Effects of Zeolite Framework Topology on Cu(I) Oxidation and Cu(II) Reduction Kinetics of NO_x Selective Catalytic Reduction with NH_3

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SUMMARY

The low-temperature (<523 K) selective catalytic reduction (SCR) of nitrogen oxides proceeds on Cu-zeolites, wherein Cu cations are solvated by NH_3 and form ion-pairs with anionic lattice charges at framework Al centers. The ionic tethering of NH_3-solvated Cu ions confers regulated mobility within microporous voids, which strongly influences the pairability of Cu ions and thus SCR reactivity, yet the influence of zeolite framework topological features is not well understood. We combine steady-state kinetics and *operando* and transient X-ray absorption (XAS) measurements on different Cu-zeolite topologies to measure SCR rate constants and fractions of SCR-active Cu sites, together with statistical simulations and *ab initio* dynamics simulations, to show that changes in void size and shape among 3D cage-window zeolites have subtle effects on Cu ion pairability and SCR reactivity, but that decreasing pore dimensionality to 2D or 1D networks imposes more severe restrictions on Cu ion pairability that lowers SCR reactivity.

INTRODUCTION

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia using Cu-chabazite (Cu-CHA) zeolites is the primary component of the commercially used NO_x abatement strategy in heavy-duty lean-burn diesel engines. NO_x emission regulations are becoming more stringent globally.[1] Most NO_x emissions occur under low-load and idle conditions at which exhaust temperatures are <473 K, motivating research to identify how catalyst properties influence the underlying kinetic and mechanistic factors that determine SCR reactivity under these conditions.

The CHA framework contains one unique crystallographic tetrahedral site (T-site) located at the vertex of three 8-membered ring (8-MR) windows; Al atoms substituted for Si atoms at these T-sites generate anionic charges in the lattice, endowing the capability to charge-compensate cationic Cu cations and complexes. At reaction conditions relevant to practical low-temperature SCR operation (3–17 kPa O_2, 0.005–0.1 kPa NO and NH_3, 10 kPa H_2O, <523 K), computational and experimental data indicate that Cu ion sites are solvated by NH_3 to form NH_3-coordinated Cu complexes[2-8] (e.g., $Cu^{II}(NH_3)_4$, $Cu^{II}(OH)(NH_3)_3$ $Cu^{I}(NH_3)_2$) that serve as reaction intermediates in a Cu^I/Cu^{II} redox cycle. *Ab initio* molecular dynamics (AIMD) simulations reveal that these NH_3-coordinated cationic Cu complexes are tethered to anionic $[AlO_4]^-$ centers, are mobile within the *cha* cage,[5] and can migrate through 8-MR windows into adjacent cages with moderate energy costs.[3,5,8-10] Metadynamics and umbrella sampling simulations estimate that a $Cu^I(NH_3)_2$ complex can migrate from its conjugate Al site and through the 8-MR windows of CHA into adjoining *cha* cages, up to a distance of ~10 Å, with a free energy barrier of ~20 kJ mol^{-1} if the destination cage is vacant and ~ 35 kJ mol^{-1} if the destination cage is occupied.[3,11] Apparent activation barriers for low-temperature SCR are measured to be ~40–100 kJ mol^{-1},[3,5,6,10,12-14] implying that $Cu^I(NH_3)_2$ diffusion among the three *cha* cages adjacent to the conjugate Al site is facile relative to the other steps in the low-temperature SCR cycle.

The mobility of $Cu^I(NH_3)_2$ complexes within zeolitic void spaces becomes particularly consequential for the kinetics of the low-temperature Cu^I oxidation half-cycle, which is generally accepted to proceed via a dual-site mechanism that involves Cu ion pairing and the formation of an O_2-bridged binuclear Cu intermediate.[3,15,16] Rate constants of Cu^I oxidation and Cu^{II} reduction can be isolated by measuring the dependence of SCR rates on O_2 pressure, given that O_2 is only a reactant in the oxidation half cycle, and extrapolating rate data to limiting kinetic regimes that are first-order and zero-order in O_2 pressure, respectively.[17,18] Steady-state Cu^I oxidation rate constants (k_{first}, per total Cu, 473 K) increase monotonically over an order-of-magnitude (>15×) as the density of Cu ion sites increases in Cu-CHA (0.078–0.35 Cu per 1000 $Å^3$),[17] inconsistent with a single-site mechanism. Transient X-ray absorption spectroscopy (XAS) experiments of O_2-assisted $Cu^I(NH_3)_2$ oxidation (10 kPa O_2, 473 K) of pre-reduced Cu-CHA samples reveal the presence of a recalcitrant fraction of Cu^I that is unable to oxidize at long times, and that the amount of recalcitrant Cu^I decreases with increasing Cu density.[3,7] Statistical simulations rationalize this behavior as the consequence of the finite spatial footprint occupied by the ionically tethered $Cu^I(NH_3)_2$ complex and the intrinsic physical or dynamic functional isolation of a fraction of such Cu^I sites from another Cu^I site necessary to pair and form binuclear O_2-bridged complexes. EXAFS spectra of Cu-CHA measured at the end state of O_2-assisted oxidation treatments confirm the presence of Cu–Cu second-shell scattering characteristic of binuclear O_2-bridged dicopper complexes.[3,16,19] In contrast, transient XAS experiments report Cu^I sites in pre-reduced Cu-CHA to be completely oxidized to Cu^{II} upon exposure to NO_2 (0.01 kPa NO_2, 473 K),[3] consistent with a single-site oxidation mechanism that forms $Cu^{II}(NO_2)^-$.[20] The fraction of O_2-oxidizable

Cu^I sites, taken as a proxy for the fraction of active Cu sites during low-temperature SCR, increases systematically with Cu ion density in CHA zeolites and reflects the non-mean field behavior of solvated and mobilized Cu active sites during low-temperature SCR.

Conversely, the preponderance of data from kinetic and spectroscopic interrogations of the Cu^{II} reduction half-cycle and density functional theory (DFT) calculations are best described by a single-site mechanism. Steady-state Cu^{II} reduction rate constants (k_{zero}, per total Cu, 473 K) are similar (within ~2.5×) across a range of Cu densities and show a weakly positive dependence on Cu ion density in Cu-CHA samples (0.078–0.35 Cu per 1000 Å^3)[17] that closely resembles the increasing fraction of SCR-active Cu sites (i.e., O_2-oxidizable Cu) with Cu ion density.[17] Moreover, on the same series of Cu-CHA zeolites of varied Cu ion density, transient XAS experiments indicate that all Cu^{II} sites are reduced to the Cu^I state in NO and NH_3 (0.03 kPa NO, 0.03 kPa NH_3, 473 K),[3] consistent with a DFT-computed single-site reduction mechanism that forms $Cu^I(H_2NNO)$[3,21] and a proton. Such behavior stands in contrast with the oxidation of only some Cu^I sites during transient O_2 oxidation. Cu^{II} reduction has been proposed to also involve participation of two Cu^{II} ions, based on inferences from transient reduction data,[22] but such proposals are inconsistent with steady-state k_{zero} values (per total Cu) that are insensitive to Cu ion density and with the unity fraction of NO+NH_3-reducible Cu^{II} sites across Cu densities.

The observed sensitivity of apparent Cu^I oxidation rate constants and fraction of oxidizable Cu^I sites in Cu-CHA suggests that zeolite framework topology should influence the mobility and reactivity of Cu ion sites,[23] particularly for the Cu^I oxidation half-cycle.[24] Prior work aimed at assessing low-temperature NO_x-SCR "light-off" behavior has screened >25 zeolites of different topology and composition and reported variations in such behavior with topology,[25,26] and measurements of steady-state SCR rates (per Cu, 473 K, 1–16 kPa O_2) and transient Cu^I oxidation rates (473 K, 5% O_2) have been reported to be higher on Cu-CHA and Cu-*BEA compared to Cu-MFI and Cu-MOR;[27,28] yet, the underlying mechanistic influences of zeolite topology on observed SCR rate differences remain unclear. Changes to zeolite void sizes can alter barriers of certain elementary steps in the redox cycle, as indicated by DFT-calculated barriers associated with forming NH_3-solvated Cu^{II}–O_2–Cu^{II} complexes that are ~40 kJ mol^{-1} higher in *gme* cages than in larger *cha* and *aft* cages, because *gme* cages are too small to effectively solvate the transition state and result in repulsive interactions with framework atoms.[29] Additionally, changing pore size and connectivity should influence the fraction of SCR-active Cu sites via changes to Cu ion diffusion and mobility, which has been proposed to be more facile in Cu-CHA than Cu-MFI using measurements of the relaxation time of Cu ion motion by *in situ* impedance spectroscopy (483 K, 100 ppm NH_3) as a proxy for Cu ion mobility.[30,31] While these data suggest that zeolite framework topology can influence both the fraction of SCR-active Cu ion sites and the kinetics associated with various steps in the low-temperature SCR redox cycle, quantitative relationships between these variables are lacking.

