

SUPPORTING INFORMATION

Mechanistic Studies of NH₃-Assisted Reduction of Mononuclear Cu(II) Cation Sites in Cu-CHA Zeolites

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Section S1. Characterization data of Cu-CHA Samples

X-ray diffraction patterns (Figure S1) and Ar adsorption isotherms at 87 K (Figure S2) are shown for the samples; data are consistent with the expectations of the CHA framework topology. Note: Cu-CHA(15)-0.14 and Cu-CHA(15)-0.30 XRD and Ar adsorption profiles are shown in previous work.¹

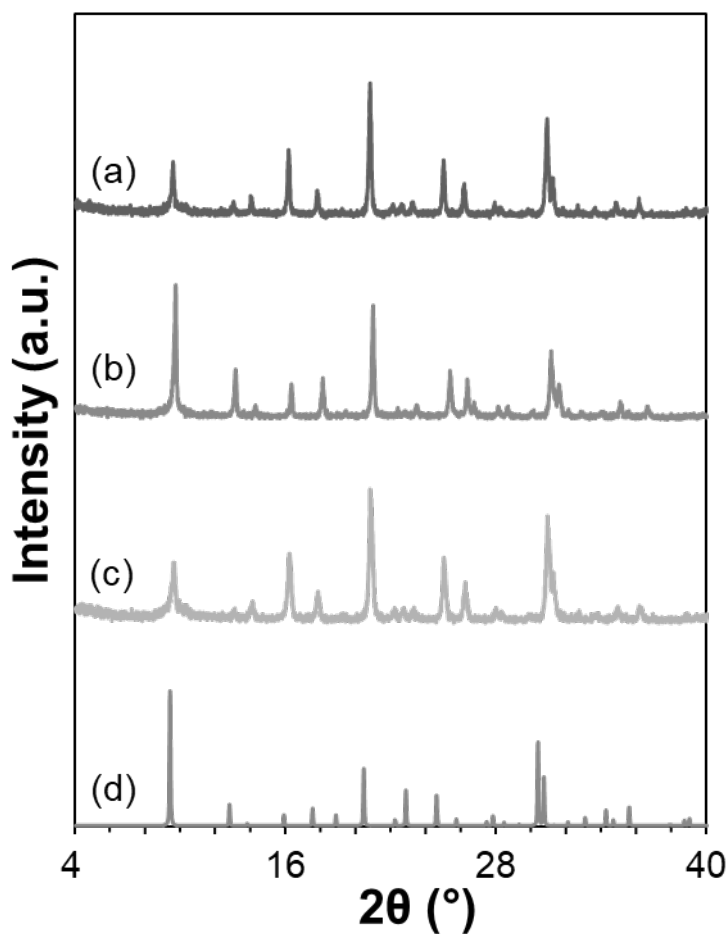


Figure S1. Powder X-Ray diffraction patterns for (a) H-CHA(25)-0.18 (b) H-CHA(15)-0.06 (c) H-CHA(9)-0.17, and (d) CHA from the International Zeolite Association (IZA)².

