Supporting Information

Solvation and Mobilization of Copper Active Sites in Zeolites by Ammonia: Consequences for the Catalytic Reduction of Nitrogen Oxides

Christopher Paolucci,[#] John R. Di Iorio,^{§,†} William F. Schneider,^{*,#} and Rajamani Gounder^{*,§}

[®]Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903 (USA) [§]Charles D. Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907 (USA)

[#]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556 (USA)

*Corresponding author e-mail addresses: rgounder@purdue.edu, wschneider@nd.edu

S2.1 NH₃-SCR and Dry NO Oxidation Rates

Table S1. NH_3 -SCR kinetic parameters measured on a series of Cu-CHA samples with Si/Al = 15 and Cu/Al varying from 0.03-0.44. Data corresponding to Figure 2a (main text). Adapted with permission from ref. 1. Copyright 2017 American Association for the Advancement of Science.

| Si/Al | Cu/Al | Cu | SCR Rate (10 ⁻³ | SCR Rate (10 ⁻³ | O ₂ | E _{app} ^b |
|-------|-------|---------------------|----------------------------|----------------------------|-----------------------|-------------------------------|
| | | /1000Å ³ | mol NO/mol Cu/s) | NO/1000Å ³ /s) | order ^a | |
| 15 | 0.03 | 0.03 | 1.8 | 0.05 | 0.8 | 47 |
| 15 | 0.08 | 0.07 | 2.3 | 0.16 | 0.7 | 50 |
| 15 | 0.10 | 0.09 | 3.3 | 0.30 | 0.7 | 56 |
| 15 | 0.12 | 0.11 | 4.5 | 0.50 | 0.7 | 56 |
| 15 | 0.19 | 0.18 | 6.5 | 1.17 | 0.5 | 60 |
| 15 | 0.25 | 0.23 | 7.8 | 1.79 | 0.4 | 63 |
| 15 | 0.37 | 0.35 | 7.4 | 2.59 | 0.4 | 66 |
| 15 | 0.44 | 0.41 | 7.8 | 3.20 | 0.3 | 74 |

^aErrors are ± 0.1 .

^bErrors are \pm 7 kJ/mol.

Table S2. NH₃-SCR kinetic parameters and dry NO oxidation rates measured on a series of Cuexchanged SSZ-13 samples with Si/Al = 4.3-4.5 and Cu/Al varying from 0.02-0.39; arranged by increasing Cu/Al). Data corresponding to Figure 2b (main text). Adapted with permission from refs. 2,3. Copyright 2014 Elsevier.

| Si/Al | Cu/Al | Cu /1000Å ³ | SCR Rate (10 ⁻³ NO/1000Å ³ /s) | SCR O ₂ order ^a | SCR E _{app} | Dry NO Oxidation Rate (10 ⁻⁴ NO/1000Å ³ /s) |
|-------|-------|---------------------------|---|--|-------------------------|--|
| 4.3 | 0.02 | 0.06 | 0.2 | 0.5 | 42 | 0 |
| 4.3 | 0.04 | 0.11 | 1.5 | 0.5 | 68 | 0 |
| 4.5 | 0.09 | 0.25 | 1.8 | 0.3 | 64 | 0 |
| 4.5 | 0.16 | 0.44 | 2.8 | 0.3 | 70 | 0 |
| 4.5 | 0.20 | 0.55 | 3.6 | 0.3 | 71 | 0 |
| 4.5 | 0.31 | 0.85 | n.m. | n.m. | n.m. | 0.5 |
| 4.5 | 0.35 | 0.96 | 2.9 | 0.2 | 71 | 1.3 |
| 4.5 | 0.39 | 1.07 | n.m. | n.m. | n.m. | 1.6 |

^aErrors are ± 0.1 .

^bErrors are \pm 5 kJ/mol.

n.m. not measured

S3.1 Energies of Cu species at 1Al and 2Al sites



Figure S1. Z₂Cu energy vs Al–Al lattice separation, relative to the lowest energy structure (3NN 6-MR). Symbol color indicates connectivity distance: red–1NN, green–2NN, blue–3NN, orange–4NN, black–5NN. Lowest-energy structures and corresponding Cu–O_f distances (in Å) at each connectivity distance are shown. Atom colors: yellow–Si, green–Al, red–O, pink–H. Reproduced from ref. 4. Copyright 2018 American Chemical Society.