Here, we synthesize Cu-zeolites of varied Cu ion density on materials with 3D pore dimensionality comprised of different cage sizes and shapes than CHA (AFX, AEI) and on materials of lower pore dimensionality (2D: LEV, FER; 1D: MOR). Measurements of steady-state SCR rate constants (per total Cu) for the Cu^I oxidation and Cu^{II} reduction half-cycles are determined from rate data measured over widely varying O_2 pressures[17], and are combined with transient XAS experiments to quantify the fraction of SCR-active Cu sites, in order to disentangle the influences of framework topology on the number of active sites and the kinetics of redox half-cycles, the combination of which determines observed low-temperature SCR reactivity. Steady-state rate constants, the fraction of SCR-active Cu, and apparent Cu^I oxidation and Cu^{II} reduction rate constants on each

Cu-zeolite material are compared to a Cu-CHA sample of similar Cu ion density. We extend prior statistical and dynamic analyses to predict and interpret the SCR-active Cu sites in terms of the density, spatial distribution, and accessibility of exchanged Cu^I ions as a function of framework topology and Cu/Al ratio. These comparisons reveal the particular kinetic and mechanistic benefits to low-temperature NO_x-SCR reactivity conferred by the CHA topology, which comprises a 3D framework with an open and interconnected window-cage system that facilitates Cu ion mobility and pairability to maximize the fraction of SCR-active Cu ion sites and to effectively solvate reactive intermediates and transition states in both the Cu^I oxidation and Cu^{II} reduction half-cycles.

RESULTS AND DISCUSSION

Zeolite sample characterization and topological characteristics

Zeolite samples of different cage shape, cage size, and pore connectivity were synthesized and exchanged in their Cu-forms; sample compositions and salient characterization data are summarized in Table 1 (additional characterization data in Section S1, SI). Given that the framework Al density (i.e., framework Si/Al ratio) has been reported to influence Cu speciation,[18,32] zeolite samples of different topology were synthesized to minimize the variation in composition (Si/Al = 9-15, Table 1) within the constraints of available synthesis protocols. Each sample showed powder XRD patterns (Figures S1–S5, SI) and micropore volumes (Table S1, Figures S6–S10, SI) that were consistent with the intended zeolite topology. Cu volumetric densities are calculated using theoretical T-site densities for each framework and the Si/Al and Cu/Al of each sample (Section S2, SI). Samples are denoted Cu-ZZZ-X, where ZZZ is the three-letter IZA code for the framework topology and X is the Cu volumetric density (per 10^3 $Å^3$). Six different zeolite framework structures (CHA, AEI, AFX, LEV, FER, MOR) were examined here, and their main topological features are summarized in Scheme 1.

CHA, AEI, and AFX belong to the family of eight-membered ring (8-MR) cage-window zeolites composed solely of stacked double six-membered ring (d6r) building units (ABC-6 family),[33,34] but different ordering in d6r stacking results in different cage shapes and pore size distributions, as shown in Figure 1. The d6r stacking in the CHA framework results in cylindrical cages (7.9 × 7.9 Å × Å, assuming an atomic radius of 1.35 Å) that are connected via 8-MR windows (3.7 × 3.7 Å) to form a porous network with 3-D connectivity. The AEI framework topology is also constructed using the same repeating d6r building units; however, every other plane is rotated 90° about the z-axis, resulting in a pear-shaped cage connected via 8-MR windows that are slightly larger than those of CHA (Scheme 1). Finally, AFX contains cages that are both smaller (*gme*) and larger (*aft*) than the *cha* cage. The different stacking arrangement of AFX yields 8-MR windows that are slightly larger (*aft-aft*) or smaller (*aft-gme*) than those of CHA. The dimensions of the different cages are shown in Scheme 1. The void size of frameworks with homogeneous cages, such as CHA and AEI, can be described well using the maximum diameter of a sphere that can be included (7.37 Å and 7.33 Å, respectively); however, AFX has multiple void environments that are not captured by a single spherical diameter. Instead, the void space occupied by pores of a certain size can be captured by the pore size distribution, which determines the largest sphere that encapsulates a sampled point without colliding with framework atoms. Here, points are sampled with a probe radius of 1.3 Å (representing NH_3 with a kinetic diameter of 2.6 Å), and the fraction of void space that corresponds to voids of a certain size are visualized with the derivative distribution, reported in Figure 1. The majority of the CHA void space is represented by voids of ~7 Å, reflecting the homogeneous cage voids within the CHA unit cell. The AEI framework has cages with similar void size but different shape than CHA, characterized by a single peak at ~7 Å. Conversely, the AFX framework has voids that are similar in size (7.1 Å, *aft* cages) or smaller (5.2 Å, *gme* cages) than *cha* cages.

Each CHA cage is connected to six identical cages via 8-MR windows, yielding a three-dimensional (3D) framework; however, we also investigate two-dimensional (2D) and one-dimensional (1D) frameworks. LEV is chosen as a representative 2D framework because, like CHA, it is a window-cage structure in the ABC-6 topological family. The voids of LEV cages are smaller than CHA, characterized by a pore size distribution consisting of a single peak at 6.7 Å. Each LEV cage is connected to three cages via 8-MR windows, as compared to the six neighboring cages of CHA, thereby creating fewer possible diffusion pathways for species confined within zeolitic voids (Scheme 1). FER is another 2D structure with interconnected 10-MR and 8-MR channels. The dimensions of the 8-MR and 10-MR channels are larger than the 8-MR windows of CHA, however, the void space of FER is smaller than that of the CHA cages and ranges from 5–5.4 Å. Finally, MOR is a 1-dimensional structure with 12-MR channels and 8-MR side pockets and has a larger void (6.3 Å, channel system) and a smaller void space (4.8 Å, 8MR side pockets).

Influence of cage shape and cage size in 8-MR zeolites on transient and steady-state SCR kinetics

The effects of cage size on SCR rate constants were assessed by comparing steady-state and transient kinetic behavior on Cu-AFX to Cu-CHA. Steady-state SCR rates (per Cu) on two Cu-AFX samples of different Cu density show a Langmurian dependence on dioxygen pressure (Figs. 2a, 2b), consistent with rates limited by the Cu^{I} oxidation half-cycle in the low O_2 pressure limit and rates limited by the Cu^{II} reduction half-cycle in the high O_2 pressure limit, as in the case of Cu-CHA.[17] Apparent rate constants for the Cu^{II} reduction-limited regime (k_{zero}) and Cu^{I} oxidation-limited regime (k_{first}) were determined by fitting rate data to the empirical Langmurian model used in our previous work (details in Section S.4, SI),[17] and are summarized in Table 2. Values of k_{first} and k_{zero} for Cu-AFX-0.27 and Cu-AFX-0.32 were compared to those for Cu-CHA samples with similar Cu density (within ~10%; Cu-CHA-0.29 and Cu-CHA-0.31, respectively) and shown as rate constant ratios in Figure 2c. Values of k_{first} are 1.8–2.6× lower while k_{zero} is ~1.5× lower on Cu-AFX compared to their respective Cu-CHA counterparts (Fig. 2c). The slightly lower rate constants (within 1.5–3×) on AFX relative to CHA may reflect lower kinetic constants associated with apparent Cu^{I} oxidation and Cu^{II} reduction half-cycles or a lower fraction of SCR-active Cu sites, as probed next using transient XAS techniques.

