Effect of Ceria on the Sulfation and Desulfation Characteristics of Lean NO$_x$ Trap Catalysts

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Background: Ceria in LNT catalysis

• Role of ceria:
  - OSC for stoichiometric operation in lean-burn gasoline engines
  - Water-gas shift activity for \( \textit{in situ} \) \( \text{H}_2 \) generation:
    » facilitates LNT regeneration at low temperatures
    » facilitates LNT desulfation at moderate temperatures
  - \( \text{NOx} \) storage at low temperatures (<350 °C)

• Use of ceria may prove critical for low temperature applications, e.g., LD diesel (typical FTP temperatures of ~150-340 °C)

• Role of ceria largely ignored in literature LNT studies

Objectives

• Understand role of ceria in mitigating sulfur deactivation of LNT catalysts
• Quantify effect of ceria in fresh and aged catalysts
  - This talk will focus on fresh/degreened catalysts
• Study divided into two parts:
  - Powder model catalysts: Pt/Ba/Al₂O₃ with and without added Pt/CeO₂
    - DRIFTS and microreactor
  - Monolithic model catalysts
DRIFTS STUDY
Part I: Powder model catalysts

- DRIFTS studies performed in an environmental cell:
  - *in situ* observations during LNT sulfation and desulfation

- Experiments also performed in a microreactor equipped with mass spectrometer:
  - measurement of NOx storage capacity after sulfation and desulfation
  - temperature-programmed desulfation

- Two catalysts were prepared:
  (1) 1 wt% Pt / 20 wt% BaO / Al₂O₃ (“PBA”)
  (2) 1 wt% Pt / 20 wt% BaO / Al₂O₃ (74 wt%) + 1 wt% Pt / CeO₂ (26 wt%), physical mixture (“PBAC”)
Sulfation of PBA without added H₂O

1418, 1323 cm⁻¹: mono-/bidentate Ba nitrate
1130 cm⁻¹: surface/bulk Ba sulfate
1560 cm⁻¹: Al-based nitrate

- 300°C, 27 ppm SO₂
- Strong nitrate bands
- Slow formation of surface Ba sulfate


1168 cm⁻¹ = bulk Ba sulfate
1107 cm⁻¹ = surface Ba sulfate
Sulfation of PBA with added H$_2$O

1420/1320 cm$^{-1}$: mono-/bidentate Ba nitrate

1122 cm$^{-1}$: surface/bulk Ba sulfate

- 300°C, 27ppm SO$_2$
- Strong sulfate bands $\Rightarrow$ H$_2$O facilitates sulfate formation
- Reduction in intensity of nitrate bands towards end of experiment $\Rightarrow$ displacement of nitrate by sulfate
Sulfation of PBAC without added H$_2$O

- 1542, 1516 cm$^{-1}$: Ce monodentate nitrate
- 1414, 1323 cm$^{-1}$: Ba mono-/bidentate nitrate
- 1140 cm$^{-1}$: surface/bulk BaSO$_4$

- 300°C, 27ppm SO$_2$
- Strong nitrate bands
- Slow formation of surface Ba sulfate
- Shift in location of sulfates from 1130 to 1140 cm$^{-1}$...ceria impact
Sulfation of PBAC with added H₂O

- 1538, 1508 cm⁻¹: Ce monodentate nitrate
- 1413, 1325 cm⁻¹: mono-/bidentate Ba nitrate
- 1114 cm⁻¹: surface/bulk BaSO₄

- 300°C, 27ppm SO₂
- Spectra similar to those of PBA sulfated in absence of water...but with much greater nitrate/sulfate ratio
- sulfate location shifts from 1122 to 1114
Sulfation of Pt/CeO$_2$ with added H$_2$O

- 1540 and 1516 cm$^{-1}$: Ce monodentate nitrate;
- Other bands due to Ce sulfate and sulfite species

- 300°C, 27 ppm SO$_2$
- Strong sulfate bands
- Reduction in intensity of nitrate bands towards end of experiment ⇒ displacement of nitrate by sulfate
Comparison of sulfation behavior

Sulfate/Nitrate ratio
- PBA (w/o H₂O): 0.38
- PBAC (w/o H₂O): 0.40
- PBA (w/ H₂O): 2.43
- PBAC (w/ H₂O): 0.51

- Addition of H₂O significantly increased the formation of sulfate relative to nitrate for PBA

  → H₂O improved the Ba dispersion, resulting in greater SOₓ uptake by Ba phase?

