Modeling Sulfur Poisoning of NH$_3$-SCR over Cu-SSZ-13

Yasser Jangjou

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Acknowledgment

- Epling Research Group at University of Virginia
- Dr. Chaitanya Sampara
- Di Wang, Ashok Kumar, Junhui Li from Cummins, Inc.
Background

- $\text{SO}_x$ inhibits low-temperature (< 350 °C) SCR activity of Cu-CHA.

- Sulfur poisoning over Cu-CHA seems to be reversible in nature, known as deSOx.

References:
4- Y. Jangjou, D. Wang, A. Kumar, J. Li, W. S Epling, ACS Catalysis 10 (2016)
Background

- Two different S-containing species form:

  1. **Ammonium sulfate** and **Cu sulfate** species when NH$_3$ and SO$_2$ are both present and

  2. **Cu sulfate** when only SO$_2$ is present.

Objective

Develop a NH$_3$-SCR kinetic model:

✔ Capable of describing experimental behavior of fresh, sulfated and regenerated (deSO$_x$) Cu-SSZ-13

✔ That is mechanism based
SCR Model: Single site approach

model catalysts:
Cu-SSZ-13_SAR_30
Cu-SSZ-13_SAR_6
Commercial Cu-SSZ-13

Fresh
After deSOx @ 500 °C
Sulfated
SCR Model: Single site approach
SCR Model: Single site approach

Step 1- SCR model – Fresh or DG
SCR Model: Single site approach

Step 1- SCR model – Fresh or DG  ✓

Step 2- S poisoning

Step 3- DeSOx  ❌
SCR Model: Single site approach

Step 1- SCR model – Fresh or DG
Step 2- S poisoning
Step 3- DeSOx

Cu-SSZ-13_SAR_6

Failed to capture deSOx
A Critical Step Prior to the Kinetic Modeling

Experimentally answering remaining questions on S poisoning mechanism, such as:

How do Z2Cu and ZCuOH respond to sulfur poisoning?
What is the nature of the S-Cu complexes?

Courtesy of Feng Gao, PNNL
Experimental Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu$^{2+}$ : Cu$_{\text{tot}}$</th>
<th>[CuOH]$^{+}$ : Cu$_{\text{tot}}$</th>
<th>Cu$^{2+}$ : Cu$_{\text{tot}}$</th>
<th>[CuOH]$^{+}$ : Cu$_{\text{tot}}$</th>
<th>H$_2$-TPR</th>
<th>DRIFTS</th>
<th>Sulfur TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-SSZ-13-SAR-6</td>
<td>0.61</td>
<td>0.31</td>
<td>0.36</td>
<td>0.64</td>
<td>0.8</td>
<td>0.2</td>
<td>0.65</td>
</tr>
<tr>
<td>Cu-SSZ-13-SAR-30</td>
<td>0.36</td>
<td>0.64</td>
<td>0.37</td>
<td>0.63</td>
<td>0.34</td>
<td>0.66</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Sample on site 1

Sample on site 2

Ammonium sulfate

Copper sulfate

Cu-SSZ-13 SAR=6

Cu-SSZ-13 SAR=30
Kinetic Modeling Approach

1. SO$_2$ Adsorption/Desorption
2. NH$_3$ Adsorption/Desorption
3. Ammonium Sulfate Formation/Decomposition
4. Fresh SCR
5. Sulfated SCR + Regeneration

A reaction mechanism assumed based on experimental data

Kinetic Parameters estimated using experiments

Packed-Bed Reactor model is solved using GT-SUITE

Model Validation

Model output comparison with experimental data
Kinetic Modeling Approach:

1. SO₂ Adsorption/Desorption
2. NH₃ Adsorption/Desorption
3. Ammonium Sulfate Formation/Decomposition
4. Fresh SCR
5. Sulfated SCR + Regeneration

A reaction mechanism assumed based on experimental data.

Kinetic Parameters estimated using experiments.

Packed-Bed Reactor model is solved using GT-SUITE.

