SUPPORTING INFORMATION

Influence of ZCuOH, Z\textsubscript{2}Cu, and extraframework Cu\textsubscript{x}O\textsubscript{y} species in Cu-SSZ-13 on N\textsubscript{2}O formation during the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}

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Section S1: Reactor rig flow diagram and example kinetic measurements

Figure S1 shows a flow diagram of our reactor system. All tubing was stainless steel, except short portions for non-corrosive and non-toxic gases such as N$_2$, CO$_2$, and O$_2$. Water was introduced by flowing N$_2$, O$_2$, and CO$_2$ through a PermaPure MH® humidifier. Flow rates of all gases (other than water) were controlled using mass flow controllers (Brooks Instrument® and Porter Instrument) and measured using a soap-film bubble flow meter (Bubble-O-Meter, NIST certified). All stainless steel lines downstream of the humidifier were wrapped with heat-tape (BriskHeat® BWH series high temperature heavy insulated heating tape; 0.5 inch width, 24 – 72 inch length, 470 W) and insulation tape (Cotronics Corp. Thermeez woven insulation tape 1/32 inch thick x 1 inch wide) and maintained at 373 K using variable AC transformers to prevent the condensation of H$_2$O. NO was introduced to the stream prior to entering the preheater (which is a simple tubing coil within a furnace heated to 200°C). Immediately downstream of the preheater, NH$_3$ is introduced to either the bypass or the flow reactor via a three-way-valve to minimize the formation of NH$_3$NO$_3$. Quartz chips (~2 to 3 mm diameter) were placed on a stainless steel mesh above the reactor to induce turbulence and thus plug flow. Before entering the reactor, all gases (except NH$_3$ to avoid side reactions) were mixed and preheated to 473 K.

**Figure S1.** Flow diagram of the reactor used for SCR kinetic measurements.
Figure S2. NO concentration and catalyst temperature raw data collected on a fresh Cu-SSZ-13 with Si:Al = 25, Cu wt% 1.5 with a total flow rate of 1150 mL min$^{-1}$ and reactor loading of 6.5 mg catalyst. The two gaps in the NO concentration at ~16 and 17 hours were due to the FTIR detector warming up due to the temporary absence of liquid nitrogen cooling the detector.
Figure S3. NO concentration raw data collected on a fresh Cu-SSZ-13 with Si:Al = 25, Cu wt% 1.5 with a total flow rate of 1150 mL min$^{-1}$ and reactor loading of 6.5 mg catalyst. NO concentrations were varied between 150 and 2000 ppm.
Section S2: NH$_3$ Titration Results on our Z$_2$Cu and ZCuOH model catalysts

Figure S4. Selective NH$_3$ titration of Brønsted acid sites of Z$_2$Cu and ZCuOH model materials (red border) used in this study plotted with the rest of the NH$_3$ titration results reported in Paolucci et al.$^1$. 
Section S3: Cu(OH)$_2$ precipitation equilibrium constant ($K_{sp}$) derivation

Cu(OH)$_2$ precipitation reaction:

$$Cu^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightleftharpoons Cu(OH)_2 (s) \quad \text{(Equation S1)}$$

Equilibrium constant for Cu(OH)$_2$ formation:

$$K_{sp} = \frac{[Cu_2(OH)_2]}{[Cu^{2+}][OH^-]^2} \sim \frac{1}{[Cu^{2+}][OH^-]^2} \quad \text{(Equation S2)}$$

Definition of pH:

$$pH = -\log[H^+] \quad \text{(Equation S3)}$$

Solubility dissociation constant for water:

$$K_w = [OH^-][H^+] \sim 1 \times 10^{-14} \frac{mol}{dm^3} \text{ @ RT} \quad \text{(Equation S4)}$$

$$[OH^-] = \frac{K_w}{[H^+]} \quad \text{(Equation S5)}$$

Combine:

$$K_{sp} = \frac{1}{[Cu^{2+}](\frac{K_w}{10^{-pH}})^2} \quad \text{(Equation S6)}$$

Linearized:

$$pH = -\log_{10} \left( K_w K_{sp}^{\frac{1}{2}} \right) - \log_{10} ([Cu^{2+}]) \quad \text{(Equation S7)}$$
Section S4: Precipitation curves for Cu(CH₃COO)₂ and CuSO₄