Transient XANES and EXAFS experiments were used to independently measure the fraction of active Cu (Cu_{active}) and the apparent rate constants associated with Cu^{I} oxidation with O_2 (k_{ox}) and Cu^{II} reduction with NO and NH_3 (k_{red}). First, the Cu-AFX-0.32 sample was oxidized in flowing O_2 (10 kPa, 673 K) to convert all Cu ions to framework-bound Cu^{II} species, as evidenced by EXAFS spectra that are characteristic of framework-bound Cu ions with a second-shell Cu–Si/Al scattering feature at ~2.5 Å (Section S5, SI). The sample was then exposed to flowing NO and NH_3 (0.03 kPa NH_3, 0.03 kPa NO, 473 K); after ~500s of NO and NH_3 exposure, all Cu^{II} sites were reduced to $Cu^{I}(NH_3)_2$, as evidenced by EXAFS spectra that show a first-shell Cu–O/N coordination number of ~2.6 and the disappearance of the second-shell Cu–Si/Al scattering feature (Fig. S18, SI). The fraction of Cu^{II} sites quantified from linear-combination XANES fitting during the first Cu^{II} reduction transient on Cu-AFX-0.32 is shown in Figure 3, and the ability of NO and NH_3 to reduce nearly all (>0.90) Cu^{II} sites to the Cu^{I} state in AFX is consistent with previous measurements on CHA samples of varying Cu density[3] (Table 2). Based on previous work in Cu-CHA, reduction transients are always best-fit to models that are first-order in Cu^{II}. Out of thoroughness, we assessed whether the first reduction transient in Cu-AFX (and all Cu-zeolites) could be described by models that are either first-order or second-order in Cu^{II} concentration, however, this transient on Cu-AFX is not well-described by either rate model (determined by the sum of square errors >0.1 on both fits, Table S4, SI). Such behavior may reflect the convolution of NH_3 solvating multinuclear Cu sites, possibly present on the sample, with Cu^{II} reduction behavior.

After the initial reduction transient, $Cu^I(NH_3)_2$ species in Cu-AFX-0.32 were exposed to O_2 (10 kPa and 473 K), and transient oxidation to the Cu^{II} state was quantified by XAS and shown in Figure 3. EXAFS spectra at the end of the oxidation transient show a first-shell Cu–O/N coordination that increases to ~3.6 and the appearance of a feature at ~2.5 Å consistent with second-shell Cu–Cu scattering (Fig. S19, SI); similar observations in Cu-CHA have been attributed to formation of NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ species. Within ~700s of O_2 exposure, the fraction of Cu^{II} approached a steady-state value of 0.91 ± 0.05, which is comparable to the fraction of O_2-oxidizable Cu^{II} quantified in Cu-CHA-0.31 (0.85 ± 0.05, Table 2). The fraction of active Cu is calculated as the difference in the fraction of reduced Cu^{II} ($Cu_{reducible}$) and recalcitrant Cu^I at the end of the first and second transients, respectively (Fig. 3 and Table S6, SI). For Cu-CHA, all Cu ions are assumed to be reducible, consistent with our prior work.[17] Values of Cu_{active} are reported in Table 2 and are identical for Cu-AFX-0.32 (0.84 ± 0.1) and Cu-CHA-0.31 (0.85 ± 0.05). These data indicate that $Cu^I(NH_3)_2$, when present at similar volumetric densities, can form a similar number of SCR-active Cu sites within the 3D cage-window topologies of AFX and CHA.

The transient rate of Cu^{II} formation on Cu-AFX-0.32 during the O_2 oxidation transient is best described by a rate model that is second-order in Cu^I (Section S6, SI), as in the case of Cu-CHA samples (0.078–0.35 10^3 $Å^3$).[3,17] The apparent Cu^I oxidation rate constant (k_{ox}) is 3.7× lower on Cu-AFX-0.32 than Cu-CHA-0.31, and this resembles steady-state k_{first} values that are 1.8× lower on Cu-AFX-0.32 than Cu-CHA-0.31 (Table 2). The apparent oxidation rate constant, k_{ox}, reflects kinetics associated with $Cu^I(NH_3)_2$ diffusion through the 8-MR windows and its subsequent pairing to form NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ complexes. Given that Cu_{active} is identical in Cu-CHA and Cu-AFX (Table 2), and that both frameworks consist of 8-MR windows of similar dimensions (Scheme 1), $Cu^I(NH_3)_2$ diffusion barriers are expected to be similar for the two frameworks. Thus, lower k_{ox} values might suggest that the transition state to form the NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ intermediate is less stable within the voids of AFX, which are either similarly sized (7.1 Å) or smaller (5.2 Å) than the voids of CHA (7 Å, Fig. 1). Such an interpretation is qualitatively consistent with DFT-calculated energies of pairs of $Cu^I(NH_3)_2$ within the same cage and formation barriers of NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ binuclear intermediates that are 20–40 kJ mol^{-1} less stable in smaller *gme* cages compared to larger *cha* and *aft* cages.[29]

Finally, after the O_2-assisted Cu^I oxidation of Cu-AFX-0.32, which should result in some fraction of NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ species,[3,7,8,16,35] a second Cu^{II} reduction transient is measured in NO and NH_3 to compare the kinetics of Cu^{II} reduction from a predominantly mononuclear Cu^{II} state ($k_{red,1}$) or binuclear Cu^{II} state ($k_{red,2}$, Fig. 3). The first Cu^{II} reduction transient is measured after a high temperature oxidation treatment, where Cu^{II} ions are framework-bound; as such, the apparent rate constant, $k_{1,red}$, may reflect processes involved with both solvating framework-bound Cu^{II} ions with NH_3 and reducing NH_3-solvated Cu^{II} ions with NO. During the first NO+NH_3 reduction, the transient rate of Cu^{II} disappearance is not well-described by rate models that are either first-order or second-order in Cu^{II} concentration, evidenced by large residual sum of squared errors between the measured data and rate-model fits (Table S4, SI). Such behavior can be rationalized by the influence of NH_3 exposure of oxidized Cu-zeolite samples, as *in situ* UV-Visible spectroscopy experiments show that introducing NH_3 prior to NO to fully solvate Cu^{II} sites results in faster Cu^{II} reduction rates than when NH_3 and NO are introduced together (Section S8, SI). Conversely, the second reduction transient is measured on a sample that contains predominantly NH_3-solvated mononuclear Cu^{I} and binuclear Cu^{II} species. In the second reduction transient, within ~280s of NO and NH_3 exposure, all Cu^{II} species were reduced to Cu^{I} (Fig. 3), which is faster than the time required in the first reduction transient (~500s) to cause reduction to Cu^{I}. Different studies reported previously from our group[17] have measured $k_{red,1}$ and $k_{red,2}$ values for a series of Cu-CHA samples with varying Si/Al (6–25) and Cu density (0.08–0.35) (Fig. S42, SI). The rate constants of the second reduction transients are, on average, 1.3× higher than for the first reduction transients, indicating that Cu^{II} reduction can occur from both the mononuclear or binuclear state, and at faster rates from the binuclear state. Despite faster reduction kinetics, the fraction of Cu^{I} is nearly identical after the end of the first and second reduction transients (0.10 ± 0.05 and 0.04 ± 0.05, respectively), reflecting a consistent fraction of reducible Cu^{I} sites on both CHA and AFX.

To assess the effects of cage shape on SCR kinetics, steady-state rates (473 K, per Cu) were measured as a function of dioxygen pressure on three Cu-AEI samples and compared to Cu-CHA samples at similar Cu densities (Fig. 4a–c). SCR rates (per Cu) show a Langmurian dependence on O_2 pressure in Cu-AEI, akin to observations on Cu-CHA. Moreover, *operando* XAS measurements of Cu-AEI-0.25 show that increasing O_2 pressure also increases the steady-state Cu^{II} fraction, reflecting a transition of Cu^{I} oxidation-limited to Cu^{II} reduction-limited rates with increasing O_2 pressures, as previously reported on Cu-CHA[17] (Fig. 4d). Values of k_{first} are systematically lower (by ~1.7×), while values of k_{zero} are similar and vary non-systematically (within 1.3×), on Cu-AEI compared to Cu-CHA of similar Cu density (Table 2, Fig. 4e). Together, these data indicate that Cu ions show similar kinetic behavior when confined within either AEI or CHA, although with systematically lower rates (by 2×) for AEI in kinetic regimes limited by the Cu^{I} oxidation half-cycle.

