Structure/Activity Relationships in Cu/CHA-Based NH₃ SCR Catalysts

Feng Gao, Yilin Wang, Márton Kollár, Eric Walter, János Szanyi, Chuck Peden
Institute for Integrated Catalysis
Pacific Northwest National Laboratory
Location for Cu in SSZ-13 catalysts at low Cu loadings

“Cu/SSZ-13 contains mononuclear Cu$^{2+}$ species, located in the face of the double-6-ring subunit of the zeolite after calcination where it remains under reaction conditions”


This location also identified in:


Higher Cu loadings result in multiple Cu locations in the zeolite cages.

a = b = 13.719 Å

\[ c = 14.953 \ Å \]

\[ d = 3.8 \ Å \]
Effect of Cu Loading on the Reduction of Cu Species in Cu/SSZ-13 Zeolites Catalysts

At low loading, only a single H₂ TPR reduction peak at ~340 ºC.

At higher loadings, a second TPR peak at ~230 ºC.

Reduction of Cu⁺ to Cu⁰ does not occur until T>800 ºC (data not shown).


Perturbation of Zeolite Framework Vibrations also Suggest Multiple Cu Sites

IR peak at ~940 cm\(^{-1}\) in T-O-T (Si-O-Si, Si-O-Al) region grows in with Cu loading.

This ~940 cm\(^{-1}\) peak is removed first during H\(_2\) reduction, followed by loss of ~899 cm\(^{-1}\) peak.

Two Cu\(^{+2}\) locations as a function of loading are clearly evident in FTIR spectra after NO adsorption.

EPR results also strongly suggest two Cu species as a function of loading.

A couple more significant open questions...

- Cu at low loadings is more difficult to reduce.
- In presence of 1% H₂O, H₂-TPR shows only low-temp peak for all Cu loadings.
- It appears Cu species may move under reaction conditions.
- Relevant to catalytic reactivity?

The “Seagull” Shape in Conversion-Temperature Curves

Example: Standard SCR on Cu-SAPO-34 at a relatively high SV.

- Some industrial colleagues indicated that this phenomenon only occurs for Cu-SAPO-34.
- However, we found this same effect at lower Cu-SSZ-13 catalysts at lower Cu loadings.
Dependence of SCR Performance on Cu Loading for SSZ-13 Catalysts

- The ‘Seagull’ shape is present for both Cu-SSZ-13 and Cu-SAPO-34.
- On high Cu loading samples (IE level > 60%), the seagull ‘flies away’.

What might be responsible for the drop in reactivity between 250 and 350 °C?

Behind the ‘Seagull’ Shape

Key questions:

1. Is this caused by mass transfer limitations, or reactant or product inhibitions? – NO

2. Is this caused by changes in reaction mechanisms as a function of reaction temperature?

3. Or is this intrinsically correlated with changes in the nature and/or location of the catalytically active centers?
SSZ-13 with very low Cu loadings

Why very low Cu loadings?

(1) Hope to minimize mass transfer limitations.

(2) Simplify the catalysts: eliminate Cu-Cu interactions, eliminate multiple Cu positioning.

(3) Verify that we still see the seagull shape.

Cu loadings determined with EPR using standard solutions of Cu(II)-imidazole.
‘Seagull’ shape especially evident at low Cu loaded SSZ-13 catalysts

Considering just temperatures below 300 ºC:

- Why NO\textsubscript{x} conversions drop from 250 to 300 ºC?
- Why large increase in NO\textsubscript{x} conversions above 350 ºC?

Key questions:

1. Is this caused by mass transfer limitations, or reactant or product inhibitions? – NO

2. Is this caused by changes in reaction mechanisms as a function of reaction temperature?

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Low-Temperature Reaction Kinetics

Does the reaction mechanism change from 250 to 300 °C?

If yes, we might expect some change in the power-law pressure dependence

- In this temperature range: \( r \propto P_{NH_3}^0 P_{NO}^1 \)
- What about changes in the nature of Cu? Recall that Cu is more readily reduced in the presence of water.

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Behind the ‘Seagull’ Shape

Key questions:

1. Is this caused by mass transfer limitations, or reactant or product inhibitions? – NO

2. Is this caused by changes in reaction mechanisms as a function of reaction temperature? – NO

3. Or is this intrinsically correlated with changes in the nature and/or location of the catalytically active centers?
   - FTIR, Synchrotron XRD, and EPR studies…
Two Perturbed Zeolite Framework Vibrations also Suggest Multiple Cu Sites

These spectra were for catalysts that had been oxidized and cooled in O\textsubscript{2}/N\textsubscript{2} gas mixtures.

What do the spectra look like for an 80% Cu-exchanged catalyst when water is also present?

FTIR Clearly Shows Loss of Water During Calcination to 400 ºC

- Molecular water fully desorbed above 220 ºC
- Loss of water brings about significant changes to the zeolite T-O-T vibrations.

Changes in the framework vibrations caused by Cu ion relocation towards the zeolite framework

CHA unit cell parameter change caused by dehydration and subsequent Cu ion movement

EPR data also evidence these changes

Behind the ‘Seagull’ Shape

Key questions:

1. Is this caused by mass transfer limitations, or reactant or product inhibitions? – NO

2. Is this caused by changes in reaction mechanisms as a function of reaction temperature? – NO

3. Or is this intrinsically correlated with changes in the nature and/or location of the catalytically active centers? – Likely YES

• So, what is the nature and structure of the active and hydrated Cu species?
Results for low Cu-SSZ-13 catalysts indicate reactivity very sensitive to loading.

- Convert NOx conversions to TOFs based on total Cu.
- Drop in TOFs at higher loadings due to the intra-particle diffusion limitations.
- Why do TOFs increase for the very low Cu loaded catalysts?

Experimental TOFs difficult to explain by only considering Cu ion monomers.

1st

![Graph 1]

2nd

![Graph 2]

3rd

![Graph 3]

4th

![Graph 4]

Low T NOx conversions versus Cu loading best fit by using the square of the Cu loading!

Our results suggest the following model for active Cu structures as a function of temperature:

- At temperatures < 250 °C, water and/or ammonia ‘mobilizes’ Cu leading to formation of highly active dimeric species.
- At higher temperatures, coordinated water and/or ammonia ‘desorbs’, Cu dimers ‘dissociate’, and monomeric Cu ion migrate back to zeolitic ion exchange sites.

Summary and Conclusions

- Cu/SSZ-13 catalysts display outstanding performance for NH₃ SCR relative to other Cu/zeolite-based catalysts, including considerably lower sensitivity to high-temperature hydrothermal aging.

- The nature of the active Cu site in CHA zeolites is an active area of research.
  - Two different Cu species within Cu/SSZ-13 were identified by H₂ TPR, EPR and FTIR.
  - The relative distribution of Cu species is dependent on Cu loading levels and reaction conditions.
  - Dimeric Cu species appear to be the active Cu species at lower (<250 °C) reaction temperatures where significant amounts of adsorbed water are present.

- The mechanism of NH₃ SCR may involve the facile reduction of reactive Cu⁺² species by NO.
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