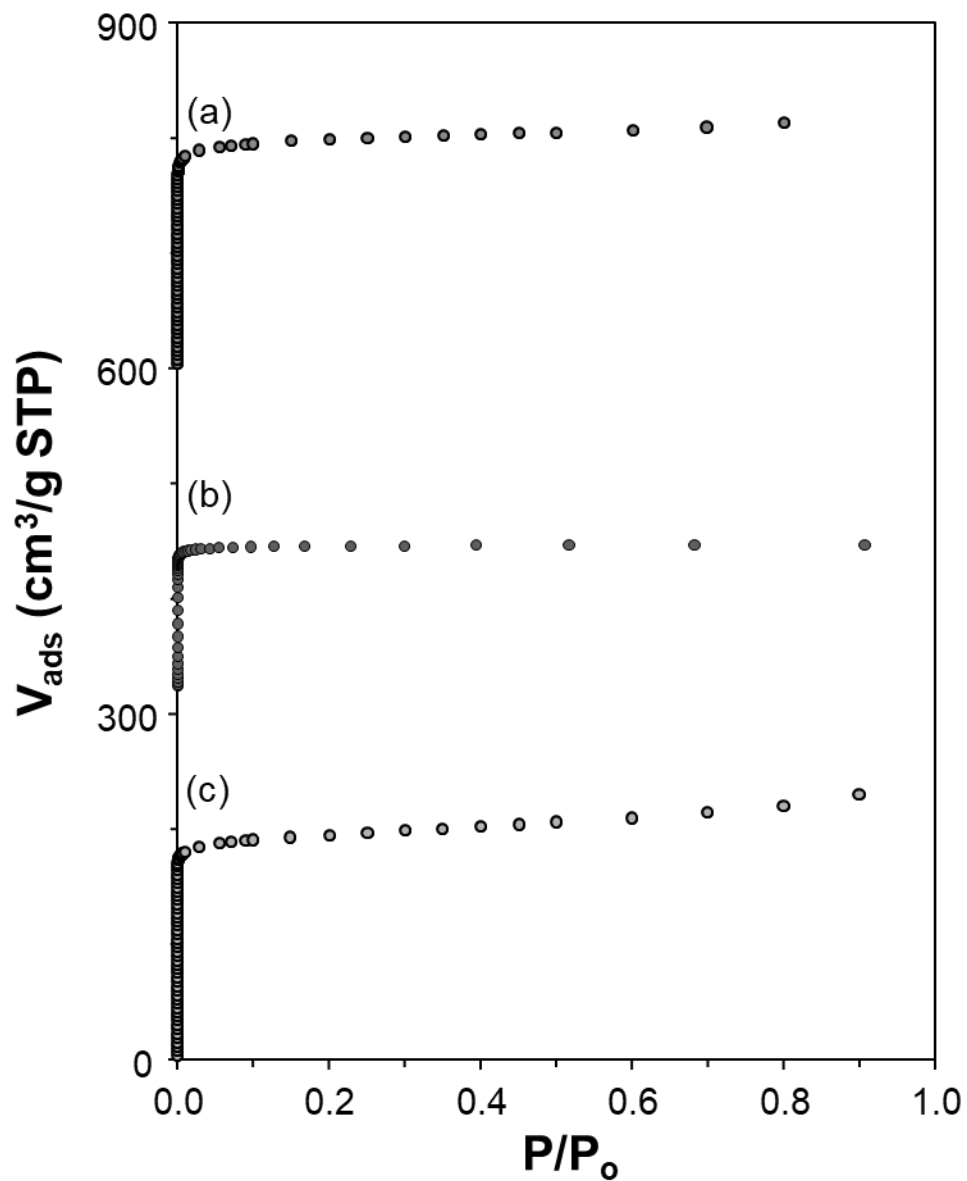


Figure S2. Ar adsorption isotherms measured at 87 K on for (a) H-CHA(25)-0.18 (b) H-CHA(15)-0.06, and (c) H-CHA(9)-0.17. Isotherms are offset by $300 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

Table S1. Number of Brønsted acid sites on H-CHA and Cu-CHA for each sample, and micropore volumes determined from Ar adsorption isotherms (87 K).

Sample ^a	Si / Al ^b	Cu / Al ^b	H ⁺ / Al ^c	H ⁺ _{residual} / Al ^d	Micropore Volume (cm ³ gcat ⁻¹) ^e
Cu-CHA(25)-0.18	25	0.37	0.98	0.56	0.25
Cu-CHA(9)-0.17	9	0.11	0.89	0.55	0.22
Cu-CHA(15)-0.14	15	0.18	0.98	0.70	0.18*
Cu-CHA(15)-0.06	15	0.06	1.01	0.98	0.18
Cu-CHA(15)-0.30	15	0.37	0.98	0.51	0.18*

^a Sample nomenclature is Cu-CHA(X)-Y. X = Si/Al, Y = Cu/cage.

^b Al content was determined by AAS or ICP and Si content was determined from unit cell of CHA calculations. Uncertainty is $\pm 10\%$.

^c H⁺/Al measured on parent H-CHA zeolite.

^d H⁺/Al measured after ion-exchange with Cu²⁺.

^e Micropore volumes calculated by analyzing the semi-log derivative plot of the Ar adsorption isotherm ($\partial(V_{ads})/\partial(\ln(P/P_0))$ vs. $\ln(P/P_0)$) for the H-CHA samples.

* Micropore volumes previously reported on a representative parent CHA sample by Paolucci et al.¹

