On kinetic modeling of change in active sites upon hydrothermal aging of Cu-SSZ-13

CLEERS 2019 Workshop

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Outline

- Motivation and Background
- Modification of reaction rate forms to account for active site dynamics
- Developing constitutive relations for Hydrothermal Aging of Cu-SSZ-13
- Summary and Future Work
Motivation – Tailpipe NO\textsubscript{x} and Durability Requirements

Future Application Challenges

GHG Reduction
Engine efficiency
Electrification
Fuel type
...

Real World 90%NO\textsubscript{x}
Add heat/CDA/bypass
Sustained LT
Cold start

2024+
Challenge

Emission Warranty Extension

Overall approach to meet these challenges includes
a) Adaptable Controls
b) Improved understanding and modeling of real world aging
c) Improved Component durability (higher resistance to real world aging)

<table>
<thead>
<tr>
<th>Class</th>
<th>2022</th>
<th>2027 (forecast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD</td>
<td>5Y 350K miles</td>
<td>14Y 800K miles</td>
</tr>
<tr>
<td>MD</td>
<td>5Y 150K miles</td>
<td>14Y 400K miles</td>
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</tbody>
</table>
Active Sites in Cu-SSZ-13 and influence of aging

Two chemically distinct monomeric Cu\(^{2+}\) active sites in Cu-SSZ-13; typically solvated and mobile under reaction conditions; undergo redox during SCR (Cu\(^{1+}\) observed during standard SCR)

### Hydrothermal Aging

Mild-hydrothermal aging leads to decrease in number density of ZCuOH sites (\(\Omega_{ZCuOH}\)), and concomitant increase in number density of \(Z_2Cu\) sites (\(\Omega_{Z2Cu}\)) \[1\]. Severe HTA leads to dealumination, increase in CuO\(_x\), and eventually structural collapse

#### ZCuOH

![ZCuOH](image)

#### \(Z_2Cu\)

![\(Z_2Cu\)](image)


#### Sulfur Poisoning

Sulfur selectively poisons Copper sites. ZCuOH stores more sulfur and is harder to regenerate relative to \(Z_2Cu\) \[2\]


Classical Conservation Equations for Monolith Reactors

Monolith reactors can be modeled as plug flow reactors. Equations below are sufficient to describe SCR behavior under realistic operating conditions.

\[
\begin{align*}
\mathbf{u} \frac{\partial y_i}{\partial z} &= -4 \frac{k_{m,i}}{d_{hyd}} (y_i - y_{i,wc}) \\
\frac{v_{j,i} r_j}{C_0} &= -D_{eff} \frac{\partial^2 y_{i,wc}}{\partial x^2} \\
\Omega_m \frac{\partial \theta_k}{\partial t} &= v_{j,i} r_j
\end{align*}
\]

subject to

\[
k_{m,i} (y_i - y_{i,wc}) = -D_{eff} \frac{\partial y_{i,wc}}{\partial x} \text{ at } x = 0
\]

**Nomenclature**

- \(d_{hyd}\): Hydraulic diameter of the channel (m)
- \(C_0\): Total molar concentration (mol/m³)
- \(D_{eff}\): Effective diffusion coefficient in the washcoat (m²/s)
- \(r_j\): Reaction rate for reaction \(j\) (mol/m²s⁻¹)
- \(k_{m,i}\): Mass transfer coefficient of species \(i\) (mol/m²s⁻¹)
- \(u\): Gas velocity (m/s)
- \(y_i\): Mole fraction in the gas bulk of species \(i\)
- \(y_{i,wc}\): Mole fraction on the surface of species \(i\)
- \(\Omega_m\): Surface site density of storage site \(m\) (mol/m²s⁻¹)
- \(\theta_k\): Coverage of surface species \(k\)
- \(v_{j,i}\): Stoichiometric coefficient of species \(j\) in reaction \(i\)

**Figure:**

- **Cumulative NOx:**
  - SCR-In NOx
  - SCR-Out Exp
  - SCR-Out Model

- **NH₃ Slip:**
  - SCR-Out Exp
  - SCR-Out Model

References:
Incorporating Aging in Conservation Equations

- Aging induces changes in catalyst state. These changes can be modeled in a classical framework by deriving:

a) Constitutive relations/rate expressions for quantitative changes of all chemically distinct active sites

b) Intrinsic, site specific turnover rates for conversion of gas species on each active site

\[ \frac{\partial \theta_k}{\partial t} = v_{ji} r_j \]

\[ \Omega_m' (t_{age}, T_{age}, SOx ...) \frac{\partial \theta_k}{\partial t} = v_{ji} r_j'(t_{age}, T_{age}, SOx ...) \]