Figure S5. Precipitation pH curves for Cu(CH₃COO)₂ (red squares) (98%, Sigma-Aldrich) using drop-wise 0.1 M NH₄OH as a base to increase the pH. If final equilibrium pH and Cu molarities fall above the curve, Cu(OH)₂ precipitates were observed. If final equilibrium pH and Cu molarities fall below the curve, then all Cu species are aqueous. A Kₛₚ value of 2.4×10⁻¹⁸ ± 2.0×10⁻¹⁸ L² mol⁻² was measured by fitting the experimental data to a thermodynamic solubility model (Equation S6).
Figure S6. Precipitation pH curves for CuSO₄ (red squares) (≥ 99%, Sigma-Aldrich) using drop-wise 0.1 M NH₄OH as a base to increase the pH. If final equilibrium pH and Cu molarities fall above the curve, Cu(OH)₂ precipitates were observed. If final equilibrium pH and Cu molarities fall below the curve, then all Cu species are aqueous. A $K_{sp}$ value of $4.1 \times 10^{21} \pm 3.9 \times 10^{21}$ $L^2 mol^{-2}$ was measured by fitting the experimental data to a thermodynamic solubility model (Equation S6)
Section S5: Formation of Cu$_x$O$_y$ species in Cu-ZSM-5 and Cu-Beta zeolites after aqueous Cu-exchange in Cu(NO$_3$)$_2$ and subsequent calcination

NH$_4$-ZSM-5 with Si:Al = 12.5 (CBV 2314) and Si:Al = 30 (CBV 5524G) was purchased from Zeolyst International, Inc. Beta with Si:Al = 11.5 was synthesized according to a recipe reported by Chang et al. $^2$. The procedure to obtain H-Beta from as-synthesized Beta is identical to the procedures reported for SSZ-13. Commercial NH$_4$-ZSM-5 only required the last calcination step to obtain H-ZSM-5. The H-Beta and H-ZSM-5 were then utilized for aqueous Cu-exchange using the same procedure used for H-SSZ-13 in the main text.

Figure S7. Zoom-in of Figure 3. Equilibrium concentration of Cu(NO$_3$)$_2$ and pH after aqueous Cu-exchange of SSZ-13. Hollow shapes represent Cu-exchanged zeolites that did not exhibit black Cu$_x$O$_y$ clusters after calcination. Filled black shapes represent Cu-exchanged zeolites that did exhibit black Cu$_x$O$_y$ clusters after calcination. The precipitation pH for Cu(NO$_3$)$_2$ is represented by the best-fit precipitation curve model (light red trace).
Figure S8. Aqueous Cu-exchange with Cu(NO$_3$)$_2$ of Cu-ZSM-5 Si:Al = 12.5 (triangles) and Si:Al = 30 (circles) and whether the formation of extraframework Cu$_x$O$_y$ species were observed (filled shapes) or not observed (hollow shapes) after calcination in 20% O$_2$/N$_2$ at 773 K.

Figure S9. Aqueous Cu-exchange of Cu-Beta with Si:Al = 11.5 with Cu(NO$_3$)$_2$. Three samples were synthesized and the formation of extraframework Cu$_x$O$_y$ species were not observed after calcination in 20% O$_2$/N$_2$ at 773 K under the conditions used.
Figure S10. Aqueous Cu-exchange of Cu-zeolites using Cu(CH$_3$COO)$_2$ from literature. Grünert et al $^3$ exchanged ZSM-5 materials with 0.01 M Cu(CH$_3$COO)$_2$ at a pH 6 and did not observe Cu$_x$O$_y$ species on their Cu-ZSM-5 catalysts (hollow triangle). Mihai et al $^4$ exchanged four Beta materials with molarities ranging from 0.01 to 0.1 M Cu(CH$_3$COO)$_2$ at a pH 6 and did not observe Cu$_x$O$_y$ species on their Cu-Beta (hollow squares).
Section S6: UV-visible characterization of Cu-SSZ-13

Figure S11. Image of calcined SSZ-13 with Cu wt%’s of 0.0, 2.0, 3.6, and 7.4 (from left to right). The red tint around H-SSZ-13 (Cu wt% = 0) is unfortunately due to refraction of the red permanent marker used to label the outside of the vial.

Figure S12. Diffuse Reflectance UV-Visible-NIR spectra of calcined Cu-SSZ-13 Si:Al = 4.5 with Cu wt% of 18.9.
Section S7: XRD characterization of Cu-SSZ-13

Figure S13 plots XRD spectra of all Cu-SSZ-13, Cu(OH)$_2$, and CuO samples tested. All spectra were collected less than 48 hours after synthesis except for Cu-SSZ-13 Cu wt% = 18.9, which was stored under ambient conditions for 5 years prior to collecting the XRD spectra as is. Spectra of CuO from Sigma Aldrich and Mallinkrodt were also collected as is from the manufacturer.

Figures S14 and S15 compares Cu(OH)$_2$ and CuO features, respectively, with that of Cu-SSZ-13 Cu wt% 18.9. Interestingly, we see Cu(OH)$_2$ features in the Cu-SSZ-13 Cu wt% 18.9 sample, which is surprising. We presume that either the sample was not fully calcined prior to storage and testing, or over the course of 5 years, exposure to ambient conditions re-converted some of the CuO back to Cu(OH)$_2$.

