Pre-Competitive Catalysis Research: Fundamental Sulfation/Desulfation Studies of Lean NOx Traps

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U.S. DEPARTMENT OF
ENERGY

OAK RIDGE NATIONAL LABORATORY
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Project Overview

Timeline

- Project is ongoing but re-focused each year to address current DOE and industry needs
  - FY10 focus: LNT dopant study
  - FY09 focus: Component LNT study
  - FY08 focus: Desulfation of sectioned LNTs and sulfur coverage on Pt

Barriers

- Fuel penalty
  - Regeneration & desulfation of emission controls require extra fuel consumption
- Durability and Cost
  - Large built-in PGM margin required to meet durability requirements/emissions standards

Budget

- Funding received
  - FY09: $100K
  - FY10: $200K
    - $150K allocated to date
- Anticipate similar funding for FY11

Partners

- Collaborators and their roles
  - CLEERS: evaluation protocols
  - Center for Nano-phase Material Science (CNMS): catalyst synthesis
  - Umicore: catalyst supplier

Relevance and Objectives

- LNTs are attractive for the reduction of NOx emissions in both lean-gasoline and diesel applications
  - No additional injection ports or reductant storage necessary

- LNTs have been introduced commercially, **BUT…**

HIGH COSTS AND DURABILITY LIMIT FURTHER IMPLEMENTATION

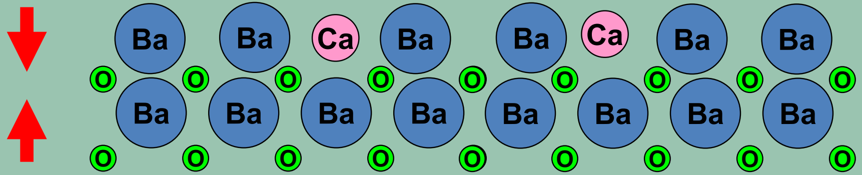
Objectives:

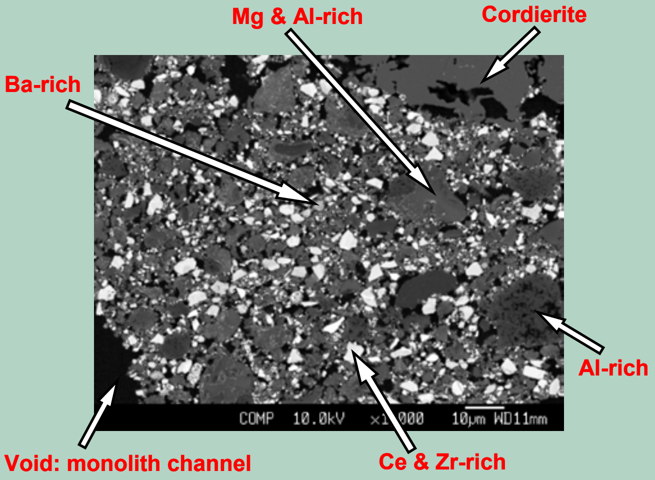
- Investigate methods for improving performance and/or durability of LNTs, such that PGM costs can be reduced
- Determine role of individual components in a commercial LNT during desulfation of lean NOx traps to improve understanding

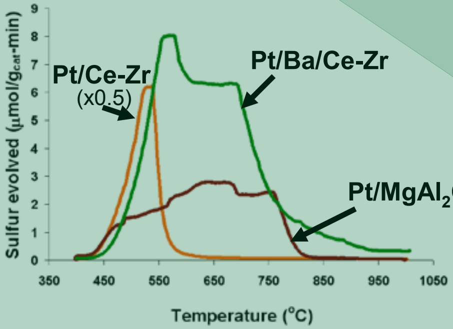
Two-tiered Approach

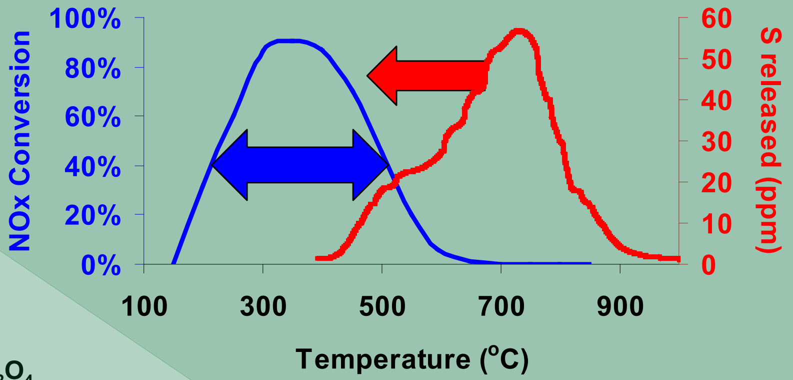
- Explore mixed metal oxides for storage phase of LNTs; Ba substitution
- Identify material effects and attempt to correlate to performance changes
- Work with CNMS (BES funded user center)
- Synthesize LNTs using aqueous techniques

umicore Automotive Catalysts









- Commercial catalysts are complex; made of several phases or components
  - Formulations derived from empirical and fundamental catalysis research
- Investigate functionality of individual components during sulfation and desulfation

Milestones for FY 2010

- Publish the collaborative effort with the Center for Nanophase Material Science on Ba-dopant effects on LNT performance (September 2010).
  - Submitted April 2010 to Catalysis Today

- Publish efforts on Umicore component sulfation/desulfation study (September 2010).
  - On target, manuscript being circulated amongst co-authors

Summary of Technical Accomplishments

- Confirmed the improvement in performance and desulfation properties with 5%mol Ca introduction into the BaO storage phase of an LNT catalyst