Transient reduction and oxidation XAS experiments were performed to provide more insight into the lower steady-state Cu^{I} oxidation rate constants (k_{first}) on Cu-AEI compared to Cu-CHA, and are shown in Figure 5. The sample was first oxidized in flowing O_2 (10 kPa, 673 K) to convert Cu ions to framework-bound Cu^{II} and was then exposed to flowing NO+NH_3 (0.03 kPa NO, 0.03 kPa NH_3, 473 K) to reduce Cu ions to the Cu^{I} state. After ~900 seconds of NO+NH_3 exposure, all Cu^{II} ions are reduced to Cu^{I}; however, the transient behavior is not well-described by rate laws that are either first-order or second-order in Cu^{II} concentration, possibly reflecting the convolution of NH_3 solvation and reduction behavior (Fig. S21, SI). After reduction, the EXAFS spectra shows only a first-shell scatter peak with a Cu–O/N coordination number of ~2.4, which is consistent with observations in Cu-CHA[5] and formation of $Cu^{I}(NH_3)_2$.

After the first reduction transient, the sample is exposed to flowing O_2 (10 kPa, 473 K), but a sub-unity fraction of Cu^{I} (~0.80, Fig. 5 and Table S3, SI) re-oxidizes to Cu^{II}. The transient rate of Cu^{I} oxidation on Cu-AEI-0.25 is best-fit to a model that is second-order in Cu^{I}, with a k_{ox} value that is within the error of Cu-CHA-0.23. After oxidation, the Cu–O/N first-shell coordination number increases to 3.8 and a second-shell Cu–Cu scattering feature at 2.5 Å appears, consistent with formation of NH_3-solvated Cu^{II}–O_2–Cu^{II} structures. Typical EXAFS analysis in R-space, however, cannot distinguish between Cu–Si/Al scattering with framework atoms and Cu–Cu scattering because both scattering paths occur at ~2.5 Å. To resolve these contributions, the k^2-weighted EXAFS signal can be combined with R-space information with a wavelet transform to visualize different atomic elements in k and R space simultaneously, as has recently been used in Cu-zeolites[16,19,35-38] and performed here for Cu-AEI, because this sample has the highest quality EXAFS spectra (Section S5, SI). Cu–Cu scattering contributions are localized at ~7 $Å^{-1}$ in k-space and do not overlap with contributions from Cu–Si/Al framework atom scattering localized at 4 $Å^{-1}$ in k-space. Upon oxidation of Cu-AEI, the wavelet transform shows appearance of a small feature at 7 $Å^{-1}$, corresponding to Cu–Cu scatter, with a bond distance of ~2.5 Å (Fig. 5c). This suggests that the appearance of second-shell scatter at 2.5 Å in R-space can be attributed, at least in part, to the formation of NH_3-solvated $Cu^{II}–O_2–Cu^{II}$ complexes in Cu-AEI, as also reported on Cu-CHA.[3,19]

The fraction of Cu_{active} on Cu-AEI-0.25 (0.75 ± 0.1) is similar to that on Cu-CHA-0.23 (0.85 ± 0.05, Table 2) and Cu-AFX-0.32 (0.84 ± 0.10, Table 2), suggesting that topological differences between 3D cage-window topologies only weakly influence the fraction of O_2-oxidizable $Cu^I(NH_3)_2$ complexes. The fraction of O_2-oxidizable Cu^I, as measured by XAS in a series of Cu-CHA samples of varying Cu density, can be rationalized by accounting for the fraction of Cu^I pairs separated by one cage (i.e., transit of one Cu^I away from its host Al center and through an 8-MR window to an adjacent cage).[18] The same statistical models are applied here to count the number of ring transits necessary for a fraction of Cu^I to find a partner Cu^I site (details in Section S.9, SI) in Cu-AEI and Cu-AFX topologies. Briefly, the models capture the location of Al in the framework lattice, the association of Cu^I with those Al, and the accessibility of Cu^I to each other based on the number of cages that must be traversed (illustrated for CHA, AEI, and AFX in Fig. S48, SI). We distributed Al randomly subject to Löwenstein's rule to the target Si/Al ratio and randomly assigned Cu^I to Al to the target Cu/Al ratio. We sequentially titrated Cu^I pairs based on the number of cage separations, and titrations were conducted from 0 to 0.4 Cu/1000$Å^3$ in increments of 0.01 Cu/1000$Å^3$.

Figure 6a–c reports the oxidizable Cu^I fraction for a given maximum number of cage transits across CHA, AEI, and AFX, respectively, as a function of the Cu volumetric density. The blue region indicates Cu that are anchored to Al shared by a common cage; successive colored regions indicate anchored Cu that must pass through increasing numbers of 8-MR windows to access one another. Figure 6a displays the results for CHA, which are consistent with our prior results,[18] wherein the experimentally measured Cu_{active} fraction corresponds within error to the fraction of Cu^I that are at most separated by one cage. This separation is consistent with the 9 Å migration distance inferred from our earlier transient O_2-assisted oxidation experiments and models.[3] This result highlights that apparent oxidation rates, measured during transient and potentially steady-state experiments, convolute reactions of Cu^I ions that must make different transits to react, and further that the relative proportions of Cu^I ions that react change with increasing Cu density. Thus, higher apparent Cu^I oxidation rates with increasing Cu density potentially reflect both a higher fraction of reactive Cu^I and Cu^I that are maximally proximal.

Figure 6b shows titration results for AEI. CHA and AEI share the same topology and connectivity, so the simulation results are identical. The experimentally measured oxidizable fraction of Cu^I lies within the window, but below the top, of the single 8-MR accessible Cu^I (red region), potentially suggesting some other factor that may limit Cu^I pairability in AEI. These differences may also reflect differences in the Al distribution in CHA and AEI samples synthesized experimentally. To test the sensitivity of the fraction of oxidiziable Cu^I sites to Al distribution, we extracted the extrema across all realizations of the Al distribution in AEI and performed simulated Cu^I titrations (results shown in Fig. S49, SI), which indicated that the fraction of oxidizable Cu^I is weakly sensitive to Al distribution. To explore the extent to which the real physical separation of Al influences Cu^I pairability, we compared the distance distribution of Cu separated by zero and one cages in CHA versus AEI (results shown in

Fig. S50, SI), but the results are indistinguishable. Thus, small differences in experimentally measured oxidation reactivity between CHA and AEI reflect differences not captured by topology.

Figure 6c shows titration results for AFX. AFX is comprised of larger *aft* and smaller *gme* cages; we assume that Cu^I preferentially occupy and transport through the latter. This assumption leads to the same conclusion that the oxidizable Cu^I fraction corresponds to Cu^I separated by at most one *aft* cage. The number of these sites in AFX is similar to that in CHA and AEI at the measured Cu/Al ratio of 0.32, although it is expected to decrease more rapidly with decreasing Cu density than on CHA and AEI. The Cu distance distribution in AFX shows a tail to greater distances than in CHA (Fig. S51, SI), suggesting that differences in oxidation rates may reflect differences in distances that Cu^I must travel from anchoring Al to pair with another Cu^I.

Overall, these steady-state and transient data suggest that topological changes to cage shape among 3D 8-MR window-cage zeolites (CHA, AEI, AFX), compared at similar Cu ion densities, weakly influence the fraction of SCR-active Cu ion sites and rates of Cu^{II} reduction reactions. The oxidizable fraction of Cu^I on all three frameworks appears to correspond to Cu^I pairs separated by no more than one cage. Apparent transient rate constants for Cu^I oxidation with O_2 (k_{ox}) are comparable or lower on AEI and AFX than on CHA, and by similar factors as steady-state rate constants measured in Cu^I-oxidation limited regimes (k_{first}). Oxidation rates likely convolve contributions of Cu^I that travel across zero or one cage to pair, and differences in the physical distances of anchoring Al sites. Lastly, as noted elsewhere,[18] oxidation rates are sensitive to Al as well as Cu density, and these material properties may influence observed differences among the cage-window frameworks.

Influence of pore dimensionality on transient and steady-state SCR kinetics on Cu-zeolites

To investigate the effects of framework dimensionality on SCR kinetics, SCR rates (per total Cu) were measured with varying dioxygen pressure on Cu-LEV-0.18 and compared to previously reported data on Cu-CHA-0.17 (Fig. 7). Even at the highest O_2 pressures studied (60 kPa), SCR rates on Cu-LEV are near first-order in O_2 pressure, suggesting that Cu^I oxidation is significantly slower on Cu-LEV than Cu-CHA. The ratios of k_{first} and k_{zero} values on Cu-LEV-0.18 compared to Cu-CHA-0.17 are shown in Fig. 7b and reported in Table 3, and rate constants are nearly an order-of-magnitude lower on Cu-LEV. Such differences reflect the more substantial impact on SCR reactivity when decreasing the pore dimensionality from 3D to 2D, as compared to cage shape and size within 3D pore networks of 8-MR cage-window zeolites.

