	$2NH_3+3/2O_2 \rightarrow N_2+3H_2O$	$R_6 = k_6 C_{O2}\,\theta\,\Omega$
7	NO-NO_2 Oxidation	$NO+1/2O_2 \Leftrightarrow NO_2$	$R_7 = k_{7,f} C_{NO} C_{O2}^{1/2} - k_{7,b} C_{NO2}$

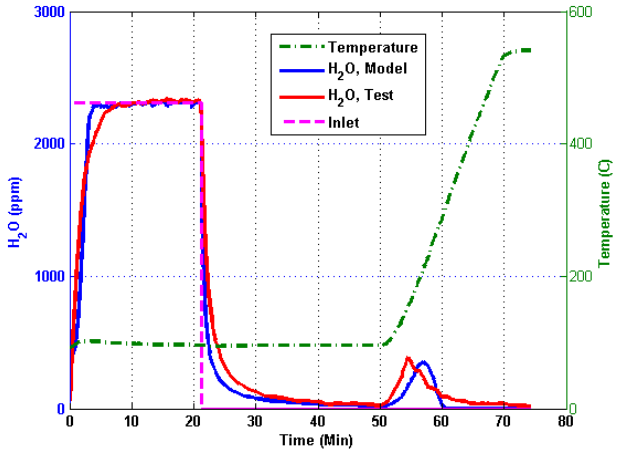
H_2O Inhibition Modeling



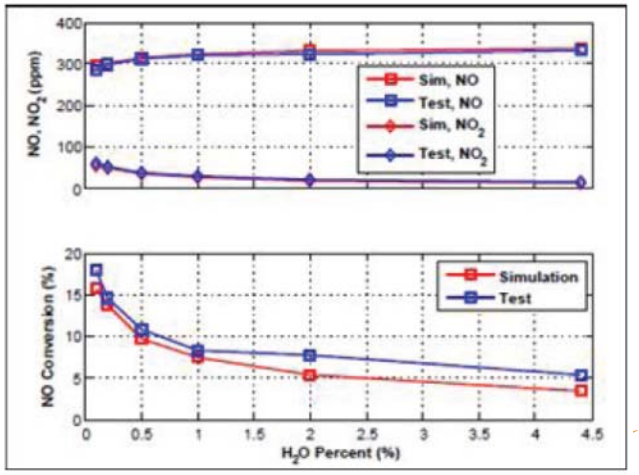
Effect of H_2O on SCR Reactions



Effect of H_2O on NO Oxidation



H_2O Storage Model

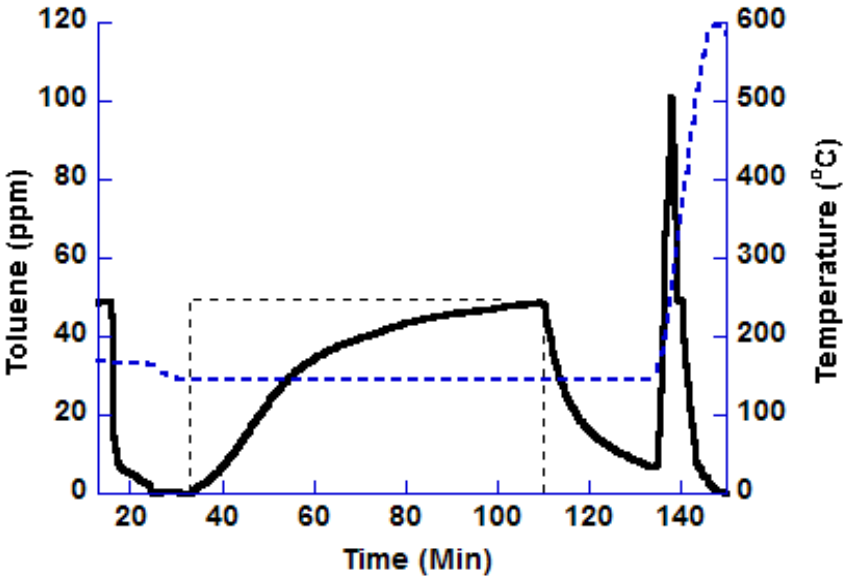


Model for H_2O Inhibition of NO oxidation

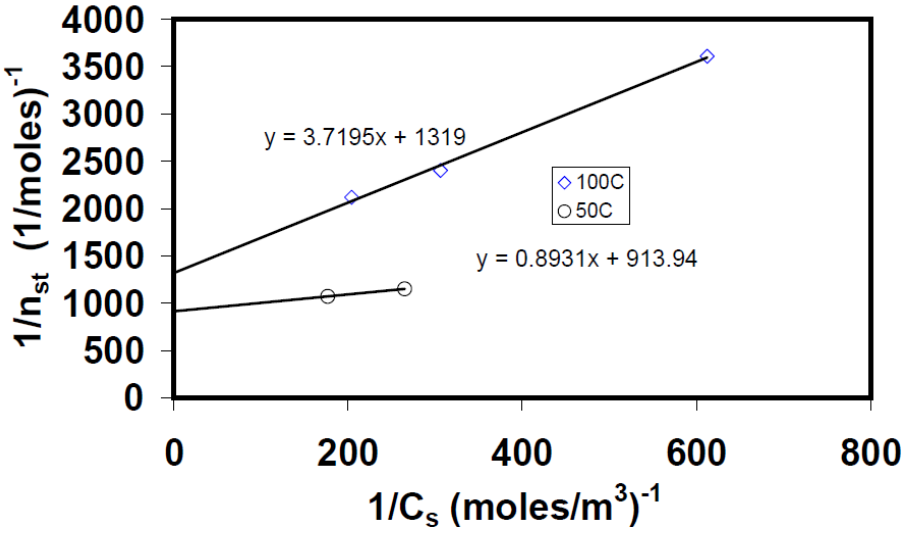
Hydrocarbon Storage Model: Toluene

T(°C) / C(ppm)	50	100	150
50		X	X
100	X	X	X
150	X	X	X

Test Matrix



Typical Adsorption Test



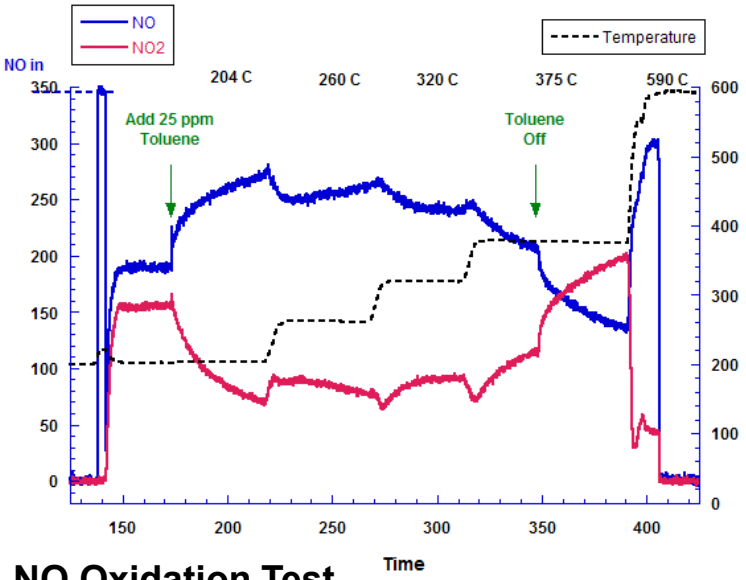
Langmuir Isotherms

$$n_{st,eq} = \int_0^{t_{eq}} (\dot{n}_{C_7H_8,in} - \dot{n}_{C_7H_8,out})dt$$

$$\frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T)c_{s,C_7H_8}N_{total}}$$

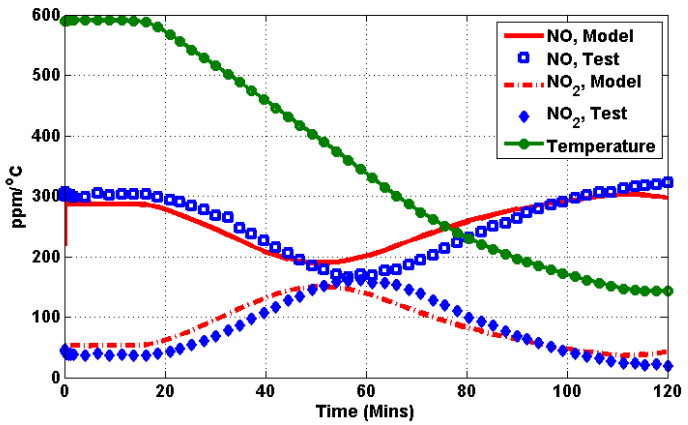
Storage rate parameters are obtained through approximation of Langmuir isotherms.

Toluene Inhibition on NO and NH_3 Oxidation

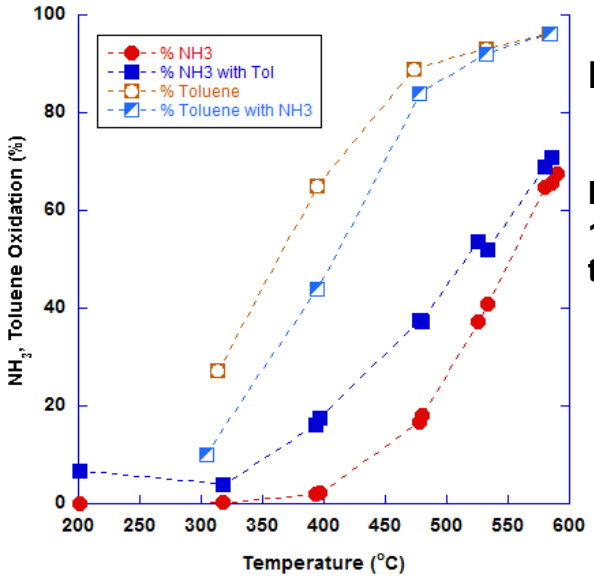


NO Oxidation Test

Feed: 350 ppm NO, 14% O_2, 25 ppm toluene (175

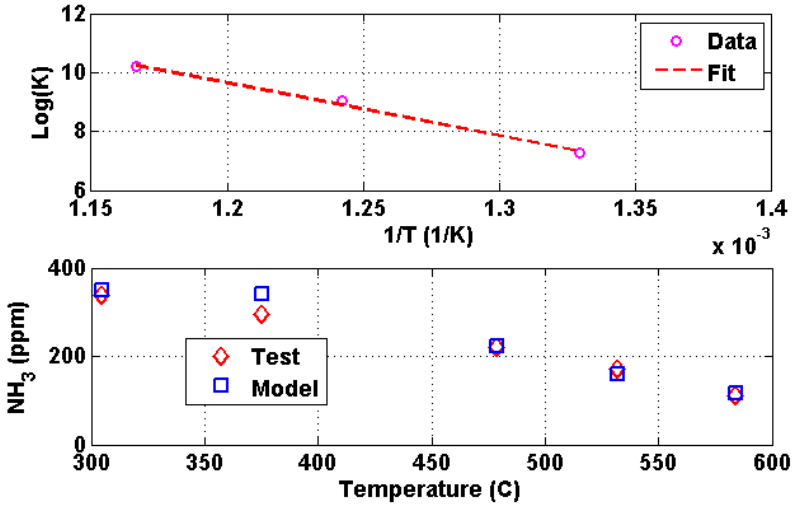


Model Validation on Temperature Ramps



NH_3 Oxidation Test

Feed: 350 ppm NH_3, 14% O_2, 50 ppm toluene (350 C1)



