Performance Characterization of Cu/Zeolite and Fe/Zeolite Catalysts for the SCR of NOx

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Motivation

The durability requirements and diverse operating conditions of light-duty compared to heavy-duty vehicles make it necessary to understand the differences between SCR formulations.

Parameters studied include:

- Durability to active DPF regenerations.
- Robustness to occasional over-temperature.
- Impact of NO₂/NOx, O₂ level, SV, and NH₃ storage.
- Influence due to sulfur and hydrocarbon poisoning.
Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

OUTLINE:
1. SCR Catalyst Description
2. Durability/Robustness
3. Factors Affecting SCR Activity
SCR Catalyst Description

1) **Cu/Zeolite**
   - 400/6.5 CPSI
   - 2006 state of the art supplier formulation
   - Optimized zeolite formulation for stabilizing Cu

2) **Fe/Zeolite**
   - 400/6.5 CPSI
   - 2006 state of the art supplier formulation
   - Optimized zeolite formulation for stabilizing Fe

**NOTE:** Cu and Fe SCR formulated with the same zeolite-type.

3) **Vanadium Based**
   - Commercially available
   - $V_2O_5$-$WO_3$ on corrugated TiO$_2$ carrier
Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

**OUTLINE:**
1. SCR Catalyst Description
2. Durability/Robustness
3. Factors Affecting SCR Activity
Standard Hydrothermal Aging (HTA)

**Purpose:** Develop hydrothermal aging (HTA) representative of time at temperature conditions typical during active DPF regeneration events.

<table>
<thead>
<tr>
<th>Hydrothermal Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>14% $O_2$</td>
</tr>
<tr>
<td>4.5% $H_2O$</td>
</tr>
<tr>
<td>5% $CO_2$</td>
</tr>
<tr>
<td>0 ppm $SO_2$</td>
</tr>
<tr>
<td>balance $N_2$</td>
</tr>
<tr>
<td>Flowrate = 6.44L/min</td>
</tr>
<tr>
<td>Sample Size = 1.0” D x 1.0”L</td>
</tr>
<tr>
<td>Space Velocity = 30,000/hr</td>
</tr>
<tr>
<td><strong>Temperature = 670°C</strong></td>
</tr>
<tr>
<td><strong>Time = 64 hrs</strong></td>
</tr>
<tr>
<td>Standard aging unless otherwise noted</td>
</tr>
</tbody>
</table>
Standard SCR Baseline Evaluation

**Purpose:** Determine activity window for NOx conversion versus temperature for the worst case NO only evaluation (0% NO\textsubscript{2}/NOx ratio).

<table>
<thead>
<tr>
<th>Steady State Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 ppm NO</td>
</tr>
<tr>
<td>350 ppm NH\textsubscript{3}</td>
</tr>
<tr>
<td>14% O\textsubscript{2}</td>
</tr>
<tr>
<td>4.5% H\textsubscript{2}O</td>
</tr>
<tr>
<td>5% CO\textsubscript{2}</td>
</tr>
<tr>
<td>0 ppm SO\textsubscript{2}</td>
</tr>
<tr>
<td>bal N\textsubscript{2}</td>
</tr>
<tr>
<td>S.V. = 30,000 hr\textsuperscript{-1}</td>
</tr>
<tr>
<td>T = 150 - 600°C</td>
</tr>
<tr>
<td>ANR = 1.0 (NH\textsubscript{3}/NOx)</td>
</tr>
</tbody>
</table>

*Standard evaluation unless otherwise noted*
Base metal/zeolite SCR formulations were found to be more thermally stable than a vanadium-based formulation at temperatures typical of diesel applications.
SCR Reaction Activity Profile

NOx and NH₃ Conversion, N₂O Formation, and NH₃ Slip

Cu/zeolite

Fe/zeolite

- Cu/zeolite is more activity below 350°C and generates high levels of N₂O.
- Fe/zeolite is more activity above 350°C and generates very low N₂O.

4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O  "Standard" Reaction

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Thermal Durability as a Function of Mileage

Effect of thermal aging at 670°C

Cu/zeolite

- Cu/zeolite deactivates from 80% to 60% NOx conversion at 175°C.

Fe/zeolite

- Fe/zeolite deactivates from 70% to 50% NOx conversion at 225°C.
Impact of $O_2$ and $H_2O$ Levels During Aging

HTA 64hr/670°C: 2% $O_2$/10% $H_2O$ vs. 14% $O_2$/5% $H_2O$

Cu/zeolite

Fe/zeolite

- Vehicle high load and cDPF events can cause low $O_2$ and high $H_2O$ levels.
- Both Cu and Fe/zeolite show mild deactivation with 2% $O_2$ & 10% $H_2O$. 
HTA with Longer Time & Lower Temp.

64hrs/670°C vs. 2000hrs/550°C

Cu/zeolite

- Cu/zeolite deactivates significantly at low T and improves at high T.

