A Comparative Study between Real-world and Accelerated Lab Aging of Cu/SSZ-13 SCR Catalysts

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Introduction

2018 roadmap of the U.S. DRIVE Partnership

Emission control technology research needs for combustion strategies. (✓=need for emission-control technology, ?=further research required to determine applicability)

<table>
<thead>
<tr>
<th>Low Temperature Combustion</th>
<th>Dilute Gasoline Combustion</th>
<th>Clean Diesel Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTC-G (Gasoline Fuel)</td>
<td>S-GDI (Stoichiometric)</td>
<td>L-GDI (Lean)</td>
</tr>
<tr>
<td>Lean NOx Catalysts</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Three-Way Catalyst</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>CO/HC Oxidation Catalysts</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>HC Traps</td>
<td>✓</td>
<td>?</td>
</tr>
<tr>
<td>Passive NOx Adsorbers</td>
<td>✓</td>
<td>?</td>
</tr>
<tr>
<td>Particulate Filters</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Multifunction Devices/Systems</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
Traditionally, hydrothermal and sulfur aging have been identified as two degradation modes of Cu-zeolite SCR catalysts [1-4].

SCR catalysts with history of high mileage show characteristics different from traditional accelerated aging, i.e., hydrothermal aging (HTA).

Future extended aftertreatment system durability and further stringent emissions need accurate predictive aging and performance models, for which deeper understanding of aging mechanisms than our current comprehension are required.


Year one focus: Understand gaps between real-world and laboratory accelerated aging.

The analysis of high mileage Cu-CHA catalyst showed changes in catalyst functions that cannot be explained by HTA alone.

Presence of SOx during HTA further contributes to Cu-CHA aging.

The underlying aging mechanisms in real-world SCR components are not well-understood.

- Additional poisons beyond sulfur;
- Additional pathways for Cu deactivation, beyond HTA;
- Multiple pathways for zeolite support degradation;
- Interaction of deactivation pathways.

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Impact of aging on active copper

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Cu content ICP (wt%)</th>
<th>Cu content XPS (wt%)</th>
<th>S content ICP (wt%)</th>
<th>S content XPS (wt%)</th>
<th>Isolated Cu(II) EPR (wt%)</th>
<th>Reducible Cu NO+NH₃ titration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-greened</td>
<td>2.31</td>
<td>2.62</td>
<td>-</td>
<td>-</td>
<td>1.39</td>
<td>2.27</td>
</tr>
<tr>
<td>HTA</td>
<td>2.42</td>
<td>2.93</td>
<td>-</td>
<td>-</td>
<td>1.41</td>
<td>2.27</td>
</tr>
<tr>
<td>HTA+SOx</td>
<td>2.38</td>
<td>3.89</td>
<td>0.14</td>
<td>0.15</td>
<td>1.10</td>
<td>2.09</td>
</tr>
<tr>
<td>HM1</td>
<td>2.42</td>
<td>3.39</td>
<td>0.22</td>
<td>0.25</td>
<td>0.87</td>
<td>1.48</td>
</tr>
<tr>
<td>HM2</td>
<td>2.50</td>
<td>2.88</td>
<td>0.31</td>
<td>0.40</td>
<td>1.00</td>
<td>1.82</td>
</tr>
<tr>
<td>HM3</td>
<td>2.50</td>
<td>2.77</td>
<td>0.58</td>
<td>0.64</td>
<td>0.99</td>
<td>1.54</td>
</tr>
</tbody>
</table>

- Cu and S quantification via ICP and XPS are consistent.
- However, quantification of SCR active Cu sites via EPR or NO+NH₃ titration results in rather large discrepancy.
- Yet, both methods suggest that S-containing samples have fewer SCR active sites than DG and HTA samples.
Discrepancy between EPR and NO+NH₃ titration

- EPR detects isolated Cu(II) cations in the catalysts; NO+NH₃ titration detects reducible Cu species in the catalysts.
- The discrepancy suggests that all samples contain EPR silent CuₓOᵧ species that are readily reducible during NO+NH₃ titration.
- This is supported by SCR tests, H₂-TPR, and “reverse” ion exchange (exchange catalyst with NH₄NO₃ solution).

Both high-T SCR selectivity drop and H₂-TPR peak area analysis suggest the presence of CuₓOᵧ species. Their precise quantification is not straightforward. CO titration in progress.
H₂-TPR: Nature of reducible species in Cu-CHA with different aging history

- A reduction peak centered at 386 °C only appears in field-aged samples. The HTA+SOx sample shows a similar peak at 464 °C.
- Since these reductions are unique to S-containing catalysts, possible origin for this reduction peak: Cu-sulfates. H₂ consumption quantification suggests Cu reduction and not SOx reduction.
- Field-aged and HTA+SOx samples have a unique reduction that may be described by the reaction: CuSO₄ + H₂ → Cu(0) + H₂SO₄. However, It is not clear what causes the difference in reduction temperatures between field-aged and HTA+SOx samples.
- Nature of sulfur species is likely Cu-sulfate formation.
Strong Cu reduction already at 300 °C; continuous Cu reduction at higher temperatures.

Minor sulfate reduction below 500 °C. SO₂ and H₂S desorption above 600 °C.
Similar reduction behavior to that of HM3, suggesting the same nature of sulfur poisoning in accelerated aged and high mileage samples.

This similarity, however, does not help elucidating $H_2$-TPR difference between HM and HTA+SOx.
Turnover rates (mol NOx/mol Cu/s) calculated using reaction data collected under kinetic control using active site concentrations based on EPR and NO+NH₃ titration, respectively.

Both methods lead to the same conclusion that high mileage catalysts display lower TORs than lab-aged catalysts.

However, more work is needed to further differentiate contributions from isolated Cu and CuₓOᵧ species.
Arrhenius plots of TOR (Cu\textsuperscript{2+}-EPR basis) show decrease of apparent activation energies ($E_a$ \textsubscript{app}) from lab-aged to field-aged samples.

- Activation barriers are more readily overcome with sulfur poisoning? Obviously not.
- With sulfur poisoning, the oxidation half-cycle of standard SCR ($2\text{Cu}^\text{I} + \text{O}_2 + \text{NO} \rightarrow 2\text{Cu}^\text{II}$) gains more control in rate-limiting.
Model catalysts, that simulate the features of high mileage Cu-CHA, are prepared and being evaluated.

- **H$_2$-TPR**
- **XRD**
- **NH$_3$-TPD**
Conclusions

- HTA do not account for the changes in all the underlying functions observed in high mileage Cu-CHA catalysts.
- Sulfur species, likely in the form of Cu-Sulfate, are ubiquitous in high mileage Cu-CHA catalysts. Other possible poisons are absent based on wide scan XPS analysis.
- Laboratory accelerated hydrothermal aging in the presence of SOx introduces the same type of sulfur poison (i.e., Cu-sulfate); therefore, mimics field-aging much better.
- Sulfur poisoned Cu appear to escape both EPR and NO+NH\textsubscript{3} titration, i.e., SCR active site concentration decreases upon sulfur poisoning.
- SCR kinetics studies demonstrate that SCR active site concentration decrease for field-aged catalysts triggers stronger involvement of the Cu\textsuperscript{I} oxidation to Cu\textsuperscript{II} step in rate limiting, thus decreasing low-temperature deNOx efficiency.
- Solid-state NMR and in situ EPR studies will be carried out next to gain additional molecular level understanding of these catalysts. PNNL “model” powder SCR catalysts are also being investigated to assist our better understanding of the commercial catalysts.
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Thanks!