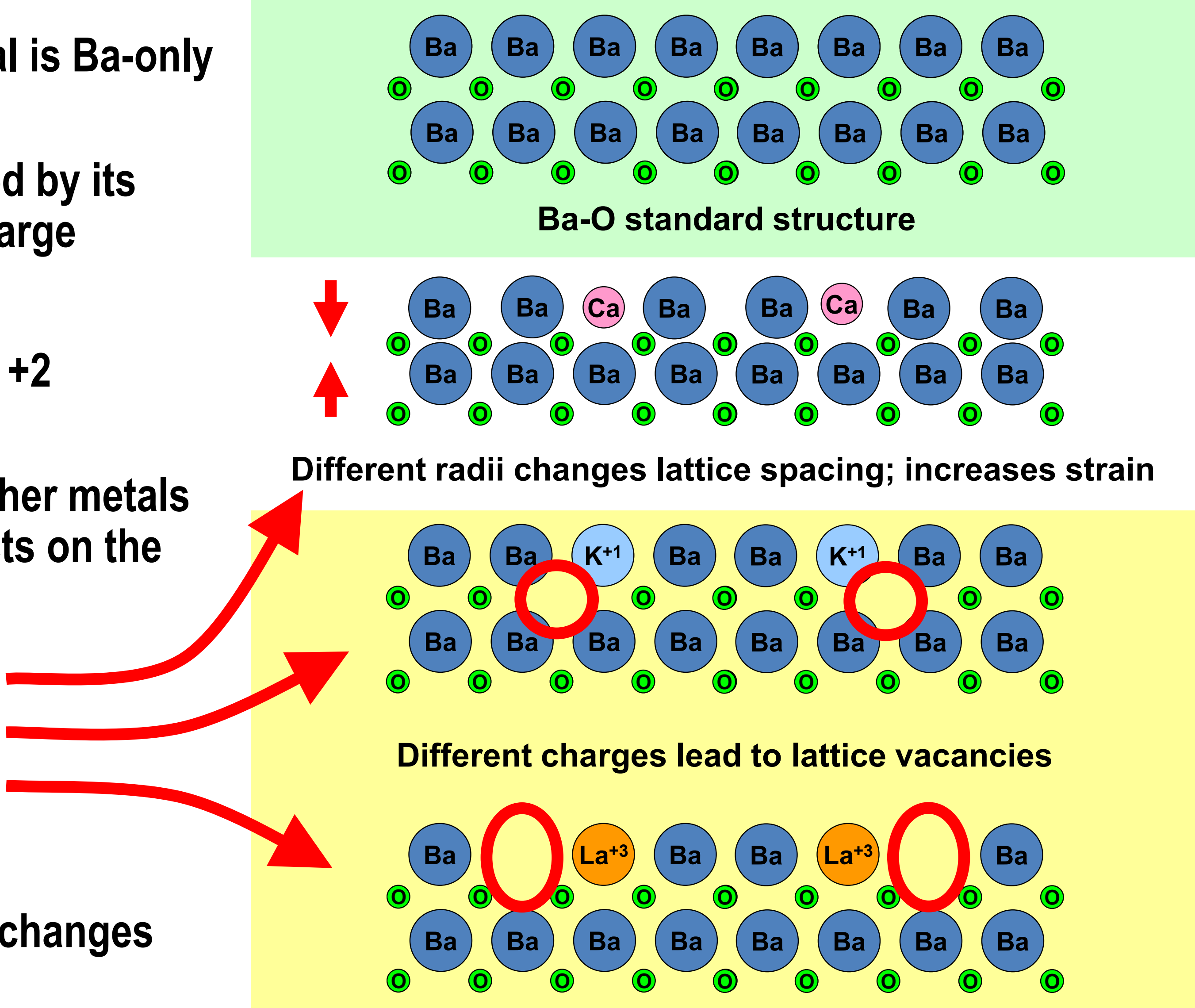
- Demonstrated sequential effect of Ca addition from 5% to 100%
  - Improvement is due to a synergistic effect as Ca-only catalyst results in higher desulfation temperatures

- Determined sulfur stability and desulfation characteristics of individual components of a commercial LNT catalyst
  - several findings, two to be discussed
  - see supplemental slides for additional details

Impact of Dopants in Ba-based LNT Catalysts

Can Ba storage/release chemistry be modified by lattice substitutions?

- Typical storage material is Ba-only
- BaO structure is defined by its covalent radius and charge
  - $r_{Ba} = 2$ Å
  - Charge in Lattice = +2
- Substituting Ba with other metals can have multiple effects on the material structure
  - Lattice spacing
  - Oxygen vacancies
  - Ba-vacancies
- Do nanoscale material changes affect performance?