Fe/zeolite

- Fe/zeolite deactivates slightly at low temp. and remains stable at high T.
HTA with Shorter Time & Higher Temp.
(Robustness to Occasional DPF Over-Temperature)

Determination of Never-To-Exceed (NTE) Temperature

Cu/zeolite

Fe/zeolite

- Cu/zeolite deactivates rapidly with increasing temperature, NTE = 775°C.
- Fe/zeolite is much more stable, NTE = 925°C.
Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

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### Standard Aging and Evaluation Conditions

**Purpose:** Determine SCR temperature activity window

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<thead>
<tr>
<th>Hydrothermal Aging</th>
<th>Steady State Evaluation</th>
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</thead>
<tbody>
<tr>
<td>14% O₂</td>
<td>350 ppm NO</td>
</tr>
<tr>
<td>4.5% H₂O</td>
<td>(NO₂/NOₓ = 0%)</td>
</tr>
<tr>
<td>5% CO₂</td>
<td>350 ppm NH₃</td>
</tr>
<tr>
<td>0 ppm SO₂</td>
<td>14% O₂</td>
</tr>
<tr>
<td>bal N₂</td>
<td>4.5% H₂O</td>
</tr>
<tr>
<td>S.V. = 30,000 hr⁻¹</td>
<td>5% CO₂</td>
</tr>
<tr>
<td>T=670°C</td>
<td>0 ppm SO₂</td>
</tr>
<tr>
<td>64 hrs</td>
<td>bal N₂</td>
</tr>
<tr>
<td></td>
<td>S.V. = 30,000 hr⁻¹</td>
</tr>
<tr>
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<td></td>
<td>ANR = 1.0 (NH₃/NOₓ ratio)</td>
</tr>
</tbody>
</table>

*Aging and evaluation conditions unless otherwise noted.*
Effect of NO\textsubscript{2}/NO\textsubscript{x} Ratio on Activity

NO\textsubscript{x} Conversion vs. Temperature

- NO\textsubscript{x} performance is significantly improved for both Cu and Fe SCRs.
- At low T, Fe/zeolite is more sensitive to the NO\textsubscript{2}/NO\textsubscript{x} ratio than Cu.
Effect of O₂ Concentration (2-14% O₂)

NOx Conversion vs. Temperature

Cu/zeolite

Fe/zeolite

● Both Cu and Fe light-off NOx activity NOx drops as the [O₂] decreases.

Recall: 4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O "Standard" Reaction

● High T NOx conversion is not affected in O₂ range tested (2-14%)
**NH₃ Oxidation in the Absence of NOx**

**NH₃ Oxidation and By-product Formation vs. Temperature**

**Cu/zeolite**

- Cu/zeolite is active for NH₃ oxidation above 300°C (95% selectivity to N₂).
- Fe/zeolite demonstrates similar behavior but much less active.

**Fe/zeolite**
Effect of Increasing Space Velocity

NOx Conversion and NH₃ Slip vs. Temperature

Cu/zeolite

Fe/zeolite

- Cu/zeolite NOx activity is reduced at low T but unaffected above 425°C. In addition, no NH₃ slip is observed above 450°C.
- Fe/zeolite NOx activity is reduced for the entire temperature range while NH₃ slip becomes more of an issue.
Base-metal/zeolites store high levels of NH₃ at low T and less as a f (T).

Cu/zeolite stores up 2x more NH₃ than the Fe/zeolite formulation.
Impact of NH₃ Exposure Level

NOx Conversion vs. Temperature

Cu/zeolite

Fe/zeolite

- Exposing SCR catalysts to less than the saturated value of NH₃ results in a loss of NOx performance.
- Cu/zeolite is more sensitive to NH₃ storage than Fe/zeolite.
Sulfur Poisoning and Regeneration

NOx Conversion vs. Temperature

Cu/zeolite  
20% NO\textsubscript{2}/NO\textsubscript{x}  
Fe/zeolite

- 29g S/L exposure (24hrs ~ 120k miles) was more significant on the Cu/zeolite than Fe/zeolite.
- NOx performance recovered after short 650°C lean exposure.
DeSOx was achieved by temperature programmed desorption in the presence of oxygen.

Consistent with active DPF regenerations, Cu/zeolite requires 650°C to remove most of the sulfur.
Hydrocarbon Poisoning at 200°C

NOx Conversion vs. Elapsed Time

Cu/zeolite

- 225ppm Benzene
- 700ppm Propylene
- 50ppm n-Decane

Fe/zeolite

- HC Injection turned on

T = 200°C

- HC exposure significantly impacts NOx conversion for both Cu and Fe.
- n-Decane is most severe for Cu while benzene is most severe for Fe.
Hydrocarbon Poisoning at 300°C

NOx Conversion vs. Elapsed Time

Cu/zeolite

Fe/zeolite

- HC exposure results in an instant inhibition of the NO + NH₃ SCR reaction.
- Propylene is most severe for Cu while benzene is most severe for Fe.
Summary

- Both Cu and Fe formulations are durable under typical DPF generations conditions (<670°C).

- Cu rapidly deactivates above 750°C while Fe rapidly deactivates above 900°C.

- Cu is more active at low temperature whereas Fe is more active at high T.

- Cu is least sensitive to NO₂ to achieve high NOx conversion.

- Both Cu and Fe oxidize NH₃ with high selectivity to N₂.

- At high SV, Fe slips excess NH₃ while Cu does not.

- Cu requires a larger amount of pre-stored NH₃ to achieve high NOx conversion at low temperature.

- Cu and Fe are adversely impacted by sulfur and HC. However, poisoning is reversible with frequent active DPF regenerations.
Thank you for your attention!

QUESTIONS?

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