Section S2. NO+NH₃ Titrimetric Methods

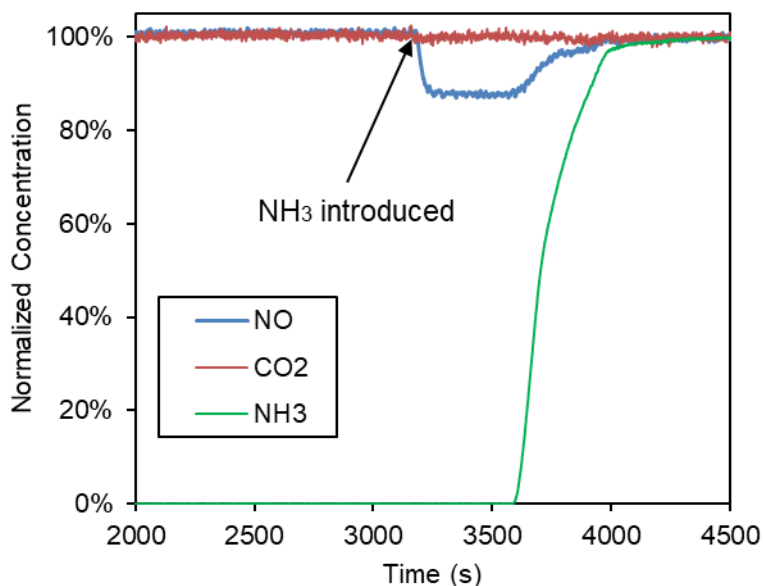


Figure S3. Normalized concentrations of NO, CO₂, NH₃ versus time during transient reduction experiment on a pre-oxidized Cu-CHA sample (Cu-CHA(15)-0.14) during exposure to 0.03 kPa NO and 5 kPa CO₂ (473 K, balance N₂), followed by introduction of 0.03 kPa NH₃.

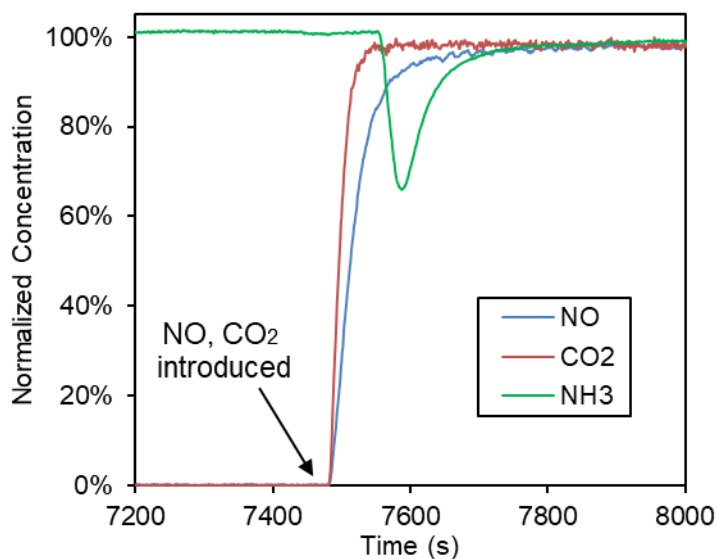


Figure S4. Normalized concentrations of NO, CO₂, NH₃ versus time during transient reduction experiment on a pre-oxidized Cu-CHA sample (Cu-CHA(15)-0.14) during exposure to 0.03 kPa NH₃ (473 K, balance N₂), followed by introduction of 0.03 kPa NO and 5 kPa CO₂.

Section S3. UV-Visible Spectroscopy

H-CHA sample was characterized with UV-Visible spectroscopy to confirm the absence of features in the d-d transition region when either no Cu is present on the sample, or the Cu is reduced to Cu(I) (d^{10}).