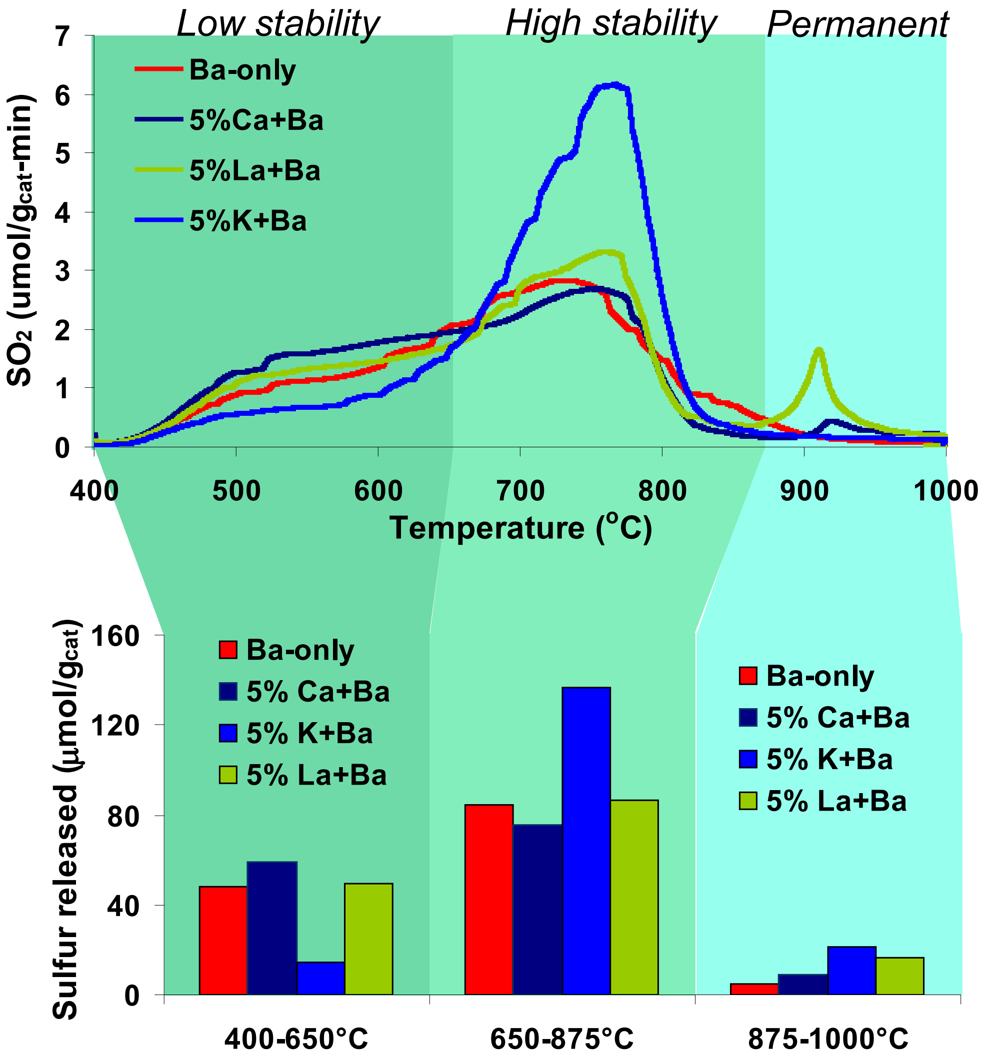
Ba-O standard structure

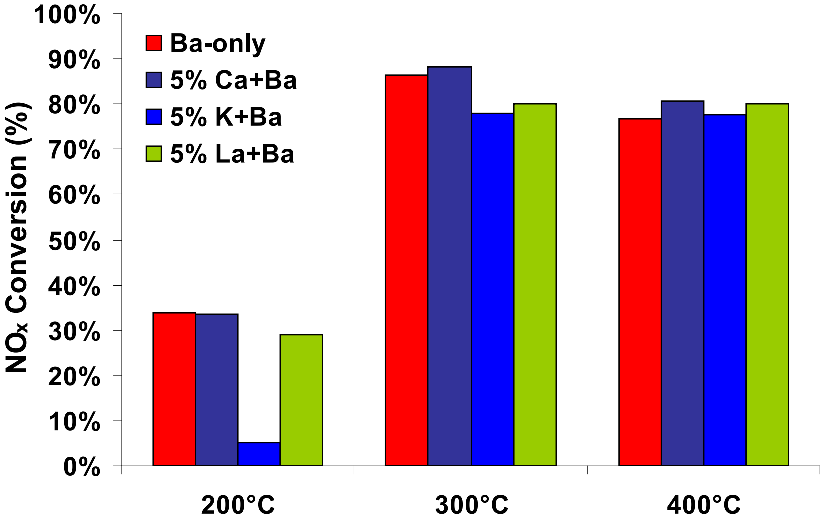
Different radii changes lattice spacing; increases strain

Different charges lead to lattice vacancies

FY2009 efforts show Ca-substitution leads to improved NSR performance and desulfation

- Ca+Ba sample yields similar NOx conversion performance to Ba-only
  - Some improvement at 300 and 400ºC compared to Ba-only
- Ca+Ba sample releases more sulfur at lower temperatures

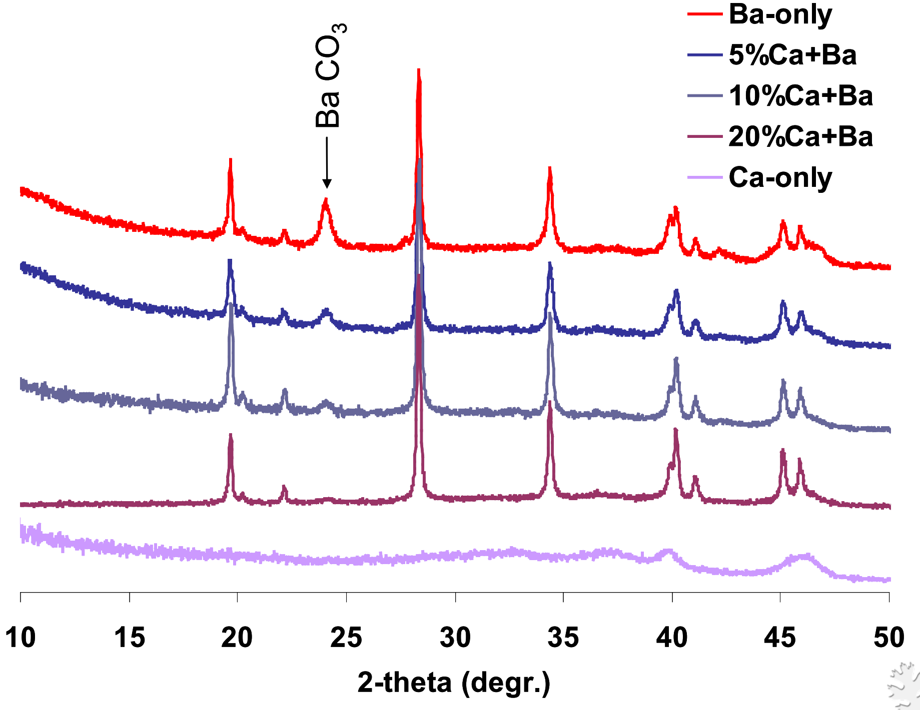




Ca-substitution expanded to study additional concentrations

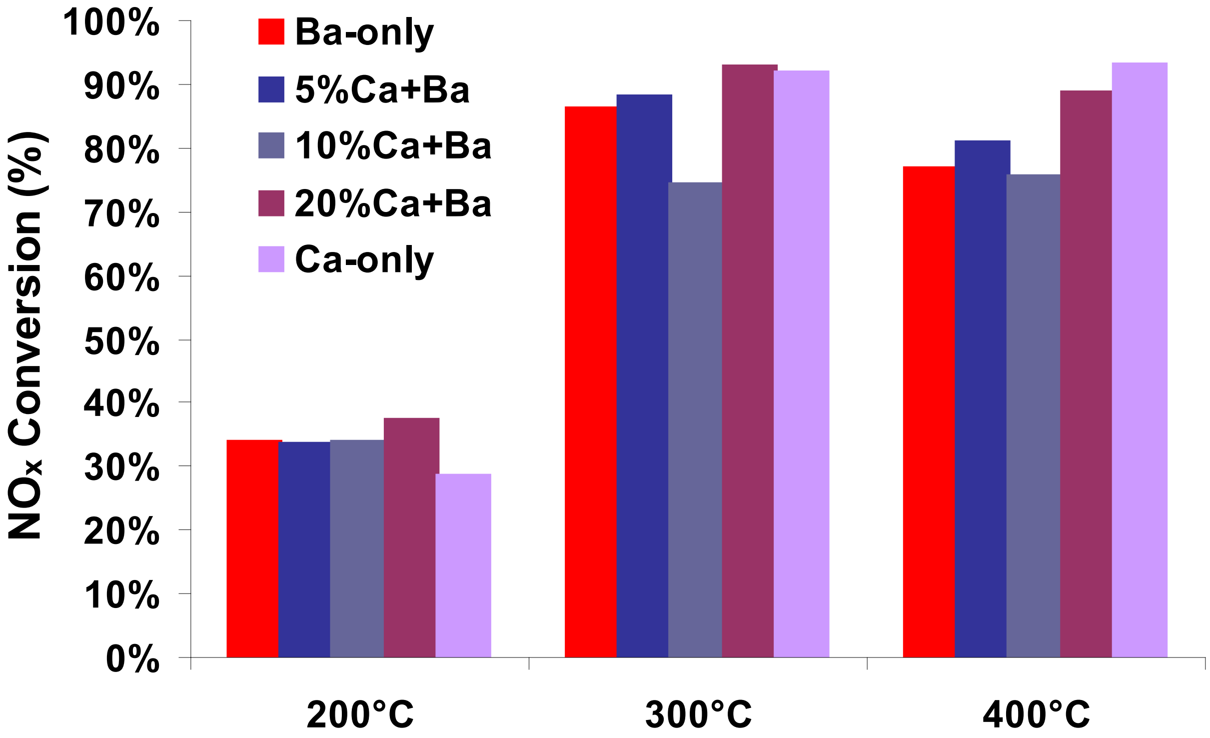
- Same base catalyst: 1.5%wt Pt/γ-Al_2O_3
- Ca substitution levels
  - 5 mol%
  - 10 mol%
  - 20 mol%
  - Ca-only
- $BaCO_3$ identified again
  - decreases with increasing Ca content
- Ca-only sample results in amorphous/nanocrystalline Ca-phase

