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

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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

- 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
  - $r_{\text{Ba}} = 2 \text{ Å}$
  - 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?
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 400°C 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-Al₂O₃
- Ca substitution levels
  - 5 mol%
  - 10 mol%
  - 20 mol%
  - Ca-only
- BaCO₃ identified again
  - decreases with increasing Ca content
- Ca-only sample results in amorphous/nanocrystalline Ca-phase

<table>
<thead>
<tr>
<th>NSR Catalyst</th>
<th>Pt (wt%)</th>
<th>Ba (mol%)</th>
<th>Ca (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al₂O₃</td>
<td>1.5%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba-only</td>
<td>1.1%</td>
<td>20%</td>
<td>0%</td>
</tr>
<tr>
<td>5%Ca+Ba</td>
<td>1.1%</td>
<td>19%</td>
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<td>16%</td>
<td>4%</td>
</tr>
<tr>
<td>Ca-only</td>
<td>1.1%</td>
<td>0%</td>
<td>20%</td>
</tr>
</tbody>
</table>
Ca-substitution continues to show some performance benefits compared to Ba

- Ca-only NSR catalyst shows significantly better performance at 400°C
  - 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

- 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

![Graph showing SO₂ Stored at 400°C](image)

![Graph showing NOₓ Conversion (%)](image)
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 Al₂O₃, CeOₓ-ZrO₂, and MgAl₂O₄ as supports
- Several groups working to understand how some of these phases contribute to LNT performance

- Our focus is on sulfation/desulfation:
  - How does Ba/Ceria-zirconia differ from Ba/alumina?
  - What is role of MgAl₂O₄?
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 SO₂ release profile

- Ceria-Zirconia supported catalysts trap more SO₂ during cycling

SO₂ 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$_2$O$_3$, but release profile is broad
  – $T_{20\%} = 464^\circ$C; $T_{90\%} = 704^\circ$C
  – Demonstrates heterogeneity of sites
• Pt/Ceria-Zirconia has sharp release profile
  – $T_{20\%} = 494^\circ$C; $T_{90\%} = 570^\circ$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: $T_{20\%} = 570^\circ$C; $T_{90\%} = 855^\circ$C
    • PBCZ: $T_{20\%} = 535^\circ$C; $T_{90\%} = 797^\circ$C

Sulfur release measured during 400-1000°C temperature ramp
Umicore catalyst has high MgAl$_2$O$_4$ content but mechanism of benefit is unknown

- Up to 40%wt MgAl$_2$O$_4$ (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 ~800°C
  - Mg-Al phase participates in sulfur trapping and perhaps transport

![Graph showing sulfur adsorption and desorption over temperature and storage time]
Collaborators and Partners

- **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

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