Figure S2. Formation free energies (ΔG_{form}) CuH_xO_y species at (left) 298 K, 2 kPa H₂O, 20 kPa O₂, and at (right) 673 K, 2 kPa H₂O, 20 kPa O₂ on the 2Al (Z₂Cu) and 1Al (ZCu) sites. Common energy reference set through Eq. (S1). Reproduced from ref. 5. Copyright 2016 American Chemical Society.

$$[Z_2CuH_2O] + [ZH] \rightarrow [ZH]/[ZH] + [ZCuOH] \quad ; \quad \Delta E = +66 \text{ kJ/mol}$$
(S1)

S3.2 Composition of Synthesized Cu-CHA Materials

Table S3. Bulk elemental analysis and fraction of isolated Cu^{2+} and Cu^{2+} (OH) sites on a series of Cu-CHA samples with varying Si/Al (4.5-25) and Cu/Al (0.03-0.59); arranged by increasing Cu/Al for a fixed Si/Al ratio. Adapted with permission from ref. 1. Copyright 2017 American Association for the Advancement of Science. Adapted from ref. 5. Copyright 2016 American Chemical Society.

| | | | H ⁺ /Al | H ⁺ /Al | | |
|-------|-------|------------------------|--------------------|--------------------|--------------------------------------|-------------------|
| Si/Al | Cu/Al | Cu /1000Å ³ | (H-form) | (Cu-form) | ZCu ²⁺ OH/Al ^a | Z_2Cu^{2+}/Al^a |
| 4.5 | 0.08 | 0.22 | 0.46 | 0.31 | 0 | 0.08 |
| 4.5 | 0.21 | 0.57 | 0.87 | 0.42 | 0 | 0.21 |
| 15 | 0.03 | 0.03 | 0.98 | 0.93 | 0 | 0.03 |
| 15 | 0.08 | 0.07 | 0.98 | 0.81 | 0 | 0.08 |
| 15 | 0.10 | 0.09 | 0.98 | 0.80 | 0.01 | 0.09 |
| 15 | 0.12 | 0.11 | 0.98 | 0.73 | 0.03 | 0.09 |
| 15 | 0.19 | 0.18 | 0.98 | 0.68 | 0.10 | 0.09 |
| 15 | 0.25 | 0.23 | 1.00 | 0.64 | 0.16 | 0.09 |
| 15 | 0.37 | 0.35 | 0.98 | 0.58 | 0.28 | 0.09 |
| 15 | 0.44 | 0.41 | 0.98 | 0.51 | 0.35 | 0.09 |
| 25 | 0.21 | 0.11 | 0.98 | 0.74 | 0.17 | 0.04 |
| 25 | 0.42 | 0.24 | 0.98 | 0.58 | 0.37 | 0.04 |
| 25 | 0.59 | 0.34 | 0.98 | 0.47 | 0.55 | 0.04 |

^aDetermined from titration of residual H^+ sites by NH_3 and thermodynamic preferences for Z_2Cu^{2+} and $ZCu^{2+}OH$ siting.^{6,7}

Titrimetric methods were developed to quantify speciation between Z_2Cu and ZCuOH site motifs, given that the former Cu sites exchange 2 H⁺ and the latter exchange only 1 H⁺. NH₃ is among the only probe bases that can fully access the microporous voids of small-pore CHA zeolites, but it adsorbs strongly on both H⁺ and Cu sites and more weakly in various physisorbed states, complicating efforts to distinguish individual site types. However, NH₃ saturation followed by H₂O purge treatments selectively retain only NH₄⁺ species, enabling quantifying residual H⁺ sites after Cu exchange.^{6,7} Cu-CHA materials expected to contain predominantly Z_2Cu or ZCuOH reveal two stoichiometric regimes (Fig. S3), corresponding to exchange of 2 or 1 H⁺ with increasing Cu²⁺ content, consistent with the preferential population of Z_2Cu before

ZCuOH sites (Fig. S2). In contrast, Co^{2+} exchanges only as Z₂Co and enumerates 2Al sites (Fig. S3), and thus titrate the same set of proximal Al as Z₂Cu.^{5,8}



Figure S3. Number of residual H⁺ sites after Cu²⁺ (solid) or Co²⁺ (open) exchange (measured by NH₃ titration) with increasing M²⁺ exchange on CHA zeolites synthesized via FAU-to-CHA interconversion (circles, Si/Al = 5), using an equimolar mixture of Na⁺ and TMAda⁺ (squares, Si/Al = 15), and using only TMAda⁺ (diamonds, Si/Al = 15). Dotted, dashed, and dot-dash lines are predicted Cu²⁺ exchange stoichiometry based on the different synthetic procedures. Reproduced from ref. 5. Copyright 2016 American Chemical Society. Reproduced from ref. 9. Copyright 2017 American Chemical Society.