NSR Catalyst	Pt (wt%)	Ba (mol%)	Ca (mol%)
Pt/Al_2O_3	1.5%	-	-
Ba-only	1.1%	20%	0%
5%Ca+Ba	1.1%	19%	1%
10%Ca+Ba	1.1%	18%	2%
20%Ca+Ba	1.1%	16%	4%
Ca-only	1.1%	0%	20%



Ca-substitution continues to show some performance benefits compared to Ba

- Ca-only NSR catalyst shows significantly better performance at 400ºC
  - 18% greater NO converted than Ba-only

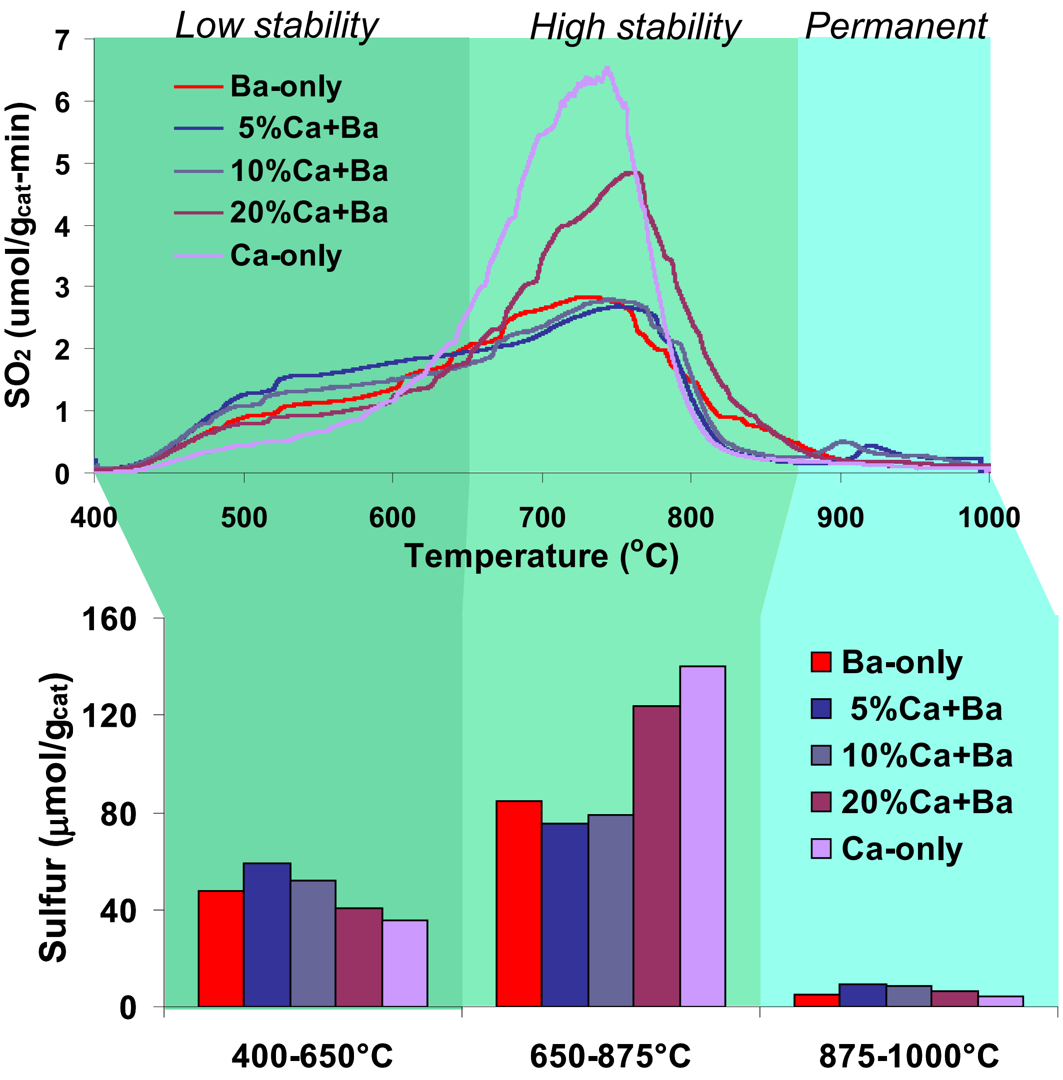


Ca-only phase results in more stable sulfates; synergistic effect occurs w/ 5-10% substitution

- Sulfate at 400°C to 5 mg S/g_{cat}
- 5% Ca+Ba releases the most sulfur at low temperatures