To interpret these differences in steady-state rate constants, transient XAS experiments were used to measure the fraction of Cu_{active} and apparent oxidation and reduction kinetics in Cu-LEV-0.18 and are reported in Figure 7c (EXAFS reported in Section S5, SI). The sample is first oxidized at high temperature in flowing O_2 (10 kPa, 673 K) then exposed to NO and NH_3 at lower temperature (0.03 kPa NO, 0.03 kPa NH_3, 473 K) to reduce Cu species to their Cu^I state. After this first reduction transient, EXAFS spectra show a first shell Cu–N scattering feature with a coordination number of 2.5, consistent with Cu ion solvation and formation of $Cu^I(NH_3)_2$. The transient rate of Cu^{II} reduction is best fit to a model that is first-order in Cu^{II} (fitting details in Section S6, SI), as in the case of Cu-CHA.[3] In contrast to Cu-CHA, however, a larger fraction of Cu^{II} ions, 0.14 (±0.05), do not reduce in Cu-LEV after exposure to NH_3 and NO.

After the initial reduction transient, the Cu-LEV sample was exposed to flowing O_2 (10 kPa, 473 K) to probe oxidation of $Cu^I(NH_3)_2$. The EXAFS spectrum at the end of the oxidation treatment shows second-shell peak at 2.5 Å characteristic of Cu–Cu scattering and an increase in the first-shell Cu–O/N coordination number to 3.7, both of which are consistent with formation of NH_3-solvated Cu^{II}–O_2–Cu^{II} intermediates (Section S6, SI). A sub-unity fraction of Cu ions, 0.69 (±0.05), are re-oxidized to Cu^{II}. The fraction of Cu_{active} is 0.55 in Cu-LEV-0.18, substantially lower than the 0.78 fraction of Cu_{active} in Cu-CHA-0.17, suggesting that a higher fraction of Cu ions are physically or functionally isolated in Cu-LEV. The rate constant for Cu^I oxidation on Cu-LEV-0.18, determined from fitting the oxidation transient to a model that is second-order in Cu^I, is within error the same as on Cu-CHA-0.17 (Table 3).

As shown in Scheme 1, while LEV has a cage-window structure, 8-MR windows only allow transit to three neighbor cages. We constructed a statistical model for pairable Cu^I that captures this hexagonal LEV cage connectivity (Fig. S47, SI) and titrated pairs following the same cage-separation priority, with the results shown in Figure 6d. Pairable Cu^I are suppressed relative to the 3D frameworks (CHA, AEI, AFX) at every value of cage separation and fails to reach unity even at six cage separations. The experimentally observed Cu_{active} is located (within uncertainty) at the top of the window of single cage separations (red region), as in the 3D frameworks. The Al-Al probability distributions are similar on CHA and LEV (Fig. S52, SI), so differences in Cu_{active} are attributable to differences in pore connectivity. Further, the statistical model predicts not only a smaller fraction of Cu^I of sufficient proximity to form Cu^I pairs on LEV, but also a greater fraction of Cu^I that must travel to a remote cage to pair and react, likely contributing to the lower observed k_{first} values.

After the oxidation transient, Cu-LEV-0.18 was exposed to flowing NO+NH_3 to measure the second NH_3-solvated Cu^{II} ion reduction transient , some portion of which are O_2-bridged binuclear Cu^{II} species (Fig. S26, SI). The rate of Cu^{II} reduction in the second transient is also best described by a rate model that is first-order in Cu^{II}; however, the rate constant of the second reduction transient, $k_{red,2}$, is ~2× faster than for the first reduction transient (Table 3). The final fraction of reduced Cu^{II} is the same after the first and second reduction transients (0.14 ± 0.05 and 0.13 ± 0.05, respectively, Table S4, SI). As observed for 3D 8-MR cage-window zeolites (Section 3.2), reduction of the binuclear Cu^{II} state is faster than the mononuclear Cu^{II} state in LEV, implying that the binuclear Cu^{II} state is more relevant to the steady-state SCR reduction half-cycle.

FER is a 2D framework like LEV, but rather than cages and windows, it is composed of 10-MR and 8-MR channels (Scheme 1) with pores that range in size from 5–5.5 Å (Fig. 1). SCR rates (per Cu) on two Cu-FER samples were measured as a function of dioxygen pressure and are reported in Figure 8, along with the SCR rates (per Cu) of Cu-CHA samples at similar Cu densities. On Cu-FER-0.09, SCR rates are nearly first-order in the O_2 pressure range examined here, indicating that rates are limited by Cu^I oxidation across the range of O_2 pressures studied. On Cu-FER-0.19, however, SCR rates show a first- to zero-order transition with increasing O_2 pressure. Such behavior is consistent with *operando* XAS experiments in Cu-CHA demonstrating the fraction of Cu^{II}, and thus the kinetic relevance of Cu^{II} reduction steps, increases with Cu ion density.[17] The O_2 pressure at which the SCR rate (per Cu) of Cu-FER-0.19 transitions to a zero-order dependence is less than that of Cu-CHA-0.17, resulting in a k_{first} value that has relatively large errors and is nearly identical to that of Cu-CHA-0.17 (Fig. 8c). Conversely, k_{first} for Cu-FER-0.09 is ~5.5× lower than Cu-CHA-0.10. These inconclusive trends among the two FER samples may also indicate an inhomogeneous Cu spatial distribution within FER samples resulting from different preferences of Cu ion siting within 8-MR and 10-MR voids of FER.

Transient XAS experiments were performed to measure the fraction of Cu_{active} and the rate constants associated with Cu^{II} reduction and Cu^{I} oxidation processes, as shown in Figure 9. After high temperature oxidation (10 kPa O_2, 673 K), the samples were introduced to flowing NO and NH_3 to measure the rate of Cu^{II} reduction. After reduction, the EXAFS spectrum of Cu-FER-0.19 shows a decrease in the magnitude of the first-shell for Cu–O/N scattering and disappearance of second-shell Cu–Si/Al scattering from framework atoms (Fig. S29, SI) reflecting formation of $Cu^{I}(NH_3)_2$. Additionally, ~20% of Cu^{II} is not reducible in both Cu-FER samples. The initial reduction transient in Cu-FER-0.09 can be fit to a model that is first-order in Cu^{II} (Fig. 9b). However, the initial Cu-FER-0.19 reduction transient is not well described by first- or second-order rate models in Cu^{II}. This may reflect higher Cu densities in FER leading to higher fractions of binuclear or multinuclear Cu-oxo clusters, which may convolute NH_3 solvation and conversion of such species to mononuclear Cu^{II} sites and their subsequent reduction to the Cu^{I} state in the initial reduction transient (Section S8, SI). Conversely, the lower Cu density in the Cu-FER-0.09 sample may lead to the presence of mostly monomeric Cu^{II} sites, resulting in more rapid NH_3 solvation of Cu and an initial reduction transient that predominantly reflects Cu^{II} reduction to the Cu^{I} state.

After the first reduction transient, both samples are exposed to 10 kPa O_2 (473 K) to measure the rate of $Cu^{I}(NH_3)_2$ oxidation (Fig. 9). In the oxidized Cu-FER-0.19 sample, the EXAFS spectrum shows an increase in first-shell coordination number from 2.8 to 4.4 and the appearance of a second-shell scattering feature at ~2.5 Å (Fig. S31, SI), and both observations are consistent with formation of an NH_3-solvated binuclear Cu complex. Both Cu-FER samples show a fraction of recalcitrant Cu^{I}, which is slightly higher in Cu-FER-0.09 (0.15 ± 0.05) than in Cu-FER-0.19 (0.09 ± 0.05). The fraction of Cu_{active} is systematically lower on Cu-FER samples relative to Cu-CHA at a similar Cu density (Table 3). The transient oxidation behavior on both samples is best described by a rate model that is second-order in Cu^{II} (Section S6, SI). The apparent oxidation rate constants are ~2× faster in Cu-FER-0.09 than Cu-FER-0.19 (Table 3); in contrast, k_{ox} values in Cu-CHA samples (0.084–0.32 Cu per 10^3 $Å^3$) systematically increase with Cu loading.