Figure S13: XRD patterns from 4° to 60° 2θ on Cu(OH)$_2$ precipitate, CuO from Mallinkrodt, CuO from Sigma Aldrich, Cu-SSZ-13 Si:Al = 4.5 with Cu wt%’s of 3.6, 7.4, and 18.9 on uncalkined and calcined materials, and H-SSZ-13 Si:Al = 4.5. All Cu-SSZ-13 materials were Cu-exchanged above the Cu(OH)$_2$ precipitation region.
**Figure S14**: XRD patterns from 10° to 30° 2θ on Cu(OH)$_2$ precipitate and calcined Cu-SSZ-13 Si:Al = 4.5 with Cu wt% 18.9.

**Figure S15**: XRD patterns from 34° to 40° 2θ on CuO precipitate and calcined Cu-SSZ-13 Si:Al = 4.5 with Cu wt% 18.9.
Section S8: Deactivation of anionic sites during low pH aqueous Cu-exchange

Figure S16. Residual H:Al\(_f\) from NH\(_3\) titrations on oxidized Cu-SSZ-13 samples versus the Cu:Al\(_f\) of Si:Al = 5 exchanged at a pH of 5 (black diamonds) and exchanged with no pH control (pH ranges between 1 to 2) (hollow diamonds). Dashed lines are model predictions \(^1\).

When low concentrations of Cu(NO\(_3\))\(_2\) (0 to 0.05 M, corresponding to a slurry pH between 1.8 and 2.3) are present during aqueous-phase Cu exchange of H-SSZ-13 (Si:Al = 4.5) at ambient conditions, a 40 to 80% decrease in the number of Brønsted acid sites relative to the parent SSZ-13 (Figure S16) is observed. This decrease could be due to significant structural changes in Al framework atoms (e.g. dealumination) in high Al content H-SSZ-13 zeolites (Si:Al = 4.5) at low pH values (pH 1 to 2) and low concentrations of Cu\(^{2+}\) cations (80% loss in H\(^+\) sites when no Cu is present), which is consistent with reports of cation exchange with H\(^+\) sites to stabilize framework Al against dealumination \(^5,6\). The addition of NH\(_4\)OH to maintain a pH of 5 during the exchange of low concentrations of Cu cations mitigated Al structural changes and only resulted in a decrease of 25% of the number of Brønsted acid sites (black diamonds). We previously reported the loss of ~0.25 H\(^+\):Al for the H-SSZ-13 sample with Si:Al=5 and Cu:Al=0.02, which is much larger than expected from the molar Cu\(^{2+}\):H\(^+\) 2:1 exchange stoichiometry (expected loss of 0.04 H\(^+\):Al for a Cu:Al=0.02) \(^7\). These results indicate that when the pH and Cu molarity is too low, simultaneous structural changes to anionic zeolite exchange sites (framework Al) occur during aqueous Cu-exchange.
Section S9: Kinetics of SCR and N₂O formation

Figure S17. Standard SCR (300 ppm NO, 300 ppm NH₃, 10% O₂, 2.5% H₂O, 8% CO₂, in balance N₂, at 200°C) rate, and apparent activation energy (collected between 150 and 270°C on unsulfated Cu-SSZ-13 samples with low Cu loadings (< 1 wt%). The catalyst with the lowest Cu and Al density (0.1 Cu wt%, Si:Al = 100) exhibited a drop in the apparent activation energy compared to other catalysts (Cu wt% from 0.2 to 0.8, Si:Al from 4.5 to 100)
**Figure S18.** NO orders versus Cu wt% during standard SCR conditions (150 to 450 ppm NO, 300 ppm NH₃, 10% O₂, 7% CO₂, 2.5% H₂O, balance N₂, 473 K). Cu-SSZ-13 with Si:Al molar ratios of 4.5, 15, 25, and 100, and Cu wt% between 0 and 19 were synthesized and used. The unshaded shaded area between 0 to 4 wt% represents samples with all Cu as ionic Cu²⁺/Cu¹⁺ species. The grey shaded area between 4 to 19 wt% represents samples that contain bulk CuₓOᵧ species.