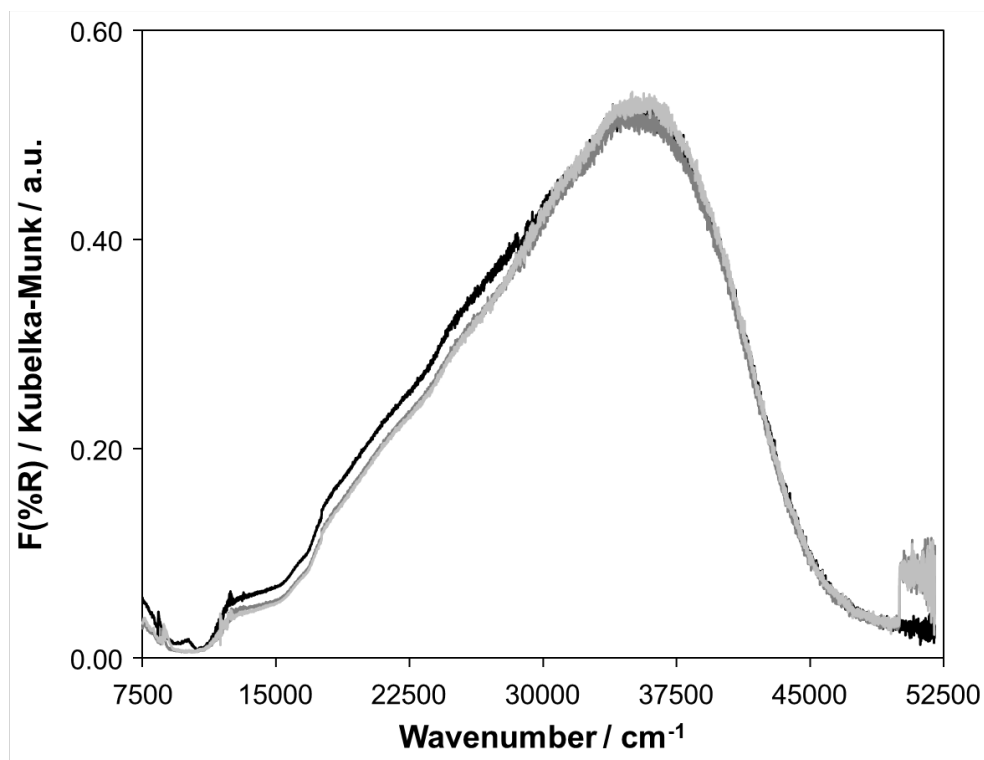


Figure S5. UV-Visible spectra collected on H-CHA (Si/Al = 15) in the presence of O₂ (21 kPa), NH₃ (0.042 kPa in balance He), or NO+NH₃ (0.042 kPa each in balance He) at 473 K.

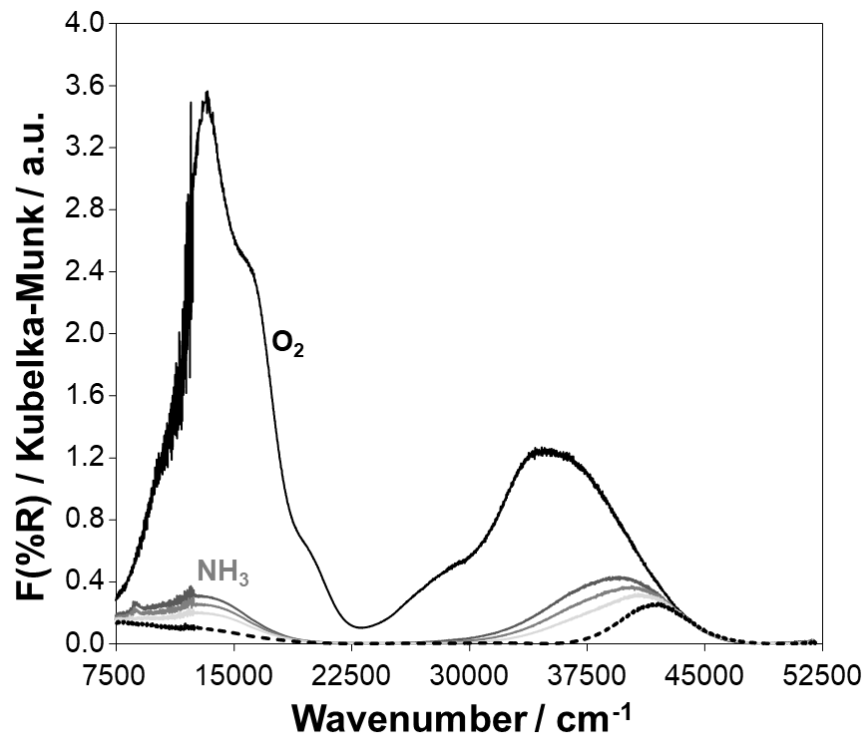


Figure S6. *In situ* UV-Visible spectra collected on Cu-CHA(25)-0.18 in the presence of O₂ (21 kPa, black spectrum), NH₃ (0.042 kPa, balance He) shown in increasing time from dark to light grayscale, and NO + NH₃ (0.042 kPa each, balance He) shown with dashed black lines at 473 K.

