Oxidation State Optimization for Maximum Efficiency of NOx Adsorber Catalysts

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Haiying Chen, Howard Hess, Shadab Mulla Johnson Matthey
LEV II-ULEV Certified System with Cummins 6.7L Engine and A/T System

<table>
<thead>
<tr>
<th>System Function</th>
<th>Close-Coupled Oxidation Catalyst (CCC)</th>
<th>Lean NOx Trap Catalyst (LNT)</th>
<th>Diesel Particulate Filter (DPF)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lean</strong></td>
<td>HC, CO, NO Oxidation</td>
<td>NOx trapping</td>
<td>Soot trapping</td>
</tr>
<tr>
<td><strong>De-NOx</strong></td>
<td>Residual $O_2$ removal</td>
<td>NOx release</td>
<td>Regeneration slip species removal</td>
</tr>
<tr>
<td></td>
<td>In situ POX, WGS</td>
<td>NOx &gt; $N_2$ reduction</td>
<td></td>
</tr>
<tr>
<td><strong>De-SOx</strong></td>
<td>Lean/rich cycling</td>
<td>Sulfur release</td>
<td>Regeneration slip species removal</td>
</tr>
<tr>
<td></td>
<td>HC oxidation - Heat</td>
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<td></td>
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<tr>
<td><strong>De-Soot</strong></td>
<td>HC oxidation - Heat</td>
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<td>PM oxidation</td>
</tr>
</tbody>
</table>

- Complex multi-component, multi-functional catalyst
- Major advances in the fundamental understanding and application of the technology
**Fundamental challenges**:[1]

- Multi-component, multi-functional catalyst:
  - At least 3 components, with different functions
  - Both red-ox and acid-base catalyst chemistry
- 5 sequentially-coupled process
- Memory effects

**Short-term memory**

- Amount of NOx on the catalyst
- Spatial profile of reactions

**Mid-term memory**

- Amount and form of sulfur
- Slow, reversible morphological changes
  - Ba redistribution
  - Ba aluminate formation and break-up
  - **Oxidation state of Rh**

**Long-term memory**

- Thermal deactivation (Pt sintering, loss of Pt/Ba interface)

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**NOx Adsorber Technology**

- **Lean (Rh oxidation):**
  \[ 4Rh + 3O_2 \rightarrow 2Rh_2O_3 \]

- **Rich (Rh reduction):**
  \[ Rh_2O_3 + 3H_2 \rightarrow 2Rh + 3H_2O \]
  \[ Rh_2O_3 + 3CO \rightarrow 2Rh + 3CO_2 \]
  \[ 3Rh_2O_3 + C_3H_6 \rightarrow 6Rh + 3H_2O + 3CO_2 \]

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Outline

- What is the function of Rh in the catalyst (why Rh is important)
- How important is Rh oxidation state
- Rh oxidation
  - temperature and duration
- Rh reduction
  - Role of reductant speciation, temp, richness
Why Rh is Important?

- Reduced metal has better reactivity than oxidized metal.
- Rh is more active than Pt for NO reduction by CO.
- The reactivity of Rh is much more sensitive to its oxidation state than Pt.

Rh is the key component for NO reduction in the presence of CO.
How Important of Rh Oxidation States

- Rh is the key component for NO reduction in LNT catalysts.
- NO dissociation is the rate-limiting step of NO reduction.

- Oxidized Rh has substantially fewer sites for NO adsorption.
- The adsorbed NO is more difficult to dissociate on the oxidized Rh.
  - Fewer adjacent sites for NO dissociation
  - Thermodynamically less favorable

Effect of Temperature on “Memory” of Rh Function

- The reduced Rh is more active for NO reduction than oxidized Rh.
- The memory effect is highly dependent on temperature.

### Graphs

1. Rich, 280°C, NOx conv. 75.1%
   Lean, 280°C, NOx conv. 62.8%

2. Rich, 350°C, NOx conv. 89.3%
   Lean, 350°C, NOx conv. 90.0%
Effect of Reductant Type on “Memory” of Rh Function

- H₂ is very effective for both NOx release and NOx conversion to N₂.
- CO is effective for NOx release but not as effective for NOx conversion to N₂, compared with H₂.
- C₃H₆ is not effective for either NOx release or NOx conversion.
Experimental Procedure

- **Lean**
- **Rich**
- **50s Lean/ 10s Rich**
- **He**

### Gas species

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Rich</th>
<th>Lean</th>
</tr>
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<tbody>
<tr>
<td>NOx</td>
<td>200 ppm</td>
<td>200 ppm</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>2000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>1.25%</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>4.00%</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>0.00%</td>
<td>5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5 %</td>
<td>5 %</td>
</tr>
<tr>
<td>CO₂</td>
<td>5 %</td>
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**Effect of Temperature on Rh Oxidation**

- $T_{50} = 184^\circ C$ for reduced Rh vs. $T_{50} = 223^\circ C$ for oxidized Rh
- One-minute lean exposure at high temperature can cause Rh oxidation

- **Reduced Rh**: pretreat sample at 400°C, 20 L/R cycles with NO and cool down in rich condition to 140°C w/o NO
Effect of Temp on Rh Oxidation

- $T_{50} = 184°C$ for reduced Rh vs. $T_{50} = 230°C$ for oxidized Rh
- One-minute lean exposure at high temperature can cause Rh oxidation
Experimental Procedure

**Gas species**

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<tr>
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<td>0.00 %</td>
<td>5%</td>
</tr>
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- The Rh reach its most reduced state at 300ºC.
- The exposure to temperature higher than 300ºC will partially oxidize the reduced Rh.

Note: NO present during the lean oxidation at 650C, cool down to target temp and 5 L/R cycles at the target temperature.
Effect of Rh Redox States on \( \text{C}_3\text{H}_6 \) Oxidation

- Rh oxidation state affects both NO reduction and HC oxidation on NOx adsorber catalyst.
Continued improvements in the understanding of the underlying chemistry of LNT operation and lifecycle offer opportunities for further system efficiency improvements

- Operation
- Catalyst design
Catalyst Technology Team

- **Cummins**
  - Neal Currier
  - Aleksey Yezerets

- **Johnson Matthey**
  - Haiying Chen
  - Howard Hess
  - Shadab Mulla

*Many other colleagues at Cummins and JM*