Arrhenius Plot and Model Validation

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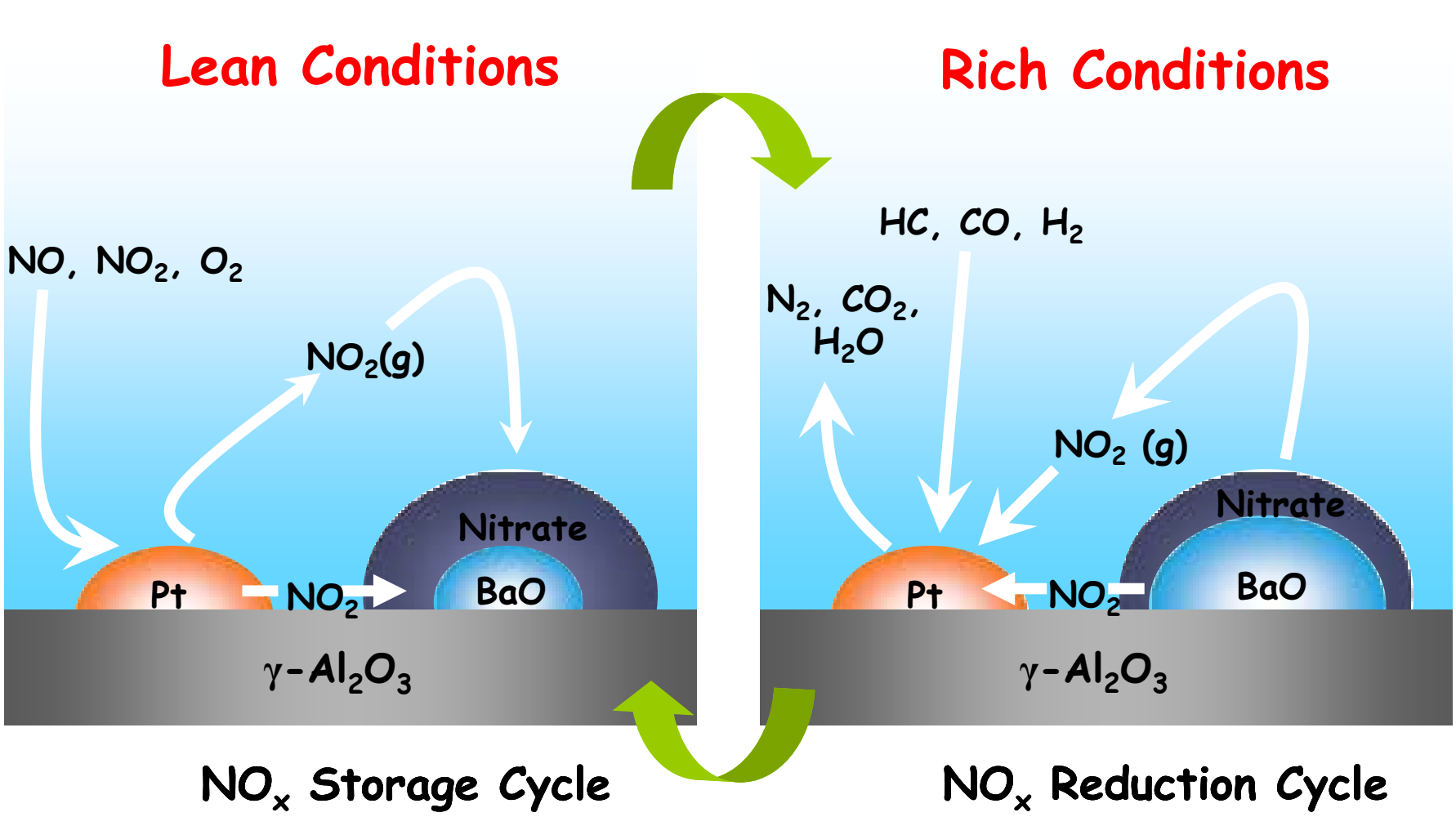
Lean NOx Trap Fundamentals

NO_x Storage/Reduction (NSR) Catalysis



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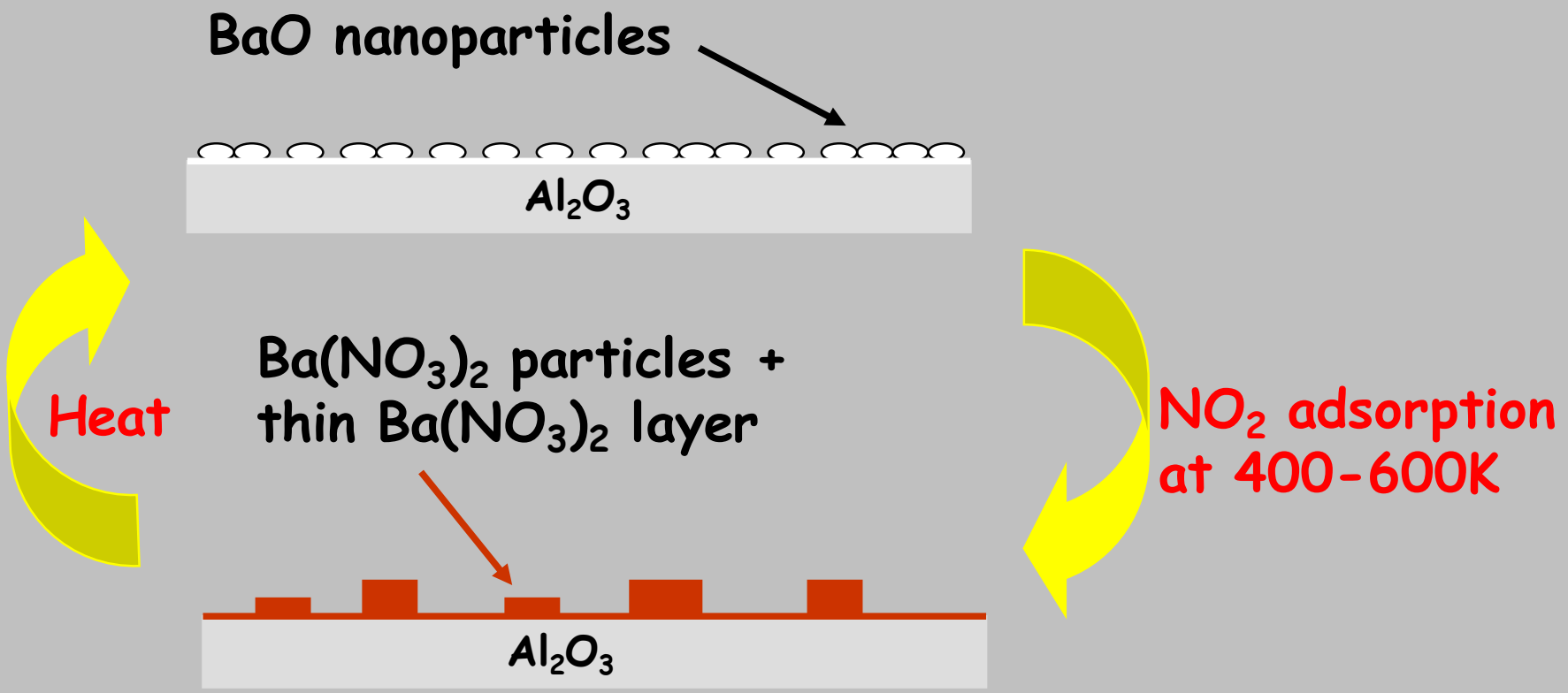
Morphology Changes During Operation Indicate an Important Role for the BaO/Alumina Interface

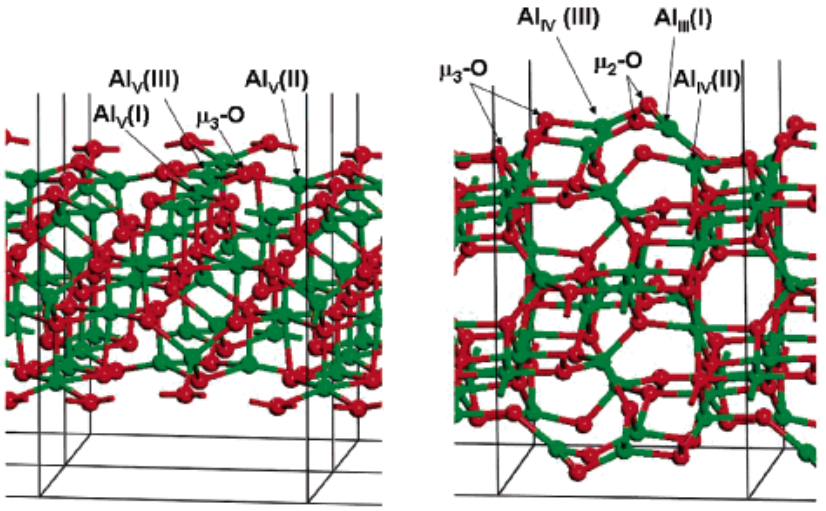


Szanyi, Kwak, Hanson, Wang, Szailer, Peden,
J. Phys. Chem. B **109** (2005) 7339-7344.

Introduction

- Surface structures and chemistry of gamma-alumina, are not easily studied – even their bulk structures remain a topic of some controversy – because of low crystallinity and small particle sizes.

Two Stable γ-Al_2O_3 Surfaces



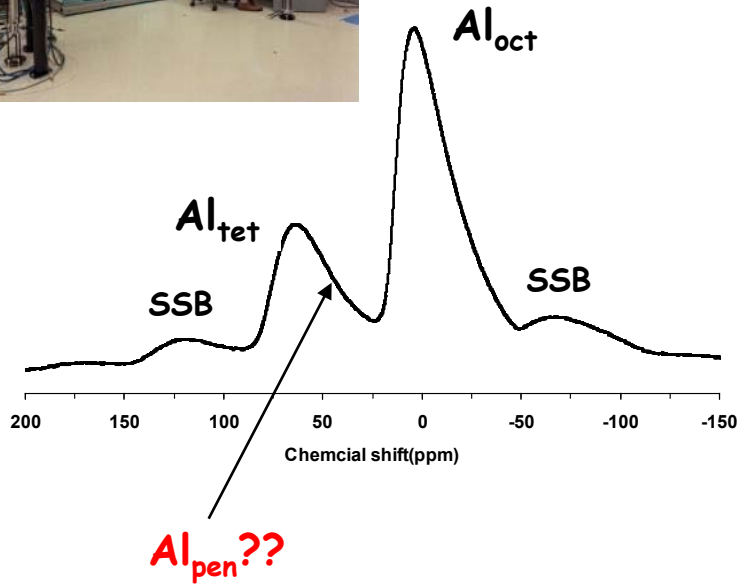
γ-Al_2O_3(100) γ-Al_2O_3(110)

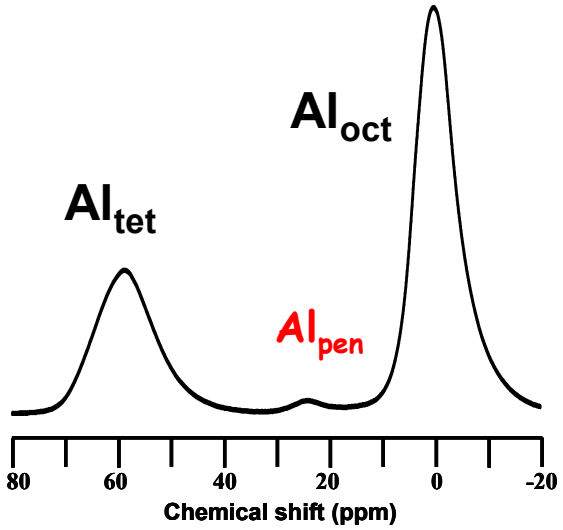
S.H. Kim, D.C. Sorescu, O. Byl, and J.T. Yates, Jr., *J. Phys. Chem. B* **2006**, *110*, 4742.

