Studies of LNT Sulfation and Desulfation at PNNL

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Fundamental LNT sulfation/desulfation studies at PNNL

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)

XPS, H\textsubscript{2} TPRX, TEM/EDX, NO\textsubscript{2} TPD..

Simple catalytic system: Pt-BaO/Al\textsubscript{2}O\textsubscript{3} prepared at PNNL
Ba loading, sulfur loading, H\textsubscript{2}O/CO\textsubscript{2} effects on sulfation/desulfation mechanism
Overview of CRADA project

CRADA between PNNL and Cummins Inc., which involves a significant collaboration with catalyst supplier, Johnson Matthey Environmental Catalyst Technology Division.

Project first initiated in February 2003 (for 5 years); Second phase CRADA agreement signed through 2011.

Goals

1st phase: Develop an understanding of the mechanisms of Lean-NOx Trap (LNT) deactivation due to high temperatures and the presence of sulfur species in the exhaust.

2nd phase: Investigate the performance and degradation mechanisms of next-generation LNT catalysts that maintain performance at higher temperatures.
Key Questions (HOW rather than WHY)

- How to find the optimum condition for regeneration, in other words, how to decouple the desulfation and thermal aging?
- How does sulfation/desulfation affect the catalytic activity of LNTs?
- How can sulfation/desulfation be usefully studied for practical monolith LNT catalysts?

Approach

1. Three samples (from JM): sulfated
   - Simple model “Pt-BaO/Al_{2}O_{3}” catalyst
   - Enhanced model “Pt-BaO/CeO_{2}-Al_{2}O_{3}” catalyst
   - Commercial LNT samples (monolith type)
2. Designed reaction protocol for activity measurements
3. Characterization of Catalysts: XRD, TEM, H_{2} TPRX
Sulfur poisoning and the subsequent effects

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\begin{align*}
\text{Pt} \\
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 \\
\text{SO}_2 + \text{O}_2 & \rightarrow \text{SO}_3 \rightarrow \text{BaSO}_4
\end{align*}
\]

Low levels of SO\(_2\) in the exhaust cumulatively deposit onto the barium sites, gradually converting these sites into BaSO\(_4\) rather than Ba(NO\(_3\))\(_2\).

→ De-sulfation with reductants at high temperature required.
→ Higher temperature, more desulfation.
→ Thermal aging effects (Pt sintering and BaAl\(_2\)O\(_4\) formation)
Tradeoff Between deSOx Efficiency and Thermal Deactivation

From XRD: Pt crystalline size

- Pt sintering is directly related to the decrease in NOx uptake.
- Therefore, we need to find the optimum regeneration condition for preventing the permanent deactivation!

Decoupling of de-sulfation and thermal aging

The presence or absence of SO$_2$ in the reactants made it possible to decouple the de-sulfation and thermal aging processes.
It appears that the conversions after de-sulfation follow those of thermally aged samples above 700 °C, where the de-sulfation is almost complete. ‘Enhanced Model’ LNT shows more complete recovery of performance at 600 °C than the ‘Simple Model’ one.

Kim, Chin, Muntean, Yezerets, Epling, Currier, Chen, Hess, Peden, I&EC, 46 (2007) 2735
1. Finding the optimum condition for regeneration

2. Sulfur effects: How does sulfation/desulfation affect the $\text{NO}_x$ uptake of the two model LNT samples?
   - High sulfur loading
   - Low sulfur loading

3. Analysis of sulfur on the monolith LNT samples
Sulfation followed by *in situ* H₂ TPRX

**Simple model** “Pt-BaO/Al₂O₃” catalyst

**Enhanced model** “Pt-BaO/CeO₂-Al₂O₃” material

10% CO₂
10% H₂O
50 ppm SO₂
10% O₂ in He
100 cm³/min

0.2 g samples
At 300 °C

900 °C
8 °C/min

H₂S, SO₂ measurement by Mass Spec.

20 cm³/min
20% H₂/He

H₂ TPRX
(Desulfation behavior)
SO$_2$ uptake during the sulfation: Simple vs. Enhanced model

Compared with the “simple” model catalyst, the “enhanced” one has less uptake of SO$_2$ during the sulfation.
For both catalysts, the sulfur species deposited during the early stage of sulfation are stable against hydrogen even up to 900 °C\textsuperscript{1}.