5%Ca+Ba > 10%Ca+Ba > Ba-only
Ba-only > 20%Ca+Ba > Ca-only

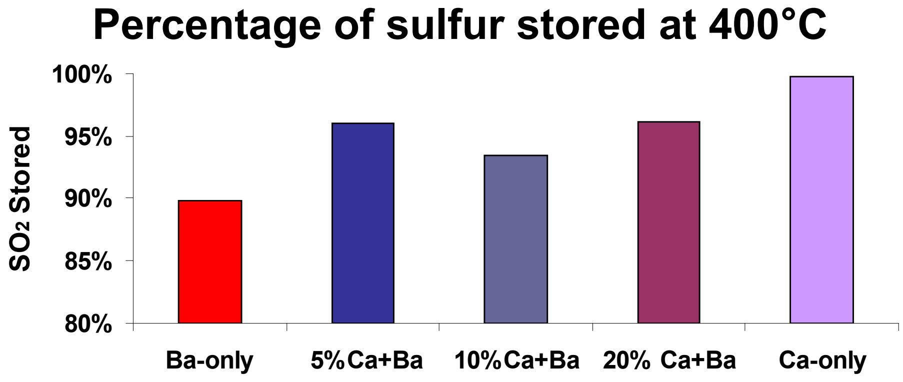
- Ca-only has the most "high-stability" sulfates
- Since Ca substitution leads to less stable sulfates there must be a synergistic effect



Although Ca-only has most stable sulfates, its performance is minimally impacted

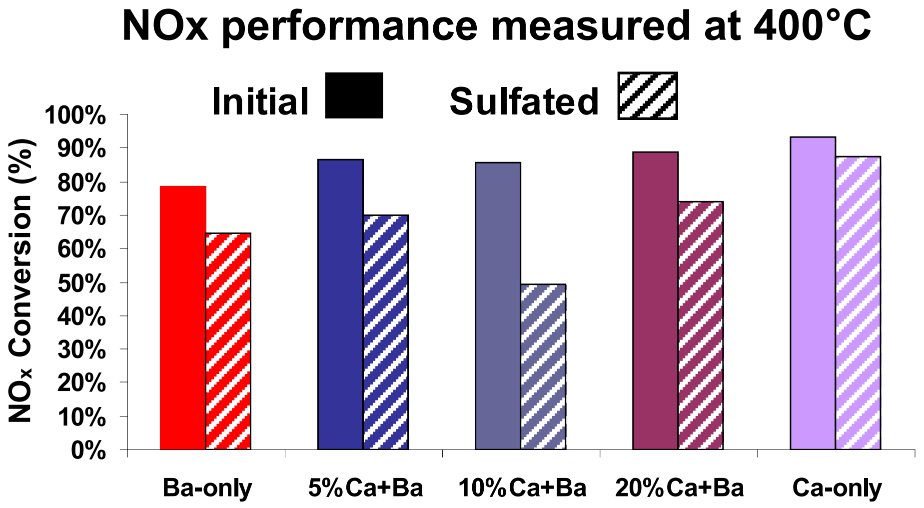
- 100% Ca-storage phase is the most sulfur adsorbant storage material
- Ba-only releases the most sulfur during rich cycle at 400°C

Percentage of sulfur stored at 400°C



- 100% Ca is most tolerant to sulfur
  - 10% Ca+Ba is most affected
- Sulfur tolerance is very important factor
  - LNT can go further between de-S
  - Fewer desulfations
    - less fuel consumed
    - less impact on PGM
    - less initial PGM needed

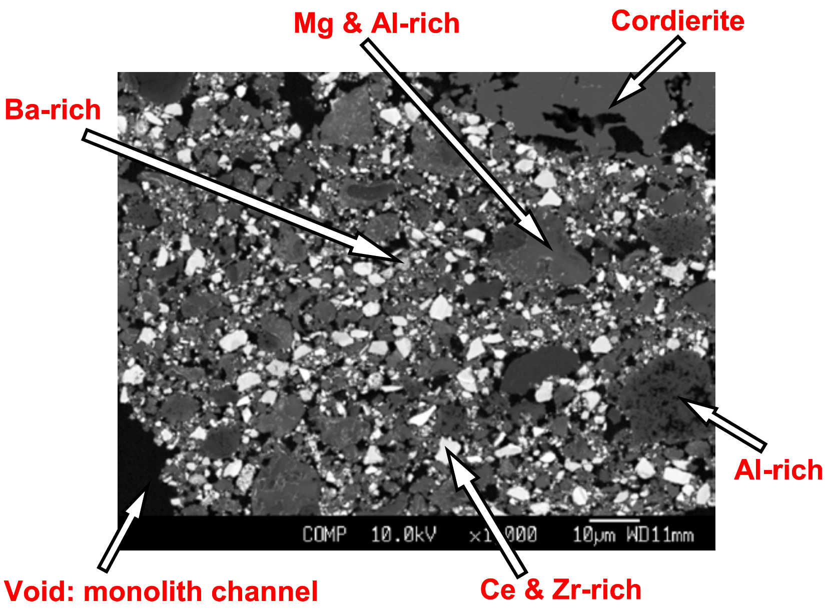
NOx performance measured at 400°C



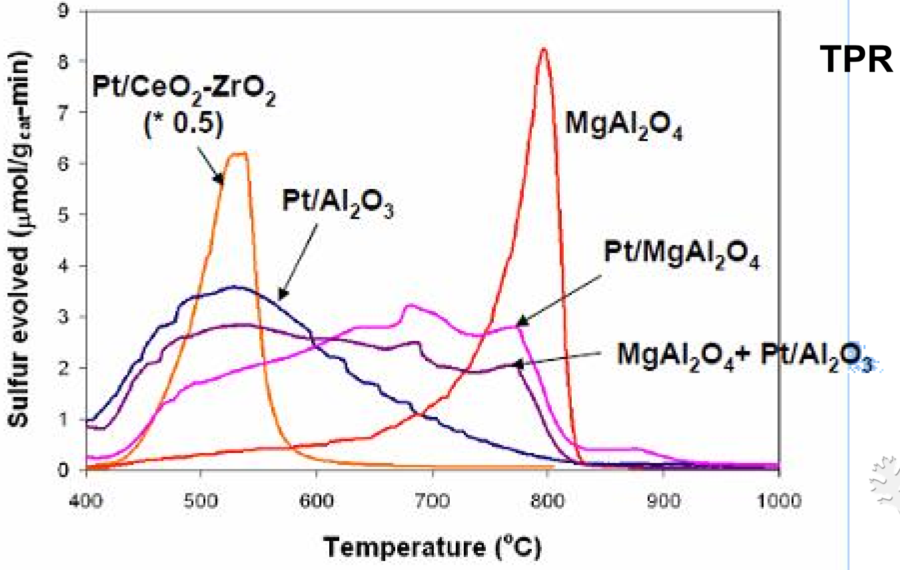
Study of functionality of commercial LNT Components