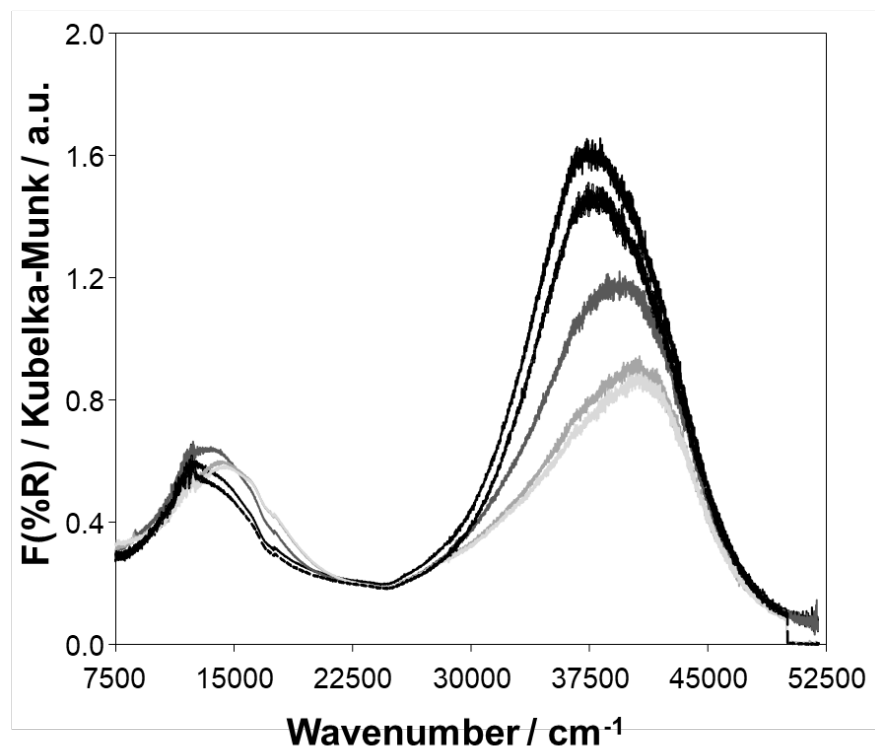


Figure S7. *In situ* UV-Visible spectra collected on Cu-CHA(15)-0.05 in the presence of O₂ (21 kPa, black spectrum), NH₃ (0.042 kPa, balance He) shown in increasing time from dark to light grayscale, and NO + NH₃ (0.042 kPa each, balance He) at 473 K.

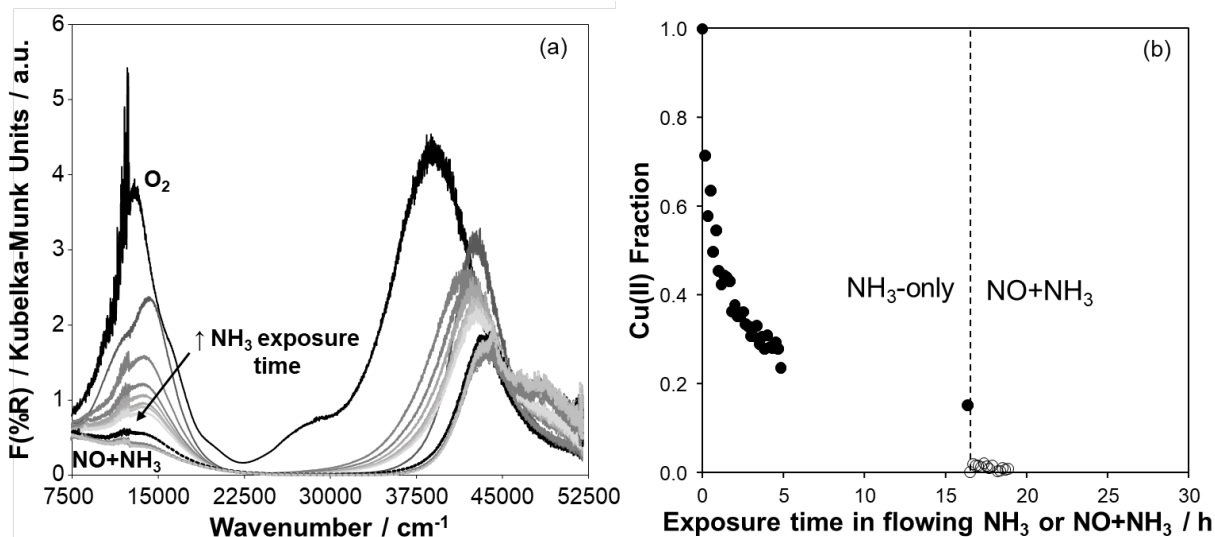


Figure S8. (a) *In situ* UV-Visible spectra (473 K) in the presence of O₂ (21 kPa), NH₃ (0.042 kPa), and balance He at 473 K (dark grey), NH₃ (0.042 kPa, balance He) shown in increasing time from dark to light grayscale, and NO + NH₃ (0.042 kPa each, balance He) shown with dashed black lines on Cu-CHA(15)-0.14, with quantification of Cu(II) estimated from integrated d-d band areas during transient exposure to NH₃-only (closed) and NO + NH₃ (open) shown in (b).

