Effects of hydrothermal aging on the properties and performance of a commercial small pore copper zeolite SCR catalyst

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Motivation

- Emission compliance is a critical barrier to adoption of high efficiency vehicle technologies
  - aftertreatment systems add cost and complexity
  - high efficiency operating regimes create new emissions challenges
    - advanced combustion modes: low exhaust temperatures, high CO and HCs
    - waste heat recovery: low exhaust temperatures
    - high efficiency diesel operating points: high NOx
    - lean gasoline: high NOx, high temperatures
    - electrification: start/stop operation
  - regulated emissions levels continue to decrease
- DOE’s aftertreatment R&D enables high efficiency vehicle architectures that provide a path to reduced petroleum consumption
- High fidelity simulation tools are essential for designing and evaluating high performance multi-component aftertreatment systems and associated operating strategies
  - better models = higher performance, lower cost systems
Approach: Support development of better aftertreatment component models

• ORNL supports model developers by
  – performing specialized experiments to measure critical catalyst parameters
  – developing reaction mechanisms
  – identifying modeling strategies

• We coordinate our efforts with partner institutions
  – for SCR systems: Maruthi Devarakonda and George Muntean at PNNL
  – ORNL provides experimental data and insights
  – PNNL develops global SCR model (see next presentation)

• Current focus:
  – identify how aging impacts critical catalyst properties and model parameters over an SCR catalyst’s useful life
  – develop mechanistic description of SCR reaction pathways and associated active sites
    • what are the key reactions
    • where are they occurring
Experimental investigations of commercially available Cu zeolite SCR catalyst

• PNNL provided Cu exchanged small pore zeolite SCR monolith
• Cut cores (2 cm diameter, 5 cm length)
• Aged in laboratory furnace under flowing 10% H₂O in Air

<table>
<thead>
<tr>
<th>core</th>
<th>T(°C)</th>
<th>time (hr)</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N/A</td>
<td>N/A</td>
<td>fresh</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>4</td>
<td>degreened</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>6</td>
<td>aged 1</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>16</td>
<td>aged 2</td>
</tr>
</tbody>
</table>

*note: aging conditions suggested by PNNL based on work with GM*

800 °C 16 hr ≈ 135000 miles*  

• Conducted CLEERS transient SCR laboratory evaluation protocol on each core in automated flow reactor
  - 550-150°C @ 50°C
  - 60000 hr⁻¹ GHSV
  - 350 ppm NOx
  - MKS Multigas 2030HS FTIR for gas analysis

CLEERS transient SCR laboratory evaluation protocol

- Designed to generate data for model calibration/validation and performance evaluation with minimal operating time

- Revised since last CLEERS workshop
  - create better-defined starting points for transient steps
  - add NO₂ SCR

- Measures:
  - SCR conversion & selectivity:
    - NO₂/NOx = 0.0, 0.5, 1.0
    - NH₃/NOx = 1.0 (others by repeating protocol)
  - NO oxidation and NO₂ decomposition
  - NH₃ oxidation by O₂
  - NH₃ storage
    - saturation capacity (with and without O₂)
    - SCR inventories
  - NH₃ stability: adsorption/desorption/TPD

note: all steps include 5% H₂O, 5% CO₂
General insights into catalyst function from experiments on degreened core sample
**NO₂/NOx controls kinetics and performance by changing reaction pathways**

- Three global pathways to N₂:
  1. **NO SCR:**
     \[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]
  2. **NO+NO₂ SCR:**
     \[ 4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]
  3. **NO₂ SCR:**
     \[ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow \frac{7}{2}\text{N}_2 + 6\text{H}_2\text{O} \]

- Assumption: \( \text{NO+NO}_2 > \text{NO} > \text{NO}_2 \)
  - holds at low T
  - not necessarily true at high T

- May need to consider contribution of NO₂ SCR even when NO₂/NOx \( \leq 0.5 \)

![Graph showing NOx conversion vs temperature with different NO₂/NOx and NH₃/NOx ratios]
NO$_2$ SCR reaction involvement impacts NH$_3$ consumption, N$_2$O selectivity

- 4:3 stoichiometry of NO$_2$ SCR reaction consumes more NH$_3$
  - particularly important under NH$_3$ limited conditions found at high T
  - requires increased dosing to compensate
  - potential explanation for drop in conversion between NO and NO+NO$_2$ SCR at high T

- N$_2$O selectivity significantly higher for NO$_2$ SCR reaction
  - N$_2$O included in proposed greenhouse gas emissions standards
NO$_2$ reactions also play a critical role at low T

- Transient concentration profiles for NO+NO$_2$ SCR reaction: 150 °C
  - 175 ppm NO, 175 ppm NO$_2$
  - start 350 ppm NH$_3$ at time = 0
- Initial consumption of NH$_3$ due to storage, reaction with NO$_2$
  - very little NO consumed
- NH$_3$ + NO$_2$ reaction generates intermediates that build up on catalyst surface (such as NH$_4$NO$_3$)
  - eventually block active sites
  - inhibit further reaction
- Low T performance limitations due to:
  - slow reaction kinetics
  - inhibition by intermediate species
High T NOx conversion limited by NH$_3$ oxidation