FER (Scheme 1) contains 8- and 10-MR channels that are not readily resolved into discrete cages. We used AIMD-based metadynamics simulations to assess the mobility of $Cu^{I}(NH_3)_2$ complexes within the large 10-MR channel (details in Section S10, SI). We compared $Cu^{I}(NH_3)_2$ ions anchored to the three symmetry-distinct channel T-sites. As shown in Fig. 59 (SI), a Cu^{I} ion is anchored to an Al T-site within the 10-MR channel with a free energy of translation <25 kJ mol^{-1} at (473 K), and once free of this barrier, Cu^{I} translates nearly freely within the channel. Based on this observation, we constructed a model in which we distributed Al and Cu on the FER framework to target densities and titrated Cu^{I} pairs located in the 10-MR channel sequentially as a function of anchoring site separation (details in Section S9.2, SI). This model (Fig. S55, SI) significantly underestimates the experimentally observed oxidizable fraction of Cu^{I} at either measured Cu density. We repeated the metadynamics simulations to assess mobility along the 8-MR channel, which resulted in a free energy profile (Fig. S59, SI) similar to that of the 10-MR channel but with a greater binding energy of 45 kJ mol^{-1}. This barrier is less than that computed for $Cu^{I}(NH_3)_2$ to migrate from its anchoring Al through a remote 8-MR in CHA,[3] suggesting that motion along the 8-MR in FER should be as facile as migration to a neighboring cage in CHA. We repeated the Cu^{I} titration calculations assuming that Cu^{I} located in either the 10-MR or 8-MR channels can participate with equal probability in Cu^{I} pairing, and the results are shown in Figure 9a. The experimentally observed SCR-active Cu^{I} in the higher density sample can be rationalized by Cu^{I} ions that migrate along both channels and have anchoring Al separated by up to 20 Å, similar to the distances expected in the cage-window frameworks above.

Considerably greater migration distances are required to account for observed SCR-active Cu^{I} in the Cu-FER-0.09 sample. To test the consequences of Al distribution in FER, we repeated the simulations by forbidding Al siting at T_3 positions, which are shared between two 8-MR channels and are not associated with any 10-MR channels, and found no change in the predicted oxidizable Cu^{I} fractions. Overall, these simulation results indicate that Cu^{I} ions likely move in two dimensions in FER and that observed differences in k_{first} in samples of different Cu densities likely reflect differences in the distances that Cu^{I} must travel to close the oxidation half-cycle.

The oxidized Cu-FER-0.19 sample, which contains some fraction of NH_3-solvated binuclear O_2-bridged Cu, was exposed to flowing NO and NH_3 to measure a second reduction transient. The rate of Cu^{II} reduction is best-fit to a model that is first-order in Cu^{II} and occurs faster than the initial Cu^{II} reduction rate. Such behavior is consistent with that of Cu-CHA, Cu-AFX, and Cu-LEV, in which the faster reduction transient for the second cycle reflects both the full solvation of Cu complexes by NH_3 at the beginning of the transient (Section S8, SI) and perhaps faster reduction kinetics from binuclear than mononuclear Cu^{II} complexes. The same fraction of Cu sites is reduced to the Cu^{I} state at the end of both the first and second reduction transient (Fig. 10b).

Finally, SCR rates are measured as a function of dioxygen on two Cu-MOR samples, a representative 1D framework, and reported in Figure 11. SCR rates (per Cu) on Cu-MOR do not transition to the zero-order regime with increasing O_2 pressure in the range studied, suggesting rates are limited by the Cu^{I} oxidation half-cycle, yielding relatively large errors in fitted rate constants of the reduction half-cycle (k_{zero}, Fig. 11 and Table 3). Values of k_{first} are 5× lower on Cu-MOR samples compared to Cu-CHA at similar Cu density, while k_{zero} values are within 1.4×. Such behavior highlights the strong influence of framework dimensionality on the kinetics of the Cu^{I} oxidation half cycle, and its much weaker influence on the kinetics of the Cu^{II} reduction half cycle.

Transient XAS experiments were performed on Cu-MOR-0.27 to provide additional insights to the Cu^{I}/Cu^{II} redox behavior and fraction of Cu_{active}. The sample was first treated in flowing O_2 at high temperature (10 kPa, 673 K) so that all Cu ions were in the Cu^{II} state and bound to the framework. Then, the sample was exposed to flowing NO and NH_3 at a lower temperature (0.03 kPa, 473 K) to measure the rate of Cu^{II} reduction. EXAFS spectra collected at the end of the first reduction transient show a first-shell Cu–N coordination number of ~2.4 and disappearance of second-shell scattering feature, both consistent with formation of $Cu^{I}(NH_3)_2$ (Section S5, SI). The first reduction transient of Cu-MOR-0.27 (Fig. 12) shows a slow rate of Cu^{II} consumption that likely reflects a convolution of rates of Cu^{II} solvation by NH_3 and Cu^{II} reduction, as observed in Cu-FER-0.19 and Cu-AFX-0.31. Despite this slow initial reduction transient, 98% of the Cu^{II} reduces to Cu^{I} and EXAFS spectra of the final state is consistent with $Cu^{I}(NH_3)_2$ (Section S5, SI).

Subsequent oxidation of $Cu^{I}(NH_3)_2$ was measured in flowing O_2 (10 kPa, 473 K). At the end of the oxidation transient, EXAFS spectra reveal that the first-shell Cu–O/N coordination number increases to ~3.6 (Table S3, SI) and the appearance of a second-shell scatter at ~2.5 Å, characteristic of NH_3-solvated $Cu–O_2–Cu$ complexes. Additionally, a fraction of Cu^{I} (0.27) is unable to oxidize to Cu^{II} because of physical or functional isolation (Fig. 12). The apparent oxidation rate constant, obtained by fitting the oxidation transient to a model that is second-order in Cu^{I}, is 2× lower than that of Cu-CHA-0.29 and is the lowest across all of the materials studied herein, which reflects the sensitivity of Cu ion mobility and pairing to the pore network dimensionality.

MOR is a 1D framework that contains uni-directional 12-MR channels (Scheme 1). We repeated the same statistical calculations on MOR, distributing Al and Cu randomly throughout the framework and, based on the FER AIMD results, assuming only Cu^{I} in the 12-MR channel have sufficient mobility to pair. Cu^{I} associated with T3 in MOR thus represent an un-oxidizable subset of about 16% of Cu that cannot participate in reaction with O_2 (details in Section S9.2, SI). Cu^{I} pairs in the 12-MR are titrated as a function of separation, and these results are shown in Figure 9b. Migration distances necessary to account for the apparent SCR-active Cu^{I} in Cu-MOR-0.27 are similar to those in Cu-FER-0.09 under this set of assumptions. In both of these frameworks, k_{first} and k_{ox} likely represent an ensemble average over binuclear Cu^{II}–O_2–Cu^{II} formed from Cu^{I} across a range of separations.

The second reduction transient on Cu-MOR-0.27, from the binuclear NH_3-solvated Cu^{II}–O_2–Cu^{II} state, occurs much faster than initial reduction, again consistent with observations for the other Cu-zeolite topologies studied herein. This suggests that reduction can occur directly from the binuclear Cu^{II} state to the same final endpoint (nearly all Cu^{I}, Fig. 10), and at rates faster than from the mononuclear Cu^{II} state. The value of $k_{red,2}$ of Cu-MOR-0.27 is lower than all of the other $k_{red,1}$ and $k_{red,2}$ values reported in Table 3. Rate constants of the single-site Cu^{II} reduction half-cycle should not depend on Cu ion mobility, so these lower rate constants may reflect the smaller sized voids in Cu-MOR compared to Cu-CHA (Fig. 1) that are too small to contain the transition states involved in Cu^{II} reduction processes thus leading to their destabilization.