Commercial LNTs are complex multicomponent devices

- CLEERS reference LNT catalyst
  - provided by Umicore
- Ba-based sample with Pt, Pd and Rh
- Relies on Al_2O_3, CeO_x-ZrO_2, and $MgAl_2O_4$ as supports
- Several groups working to understand how some of these phases contribute to LNT performance

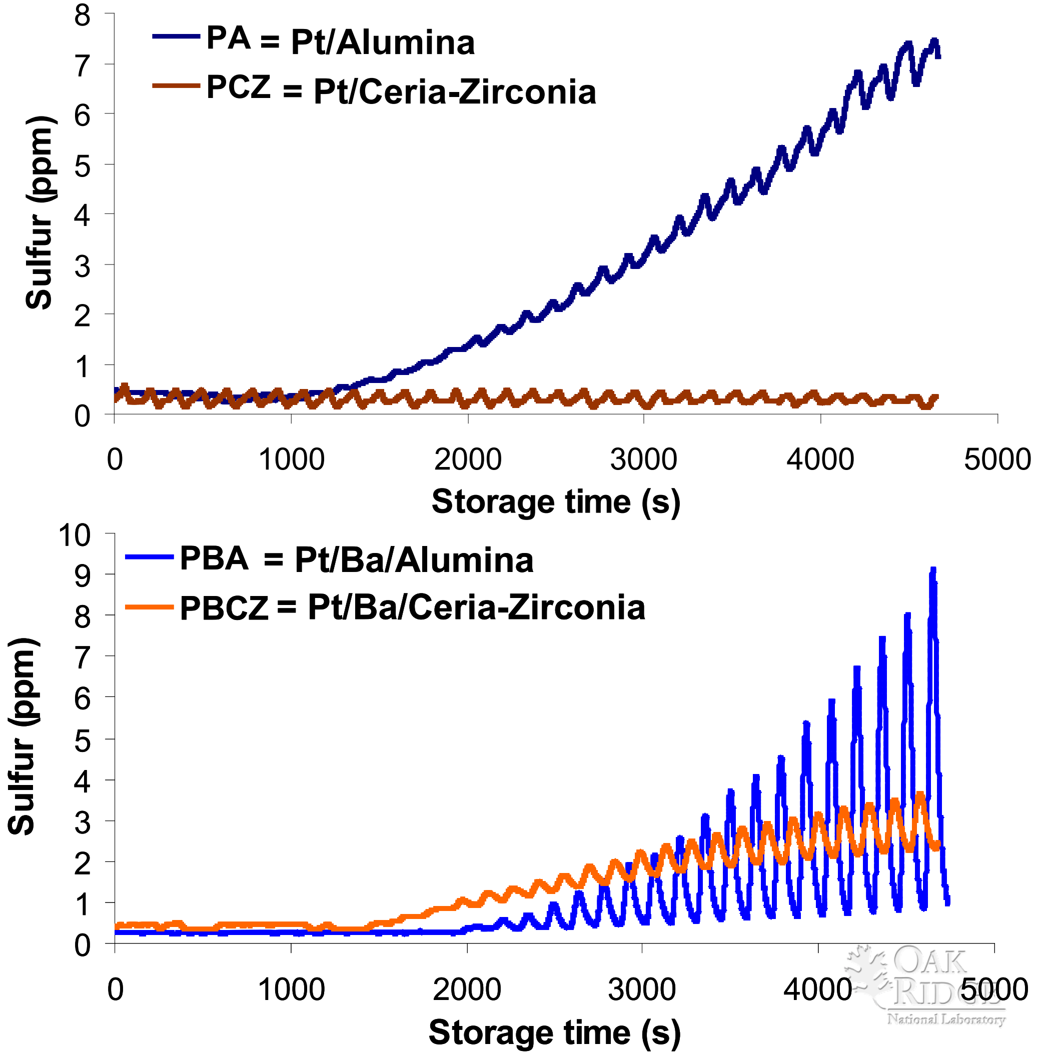


- Our focus is on sufation/desulfation:
  - How does Ba/Ceria-zirconia differ from Ba/alumina?
  - What is role of $MgAl_2O_4$?



Using Ceria-Zirconia vs. Alumina as a support impacts LNT chemistry

- Umicore catalyst relies on Ceria-Zirconia as a Ba support
  - Alumina most widely studied
- Ceria-Zirconia is a known oxygen storage component (OSC)
  - Shown to have good low temperature NOx reduction
- Sulfation studied at 400°C while cycling between lean and rich
  - PBA samples have sharp SO_2 release profile
- Ceria-Zirconia supported catalysts trap more SO_2 during cycling