Krokidis, X., Raybaud, P., Gobichon, A.-E., Rebours, B., Euzen, P., and Toulhoat, H., *J. Phys. Chem. B* **105**, 5121 (2001).

- Bulk alumina has Al^{+3} cation sites in tetra- and octa-hedral coordination. What about coordination of surface aluminum atoms?

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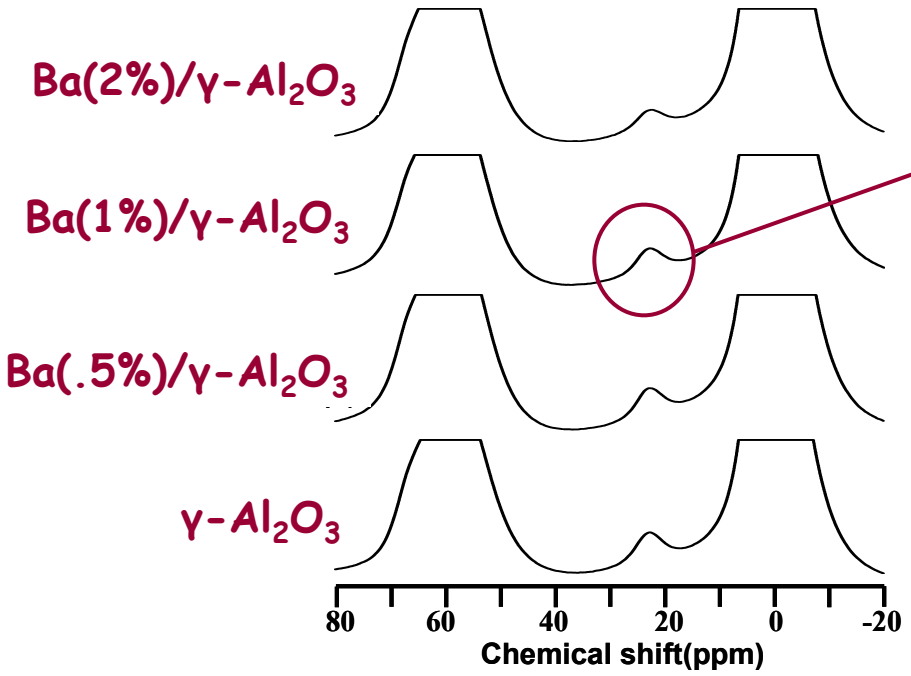
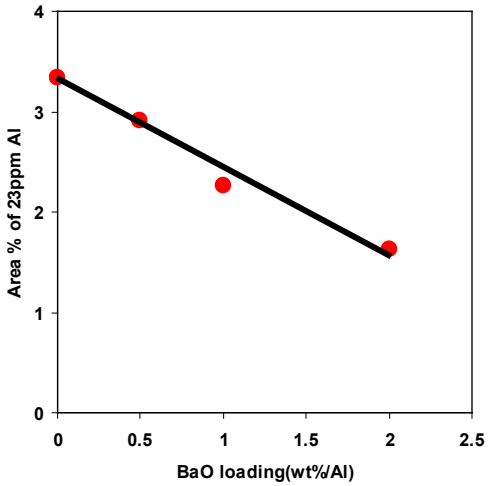
Lewis acidic 5-fold Al sites on γ-Al_2O_3 surfaces are nucleation sites for catalytic phases!

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, J. Catal. **251** (2007) 189-194.

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

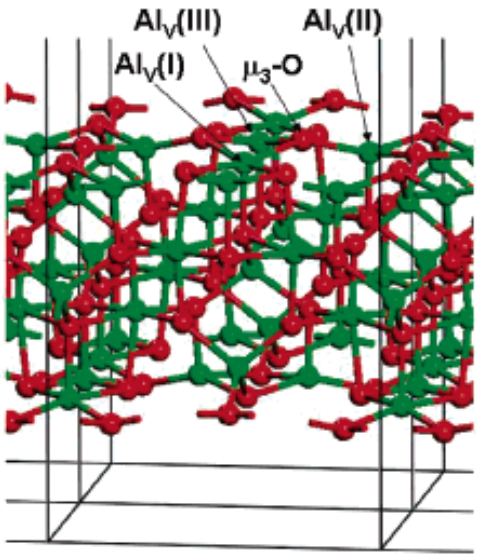
- 4 weight % loading of BaO sufficient to titrate all 5-fold Al^{+3} sites.
- Assuming that BaO forms perfect 2D clusters or domains on the 200 m^2/g γ-Al_2O_3 substrate, 1 ML of BaO will be reached at ~25% weight loading.

1ML BaO/Al_2O_3

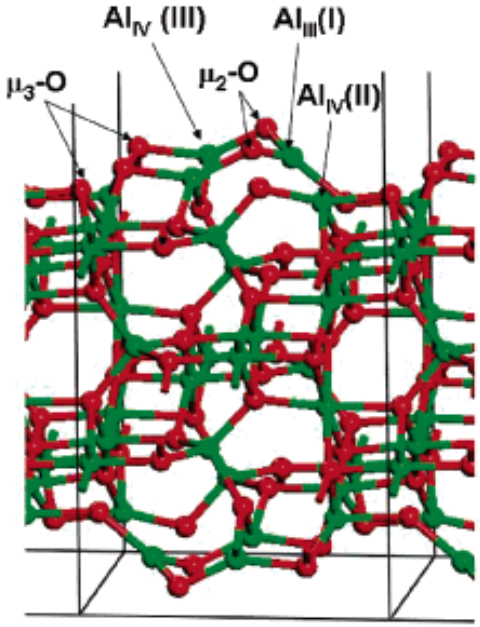
- Thus, ~16% (4÷25) of the alumina surface consists of 5-fold Al^{+3} sites.

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

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



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?

Additional evidence for reaction only on (100) surfaces obtained from low-energy ion scattering (LEIS) and high-resolution STEM.

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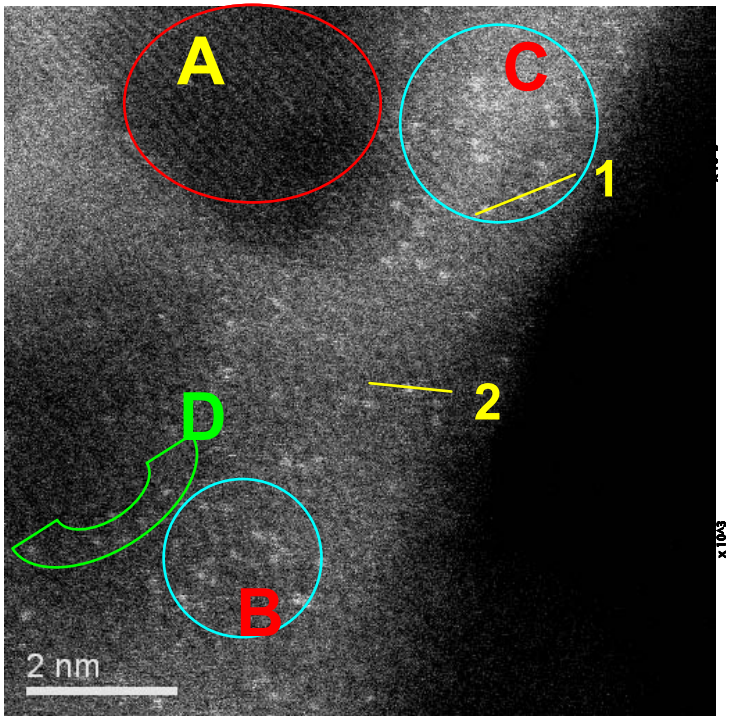
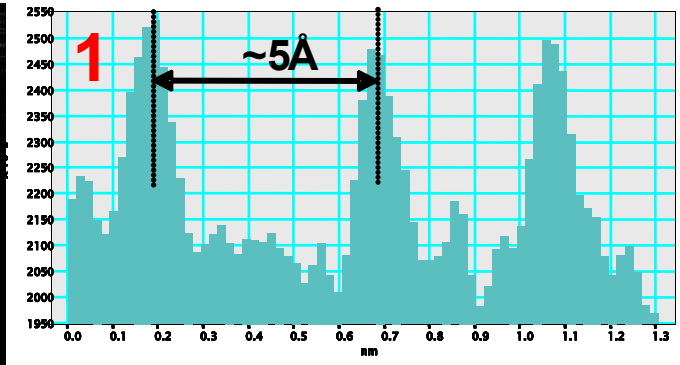
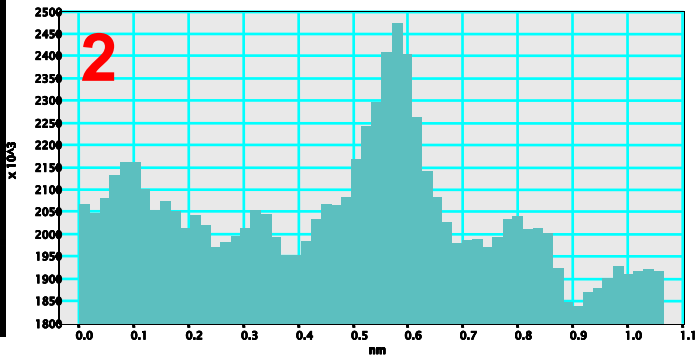
Ultra-high resolution STEM (aberration-corrected) shows BaO monomers at low loading