Contrasting SCR kinetic behavior on Cu-CHA to other zeolite topologies

Steady-state and transient behavior of Cu-AFX, Cu-AEI, Cu-LEV, Cu-FER, and Cu-MOR samples are consistent with previously reported observations on Cu-CHA samples of varying Cu density; non-CHA frameworks generally show a Langmurian dependence of SCR rate on dioxygen pressure, *operando* XAS (on Cu-AEI-0.25) shows that the steady-state Cu^{II} fraction increases with dioxygen pressure, and O_2-assisted oxidation transients yield EXAFS spectra consistent with the formation of NH_3-solvated binuclear Cu^{II}–O_2–Cu^{II} structures. Thus, the mechanism of low-temperature SCR appears to be invariant across these zeolite frameworks, indicating that the fraction of active Cu sites and the apparent rate constants associated with their oxidation or reduction in SCR half-cycles are the dominant factors that vary with framework topology. Among all Cu-zeolite topologies studied, transient XANES experiments showed that rate constants of the first NO+NH_3 reduction transient are systematically lower than those of the second reduction transient (Fig. S43 and S44, SI), while both result in the same final fraction of reduced Cu^{II} (Table S5, SI). These data suggest that measurement of the first reduction transient can be convoluted with other phenomena such as NH_3 solvation; as such, the second reduction is likely a more accurate reporter of Cu^{II} reduction behavior during steady state reactions in which Cu ions are NH_3 solvated. Furthermore, the faster second reduction transient, coupled with EXAFS spectra that are consistent with formation of NH_3-solvated Cu–O_2–Cu structures, implies that Cu^{II} reduction can occur directly from the binuclear state (Scheme 2).

The k_{first} and k_{zero} rate constants measured from steady-state SCR (details in Section S6, SI) are shown in Figure 13 and are generally lower on non-CHA samples. Changing the cage shape (Cu-AEI) and size (Cu-AFX) within 3D pore networks results in k_{zero} values that are within 1.5× of Cu-CHA samples of a similar Cu density and k_{first} values that are systematically lower by 1.7–2.6×, suggesting that the small topological differences caused by different cage shapes and sizes, and physical distances between Al anchoring sites,[18] are more influential for Cu^{I} oxidation half-cycle rates than Cu^{II} reduction half-cycle rates. Decreasing the pore dimensionality to 2D and

1D frameworks leads to more pronounced decreases in k_{first} (average of 3.1×) and k_{zero} (average of 1.7×); again, the effects are more pronounced for Cu^I oxidation half-cycle rates. Values of k_{zero} are nearly always higher on Cu-CHA than on other Cu-zeolites of similar Cu ion density (except for Cu-AEI-0.21, Fig. 13a), and show a weakly positive dependence on Cu ion density (but within ~3× for any given topology) that largely reflects an increase in the fraction of active Cu. In sharp contrast, values of k_{first} increase monotonically with Cu density in Cu-CHA over a much a larger range (~15×);[3] similarly, k_{first} values in Cu-AFX, Cu-AEI, and Cu-MOR increase with Cu density (Fig. 13b), reflecting rate constants of the dual-site Cu^I oxidation half cycle that are sensitive to Cu ion proximity. Notably, values of k_{first} are always higher on Cu-CHA than on other Cu-zeolites of similar Cu ion density (Fig. 13b), revealing that Cu-CHA materials maximize the steady-state Cu^I oxidation rate constant among the topologies studied herein.

The differences in steady-state k_{first} and k_{zero} values reflect an interplay between the fraction of active Cu sites and the apparent kinetics of SCR oxidation and reduction half-cycles in different void environments. The fraction of active Cu sites, determined from the difference in the number of NH_3+NO-reducible Cu^{II} sites and O_2-un-oxidizable Cu^I sites measured by transient XAS experiments, is reported in Figure 14a. Cu-AEI and Cu-AFX have nearly identical fractions of Cu_{active} to Cu-CHA zeolites at similar Cu densities, consistent with models in which Cu_{active} is associated with Cu^I ions that are separated by no more than one cage (Fig. 6). 1D and 2D frameworks, however, have systematically lower fractions of Cu_{active}. The restricted diffusion pathways thus decrease the effective volumetric footprint occupied by NH_3-solvated Cu ions within zeolite void spaces during catalysis. For example, each *lev* cage is only connected to three neighboring cages via 8-MR windows in the LEV topology (Scheme 1 and Section S9, SI), while each *cha* cage is connected to six neighboring cages via 8-MR windows in the CHA topology, with the result that each $Cu^I(NH_3)_2$ complex in LEV has restricted access to other $Cu^I(NH_3)_2$ complexes to pair and form binuclear O_2-bridged complexes. Statistical models bear out this difference quantitatively (Fig. 6). Similarly, in the FER (2D) and MOR (1D) topologies, each $Cu^I(NH_3)_2$ complex is able to translate along channel-like pores but are limited in mobility in the third dimension (e.g., dead-end pockets). The limited diffusion pathways cause each Cu ion to occupy a lower effective volumetric footprint, which is reflected in Cu_{active} values that are systematically lower in non-3D frameworks (Fig. 14a), and cause Cu species to diffuse over longer distances to form binuclear complexes (Fig. 7), which would be reflected in lower k_{ox} and k_{first} values.

Steady-state rate constants are renormalized by the observed fraction of Cu_{active} (rather than total Cu) and reported in Figure 14b. Corrected k_{zero} values are on average within 60% of Cu-CHA samples of similar Cu density, while k_{first} values are lower by an average of 40%. The differences in steady-state rate constants, after accounting for differences in Cu_{active}, can be rationalized by comparing transient oxidation and reduction behavior. Specifically, apparent oxidation rate constants from transient experiments (k_{ox}) on non-CHA samples are systematically up to 10× lower than Cu-CHA samples at comparable Cu density, consistent with k_{first} values that are sensitive to material composition and framework dimensionality (Fig. S58, SI). Oxidation kinetics measured by transient experiments can be affected by the void environment surrounding transition states that form NH_3-solvated Cu^{II}–O_2–Cu^{II} complexes, diffusion barriers of Cu ions through different rings and voids, and the distance each Cu ion is required to travel to find a pair. AIMD calculations suggest that $Cu^I(NH_3)_2$ migration free energies are weakly sensitive to topology and thus differences in k_{ox} likely reflect differences in the joint accessibility of $Cu^I(NH_3)_2$ pairs. Comparisons across frameworks are complicated by the convoluted contribution of multiple pairing pathways, as highlighted in Figures 6 and 9. In an attempt to account for these differences, we renormalized k_{zero} to the number of Cu^I ions separated by zero cages ("oxidizable Cu", blue region in Fig. 6) for the cage-window and by up to 15 Å for the channel frameworks and plotted this renormalized constant against the density of oxidizable Cu sites (Fig. S58a, SI). Values of k_{zero} renormalized in this manner are uncorrelated with the density of oxidizable Cu and sensitivies to framework topologies are not apparent, consistent with the normalization to experimentally observed Cu_{active}. Similarly renormalized values of k_{first} show a positive and nearly linear correlation with oxidizable Cu, (Fig. S58b, SI), consistent with this approximate accounting of Cu that contributes to SCR rates; further, across all compositions, k_{first} values on CHA materials exceed those of other frameworks, reinforcing the conclusion that the high symmetry of the CHA topology confers intrinsic advantages for Cu^{I} ion pairing and oxidation.

CONCLUSIONS

The pore topology and interconnectivity of zeolite supports influence the mobility and pairability of NH_3-solvated Cu ion sites, and apparent rate constants of Cu^{I} oxidation and Cu^{II} reduction in low-temperature NO_x SCR. Here, we quantitatively determine how these factors are influenced by changes in void size and shape among three-dimensional cage-window connectivity (CHA, AEI, AFX) and by changes in framework dimensionality (2D: FER, LEV; 1D: MOR). Steady-state kinetics and *operando* XAS at varying dioxygen pressures are used to isolate behavior in Cu^{II} reduction and Cu^{I} oxidation-limited regimes. Generally, 3D cage-window Cu-zeolites show similar SCR rates (per total Cu) and Cu^{II} fractions that increase with O_2 pressure, reflecting SCR redox cycles that become increasingly limited by Cu^{II} reduction at high O_2 pressures. Conversely, SCR rates on 1D (MOR) and 2D (FER, LEV) zeolites remain largely limited by the Cu^{I} oxidation half cycle in the range of O_2 pressures studied here, even at relatively high Cu densities. These observations indicate that rates of the dual-site Cu^{I} oxidation half-cycle are more sensitive to changes in framework topology than rates of the single-site Cu^{II} reduction half-cycle.

