Development of a Durable Low-Temperature Urea-SCR Catalyst for CIDI Engines

by

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.
Diesel Emissions Control

Potential light duty configuration to meet Bin 5 emissions standards

Oxidation Catalyst
NO and HC

SCR Catalyst

Particulate filter

NH₃ Slip Catalyst

Urea

H₂NCONH₂

4 NH₃ + 4 NO + O₂ → 4 N₂ + 6 H₂O (medium)

4 NH₃ + 2 NO + 2 NO₂ → 4 N₂ + 6 H₂O (fast)

Take advantage of faster kinetics to increase conversion and expand temperature window
Catalyst Development Issues

- **High Selectivity**
  - $\text{NH}_3 + \text{NO}_x + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$
  - $\text{N}_2\text{O} + \text{H}_2\text{O}$

- **Urea Decomposition to NH$_3$**
  - $\text{NH}_2\text{-CO-NH}_2(\text{l}) \rightarrow \text{NH}_3 + \text{HNCO}$
  - $\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3(g) + \text{CO}_2$

- **Minimize Competing Reactions**
  - *Low T:* $2\text{NH}_3 + 2\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 + \text{N}_2 + \text{H}_2\text{O}$
  - *High T:* $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$
  - $4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O}$
Typical Experimental Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>450-125</td>
</tr>
<tr>
<td>NO (ppm)</td>
<td>280-175</td>
</tr>
<tr>
<td>NO₂ (ppm)</td>
<td>70-175</td>
</tr>
<tr>
<td>NH₃ (ppm)</td>
<td>350</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>14</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>5</td>
</tr>
<tr>
<td>H₂O (%)</td>
<td>4.6</td>
</tr>
<tr>
<td>GHSV (h⁻¹)</td>
<td>30,000-140,000</td>
</tr>
</tbody>
</table>

- NH₃:NOₓ in the feed is 1:1
- Powder catalysts diluted 1:1 with cordierite
- 450 – 125 °C decreasing, 30 minute isothermal holds
- NOₓ conversion (%) defined as:
  \[ 100 \times \left(1 - \frac{NO_{(out)} + NO₂_{(out)}}{NO_{(in)} + NO₂_{(in)}}\right) \]
- N₂O selectivity (%) defined as: \[ \frac{N₂O}{(N₂O + N₂)} \]

20% NO₂ simulates cold-start conditions
LEP Staged Testing Protocol

Catalyst performance evaluated:
1. Fresh, using stated typical experimental conditions
2. Fresh, as a function of NO:NO\textsubscript{2} ratio
   • 100% NO to 100% NO\textsubscript{2}
3. After hydrothermal aging
   • 16 hours at typical experimental conditions at 600°C*, 700°C, and 800°C
4. After sulfur aging
   • 20 ppm SO\textsubscript{2} at 350°C* or 670°C at typical experimental conditions (minus NH\textsubscript{3}) for 24* and 48 hours

* Items in bold represent minimum performance requirement
Experimental Apparatus

MFCs

NH₃/N₂
NO₂/N₂
NO/N₂
HC
CO₂
N₂
Air
H₂O

Thermocouples

Powder
GHSV = 30,000-140,000 h⁻¹

Monolith
GHSV = 30,000 h⁻¹

Heating Tape

FTIR

GC
Hydrous Metal Oxide Synthesis

- **Hydroxide Addition**
  \[ \text{Ti-alkoxide} + \text{Si-alkoxide} + \text{NaOH} \rightarrow \text{Methanol} \rightarrow \text{soluble intermediate} \]

- **Hydrolysis**
  \[ \text{soluble intermediate} \rightarrow \text{Acetone} \rightarrow \text{Water} \rightarrow \text{NaTi}_2\text{O}_5\text{H} \downarrow \]

- **Acidification and Ion Exchange**
  \[ \text{M}^{n+} + n \text{NaTi}_2\text{O}_5\text{H} \rightarrow \text{M(Ti}_2\text{O}_5\text{H)}_n + n \text{Na}^+ \]

- **Impregnation**
  \[ \text{incipient wetness (powder)} \]

- **Activation/Pretreatment** (600°C in air for 4 h)

- **Monolith**
  \[ \text{Catalyst} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} + \text{grinding} \rightarrow \text{slurry} \]
  \[ \text{slurry} + \text{monolith} \rightarrow \text{final monolith} \]
  \[ 425^\circ\text{C in air for 4 h} \]
Effect of Synthesis Conditions on S.S.A.