  → Formation of surface HSO₃⁻ facilitates sulfate storage on Ba phase?
DRIFT spectra after desulfation at 450 °C

Desulfation conditions: 1% H₂, 5% H₂O, balance Ar, 450 °C, 5 min

- Sulfur can be fully removed from Pt/CeO₂ upon heating to 450 °C
- Residual sulfur on both PBA and PBAC is associated with the Ba phase
DRIFT spectra after desulfation at 550 °C

Desulfation conditions:
1% H₂, 5% H₂O, balance Ar, 550 °C, 30 min

- Residual sulfur associated with the Ba phase not removed at 550 °C
- 550°C limitation of the reactor
MICROREACTOR STUDY
Procedure for sulfation-desulfation experiments

- Powder reactor
- Testing procedure:
  - Pre-treat catalyst at 750 °C under 1% H₂/Ar for 1 h
  - Measure NOx storage capacity (NSC) at 300 °C under continuous lean conditions, 60 min
    (300 ppm NO, 10% O₂, 5% CO₂, 5% H₂O, GHSV = 30,000 h⁻¹)
  - Sulfate catalyst at 300 °C, 120 min
    (27 ppm SO₂)…~1 g S/L monolith equivalent…4 mg S/g_cat
  - Measure NSC as above
  - Desulfate catalyst at 700 °C, 60 min
    (1% H₂, 5% CO₂, 5% H₂O, balance Ar)
  - Measure NSC as above
PBA: Effect of sulfation on NSC

- Loss of NSC after sulfation (32% after 60 min)
- Desulfation improves NSC at short times, no effect at longer storage times
  ⇒ bulk storage sites not fully desulfated?
PBAC: Effect of sulfation on NSC

- Small loss of NSC after sulfation (8% after 60 min)
- Desulfation improves NSC at short times, no effect at longer storage times
  ⇒ bulk storage sites not fully desulfated?
## Comparison of NSC between ceria-free and ceria-containing catalysts

<table>
<thead>
<tr>
<th></th>
<th>Before sulfation</th>
<th>After sulfation</th>
<th>After desulfation</th>
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<tbody>
<tr>
<td><strong>PBA</strong></td>
<td></td>
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<tr>
<td>NOx stored (μmol/g)</td>
<td>400</td>
<td>271</td>
<td>322</td>
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<tr>
<td>Efficiency (%)</td>
<td>64</td>
<td>44</td>
<td>52</td>
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<tr>
<td><strong>PBAC</strong></td>
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<tr>
<td>NOx stored (μmol/g)</td>
<td>373</td>
<td>343</td>
<td>339</td>
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<tr>
<td>Efficiency (%)</td>
<td>60</td>
<td>56</td>
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</table>

Figures based on 60 min NOx storage time
LNT desulfation studies by TPR

Procedure:

- Pre-treat catalyst 450 °C (O₂, 15 min; then H₂, 15 min)

- Sulfate at 350 °C, lean conditions (100 ppm SO₂, 8% O₂, 5% H₂O, 5% CO₂, balance N₂)

- Desulfation by means of TPR: ramp to 800 °C (5 °C/min), continuous rich conditions (2% H₂, 5% H₂O, 5% CO₂, balance N₂)

- H₂S, SO₂ and COS monitored by CI-MS
TPR of 1 wt% Pt/Al₂O₃ sulfated to 1 g/L and 3 g/L monolith equivalent

- 1 g S/L: H₂S release peaks at 370 °C
- 3 g S/L: SO₂ release peaks at 360 °C, H₂S release at 380 °C
TPR of PBA sulfated to 1 g/L and 3 g/L monolith equivalent

- 1 g S/L: H$_2$S release peaks at 695 °C
- 3 g S/L: H$_2$S release at 380 °C, 682 °C and 772 °C