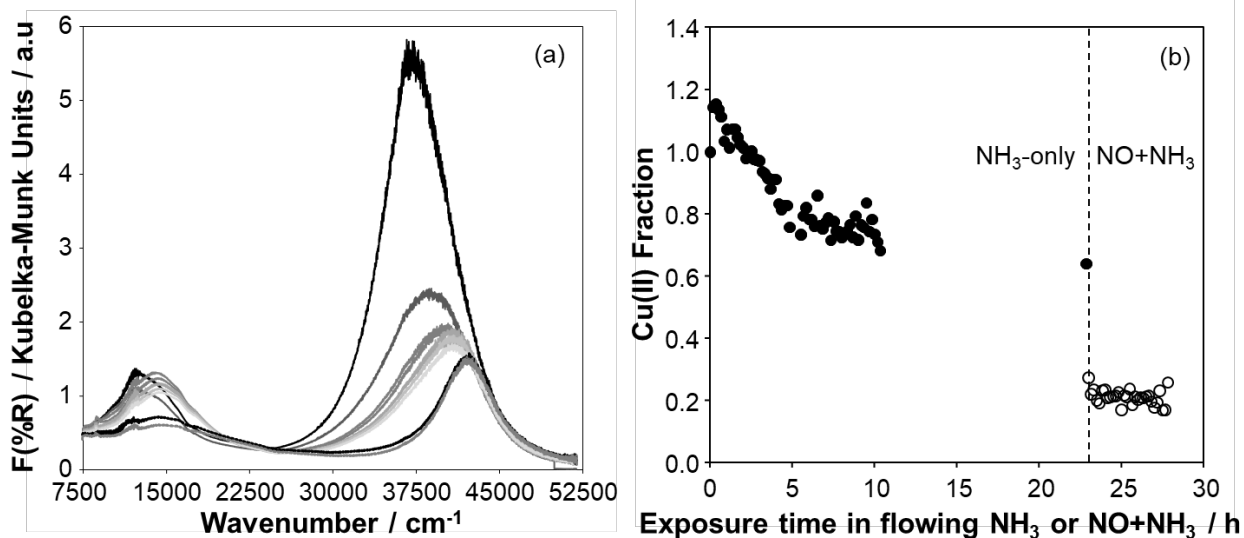


Figure S9. (a) *In situ* UV-Visible spectra (473 K) in the presence of O₂ (21 kPa), NH₃ (0.042 kPa), and balance He at 473 K (dark grey), NH₃ (0.042 kPa, balance He) shown in increasing time from dark to light grayscale, and NO + NH₃ (0.042 kPa each, balance He) shown with dashed black lines on Cu-CHA(9)-0.17, with quantification of Cu(II) estimated from integrated

d-d band areas during transient exposure to NH_3 -only (closed) and $\text{NO} + \text{NH}_3$ (open) shown in (b).

In situ UV-Visible spectra were collected with varying NO and NH_3 pressures of either 0.042 kPa or 0.094 kPa (balance He). As shown in Figure S10 below, the fraction of Cu(II) that remained after a 6 h exposure to 0.094 kPa NH_3 was approximately 0.55, while exposure to 0.042 kPa NH_3 required >10 h to reach the same extent of copper reduction. Thus, during the NH_3 -only reduction, an increase in the NH_3 pressure resulted in a more rapid reduction of Cu(II) to Cu(I) .

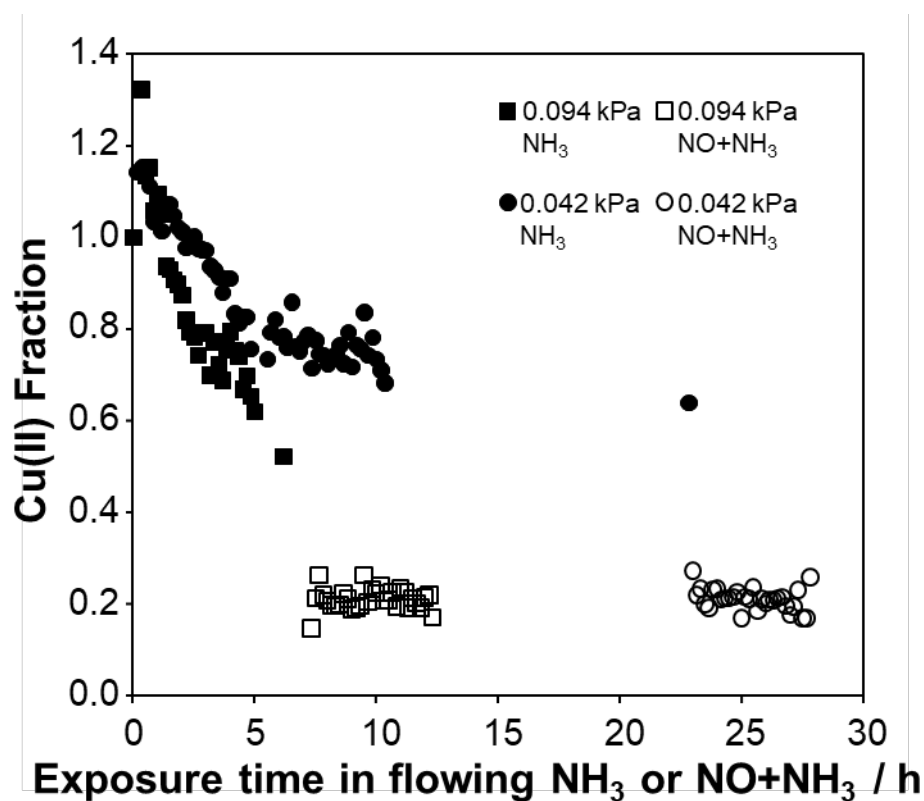


Figure S10. Cu(II) fraction as a function of time on Cu-CHA(9)-0.17 collected under different ammonia pressures of 0.042 kPa (\bullet) or 0.094 kPa (\blacksquare) at 473 K. The introduction of equivalent kPa NO to the stream is represented by the open symbols.