- In this representation, the state and behavior of each active site is defined completely by a set of variables and constants with respect to aging

<table>
<thead>
<tr>
<th>Z2Cu</th>
<th>ZCuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable : ( \Omega_{Z2Cu} ) (number density)</td>
<td>Variable : ( \Omega_{Z2Cu} ) (number density)</td>
</tr>
<tr>
<td>Constants (if fixed turnover rate) : ( A_{NH3Ads Z2Cu} ), ( \Delta S_{NH3Ads Z2Cu} ), ( \Delta H_{NH3Ads Z2Cu} ), ( A_{SCRZ2Cu} ), ( E_{aSCR Z2Cu} ) ...</td>
<td>Constants (if fixed turnover rate) : ( A_{NH3Ads ZCuOH} ), ( \Delta S_{NH3Ads ZCuOH} ), ( \Delta H_{NH3Ads ZCuOH} ), ( A_{SCRZCuOH} ), ( E_{aSCR ZCuOH} ) ...</td>
</tr>
</tbody>
</table>

- This entails a combination of reaction engineering and more fundamental approaches incorporating DFT predictions and microkinetics

- In the next few slides, we will show a first effort at developing constitutive relations for the change in active sites induced by hydrothermal aging of Cu-SSZ-13
Hydrothermal Aging Model Approach

- Site isolation approach
- 550°C-4h H-SSZ-13 data used for Brønsted acid site kinetics
- 750°C-4h Cu-SSZ-13 data used for lumped Copper site kinetics.
- 600°C-2h low temperature (<200°C) isothermal adsorption-desorption data used for Physisorbed site kinetics

Cu-SSZ-13 Architecture
Cu Loading ~ 3.1 wt.%
Si/Al ~ 10

Reactor Geometry and Boundary Conditions:
Core Size: 1” by 3”
CPSI: 300
Wall thickness: 5 mil.
GHSV: 40,000/h
NH₃: 200 ppm
Adsorption Temperature: 200°C (except physisorption)
Isothermal desorption time: 0s (except physisorption)

- NH₃ TPD data at following conditions used to quantify change in NH₃ storage ability of lumped Copper sites and number density Brønsted sites: 550°C (1h-200h), 600°C (1h-100h), 650°C (1h-8h), 700°C (1h-25h), 750°C (1h-8h)
- Change in number density of Brønsted acid sites correlated with aging time and temperature
Active Sites for NH₃ Adsorption on H-SSZ-13

- It has been shown that on H-SSZ-13, NH₄⁺ cations are NH₃–solvated below 400°C, based on in-situ vibrational spectroscopy and DFT simulations [4-5]

\[
\text{ZNH}_4 + n\text{NH}_3 \rightarrow \text{ZNH}_4.n\text{NH}_3
\]

- Furthermore, in-house experimental data for H-SSZ-13 shows indirect evidence of second order adsorption, consistent with solvation of NH₄⁺ ions by NH₃. Thus, NH₃ adsorption on Brønsted acid sites modeled as a Type-II BET isotherm

\[
\begin{align*}
\text{NH}_3 + Z \text{H} & \leftrightarrow Z.\text{NH}_4 \\
\text{r}_f - \text{SH} & = \text{k}_f - \text{SH} \theta_{\text{NH}_3} \text{Z.H} \\
\text{r}_b - \text{SH} & = \text{k}_b - \text{SH} \theta_{Z.\text{NH}_4} \text{Z.H}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_3 + Z.\text{NH}_4 & \leftrightarrow Z.\text{NH}_4.\text{NH}_3 \\
\text{r}_f - \text{WH} & = \text{k}_f - \text{WH} \theta_{Z.\text{NH}_3} \text{Z.H} \\
\text{r}_b - \text{WH} & = \text{k}_b - \text{SH} \theta_{Z.\text{NH}_4.\text{NH}_3} \text{Z.H}
\end{align*}
\]

[DFT Optimized Structures [5]]


Second Order NH$_3$-Adsorption on H-SSZ-13

- NH$_3$ release during isothermal adsorption and TPD can be described quantitatively using the Type-II BET adsorption model.