**Figure S19.** NH₃ orders versus Cu wt% during standard SCR conditions (300 ppm NO, 150 to 450 ppm NH₃, 10% O₂, 7% CO₂, 2.5% H₂O, balance N₂, 473 K). Cu-SSZ-13 with Si:Al molar ratios of 4.5, 15, 25, and 100, and Cu wt% between 0 and 19 were synthesized and used. The unshaded shaded area between 0 to 4 wt% represents samples with all Cu as ionic Cu²⁺/Cu¹⁺ species. The grey shaded area between 4 to 19 wt% represents samples that contain bulk CuₓOᵧ species.
Figure S20. $O_2$ orders versus Cu wt% during standard SCR (300 ppm NO, 300 ppm NH$_3$, 5 to 15% $O_2$, 7% CO$_2$, 2.5% H$_2$O, balance N$_2$, 473 K). Cu-SSZ-13 with Si:Al molar ratios of 4.5, 15, 25, and 100, and Cu wt% between 0 and 19 were synthesized and used. The unshaded shaded area between 0 to 4 wt% represents samples with all Cu as ionic Cu$^{2+}$/Cu$^{1+}$ species. The grey shaded area between 4 to 19 wt% represents samples that contain bulk Cu$_x$O$_y$ species.
Figure S21. NO$_2$ produced during standard SCR (300 ppm NO, 300 ppm NH$_3$, 10% O$_2$, 7% CO$_2$, 2.5% H$_2$O, in balance N$_2$ at 200°C) when the temperature, NH$_3$ concentration, NO concentration, O$_2$ concentration, or H$_2$O concentrations were independently varied. For example, for NH$_3$ dependent studies, the concentration of NH$_3$ was adjusted (by varying the NH$_3$ and N$_2$ flow rates) while maintaining a constant temperature of 200°C and NO, O$_2$, CO$_2$, and H$_2$O concentrations. 4.5 mg of Z$_2$Cu model material (Cu-SSZ-13, Si:Al = 4.5, Cu wt% = 3.9) were tested in a packed bed reactor with 1150 sccm of simulated diesel exhaust and 6.5 mg of ZCuOH model material (Cu-SSZ-13, Si:Al = 25, Cu wt% = 1.5) were tested in a packed bed reactor with 1150 sccm of simulated diesel exhaust for all NO$_2$ results shown.
Section S10: Error propagation equations

Uncertainties in measurables (masses, volumes, compositions, etc.) propagate when these measurables are used in calculations. Error propagation allows us to determine the uncertainty of functions that depend on these measurables\(^8\). The formulas used to calculate errors in this study are in Table S1. Errors for slopes (e.g. activation energies and reaction orders) were calculated using the LINEST() function in Microsoft Excel\(^9\).

Table S1. Governing equations and error propagation equations used to calculate errors.

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<th>Governing Equation</th>
<th>Variance from Error Propagation</th>
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| \( M_2 = \left( \frac{g_{\text{CuSalt}} \cdot \text{Cu wt\% } g_{\text{zeolite}}}{V_2} \right) \)  
(Equation 1) | \( \sigma_{M_2}^2 = \left( \frac{\partial M_2}{\partial g_{\text{CuSalt}}} \right)^2 \sigma_{g_{\text{CuSalt}}}^2 + \left( \frac{\partial M_2}{\partial (\text{Cu wt\%})} \right)^2 \sigma_{\text{Cu wt\%}}^2 
+ \left( \frac{\partial M_2}{\partial g_{\text{zeolite}}} \right)^2 \sigma_{g_{\text{zeolite}}}^2 + \left( \frac{\partial M_2}{\partial V_2} \right)^2 \sigma_{V_2}^2 \) |
| \( r_{NO} = \frac{(C_{\text{in}} - C_{\text{out}}) \cdot P \cdot V_{\text{total}}}{100000 \cdot RT} \)  
(Equation 2) | \( \sigma_{r_{NO}}^2 = \left( \frac{\partial r_{NO}}{\partial C_{\text{in}}} \right)^2 \sigma_{C_{\text{in}}}^2 + \left( \frac{\partial r_{NO}}{\partial C_{\text{out}}} \right)^2 \sigma_{C_{\text{out}}}^2 + \left( \frac{\partial r_{NO}}{\partial V_{\text{total}}} \right)^2 \sigma_{V_{\text{total}}}^2 \) |
| \( K_{sp} = \frac{1}{[\text{Cu}^{2+}] \cdot \left( \frac{K_w}{10^{-pH}} \right)^2} \)  
(Equation 3) | \( \sigma_{K_{sp}}^2 = \left( \frac{\partial K_{sp}}{\partial [\text{Cu}^{2+}]} \right)^2 \sigma_{[\text{Cu}^{2+}]}^2 + \left( \frac{\partial K_{sp}}{\partial pH} \right)^2 \sigma_{pH}^2 \) 
\( \sigma_{K_{sp}}^2 = \left( - \left( \frac{K_w}{10^{-pH}} [\text{Cu}^{2+}] \right) \right)^2  
\sigma_{[\text{Cu}^{2+}]}^2 
+ \left( - \left( 2^{1-pH} 5^{2 pH} \ln(10) \right) \right)^2 \sigma_{pH}^2 \) |
Section S11: References