Model Validation:
Model output comparison with experimental data.
1. SO$_2$ Adsorption/Desorption

SO$_2$ + NH$_3$ TPD ads @ 150 °C
SO$_2$ TPD ads @ 250 °C
SO$_2$ TPD ads @ 150 °C
SO$_2$ TPD ads @ 100 °C

SO$_2$ + S2 → SO$_2$-S2
SO$_2$-S2 → SO$_2$ + S2

Where S2 represents [CuOH]$^+$ site

$$r_{SO_2-ads} = f(T) \ k_{ads} \ C_{SO_2} \ \theta_{CuOH}$$

$$r_{SO_2-des} = k_{des} \ \theta_{SO_2-CuOH} \ \exp[-\frac{E_{SO_2}}{RT}]$$

Courtesy of Feng Gao, PNNL
1. SO$_2$ Adsorption/Desorption

SO$_2$-Ads @ 100 deg C + TPD

$T_{ads} = 100 \, ^\circ\text{C}$

SO$_2$ Ads @ 250 + TPD

$T_{ads} = 250 \, ^\circ\text{C}$

SO$_2$ Ads @ 150 + TPD

$T_{ads} = 150 \, ^\circ\text{C}$
1. \( \text{SO}_2 \) Adsorption/Desorption

Changed the active site density only
Part 3. Ammonium Sulfate Formation/Decomposition

Interaction of $\text{SO}_2 + \text{NH}_3$ with $\text{Cu}^{2+}$ results in formation of ammonium sulfate.

\[ \text{NH}_3 + \text{S}2 \leftrightarrow \text{S}2 - \text{NH}_3 \]

Ammonium Sulfate formation

\[ \text{S}2 - \text{NH}_3 + \text{SO}_2 + \text{NH}_3 \rightarrow \text{AS} \]

\[ \text{AS} \rightarrow \text{ABS} + \text{NH}_3 \]

\[ \text{ABS} \rightarrow \text{Z}2 + \text{NH}_3 + \text{SO}_2 \]

Ammonium Sulfate decomposition

Cu$^{2+}$ site balance:

\[ \theta_* + \theta_{\text{NH}_3} + \theta_{\text{AS}} + \theta_{\text{ABS}} = 1 \]

Reaction rates:

\[ r_{11} = a_{s2}k_{11}\theta_{\text{AS}} = a_{s2}A_{11}e^{\left(-\frac{E_{b,11}(1-\alpha_1\theta_{\text{AS}})}{RT_s}\right)}\theta_{\text{AS}} \]

\[ r_{12} = a_{s2}k_{12}\theta_{\text{ABS}}^2 = a_{s2}A_{12}e^{\left(-\frac{E_{b,12}}{RT_s}\right)}\theta_{\text{ABS}}^2 \]

\[ r_{13} = a_{s2}k_{13}C_{\text{NO}}\theta_{\text{S}2-\text{NH}_3} = a_{s2}A_{13}e^{\left(-\frac{E_{f,13}}{RT_s}\right)C_{\text{NO}}\theta_{\text{S}2-\text{NH}_3}} \]
Part 3. Ammonium Sulfate Formation/Decomposition
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Part 3. Ammonium Sulfate Formation/Decomposition

Dashed lines = Model
Solid lines = Experiment
Part 3. Ammonium Sulfate Formation/Decomposition

Different ramp rates used to validate model (tuning was done with one ramp rate)
Sulfur Adsorption Desorption

Dashed lines = Model
Solid lines = Experiment
SCR model: Multi sites model

\[ \text{Cu}^{2+} : \ 4\text{NH}_3^* + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + 4* \]

\[ \text{CuOH}^+: \ 4\text{NH}_3^* + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + 4* \]

Brønsted: \( \text{NH}_3^*_{\text{zeolite}} \rightarrow \text{NH}_3^*_{\text{Copper}} \)

Two site model needed – Cu site type defines type of sulfur formed and its stability

\[ E_1 = 88 \text{ kJ/mol} \]
\[ E_2 = 70 \text{ kJ/mol} \]

Dashed lines = Model
Solid lines = Experiment

Optimized

Changed the active site density only
SCR Model: with sulfur poisoning and regen

$Cu^{2+} \rightarrow AS$ formation + Decomposition

$CuOH^+ \rightarrow Sulfate$ formation + Decompositon

Dashed lines = Model
Solid lines = Experiment
Summary

- A mechanism-based kinetic model was developed to predict Cu-SSZ-13 sulfation and desulfation for NH\textsubscript{3}-SCR.

- The model accurately predicts sulfur concentrations during sulfur storage and release over three Cu-SSZ-13 samples.

- The model accounts for steady state NO\textsubscript{x} conversion over fresh, sulfated and regenerated (at 550 °C) Cu-SSZ-13 samples.
Thank you.


E-mail : Jangjou_Yasser@CAT.com