Section S4. *In situ* X-Ray Absorption Spectroscopy

The sample spectra were analyzed in WinXAS and normalized using first and third order polynomials for background subtraction of the pre- and post-edges, respectively. The standards used for LCF of the XANES spectra were Cu-CHA dehydrated in 21 kPa O₂ (balance He) at 723 K and Cu-CHA reduced in NO+NH₃ at 473 K, for Cu(II) and Cu(I). The Cu K-edge XANES spectra consist of several distinct features indicative of the various electronic transitions for the Cu(I) and Cu(II) oxidation states. The shoulder at 8987 eV is due to the 1s → 4p electronic transition, and the presence of features centered around 8983 eV is characteristic of the 1s → 4p transition for a two-coordinate Cu(I) complex.

Linear combination fits were determined using known standards for Cu(I) and Cu(II) as shown in Figure S11 below. The Cu(I) standard is a reduced zeolite in NO+NH₃ and the Cu(II) standard is a dehydrated zeolite. For the LCF, each spectrum was fit to include the pre-edge through the white line intensity (8.95–9.1 keV).

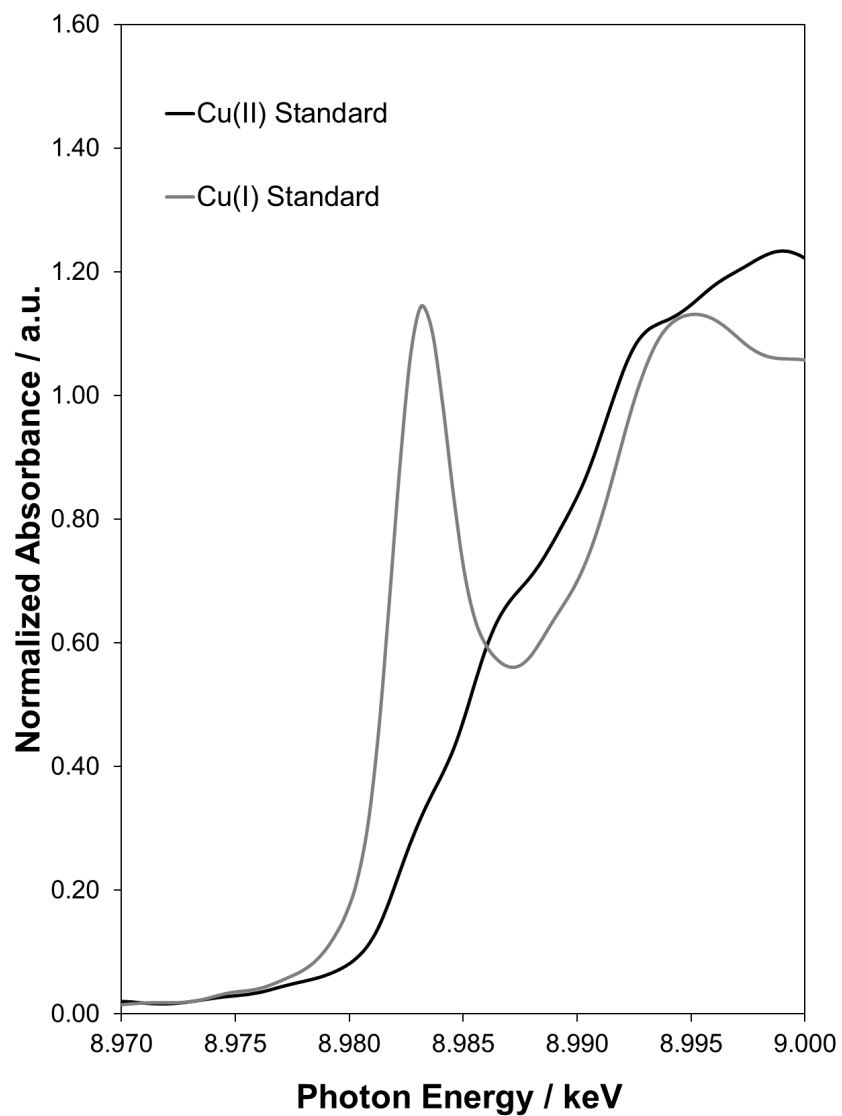


Figure S11. XANES Standards used for Cu(I) and Cu(II) for LCF of samples. The grey XANES spectrum is the Cu(I) standard (following treatment in NO and NH₃ at 473 K) and black is the Cu(II) standard (following treatment in 21 kPa O₂ at 673 K).