- Less concentrated hydrolysis solution increases resulting surface area by 30%
- May be attributed to slower rate of hydrolysis from decreased metal concentration
- Similar results seen with supports only
- No linear relationship between catalytic activity and surface area
- All samples were calcined at 600°C in air and degassed at 400°C for 14 h
Comparison of Monolith and Powder Data

- Powders tested at high SV to simulate the contact time of 25 wt.-% catalyst on monolith.
- High-loaded monoliths (>16 wt.-%) approach powder performance.

Graph showing NOx Conversion vs. Temperature (°C) with data points for powder and monoliths at different loadings:
- Powder 1:1, 50% NO₂, 140,000 h⁻¹
- Monoliths, 50% NO₂, 30,000 h⁻¹
Optimization of Catalyst Composition

- Change concentration of same two components
- Have the ability to tune catalytic performance
  - tradeoffs in low and high temperature activity

<table>
<thead>
<tr>
<th>Powder</th>
<th>NOx Conversion</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1165 / 1139/1-54C 2%CuO, 1%MnO</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1168 / 1139/3-13B 2%CuO, 2%MnO</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>1169 / 1139/3-13C 2%CuO, 4%MnO</td>
<td>200</td>
</tr>
<tr>
<td>20% NO2</td>
<td>140,000 h⁻¹</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
</tr>
</tbody>
</table>
Hydrothermal Treatment

**V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> Monolith Sample**

- SV 30,000h<sup>-1</sup>
- 50% NO<sub>2</sub>

- Minor loss in activity after short term hydrothermal treatment
- More relative activity retained with D2
- Hydrothermal treatment at feed concentration (4.6% H<sub>2</sub>O)

**Catalyst D2 Powder Sample**

- SV 30,000h<sup>-1</sup>
- 50% NO<sub>2</sub>
SO2 Tolerance

V$_2$O$_5$-WO$_3$ Monolith Sample

- SV 30,000h$^{-1}$
- 50% NO$_2$

Catalyst D2 Powder Sample

- SV 30,000h$^{-1}$
- 50% NO$_2$

- Fresh
- After 65 hrs. w/ 20 ppm SO$_2$

- Fresh
- Aged 24h, 20 ppm SO$_2$

• SO$_2$ Aging At 350 °C without NH$_3$

• Some loss in low temperature activity
Hydrocarbon Testing

- C₃ & n-C₈ suppress conversion ca. 10% above 300°C, (HC oxidation)
- No change on addition of 60 ppm toluene (>12 h TOS)
- Activity recovered when HCs removed

Graphs showing:
- V₂O₅-WO₃ Monolith Sample
  - SV 30,000 h⁻¹
  - 0% NO₂
  - NOₓ Conversion

- Catalyst D2 Monolith Sample
  - SV 30,000 h⁻¹
  - 20% NO₂
  - NOₓ Conversion

- Trends are important
- Not a direct comparison

- 117 ppm propylene
- 130 ppm n-octane
- 34 ppm propylene
- 38 ppm n-octane
Summary

• Optimizing synthesis parameters leads to enhanced catalyst surface areas
  – Nonlinear relationship between activity and surface area
• Catalyst development performed under a staged protocol
• Catalytic materials with desired properties have been identified
  – Meet stage requirements
  – Performance can be tuned by altering component concentrations
  – Optimization still necessary at low temperatures
    • Better activity and tolerance to SO2
    – V2O5-based materials ruled out because of durability issues
• Future work will focus on improving overall low temperature activity
Acknowledgments

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