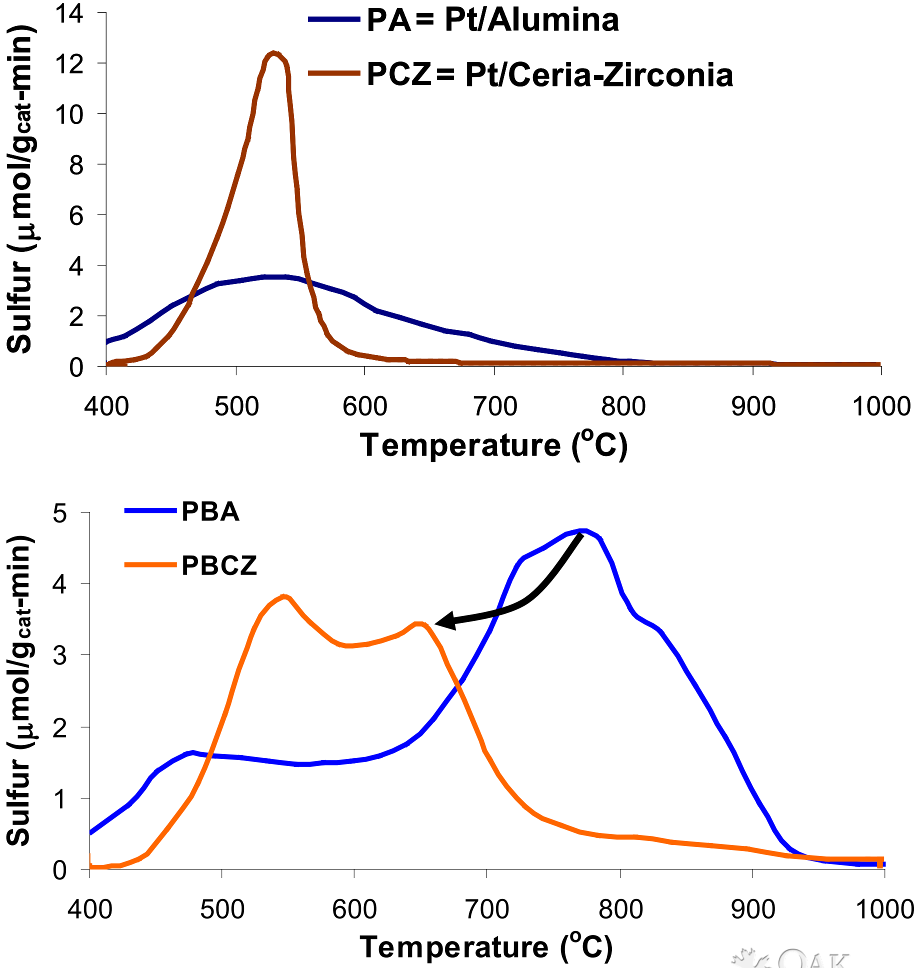


SO_2 breakthrough measured while lean-rich cycling at 400°C

Ceria-Zirconia decreases required desulfation temperature significantly

- Onset of SO_2 release is lower for Pt/Al_2O_3, but release profile is broad
  - $T_{20\%} = 464°C$; $T_{90\%} = 704°C$
  - Demonstrates heterogeneity of sites
- Pt/Ceria-Zirconia has sharp release profile
  - $T_{20\%} = 494°C$; $T_{90\%} = 570°C$
- Introducing Ba transforms release profiles
  - Only minor sulfur release observed from alumina supports
  - PBCZ sulfur releases at significantly lower temperature; 35-60°C
    - PBA: $T_{20\%} = 570°C$; $T_{90\%} = 855°C$
    - PBCZ: $T_{20\%} = 535°C$; $T_{90\%} = 797°C$

Sulfur release measured during 400-1000°C temperature ramp

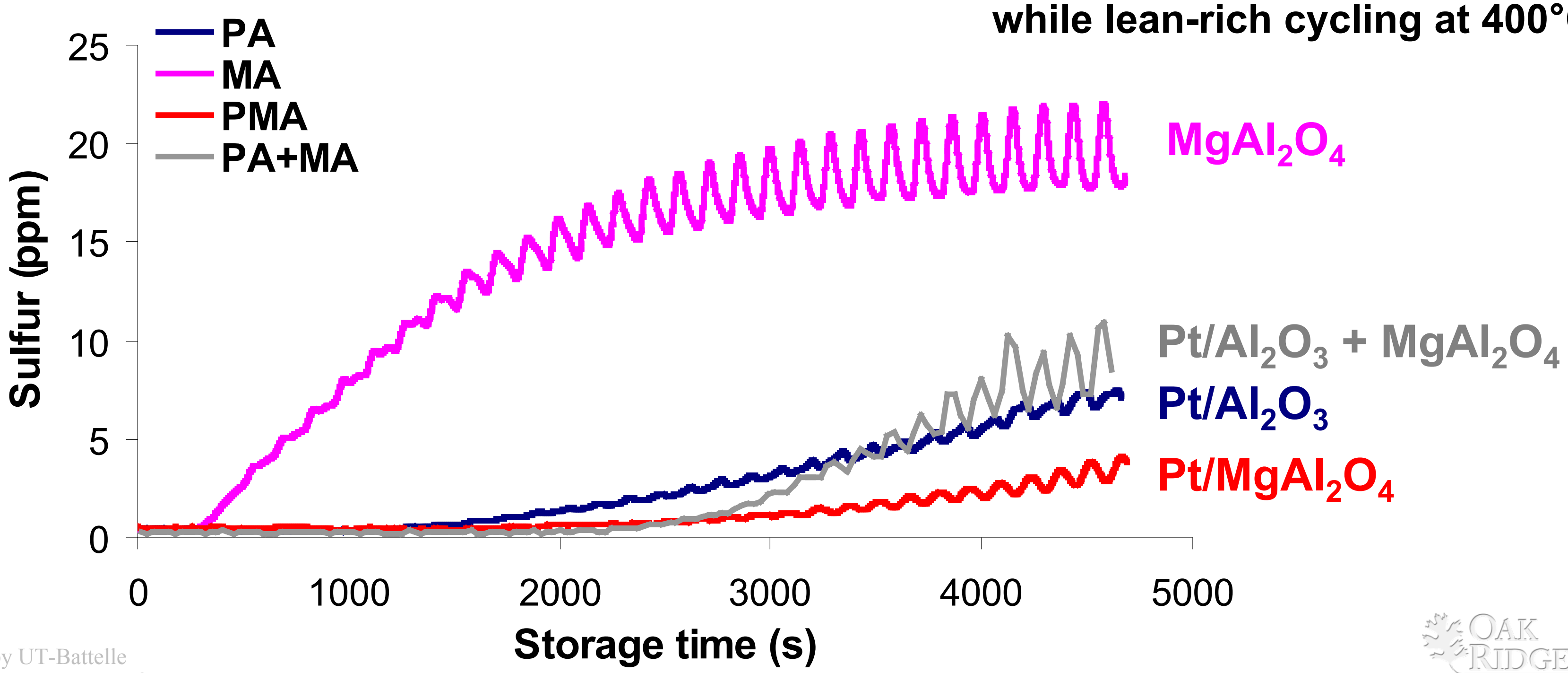


Umicore catalyst has high $MgAl_2O_4$ content but mechanism of benefit is unknown

- Up to 40%wt $MgAl_2O_4$ (MA) in the washcoat
- Not strongly-coordinated with platinum group metals (PGM)