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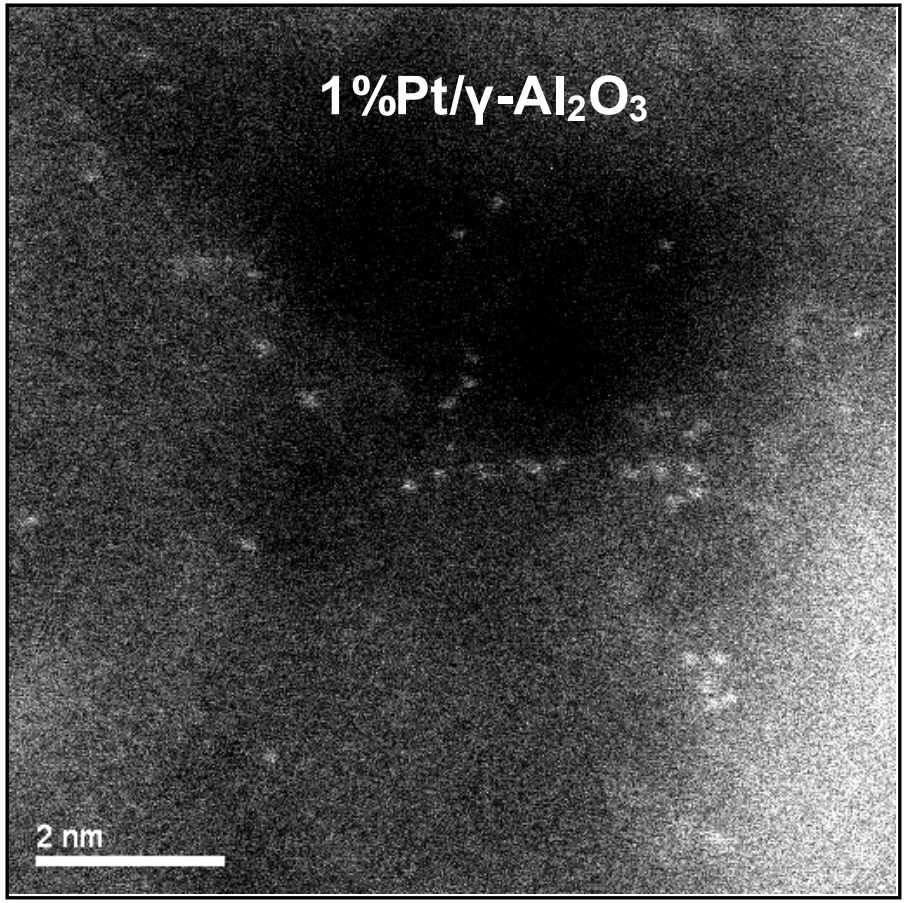
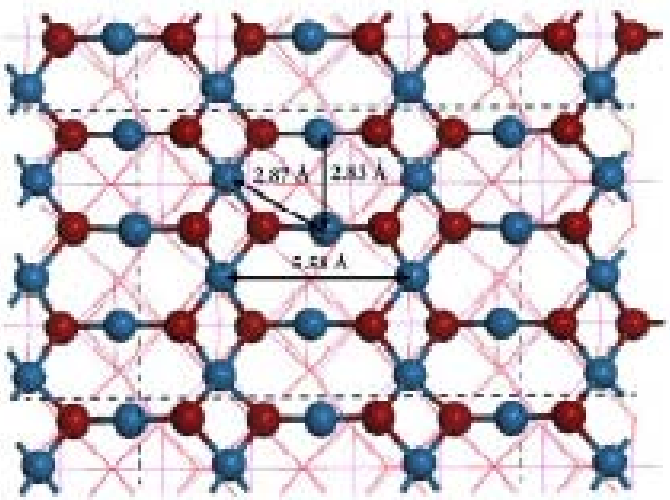
Ultra-high resolution STEM also shows that Pt can be monatomically dispersed at low loading

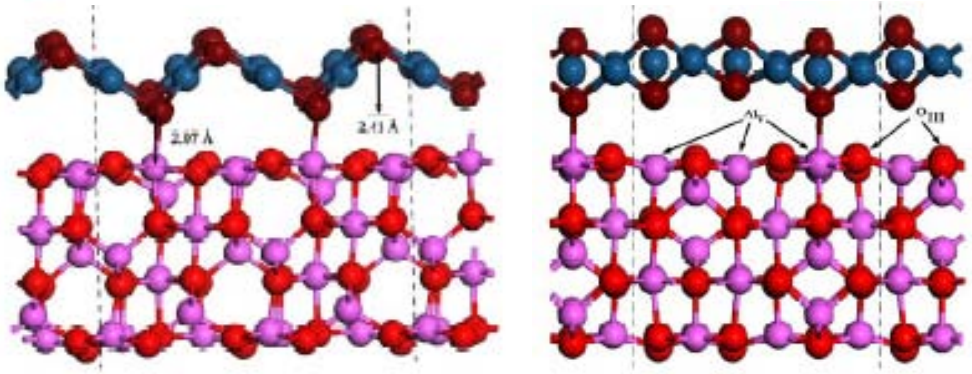


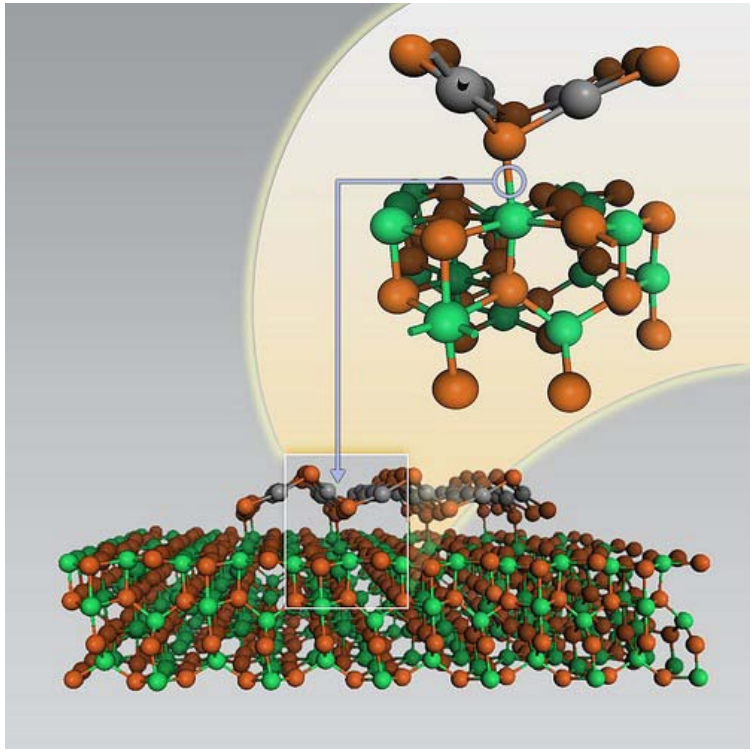
However, Pt 'clusters' on Al_2O_3 at a loading where the Pt/5-fold Al site ratio is much less than 1. Why??

JH Kwak, J Hu, D Mei, C-W Yi, DH Kim, CHF Peden, LF Allard, J Szanyi, Science **325** (2009) 1670.

DFT Calculations Identify Bonding Orientation for PtO Clusters on γ-Al_2O_3(100)







JH Kwak, J Hu, D Mei, C-W Yi, DH Kim, CHF Peden, LF Allard, J Szanyi, Science **325** (2009) 1670.

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Conclusion & Future Work

Conclusions: SCR Scope

- Characterized the effects of H2O and hydrocarbons on SCR reaction pathways over Fe-zeolite catalyst
  - No effect of ethylene and propane on NOx reduction
  - Detrimental effects of H2O, toluene and n-dodecane on Standard SCR through suppressed NO oxidation & NH3 adsorption
  - Smaller effect on Fast SCR, and no effect on NO2-SCR reactions
- Developed models to describe the inhibition effects of H2O and toluene on NOx reduction kinetics
  - Storage models were developed using Langmuir isotherms.
  - A single site kinetic model was developed and validated to predict the effects of H2O and toluene on NO oxidation and NH3 oxidation.

Conclusions: LNT Scope

- Interactions of LNT catalytic phases with the washcoat support material, alumina, have been studied
  - 5-fold Al^{+3} surface structures identified in ^{27}Al NMR spectra are active 'Lewis acid' sites for adsorption of reactant and catalyst precursor species
  - Both Ba and Pt are shown to prefer anchoring at these surface sites
- Studies of the effects of CO_2 and H_2O on performance and desulfation of model Ba-based LNTs have continued
  - The presence of CO_2 promotes the removal of sulfur species, especially at temperatures below 500 °C
  - This behavior is largely attributed to a suppression of the formation of refractory BaS phases
- Ceria as a support material for Ba-based LNTs
  - These LNT catalysts display distinct advantages but appear to lack the ability to fully desulfate because of strong interactions between ceria and sulfur oxides

Future Work

- Complete the kinetic modeling of NH_3 oxidation, NO oxidation and other SCR reactions on Fe-zeolite catalyst
- Investigate the competitive adsorption kinetics on a model Cu-zeolite SCR catalyst through experiments and modeling
- Investigate the effects of catalyst aging on kinetic parameters and physicochemical properties of a model Cu-zeolite catalyst
- Thermal transient reactor testing of model & commercial Cu-zeolite SCR catalyst
- Isocynanic acid reagent studies
  - Steady state kinetic modeling of HNCO hydrolysis and adsorption on Fe-zeolite
  - Transient reactor modeling based on HNCO injection

Future Work (con't)

- Fundamental studies of novel high temperature LNT formulations
- Complete studies of CO_2 and H_2O effects on performance and desulfation of Ba-based LNT materials
- Continue development of micro-scale DPF simulation tools, including detailed comparison to granular unit-collector theory
- Fundamental filtration experiments with repeatable lab-generated particulates and current DPF substrates

Acknowledgements

- PNNL

  Shelley Carlson, Maruthi Devarakonda, Tom Gallant, Do Heui Kim, Ja Hun Kwak, Gary Maupin, George Muntean, Ken Rappe, Nat Saenz, Janos Szanyi, Russ Tonkyn, Diana Tran, Alla Zelenyuk

- ORNL

  Stuart Daw, Todd Toops, Josh Pihl and support from the ORNL team

- Umicore

  Owen Bailey and support for SCR catalyst materials

- DOE Vehicle Technologies Program

  Gurpreet Singh and Ken Howden

Backup Slides

NOx Reaction Pathways

In addition to NH_3 adsorption and desorption on catalyst surface,

NH_3 oxidation: $2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O$

NO oxidation: $NO + 1/2O_2 \leftrightarrow NO_2$

Standard SCR: $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

NO_2-SCR: $4NH_3 + 3NO_2 \rightarrow 7/2N_2 + 6H_2O$

Fast SCR: $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

List of Kinetic Parameters

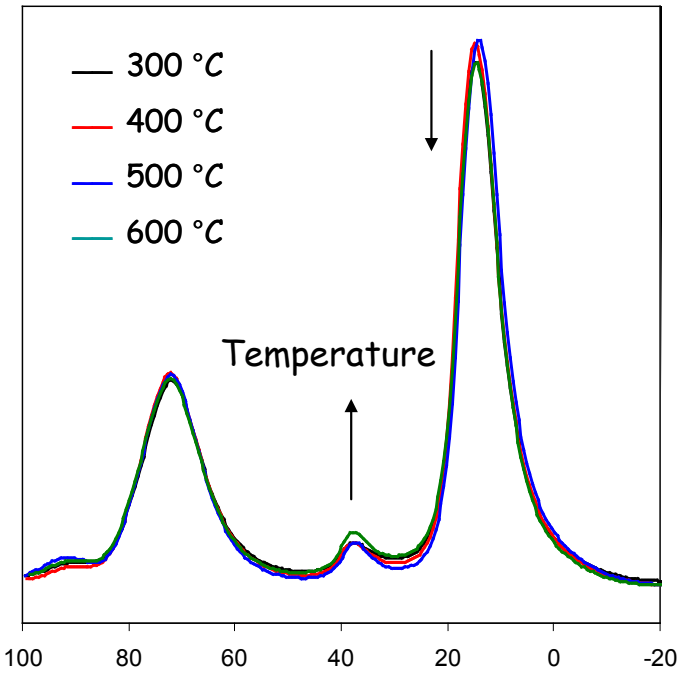
	A_{ads}	A_{des}	E_{des} (kJ/mol)	γ(-)	Ω(mol/m^3)
NH_3	83.9	2.0E5	70	0.368	46.3
H_2O	5.5	1.0E5	73	5.853	51.1
Dodecane	48.3	2.7E6	76	0.956	53.4