- 380 °C = Al$_2$O$_3$ desulfation
- 682 °C = surface BaSO$_4$
- 772 °C = bulk BaSO$_4$
TPR of PBAC sulfated to 1 g/L and 3 g/L monolith equivalent

- 463 °C = CeO₂ desulfation
- 684 °C = surface BaSO₄
- 775 °C = bulk BaSO₄

- Ba loading in PBAC = 74% of that in PBA
- But, for PBAC at 1g S/L, sulfur release from Ba phase = ca. 50% of that from PBA
TPR of 1 wt% Pt/CeO₂ sulfated to 3 g/L monolith equivalent

- CeO₂ desulfation occurs at 451 °C
MONOLITH STUDY
Monolithic catalyst compositions prepared:

### Part II: Monolithic catalysts

<table>
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<tr>
<th>Component</th>
<th>Catalyst code / Loading</th>
<th>30-0</th>
<th>30-50</th>
<th>30-100</th>
<th>Pt-100</th>
<th>Pt-50</th>
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<tbody>
<tr>
<td>Pt, g/cuft</td>
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<td>BaO, g/L</td>
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<td>CeO$_2$, g/L</td>
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<td>Al$_2$O$_3$, g/L</td>
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</tr>
</tbody>
</table>

Total washcoat loading = 260 g/L
Ford Protocol for sulfation/desulfation

- **Sample sulfation:**
  1/1 L/R cycles, 350 °C, 9 ppm SO₂, 500 pm NO, 5% O₂ (L), 10% CO₂, 10% H₂O, 15 h; equivalent to 6.2 g S/L cat.

- **Desulfation #1:**
  Rich conditions: 1.2% CO, 0.4% H₂, 10% CO₂, 10% H₂O, 5 min.; T = 675-750 °C

- **Measurement of lean NOx storage efficiency (#1):**
  5/3 minute L/R cycles, 350 °C

- **Desulfation #2**
  Measurement of lean NOx storage efficiency (#2)

- **Desulfation #3**
  Measurement of lean NOx storage efficiency (#3)

- **Sulfur “burnout”**
  Rich conditions, 10 min, 750 °C

- **Measurement of lean NOx storage efficiency (#4)**
Effect of catalyst composition on required desulfation temperature: catalyst 30-0 (no ceria)

- Required desulfation temperature for optimal NSC $\geq 750 \, ^\circ\text{C}$
Effect of catalyst composition on required desulfation temperature: catalyst Pt-100 (30 g/L ceria)

- Required desulfation temperature for optimal NSC ≈ 725 °C, vs. ~750 °C for catalyst w/o ceria (30-0)

5 min lean storage data at 350 °C
Effect of catalyst composition on efficiency of sulfur removal

Sulfation at 350 °C, continuous lean phase (1 h), sulfation to 6 g S/L

Desulfation by ramping to temp. indicated under 2% H₂, 5% CO₂, 5% H₂O (10 min hold)

- Beneficial effect of ceria confirmed
- Reduction of precious metal content has adverse effect
Conclusions (1)

- DRIFTS studies indicate that H₂O exerts a promoting effect on Ba sulfation.
- BaSO₄ formation is partially suppressed in the presence of CeO₂.
- Consequently, CeO₂-containing catalysts are better able to store NOx during/after sulfation than Ba-only formulations.
- Pt/CeO₂ can be completely desulfated at 450 °C in H₂/Ar.
- For catalyst PBA, BaSO₄ shows two decomposition maxima in H₂: ~685 °C (surface BaSO₄) and ~775 °C (bulk BaSO₄).
Desulfation of surface BaSO$_4$ occurs at a higher temperature for a physical mixture of Pt/Al$_2$O$_3$ + BaO/Al$_2$O$_3$ than for Pt/BaO/Al$_2$O$_3$ (PBA) ⇒ spillover of H$_{ads}$ facilitates decomposition of surface sulfate (as for nitrate*)

The beneficial effect of ceria with respect to LNT desulfation has been demonstrated for fully formulated monolithic catalysts

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Shazam Williams

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