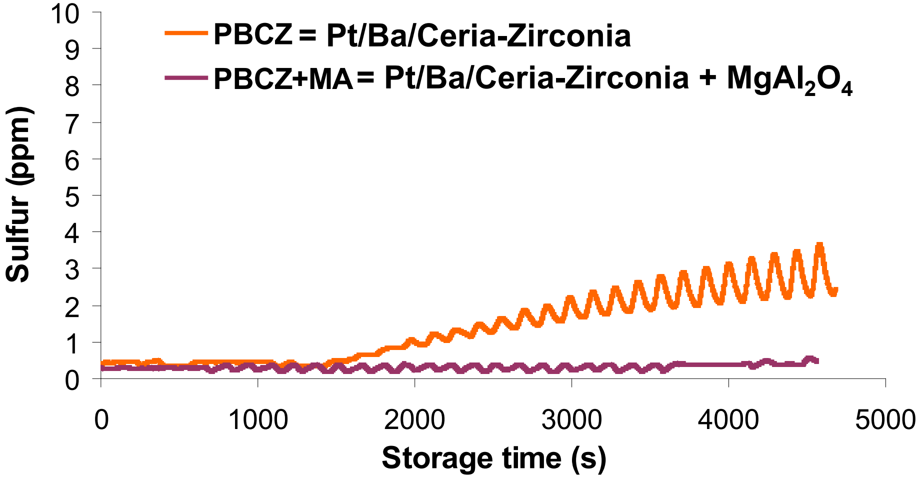
- Sulfation profile on MA-only results in fast SO_2 breakthrough
  - With PGM, it is an effective SO_2 trap (PMA)
- Physical mixture of PA+MA mimics PMA

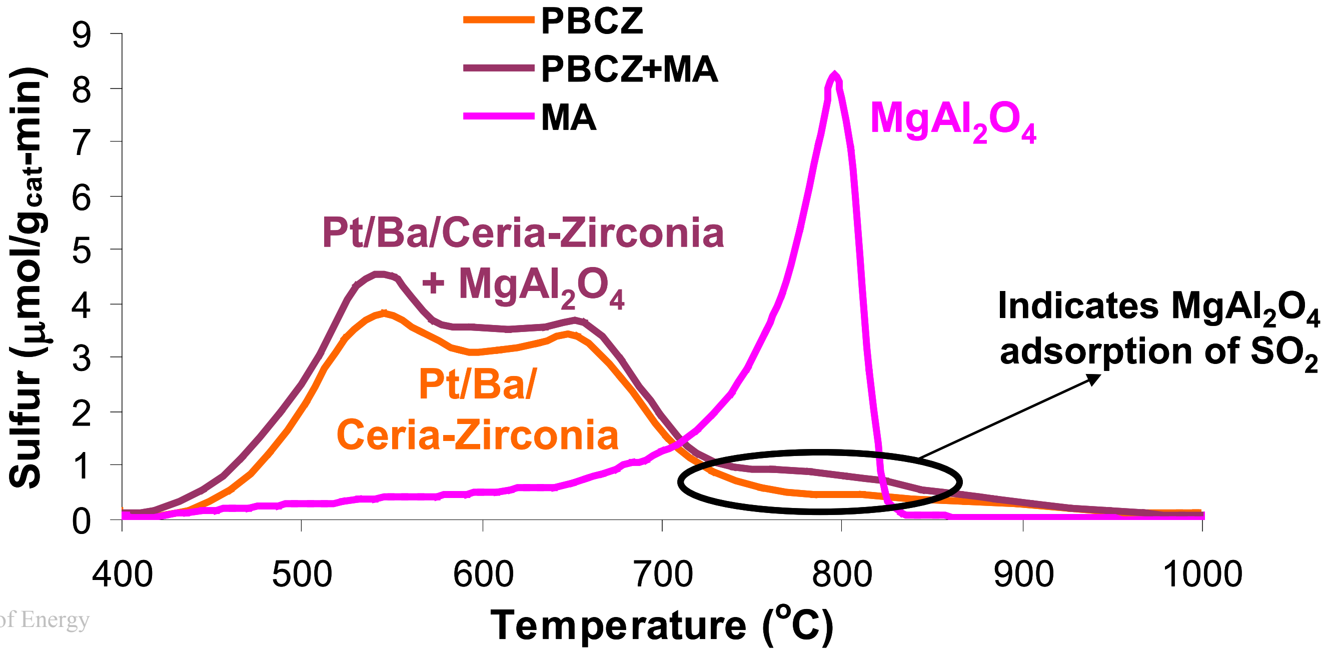
SO_2 breakthrough measured while lean-rich cycling at 400°C



Sulfation/Desulfation of Umicore-like sample suggests Mg-Al adsorbs SO_2

- **PBCZ+MA most closely mimics Umicore formulation**
- **Additional sulfur stored on PBCZ+MA**
- **Desulfation shows small amount of extra SO_2 released at ~800ºC**
  - **Mg-Al phase participates in sulfur trapping and perhaps transport**





Collaborators and Partners

CLEERS

- CLEERS
  - Discussions and evaluations protocols
- Umicore
  - Catalyst supplier for the commercial LNT
- Center for Nanophase Materials Science (CNMS)
  - Basic Energy Science funded user facility at ORNL
  - Prepared doped storage materials
  - Performed materials characterization

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Catalysts

Center for Nanophase Materials Sciences
A Highly Collaborative and Multidisciplinary
U.S. DOE Nanoscale Science Research Center

- High Temperature Materials Laboratory (HTML)
  - ORNL user facility funded by EERE
  - Additional materials characterization

html

Future Directions (Beyond FY10)

- Increase materials characterization efforts to link performance effects to material property
  - Will rely on HTML user center proposals
  - Implement DRIFTS studies to look at Ca impact on nitrate/sulfate bonding effects

- Effects of durability
  - Is benefit maintained after several thermal cycles or do the phases separate
  - Repeated sulfation/desulfation cycles
    - Only desulfate to typical desulfation temperatures, i.e. 700°C

- Support effects
  - Umicore component effort suggest changing support would affect results
  - Study Ceria-Zirconia versus Alumina

- Multicomponent studies → Tertiary oxides
  - Very interesting work recently reported from GM regarding doped perovskites with drastically reduced PGM levels

Summary

- Relevance:
  - LNTs are attractive for the reduction of NOx emissions in both lean-gasoline and diesel applications
  - High costs and durability limit further implementation of LNTs
- Approach:
  - Investigate novel formulations to guide material discovery and improve LNTs
  - Investigate functionality of individual components of commercial catalysts during sulfation and desulfation
- Collaborations:
  - Umicore catalyst supplier and collaboration with other VTP projects: CLEERS, PSAT, CRADAs, UK-CAER
  - BES-funded Center for Nanophase Materials Science (CNMS)
- Technical Accomplishments:
  - Demonstrated benefits of the addition of Ca-dopants to LNT storage phase
  - Identified functionality of components of a commercial LNT catalyst
- Future Work:
  - Increase materials characterization to help guide materials models for doped LNTs
  - Investigate support effects of Ca-doped samples; particularly ceria-zirconia
  - Explore low PGM catalysts tertiary oxide materials (GM-reported doped pervoskites)