Test Conditions

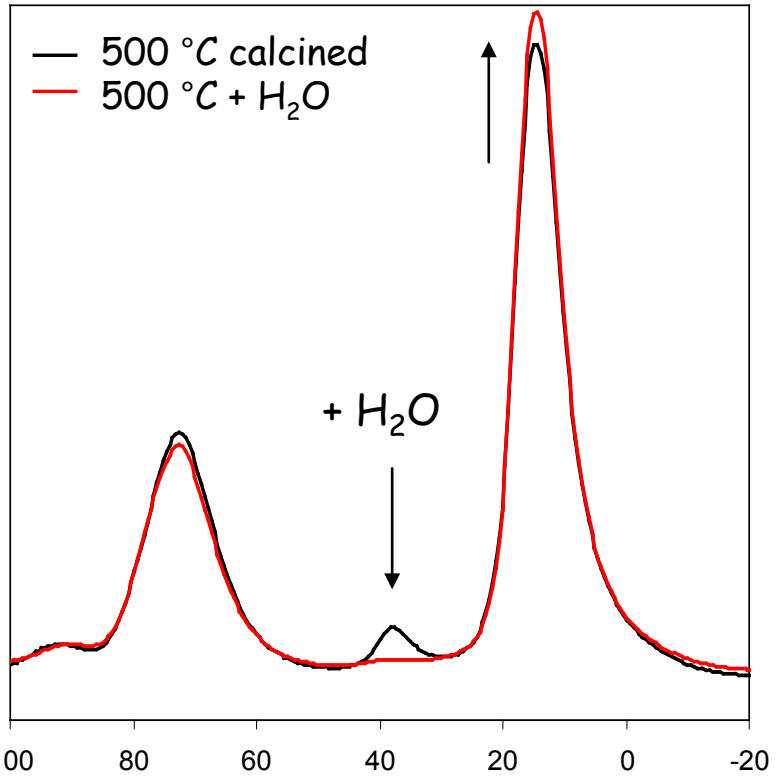
Component	Concentration
NO_x	350 ppm
NH_3	350 ppm
CO_2	0 or 5 %
O_2	14 %
Hydrocarbon ➢ C_2H_4 & C_3H_8 – combustion products ➢ Toluene – aromatic fuel component ➢ n-dodecane – long chain HC fuel component	350 ppm C1
Water	0 – 5%
N_2	balance
Space velocity	29k hr^{-1} for steady state tests 44k hr^{-1} for transient tests

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



JH Kwak, JZ Hu, DH Kim,
J Szanyi, CHF Peden, unpublished.

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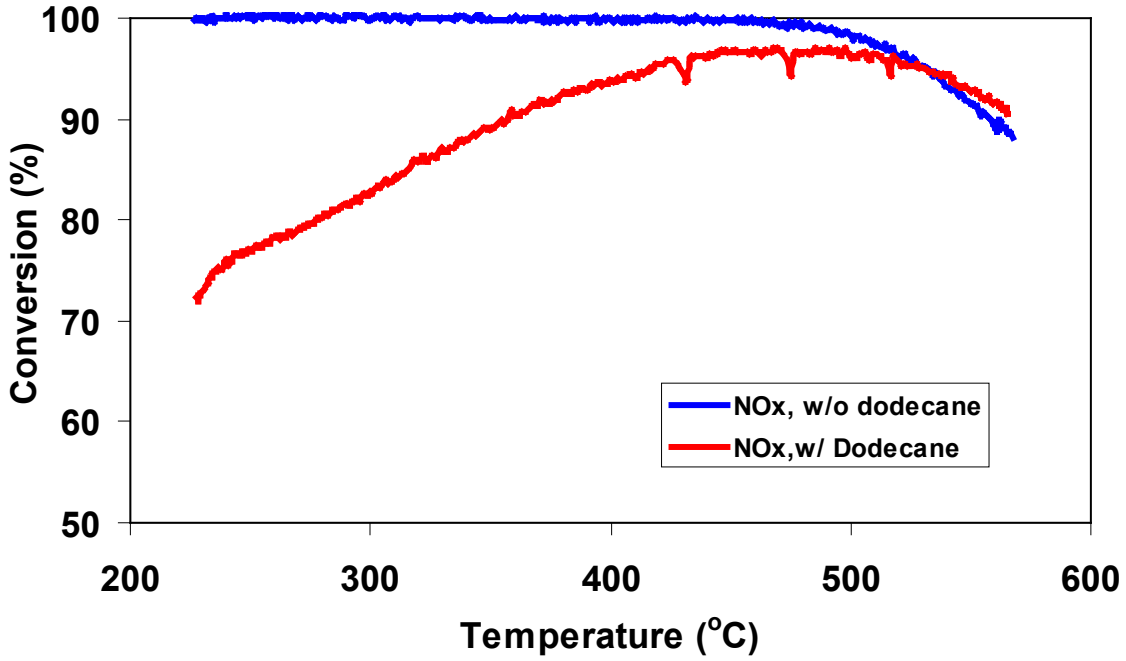
Effect of Dodecane on NOx Reduction



Feed Conditions

175 ppm NO

175 ppm NO_2

350 ppm NH_3

14% O_2

2% H_2O

29 ppm dodecane (350 C1)

- Decreased NOx reduction during temp-down ramp
- More pronounced effect on Standard SCR
- No effect on NO_2-SCR

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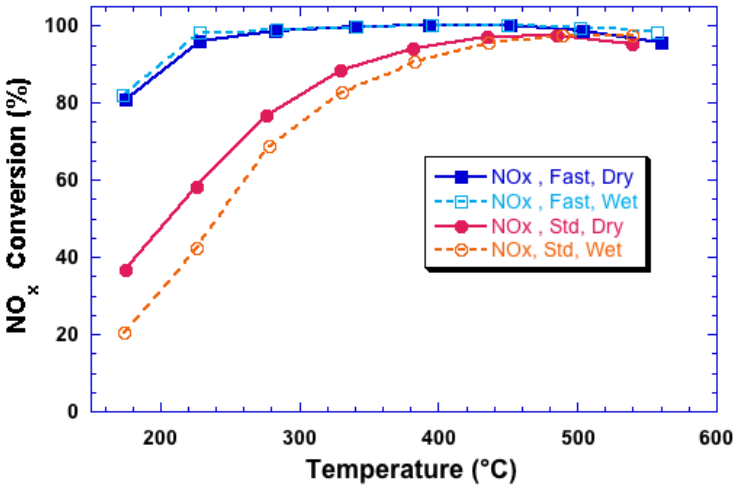
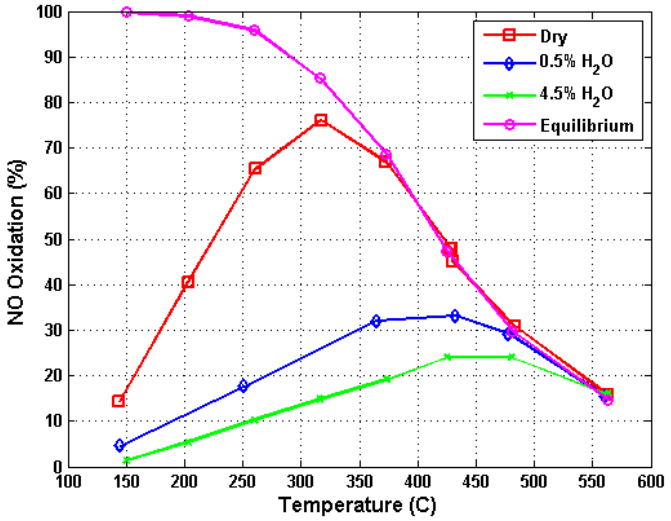
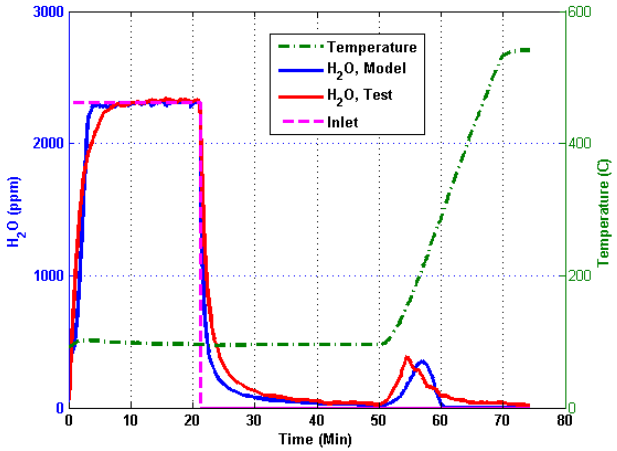
H_2O Inhibition Modeling