S7.1 Kinetic models for the transient oxidation experiments

The following equation (a detailed derivation can be found in ref.¹) was used to model the transient oxidation of Cu^+ in O₂-assisted oxidation XAS experiments:

$$Cu^{I} Fraction = \frac{[Cu^{I}(t)]}{[Cu^{I}]_{0}} = \frac{1 - [Cu^{I}]_{\infty} / [Cu^{I}]_{0}}{1 + 2k \left([Cu^{I}]_{0} - [Cu^{I}]_{\infty} \right) t} + \frac{[Cu^{I}]_{\infty}}{[Cu^{I}]_{0}}$$
(S2)

where Cu^{I} Fraction is the time-dependent Cu^{I} concentration divided by the initial Cu^{I} concentration ($[Cu^{I}]_{0}$), *k* is a pseudo-second-order rate constant, and $[Cu^{I}]_{\infty}$ is the unoxidizable, recalcitrant fraction of Cu^{I} at the end of the transient experiment.

Table S4. Apparent rate constants (*k*), recalcitrant $[Cu^+]_{\infty}/[Cu^+]_0$ fractions, and goodness of fit (R^2) to equation S2 for the data corresponding to Figure 8. Adapted with permission from ref. 1. Copyright 2017 American Association for the Advancement of Science.

| | 0.07 Cu/1000 Å ³ | 0.22 Cu/1000 Å ³ | 0.57 Cu/1000 Å ³ |
|----------------------------------|-----------------------------|-----------------------------|-----------------------------|
| $k(m^3 \mod Cu^{-1}s^{-1})$ | 0.00011 | 0.00017 | 0.00082 |
| $[Cu^{+}]_{\infty}/[Cu^{+}]_{0}$ | 0.26 | 0.10 | 0.05 |
| R^2 | 0.99 | 0.98 | 0.99 |

S7.2 Predicted recalcitrant Cu⁺ fractions from stochastic simulations



Figure S4. Snapshots taken from stochastic simulations at initial (time = 0) and final (time $\rightarrow \infty$) Cu⁺ spatial distributions corresponding to the three samples in Figure 8. Cu⁺ volumetric footprints are denoted by 9 Å–radius green spheres. Simulation results include decomposition of unoxidized Cu⁺ fraction into physically isolated (Iso) and functionally isolated (MC) components. Reproduced with permission from ref. 1. Copyright 2017 American Association for the Advancement of Science.

S7.3 Metadynamics simulation of Cu⁺(NH₃)₂ intercage diffusion



Figure S5. On left, the metadynamics-computed free energy at 473 K of $Cu^+(NH_3)_2$ in the 72–T site CHA supercell versus Cu-Al distance. The red line is the energy profile predicted from a point-charge electrostatic model, described in SM section S9. Labeled are reactant state (1) $[Cu^+(NH_3)_2$ in the same cage as A1], transition state (2) $[Cu^+(NH_3)_2$ diffusion through 8-MR], and product state (3) $[Cu^+(NH_3)_2$ in the neighboring cage without A1]. Corresponding representative $Cu^+(NH_3)_2$ configurations from the trajectories are shown on the right. Gray, Cu; green, A1; blue, N; and white, H. Reproduced with permission from ref. 1. Copyright 2017 American Association for the Advancement of Science.

S7.4 Both Cu^+ oxidation and Cu^{2+} reduction steps are kinetically relevant during "standard" SCR

SCR rates measured at low (1 kPa) O_2 pressures on Cu-CHA increase quadratically with Cu density in the entire range of Cu densities studied (Fig. S6a), because such conditions cause Cu^+ oxidation rates to become the dominant rate-limiting step (Fig. S6b). These data demonstrate that O_2 -assisted oxidation steps prevail in all Cu-CHA zeolites,¹⁰ and that the kinetic relevance of oxidation half-cycle rates to overall SCR rates depends on both Cu density and O_2 partial pressure.