- Results from typical first order Langmuir/Temkin adsorption model show that while such a model can capture the desorption peak with similar accuracy, NH$_3$ release isothermal NH$_3$ adsorption cannot be described accurately.

550°C-4h H-SSZ-13 NH$_3$ TPD

550°C-4h H-SSZ-13 Total Storage
In addition to the Strong-H and Weak-H sites, two additional sites considered for NH$_3$ adsorption:

**Copper Sites** (Temkin isotherm model)

\[ NH_3 + Cu \leftrightarrow Cu.NH_3 \]
\[ r_f^{-Cu} = k_{f-Cu}y_{NH_3}\theta_{Cu}\Omega_{Cu.NH_3} \]
\[ r_b^{-Cu} = k_{b-Cu}\theta_{Cu.NH_3}\Omega_{Cu.NH_3} \]

ZCu, Z$_2$Cu and ZCuOH sites lumped into global Copper site, due to inability of NH$_3$-TPD to resolve individual copper sites

**Physisorbed NH$_3$** (to account for increased storage at high feeds and low temperatures. Langmuir isotherm model)

\[ NH_3 + P \leftrightarrow P.NH_3 \]
\[ r_f^{-P} = k_{f-P}y_{NH_3}\theta_P\Omega_P \]
\[ r_b^{-P} = k_{b-P}\theta_P.NH_3\Omega_P \]

Isolated Cu$^{2+}$ positions from AIMD [6]

Copper and Physisorbed Site Kinetics on Cu-SSZ-13

- NH$_3$-TPD at 750°C-4h shows a primary release feature at 290°C, with a minor shoulder at 400°C
- Significant low temperature isothermal desorption attributed to a global physisorbed site. Isothermally desorbed NH$_3$ shows non-monotonic trend with increased temperature
Site-Specific Adsorption-Desorption Dynamics

- Quantitative predictions of the influence of catalyst temperature on storage of individual sites
- Steady-state total storage on 750°C-4h aged Cu-SSZ-13 compares well with model predictions

Cu-SSZ-13 NH₃ Storage at 750°C-4h

![Graph showing NH₃ storage vs. temperature for Cu-Sites, H Sites, Phys Site, and Total with experimental data points.]

Cu-SSZ-13 NH₃ Isothermal Adsorption/Desorption at 125°C

- Age: 600°C-2h
- Experiment: 1h isothermal adsorption followed by 40 minutes isothermal desorption

Cu-SSZ-13 NH₃ Isothermal Adsorption/Desorption at 200°C

- Age: 600°C-2h
- Experiment: 1h isothermal adsorption followed by 40 minutes isothermal desorption
NH₃ Adsorption Equilibrium Thermodynamics

- Estimated adsorption enthalpies and entropic penalties are aligned with DFT/AIMD predicted values in literature
- Entropic penalties in line with the notion of mobile NH₃ complexes on zeolite surface

Model Parameters

Adsorption Thermodynamics for NH₃ Storage on Individual Active Sites

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(K_{eq. at 200^\circ C})</th>
<th>(\Delta_{ads}H^0(kJ/mol))</th>
<th>(\Delta_{ads}S^0(J/mol-K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_3 + \text{Z}<em>H \leftrightarrow \text{Z}</em>\text{NH}_4)</td>
<td>8.08e+08</td>
<td>-134 ((\alpha = 0.11))</td>
<td>-113</td>
</tr>
<tr>
<td>(\text{NH}<em>3 + \text{Z}</em>\text{NH}<em>4 \leftrightarrow \text{Z}</em>\text{NH}_4, \text{NH}_3)</td>
<td>2.19e+05</td>
<td>-63</td>
<td>-31</td>
</tr>
<tr>
<td>(\text{NH}_3 + \text{Cu} \leftrightarrow \text{Cu} . \text{NH}_3)</td>
<td>3.11e+04</td>
<td>-103 ((\alpha = 0.11))</td>
<td>-111</td>
</tr>
<tr>
<td>(\text{NH}_3 + P \leftrightarrow P . \text{NH}_3)</td>
<td>1.06e+03</td>
<td>-38</td>
<td>-23</td>
</tr>
</tbody>
</table>