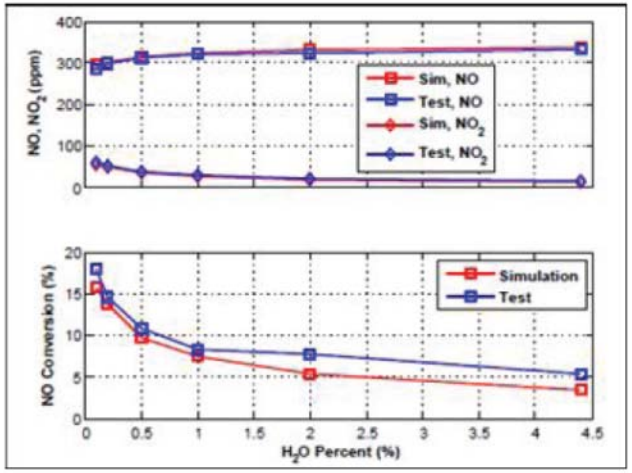
Effect of H_2O on SCR Reactions



Effect of H_2O on NO Oxidation

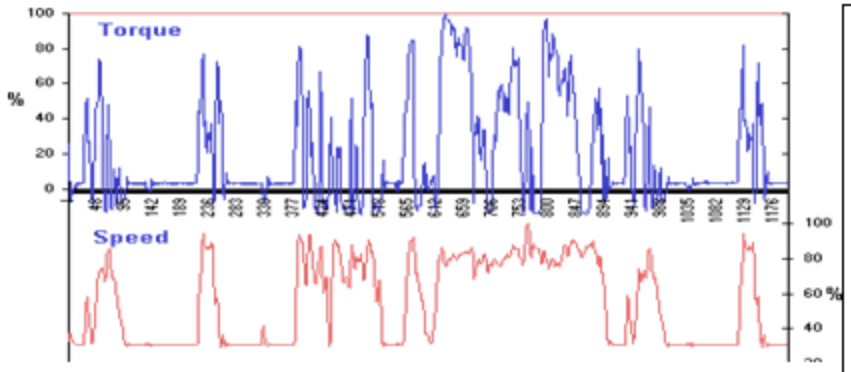


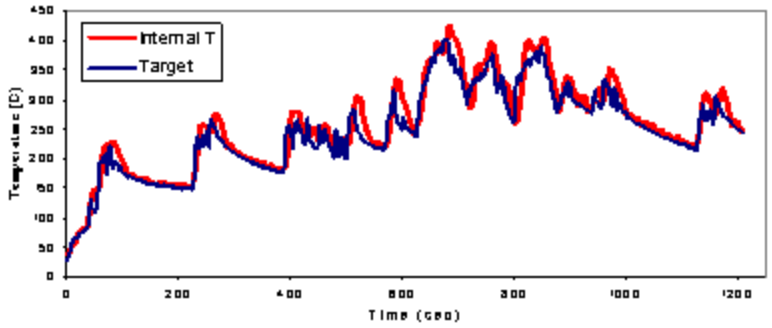
H_2O Storage Model

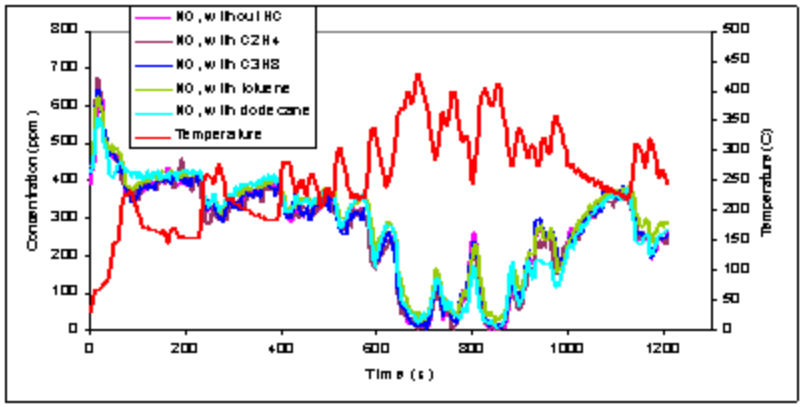


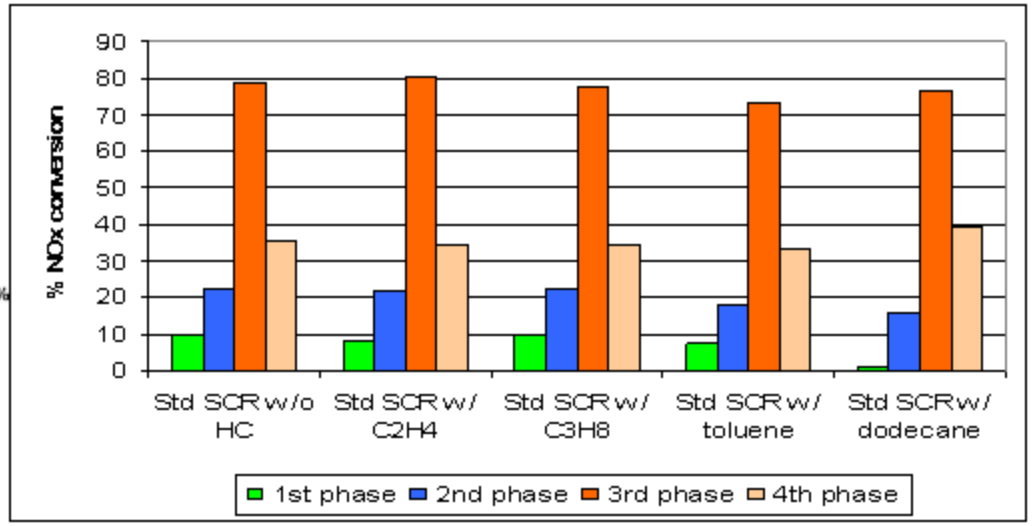
Model for H_2O Inhibition of NO oxidation

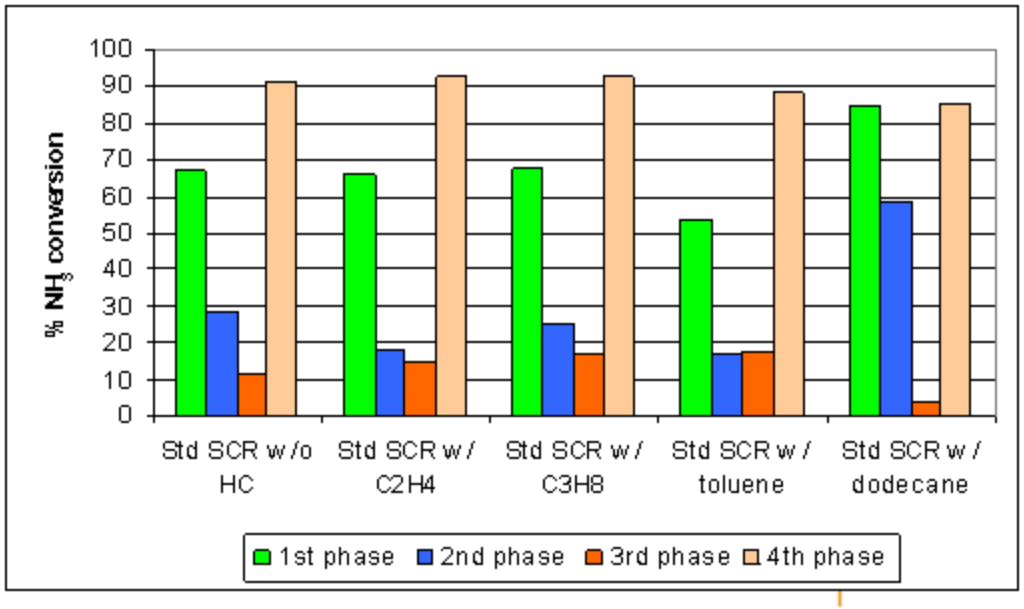
Effects of HCs under Transient Conditions



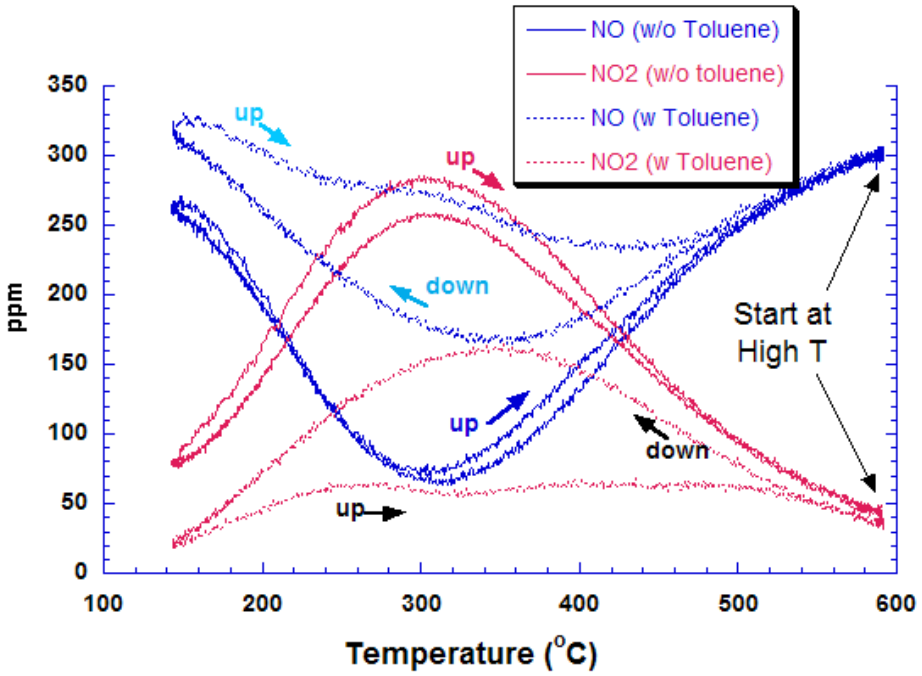


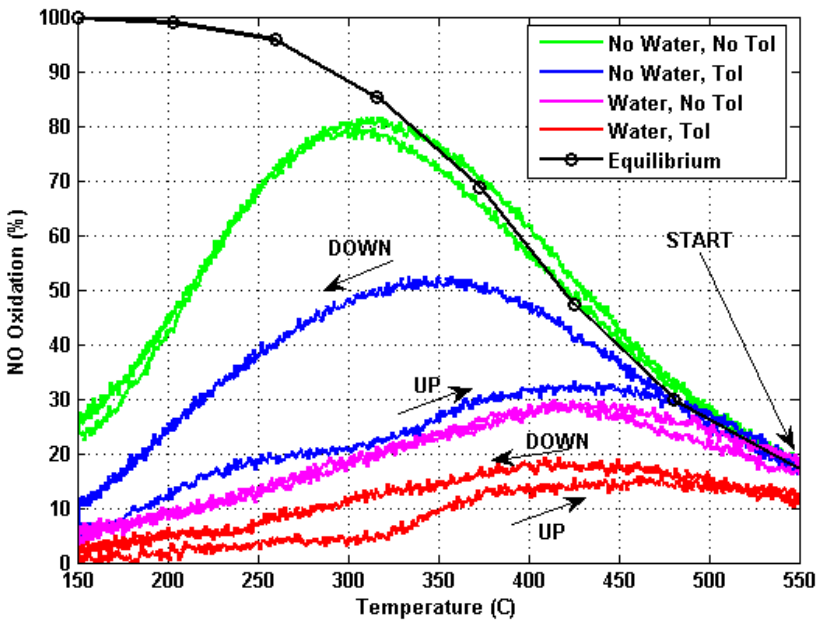






Effect of Toluene on NO Oxidation





350 ppm NO, 14% O_2, 25 ppm toluene, 2% H_2O

- More pronounced inhibition effect during temp-up ramp
- Severe inhibition in the presence of H_2O

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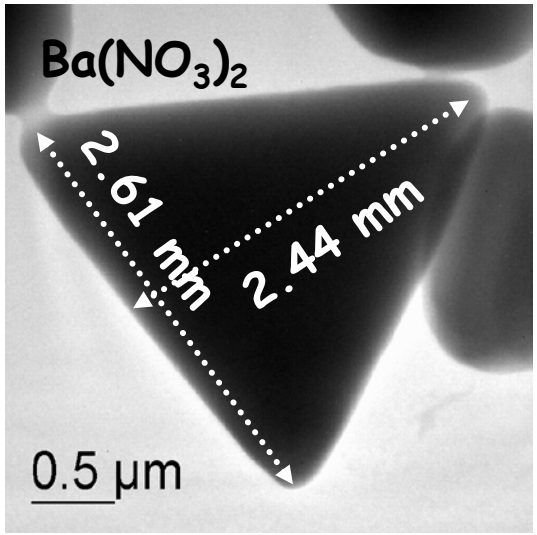
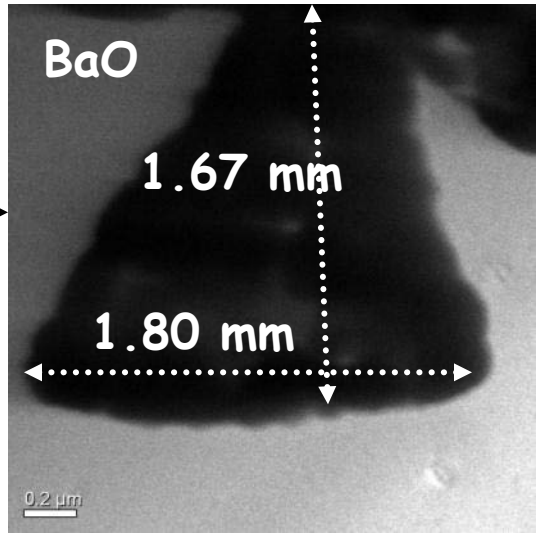
In-situ TEM observation of morphological changes in $Ba(NO_3)_2$ upon heating



Decomposition

Heating up to
800 °C in 1 torr
0.8 N_2 + 0.2 O_2



Wang, Kwak, Kim, Szanyi, Sharma, Thevuthasan, Peden, J. Phys. Chem. B **110** (2006) 11878.