**NH$_3$ conversion**

**NOx conversion**

- Increase NH$_3$/NOx
Effects of hydrothermal aging on catalyst properties
Summary of hydrothermal aging impacts on SCR NOx conversion

![Graphs showing NO SCR, NO+NO₂ SCR, and NO₂ SCR conversion vs. temperature](image)

- **NO SCR**
- **NO+NO₂ SCR**
- **NO₂ SCR**

Different symbols and colors represent various conditions such as fresh, 700°C 4h, 800°C 6h, and 800°C 16h.
Aging sensitivity varies with operating temperature and reaction pathway

- Calculated change in NOx conversion relative to fresh catalyst
- Catalyst durable under aging conditions used here: maximum drop in NOx conversion ~15%
- Magnitude of aging impact strongly depends on operating temperature
  - biggest changes at high T and near SCR light-off
  - relevance to models will depend on expected operating regimes
- Aging impact also changes with SCR pathway
  - NO+NO\textsubscript{2} different from others: minimal aging impact at low T
  - implies different active sites involved in reactions
Rates of NO oxidation and NO$_2$ decomposition decrease with aging

- Clear evidence for hydrothermal aging impact on active sites with oxidation/reduction functionality
- Consistent with loss of activity near light-off for NO and NO$_2$ SCR pathways
Outlet NO$_2$/NOx under SCR conditions could provide a sensitive aging diagnostic

- Changes in NO oxidation and NO$_2$ decomposition with aging shift NO$_2$/NOx under SCR operating conditions

- Reliable method for quantifying NO$_2$/NOx would allow measurement of catalyst state
  - enable adaptive control
Aging impacts rate and selectivity of NH$_3$ oxidation

- Further evidence for loss of sites with oxidative function due to aging
  - increased NH$_3$ oxidation not main cause of drop in high T SCR conversion after aging
  - note trend reversal after additional exposure at 800 °C

- Aging increases selectivity of NH$_3$ oxidation to NO formation (double whammy)
  - N$_2$O selectivity also increased at high T

- Could provide another sensitive indicator for catalyst state
  - for example: overdose and monitor NH$_3$ conversion at 450 °C
Aging increases SCR $\text{N}_2\text{O}$ selectivity

- $\text{N}_2\text{O}$ in proposed greenhouse gas emissions standards
  - model predictions important for design of compliant systems
- Increases in $\text{N}_2\text{O}$ at high temperatures
  - partly due to increased $\text{N}_2\text{O}$ selectivity of $\text{NH}_3$ oxidation?
Aging reduces NH₃ storage capacity

- NH₃ storage measured in the absence of O₂ or NOx
  - avoids confounding effects of NH₃ oxidation or SCR reactions
- Storage drops a bit at low temperatures, significantly at high temperatures
- Perhaps the biggest observed impact of hydrothermal aging on a catalyst property with direct model relevance
Loss of high T NH₃ storage due to shift in stability

- Uptake profiles very similar for all four aging states
  - slight loss in capacity results in earlier breakthrough
- Isothermal desorption profiles identical: no aging impact on release of “weakly bound” NH₃
- Two desorption features in TPDs, likely corresponding to two distinct storage sites
  - hydrothermal aging converts higher stability sites into lower stability sites
  - potential mechanism for modeling impact of aging on storage capacity
Small pore copper zeolite SCR catalyst decomposes N$_2$O at high temperatures

- **Experiment conditions:**
  - 30000 hr$^{-1}$: 200 ppm N$_2$O, 5% H$_2$O, 0 or 10% O$_2$
  - reductant: 1000 ppm H$_2$, 1000 ppm CO, 100 ppm C$_3$H$_8$, 667 ppm NH$_3$, or none

- N$_2$O decomposes at T > 450 °C
  - same rate with or without O$_2$
  - could explain drop in SCR N$_2$O selectivity at high T

- No evidence of NH$_3$ + N$_2$O SCR

- Other reductants slightly increase decomposition rate in O$_2$

- N$_2$O decomposition increases significantly under net reducing conditions
  - H$_2$ > CO = C$_3$H$_8$ > NH$_3$ > none
  - Implications for N$_2$O control in LNT/SCR or TWC/SCR systems
Conclusions

• NO₂ SCR may play a more important role than is typically assumed

• Hydrothermal aging impacted several SCR catalyst properties:
  – decreased SCR NOx conversion
    • at high temperatures
    • near light-off for NO and NO₂ SCR (but not NO+NO₂ SCR)
  – degraded oxidation/reduction functionality
    • reduced rates of NO oxidation, NO₂ decomposition, NH₃ oxidation
  – shifted selectivity
    • higher NO yield for NH₃ oxidation
    • higher N₂O formation for NH₃ oxidation, all SCR reactions
  – decreased NH₃ storage capacity
    • converted more stable NH₃ storage sites into less stable sites

• SCR catalyst decomposes N₂O at high T even in presence of O₂
  – net reducing conditions increase rate of decomposition

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