Recent DFT/AIMD Predictions [5, 7-8]

<table>
<thead>
<tr>
<th>(\Delta_{ads}H^0(kJ/mol))</th>
<th>(\Delta_{ads}S^0(J/mol-K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-132 to -155</td>
<td>-69</td>
</tr>
<tr>
<td>-120 to -140</td>
<td>-105 for (\text{Z}_2\text{Cu})</td>
</tr>
<tr>
<td>-40 to -70</td>
<td></td>
</tr>
</tbody>
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Modeling the change in NH₃-TPD with hydrothermal aging

- NH₃-TPD experiments indicate a monotonic decrease in high temperature peak and increase in low temperature peak with increased aging [9]

- This behavior was modeled with:
  a) Fixed turnover rates (identified previously)
  b) Increased NH₃ storage ability on Copper sites with aging
  c) Decreased number density of Brønsted acid sites with aging

Tracking Storage Capacity on Copper Sites and Number Density of Brønsted Acid Sites

- Increase in NH$_3$ storage on copper sites is linearly related to the loss of Brønsted acid sites.
- The loss of Brønsted acid sites with aging is used to develop a constitutive relationship for the evolution of these sites, yielding the hydrothermal aging equation.
Hydrothermal Aging Equation

- A linear relationship is found between the inverse Brønsted acid site density and aging time, implying a second order Arrhenius rate. The rate constant and activation energy are derived.

\[
\frac{1}{\Omega_{H_{\text{norm}}}} = 2.53 \times 10^8 \exp\left(\frac{-168733}{RT_{\text{age}}}\right) t_{\text{age}} + 1
\]

Ratio-based calculator reported previously [10]

Identical deactivation energies from two different derivation methods

Model Limitations – Copper Site Deconvolution

- Model does not explicitly predict the evolution of individual Copper sites with hydrothermal aging. However, combining model results with other characterization and experimental data can provide some insight.

- NH$_3$ adsorption at 200°C leads to replacement of approximately two framework oxygen atoms on Z$_2$Cu sites and approximately one framework oxygen atom on ZCuOH sites [9]

\[ \Omega_{Cu,NH_3} = 2\Omega'_{Z_2Cu} + 1\Omega'_{ZCuOH} \]

Known from NH$_3$-TPD model

Reducible Cu$^{2+}$ densities

- Additional characterization data on same catalyst:
  
  H$_2$-TPR on degreened catalyst [9]

  \[ \frac{\Omega'_{ZCuOH}}{\Omega'_{Z_2Cu} + \Omega'_{ZCuOH}} = 0.87 \text{ at } 550^\circ C - 4h \]

  NO + NH$_3$ titration experiments

- Correlating Brønsted acid site loss rate with individual copper site change rate:

\[ -\frac{d\Omega_H}{dt_{age}} = -\frac{d\Omega'_{ZCuOH}}{dt_{age}} + 0.31\frac{d\Omega'_{Z_2Cu}}{dt_{age}} \]

Summary and Future Work

- Modeling of SCR catalyst aging is necessary to meet the next phase of tailpipe regulations and durability requirements.

- If successfully developed and integrated with performance predictions, these models have significant applications in improved understanding and design of SCR catalysts, along with better catalyst health monitoring and control.

- These models can be enabled by intrinsic micro-kinetics for species conversion on each active site and experimental quantification of active site evolution with aging. For instance, the loss of Brønsted acid sites with hydrothermal aging can be expressed by:

\[
\frac{1}{\Omega_{H_{norm}}} = 2.53 \times 10^8 \exp\left(-\frac{168733}{RT_{age}}\right) t_{age} + 1
\]

- Constitutive relations must be discovered for the response of all chemically distinct active sites to different SCR degradation mechanisms.

- Once the catalyst state is known, the performance can be estimated using site-specific turnover rates identified through experimental and theoretical understanding.
Backup Slides
Transient and Steady-State Coverages on H-SSZ-13

- The surface coverages are plotted as a function of time (transient TPD) and temperature (steady-state). Steady-state coverages compare qualitatively well with computational results in [5].