Characteristics: particle shrinks, with a linear shrinkage of ~ 31%

Theoretical value: 32%

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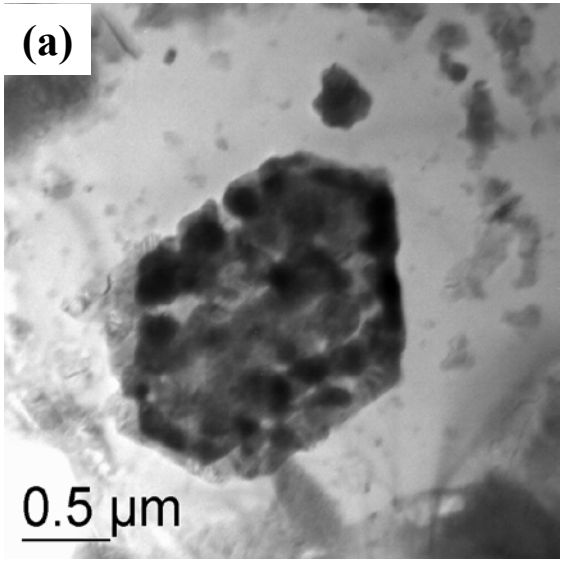
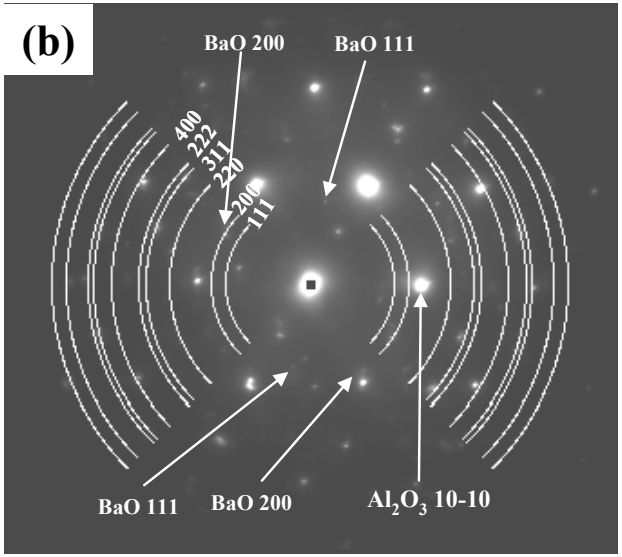
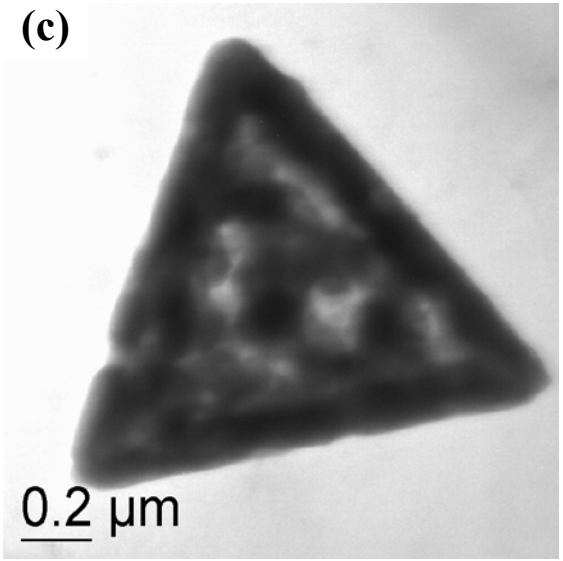
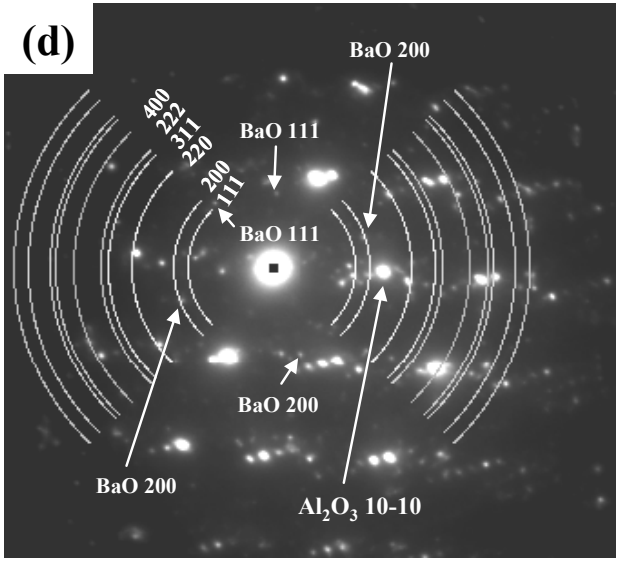
BaO maintains overall morphology of 'precursor' $Ba(NO_3)_2$ but as a collection of small particles









C.M. Wang, J.H. Kwak, D.H. Kim, J. Szanyi, R. Sharma, S. Thevuthasan, C.H.F. Peden, J. Phys. Chem. B **110** (2006) 11878.

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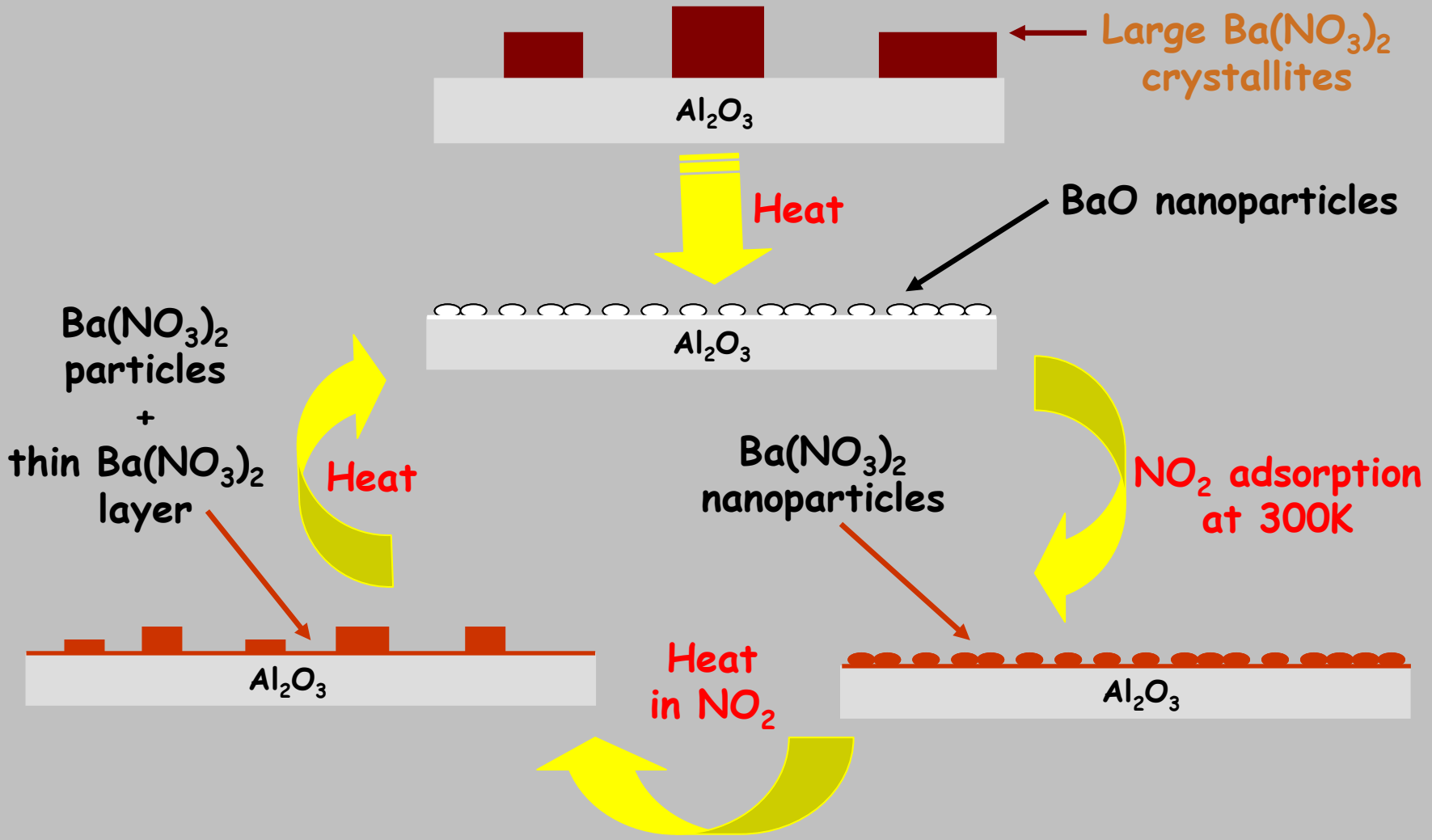
Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' $Ba(NO_3)_2$ morphologies present.



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.