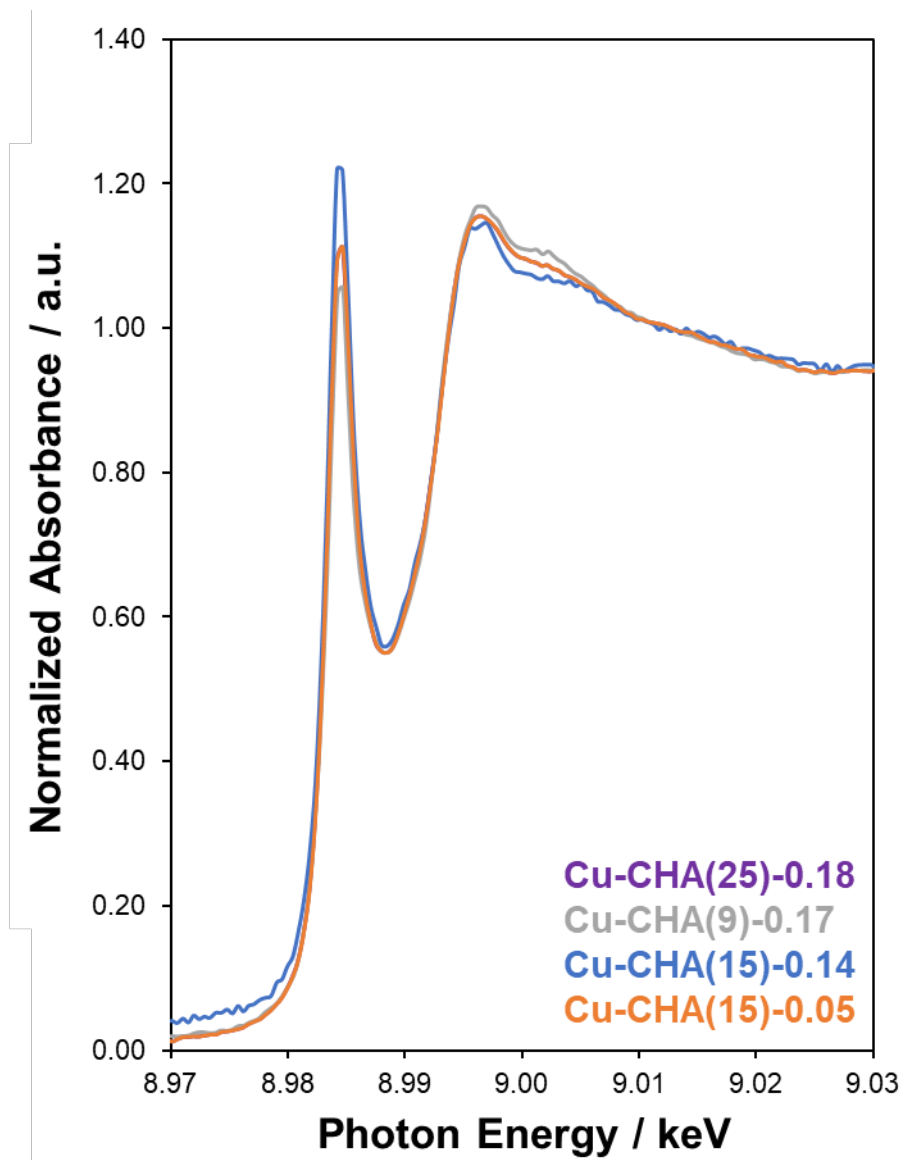


Figure S12. *In situ* XANES collected during NO+NH₃ reduction treatment at 473 K on four different Cu-CHA listed in the legend.

References

- (1) Paolucci, C.; Khurana, I.; Parekh, A. A.; Li, S.; Shih, A. J.; Li, H.; Iorio, J. R. D.; Albarracin-Caballero, J. D.; Yezerets, A.; Miller, J. T.; Delgass, W. N.; Ribeiro, F. H.; Schneider, W. F.; Gounder, R. Dynamic Multinuclear Sites Formed by Mobilized Copper Ions in NO_x Selective Catalytic Reduction. *Science* **2017**, *357* (6354), 898–903. <https://doi.org/10.1126/science.aan5630>.
- (2) Baerlocher, C. H.; McCusker, L. B. IZA Structure Commission <http://www.iza-structure.org/> (accessed 2019 -01 -30).