Transient and Steady-State Coverages on Cu-SSZ-13

- The surface coverages are plotted as a function of time (transient TPD) and temperature (steady-state)
Validation of modeling approach with steady-state Storage measurements

- Evolution of total NH$_3$ storage with hydrothermal aging can be understood using the model
- With hydrothermal aging, the significance of Brønsted acid sites as a reservoirs of NH$_3$ decreases

Surprising experimental result at 450°C being investigated further
Analytical Expressions for Total and Site Specific Storage

- The equilibrium constants on each site can be utilized to calculate site specific surface coverage using Langmuir’s adsorption isotherm

\[
BET \text{ Surface Coverage} \rightarrow \theta_{EqNH4}(y_{NH3}, T) = \frac{K_{EqSH}y_{NH3}}{1 + K_{EqSH}y_{NH3} + K_{EqWH}y_{NH3}^2}; \quad \theta_{EqNH4NH3}(y_{NH3}, T) = \frac{K_{EqSH}K_{EqWH}y_{NH3}^2}{1 + K_{EqSH}y_{NH3} + K_{EqWH}K_{EqSH}y_{NH3}}
\]

\[
\text{Langmuir/Temkin Surface Coverage} \rightarrow \theta_{Eq}(y_{NH3}, T) = \frac{K_{Eq}y_{NH3}}{1 + K_{Eq}y_{NH3}} \quad i = \text{Cu sites, Phys sites}
\]

- Once the surface coverage on each of the sites is known, the total ammonia storage can be calculated as follows:

\[
\omega_{NH3} = \left(MW_{NH3} \frac{WL}{\rho_w}\right) \left(\Omega_{Cu.NH3} \theta_{EqCu} + \Omega_{H} \left(\theta_{EqNH4} + 2\theta_{EqNH4NH3}\right) + \Omega_{p} \theta_{EqP}\right)
\]

Where \(\omega_{NH3}\) is the NH\(_3\) storage in g/L\(_{\text{cat}}\), \(MW_{NH3}\) is the molecular weight of NH\(_3\) in kg/mol, \(WL\) is washcoat loading in g/L\(_{\text{cat}}\), \(\rho_w\) is washcoat density in kg/m\(^3\) (666 for DW3136 family), \(\Omega_i\) mol/m\(^3\)\(_{\text{washcoat}}\) and \(\theta_{Eqi}\) is the equilibrium surface coverage of active site \(i\)

- In order to estimate NH\(_3\) storage as a function of aging time and temperature, \(\Omega_i\) as a function of aging time and temperature must be calculated, and this is the objective of the aging model
Model Limitations – Severe Hydrothermal Aging

- Beyond a threshold aging, there is a change in NH$_3$ storage energetics on Copper sites, characterized by a shift in the low temperature release peak from 290°C to 265°C

- Systematic analysis of NH$_3$ TPD profile shows that are at least two different phases of hydrothermal aging:

**Phase I** – Drop in ratio of high to low temperature peaks, but negligible loss of Cu$^{2+}$ (transformation of ZCuOH to Z$_2$Cu)

**Phase II** – Drop in Cu$^{2+}$ sites. Brønsted acid sites negligible. Change in energetics of low temperature sites. Loss of NH$_3$ storage

<table>
<thead>
<tr>
<th>Aging Temperature ($^\circ$C)</th>
<th>Threshold Aging Time (end of Phase-I) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>1600</td>
</tr>
<tr>
<td>600</td>
<td>400</td>
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<tr>
<td>650</td>
<td>110</td>
</tr>
<tr>
<td>700</td>
<td>35</td>
</tr>
<tr>
<td>750</td>
<td>13</td>
</tr>
<tr>
<td>850</td>
<td>2</td>
</tr>
</tbody>
</table>
Cu$^{2+}$ site Distribution as a function of Hydrothermal Age

Key Model Prediction: In the degreened state, 30-35% of the Copper does not store NH$_3$, and must therefore not exist as isolated Cu$^{2+}$.

$$Z_{Cu} (\text{wt.} \%) = \frac{\Omega_{Cu} * MW_{Cu} * V_r}{DG * 610.237}$$

$$Z_{CuOH} (\text{wt.} \%) = \frac{\Omega_{CuOH} * MW_{Cu} * V_r}{DG * 610.237}$$

Where $MW_{Cu}$ is the molecular weight of Cu in g/mol, $V_r$ is ratio of washcoat volume to reactor volume and $DG$ is dry gain in g/in$^3$. 