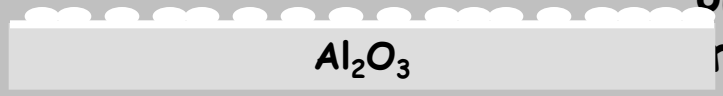
Decomposition of $Ba(NO_3)_2$ precursor requires a 500 °C calcination

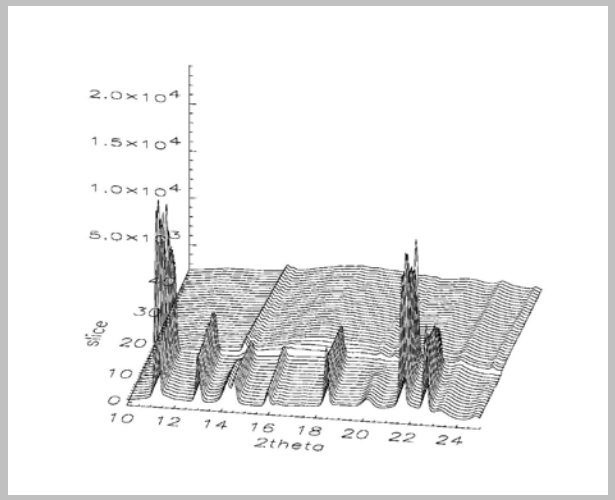
'Wet impregnation' of γ-Al_2O_3 with an aqueous $Ba(NO_3)_2$ solution; dried at 125 °C

Large $Ba(NO_3)_2$ crystallites

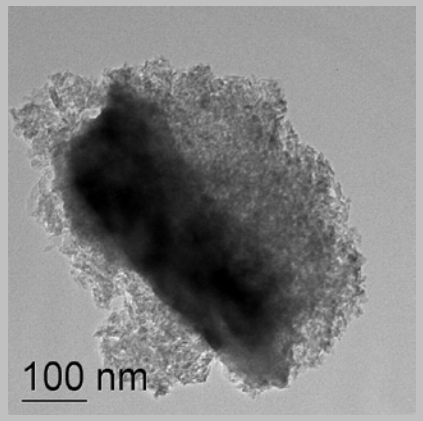
Calcined in dry air at 500 °C

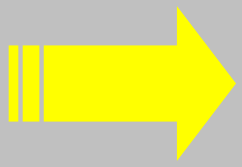
BaO nanoparticles on a BaO monolayer

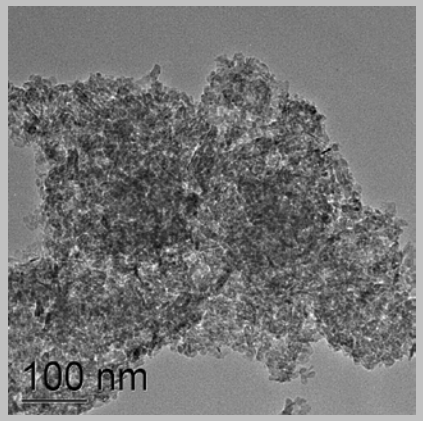


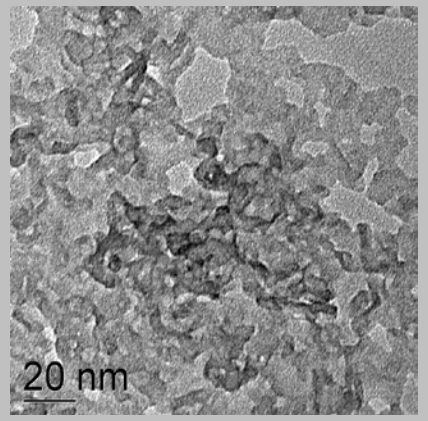


In-situ time-resolved XRD



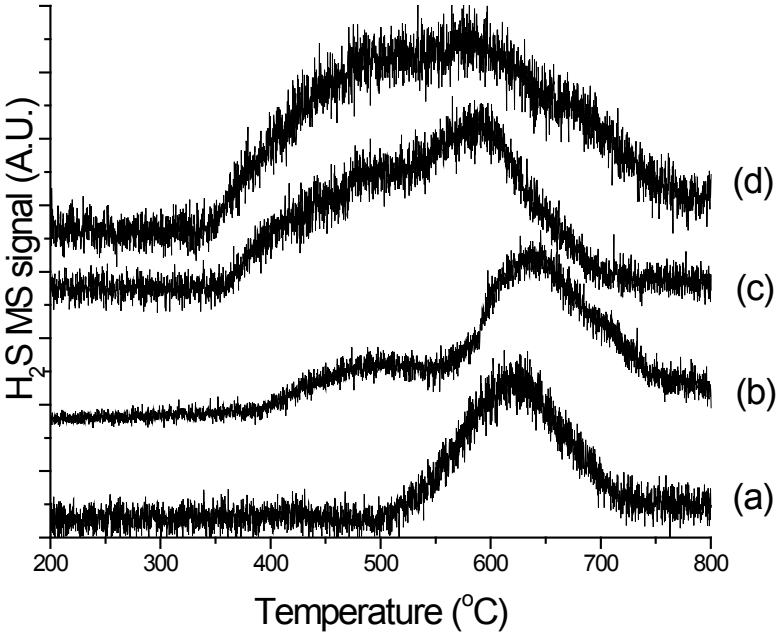






CO_2 Promotion of Desulfation of Model LNTs

	$Pt\text{-}Ba(20)/Al_2O_3$	$Pt\text{-}Ba(8)/Al_2O_3$
Sulfated	2.81	2.85
Desulfated with H_2	0.50	0.11
Desulfated with H_2/CO_2	0.30	0.03



H_2 TRPX spectra:

- **$Pt\text{-}BaO(20)/Al_2O_3$ without (a) and with (b) CO_2.**
- **$Pt\text{-}BaO(8)/Al_2O_3$ without (c) and with (d) CO_2.**

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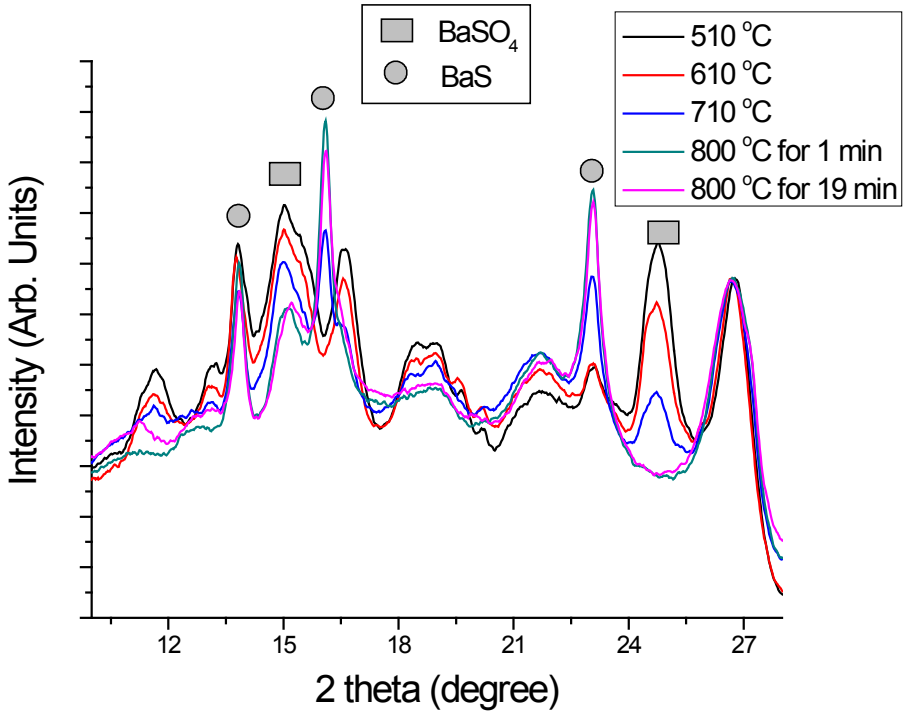
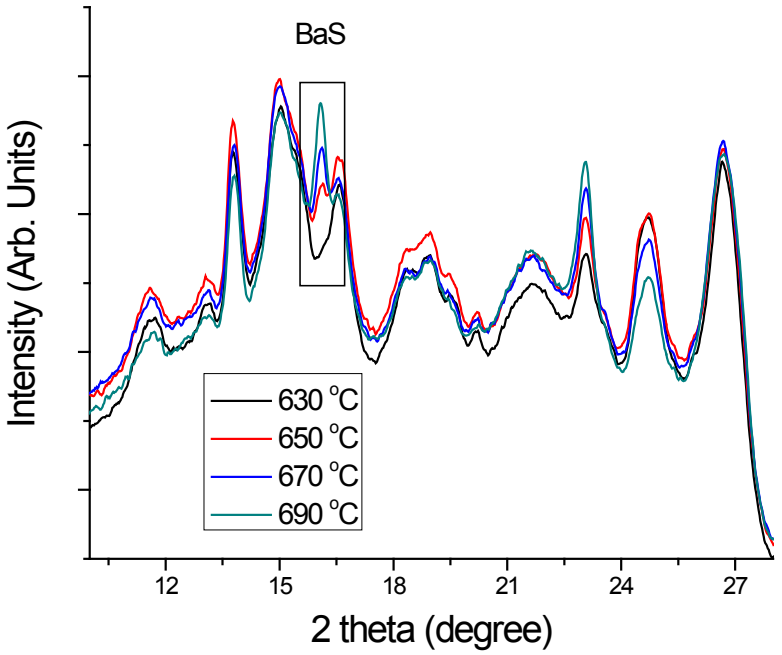
Synchrotron Time-Resolved XRD During Desulfation – Pt-BaO(20%/Al_2O_3)

TR-XRD diffractograms of pre-sulfated Pt-BaO(20)/Al_2O_3 obtained during the temperature ramping in the presence of both H_2 and CO_2.



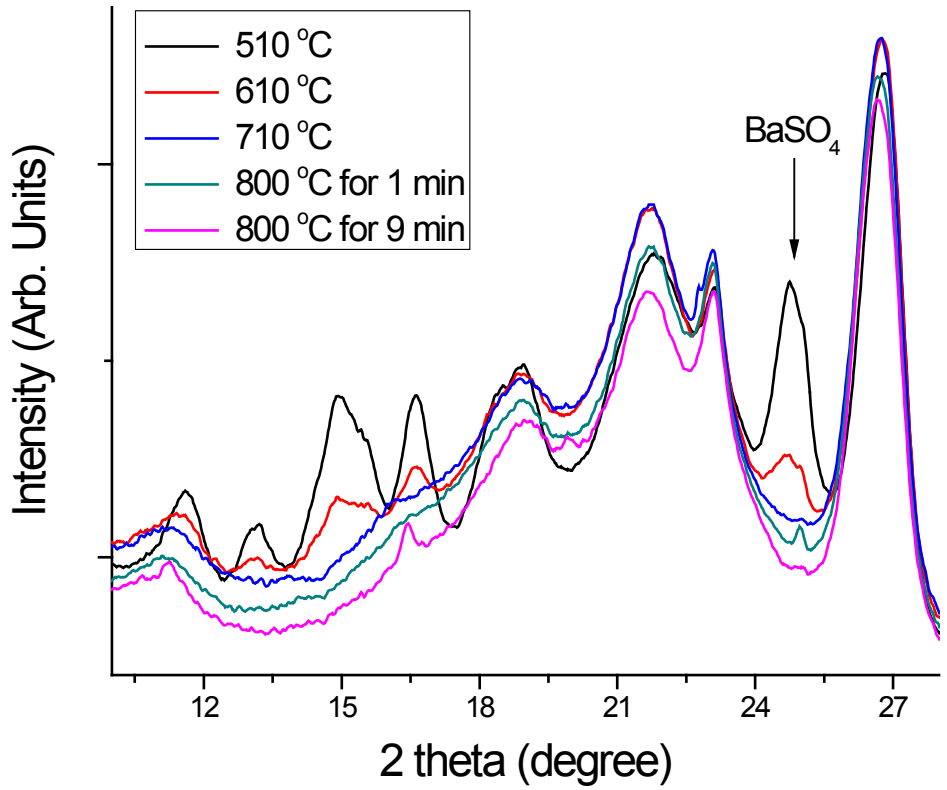
510 – 800 °C



630 – 690 °C

Synchrotron Time-Resolved XRD During Desulfation – Pt-BaO(8%/Al_2O_3)

TR-XRD diffractograms of pre-sulfated Pt-BaO(8)/Al_2O_3 obtained during the temperature ramping in the presence of both H_2 and CO_2.



510 – 800 °C