\textsuperscript{1}Kim, Szanyi, Kwak, Wang, Hanson, Engelhard, Peden, JPC C 113 (2009) 7336.
Questions: Activity changes after sulfation/desulfation

**Model vs. Enhanced samples**

- How does the catalytic activity of the two samples compare as a function of the degree of sulfation (up to 10g/L)?

- Are there any differences in the regenerated activity after de-sulfation (rich phase at 600 °C) on the heavily (10g/L) sulfated samples? Will the activity keep increasing with additional de-sulfation at 600 °C?

- How do catalysts perform for repeated desulfations after relatively low sulfur exposure?
**Reaction protocol**

**Sulfur exposure**

Lean gases (including 8 ppm SO₂) for 30 min

350 °C

5 °C/min

Lean/rich cycles for 1 hr (12 cycles)

1g/L, 2, 3, 4, ... 9 g/L

Performance measurement every 3 hrs (i.e. every 1 g/L)

**Sulfur removal**

Without SO₂

350 °C

1 Rich period for 10 min

600 °C

Lean/rich cycles for 1 hr (12 cycles)

40 min

Repeated 2 times

Total reaction time: 30 hr
Effect of sulfur exposure on the NO$_x$ uptake

- Both samples deactivate upon the exposure of SO$_2$.
- Enhanced model LNT maintains slightly better performance at high sulfur coverages.
Enhanced model catalyst has the larger amount of sulfur containing gases (H$_2$S/SO$_2$) than model one.
Most of the desorption occurred within **less than 1 min**.
2$^{\text{nd}}$ desulfation does not promote the additional removal of sulfur containing gases.
XPS confirms less amount of sulfur on the surface for the enhanced one.
Effect of de-sulfation on NO$_x$ uptake

- In spite of the similar NO$_x$ uptake after sulfation, the CeO$_2$-containing LNT sample shows superior regeneration ability.
- Multiple regenerations produce minimal improvement.
For comparison, a similar procedure without SO$_2$ was performed to see the effects of the successive thermal treatments at 600 °C.
Successive de-sulfation at 600 °C after reaction with SO₂ appears not to remove all deposited sulfur species, resulting in a gradual deactivation. Most of the deactivation is arising from SO₂, not from thermal aging.
The “enhanced” model sample is superior to the “simple” one for the removal of small amounts of $\text{SO}_2$. 
1. How does the catalytic activity of the two samples compare as a function of the degree of sulfation (up to 10g/L)?
   → Not much different; Both decrease gradually after 2 g/L sulfation. “Enhanced” model shows slightly better resistance to sulfur.

2. Are there any differences in the regenerated activity after de-sulfation (rich phase at 600 °C) on the heavily (10g/L) sulfated samples? Will the activity keep increasing with additional de-sulfation at 600 °C?
   → Definitely; “enhanced” model sample with CeO$_2$ is superior to “simple” one in this respect. Not much improvement after 1$^{st}$ pulse.

3. How do catalysts perform for repeated desulfations after relatively low sulfur exposure?
   → The “enhanced” model sample has an improved ability to remove low levels of sulfur than the “simple” one, thus maintaining higher activities.
Talk Outline

1. Finding the optimum regeneration condition

2. Sulfur effects

3. Analysis of sulfur on the monolith LNT samples
   - After sulfation/desulfation
S distribution for monolith samples

Spatial analysis of species distributions during sulfation/desulfation along the z-axis of the real monolith samples: XPS study

Cross-sectional analysis of sulfur species during sulfation along the x-y axis of the real monolith samples: SEM/EDS study
XPS analysis: sulfur distribution on monolith samples

Fresh sample
0.8021 g

Sulfation
For 8 hrs

Cut in half

1st XPS analysis

2nd XPS analysis

Desulfation

Area9
Area8
Area7
Area6
Area5
Area4
Area3
Area2
Area1

15 mm

Sulfur atomic conc. (%) vs. Length (mm) from the inlet:

- Sulfation
- After desulfation
1. Suggested reaction protocol allows us to decouple the thermal aging and sulfur effects, leading to find the optimum condition and catalyst with minimizing the thermal aging and maximizing the de-sulfation.

2. An “enhanced” model LNT that includes the promoter CeO$_2$ component has a better ability to de-sulfate than the “simple” one. Desulfation occurs at lower temperature as well, leading more readily to recovery of activity.

3. Spatial XPS analysis with monolith samples allows us to investigate sulfur distributions along the monolith length. The results demonstrate that sulfur is deposited on the inlet part of the sample and becomes more uniformly distributed after regeneration processes.
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