Figure S6. A) SCR rates (per 10^3 Å³, 473 K) measured on Cu-CHA samples at 1 (\blacktriangle), 10 (\bullet), and 60 kPa (\blacksquare) O₂ (other reaction conditions: 0.030 kPa NO, 0.030 kPa NH₃, 7 kPa CO₂, 1 kPa H₂O, balance N₂). Dashed lines are drawn through the origin and the rate on highest Cu content sample for each data series to guide the eye, illustrating that SCR rates deviate from a first-order dependence at dilute Cu density. B) Steady-state Cu⁺ fraction (Cu⁺/Cu_{tot}) at 1 (\bigstar), 10 (\bullet), and 60 kPa O₂ (\blacksquare) measured *in operando* by XAS as a function of Cu density. Reproduced with permission from ref. 10. Copyright 2020 Elsevier.

REFERENCES

- Paolucci, C.; Khurana, I.; Parekh, A. A.; Li, S.; Shih, A. J.; Li, H.; Di Iorio, J. R.; 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 NOx selective catalytic reduction. *Science* 2017, *357*, 898-903.
- (2) Verma, A. A.; Bates, S. A.; Anggara, T.; Paolucci, C.; Parekh, A. A.; Kamasamudram, K.; Yezerets, A.; Miller, J. T.; Delgass, W. N.; Schneider, W. F.; Ribeiro, F. H. NO oxidation: A probe reaction on Cu-SSZ-13. *J. Catal.* **2014**, *312*, 179-190.
- (3) Bates, S. A.; Verma, A. A.; Paolucci, C.; Parekh, A. A.; Anggara, T.; Yezerets, A.; Schneider, W. F.; Miller, J. T.; Delgass, W. N.; Ribeiro, F. H. Identification of the active Cu site in standard selective catalytic reduction with ammonia on Cu-SSZ-13. *J. Catal.* 2014, *312*, 87-97.
- (4) Li, S. C.; Li, H.; Gounder, R.; Debellis, A.; Mueller, I. B.; Prasad, S.; Moini, A.; Schneider, W. F. First-Principles Comparison of Proton and Divalent Copper Cation Exchange Energy Landscapes in SSZ-13 Zeolite. *J. Phys. Chem. C* 2018, *122*, 23564-23573.
- (5) Paolucci, C.; Parekh, A. A.; Khurana, I.; Di Iorio, J. R.; Li, H.; Caballero, J. D. A.; Shih, A. J.; Anggara, T.; Delgass, W. N.; Miller, J. T.; Ribeiro, F. H.; Gounder, R.; Schneider, W. F. Catalysis in a Cage: Condition-Dependent Speciation and Dynamics of Exchanged Cu Cations in SSZ-13 Zeolites. J. Am. Chem. Soc. 2016, 138, 6028-6048.
- (6) Di Iorio, J. R.; Bates, S. A.; Verma, A. A.; Delgass, W. N.; Ribeiro, F. H.; Miller, J. T.; Gounder, R. The Dynamic Nature of Brønsted Acid Sites in Cu–Zeolites During NOx Selective Catalytic Reduction: Quantification by Gas-Phase Ammonia Titration. *Top. Catal.* 2015, *58*, 424-434.
- (7) Bates, S. A.; Delgass, W. N.; Ribeiro, F. H.; Miller, J. T.; Gounder, R. Methods for NH₃ titration of Brønsted acid sites in Cu-zeolites that catalyze the selective catalytic reduction of NOx with NH₃. *J. Catal.* **2014**, *312*, 26-36.
- (8) Di Iorio, J. R.; Gounder, R. Controlling the Isolation and Pairing of Aluminum in Chabazite Zeolites Using Mixtures of Organic and Inorganic Structure-Directing Agents. *Chem. Mater.* **2016**, *28*, 2236-2247.
- (9) Di Iorio, J. R.; Nimlos, C. T.; Gounder, R. Introducing Catalytic Diversity into Single-Site Chabazite Zeolites of Fixed Composition via Synthetic Control of Active Site Proximity. *ACS Catal.* **2017**, *7*, 6663-6674.
- (10) Jones, C. B.; Khurana, I.; Krishna, S. H.; Shih, A. J.; Delgass, W. N.; Miller, J. T.; Ribeiro, F. H.; Schneider, W. F.; Gounder, R. Effects of Dioxygen Pressure on Rates of NOx Selective Catalytic Reduction with NH₃ on Cu-CHA Zeolites. *J. Catal.* **2020**, *389*, 140-149.