Differences in steady-state SCR rate behavior are rationalized by estimating fractions of SCR-active Cu sites and kinetics associated with each half-cycle from transient XAS measurements during Cu^{I} oxidation and Cu^{II} reduction treatments. The fraction of active Cu (i.e., O_2-oxidizable) is similar among 3D cage-window topologies (CHA, AEI, AFX), when samples are compared at a similar Cu ion density, reflecting similarities in Cu ion mobility within these pore networks. Conversely, the fraction of active Cu is systematically lower in 1D (MOR) and 2D (FER, LEV) topologies, reflecting restricted Cu ion pairability within lower dimensionality frameworks. Rate constants for Cu^{I} oxidation (k_{ox}) are also up to 10× lower on 1D and 2D topologies compared to Cu-CHA at similar Cu ion densities, while rate constants for Cu^{II} reduction (k_{red}) are only 3× lower, on average, in 1D and 2D topologies. These findings are consistent with a single-site Cu^{II} reduction mechanism, for which Cu ion mobility is less consequential than the dual-site Cu^{I} oxidation mechanism. Transient Cu^{II} reduction experiments performed after an initial high-temperature oxidation step and performed after an intermediate-temperature oxidation step that forms NH_3-solvated Cu–O_2–Cu complexes were also measured for Cu-zeolite samples and were faster for the second reduction transient on all samples. These data indicate that Cu^{II} reduction can proceed directly from NH_3-solvated Cu–O_2–Cu complexes, rather than needing to proceed via monomeric NH_3-solvated Cu^{II}, during low-temperature SCR cycles.

Statistical simulations that account for the influence of zeolite framework topology on Cu ion transit pathways were performed to provide further insights into the framework-dependent mechanistic requirements for Cu^{I} ions to pair and oxidize during low-temperature SCR. Pairwise titrations as a function of Cu density in various frameworks provide informed estimates of the proximity of SCR-active Cu^I pairs likely participating in the oxidation half-cycle. For all cage-window topologies considered here (CHA, AEI, AFX, LEV), the experimentally measured Cu_{active} fraction can be rationalized by considering Cu pairs co-located within the same cage or separated by one 8-MR window. Differences in Cu^I oxidation kinetics among these topologies reflect differences in distances traversed by Cu^I ions to form pairs during oxidation (for AFX) or reduced accessibility due to a reduction in framework dimensionality (for LEV). Among the channel topologies considered here (MOR, FER), pairwise titrations as a function of Cu density provide results consistent with prior intuition of their description as one-dimensional and two-dimensional systems, respectively, for the Cu oxidation half-cycle. Combined with experimental observations, these results underscore the impact of cage shape, size and pore-dimensionality on apparent steady-state and transient oxidation kinetics during SCR.

These experimental and computational data provide new guidance for future materials design strategies to improve low-temperature SCR catalytic reactivity. CHA (and other small-pore) zeolite frameworks provide several well-known practical benefits for commercial implementation, including improved resistance to hydrocarbon poisoning and structural degradation upon exposure to hydrothermal aging conditions, and the findings herein indicate that CHA also confers several kinetic benefits that increase rates of the low-temperature SCR redox cycle. Comparisons among all frameworks reveal that chabazite (CHA) zeolites provide maximal values of the fraction of SCR-active Cu sites and rate constants for Cu^I oxidation and Cu^{II} reduction half-cycles, when samples are compared at similar Cu ion densities. These data indicate that CHA comprises a 3D cage-window topology with appropriately sized voids that are particularly effective for low-temperature NO_x SCR, because such voids provide optimal environments to facilitate Cu ion mobility and pairability, and to stabilize mononuclear and binuclear NH_3-solvated Cu intermediates that propagate the SCR redox cycle. Therefore, while altering topological features of the host zeolite away from the CHA framework appear to decrease the effective utilization of the Cu sites exchanged onto the zeolite, approaches to alter the Cu and Al density and atomic arrangements for a given material can lead to increases in the fraction of active Cu to improve low-temperature SCR rates.

EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

Resource availability

Lead contact

Requests for further information may be directed to, and will be fulfilled by, the corresponding author Rajamani Gounder (rgounder@purdue.edu).

Materials availability

Materials and sample preparation are provided below, and in the supplemental information.

Data and code availability

Additional data are provided in the supplemental information, and in a zenodo repository located at 10.5281/zenodo.7826460

Materials and methods

Zeolite synthesis and Cu exchange

All zeolites were synthesized in-house, except for MOR that was obtained from a commercial source (NH_4-MOR; CBV21A, Si/Al = 10, Zeolyst). The parent CHA zeolites were synthesized using previously reported methods using N,N,N-trimethyl-1-adamantylammonium hydroxide (TMAdaOH) as the organic structure-directing agent (OSDA).[5] Molar ratios of 1 SiO_2 / 0.033 Al_2O_3 / 0.25 TMAdaOH / 0.25 Na_2O / 44 H_2O were used in the synthesis solution. First, an aqueous solution of TMAdaOH (25 wt%, Sachem) was added to deionized (DI) H_2O (18.2 MΩ cm) in a perflouroalkoxy alkane jar (PFA, Savillex Corp.) then stirred at ambient conditions for 0.25 h. Aluminum hydroxide ($Al(OH)_3$, grade 0325, SPI Pharma) was then added to the aqueous TMAdaOH solution. Next, a 5 M NaOH solution (16 wt% NaOH in deionized water; NaOH pellets 98 wt%, Alfa Aesar) was added dropwise to the solution and stirred for 0.25 h under ambient conditions. Finally, fumed silica (SiO_2, 99 wt%, Cabot) was added to the mixture and stirred for 2 h under ambient conditions. The final synthesis solution was then added to a 45 mL Teflon-lined stainless-steel autoclave (Parr) and placed in a forced convection oven (Yamato DKN-402C) at 433 K and rotated for 6 days at 40 RPM.

Two parent AEI zeolites were synthesized using methods adapted from previously reported procedures using *cis*-2,6,dimethylpiperidinium hydroxide (DMPOH) as the OSDA.[39,40] Molar ratios used in the two syntheses were 1 SiO_2 / 0.017 Al_2O_3 / 0.07 DMDMPOH / 0.65 Na^+ / 12.3 H_2O and 1 SiO_2 / 0.013 Al_2O_3 / 0.16 DMDMPOH / 0.28 Na^+ / 39.0 H_2O. An aqueous sodium silicate (N® type, PQ corporation) was added to DI H_2O in a PFA jar. Next, an aqueous 5 M NaOH solution was added dropwise to the solution then stirred for 0.25 h under ambient conditions. NH_4-Y zeolite (CBV500, Si/Al = 2.6, Zeolyst) was then added to the solution and stirred for 0.5 h at ambient conditions. After, the DMDMPOH was added, and the solution was stirred at ambient conditions for 2 h. The final synthesis solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave and placed in a forced convection oven at 413 K and rotated for 3 days at 40 RPM.

The parent LEV zeolite was synthesized by adapting literature procedures using 1-adamantylamine (Ada) as the OSDA.[41,42] The molar ratios used in synthesis were 1 SiO_2 / 0.024 Al_2O_3 / 0.30 Ada / 0.59 Na^+ / 10 H_2O. First, the Ada was added to DI water in a PFA jar and stirred under ambient conditions for 0.08 h. Next, H-Y zeolite (CBV720, Si/Al = 30, Zeolyst) was added to the solution and stirred until homogenized under ambient conditions. Finally, NaF (99%, Sigma Aldrich) was added to the solution which was then stirred for 2 h under ambient conditions. The solution was then transferred to a 45 mL Teflon-lined stainless-steel autoclave and placed in a forced convection oven at 423 K for 14 days.

The parent AFX sample was synthesized using 1,4-diazabicyclo[2.2.2]-octane-C4-diquaternary dibromide (DC4Br) as the OSDA.[43,44] DC4Br was synthesized following the procedure by Fickel et al.[43] The molar ratios used in zeolite synthesis were 1 SiO_2 / 0.04 Al_2O_3 / 0.5 DC4Br / 0.74 Na^+ / 44 H_2O. First, sodium silicate was added to DI water in a PFA jar. Solid NaOH (98 wt%, Alfa Aesar) was then added to the solution and the mixture was stirred at ambient conditions for 0.25 h. Na-Y zeolite (CBV100, Si/Al = 2.6, Zeolyst) was then added to the solution and stirred for 0.5 h under ambient conditions. The DC4Br was then added to the solution and the solution was stirred for an additional 0.5 h under ambient conditions. The contents of the synthesis solution were then transferred to a 45 mL Teflon-lined stainless-steel autoclave and placed in a forced convection oven at 423 K for 6 days.

The parent FER zeolite was synthesized without the use of an OSDA following literature reports.[45,46] The molar ratios used in synthesis were 1 SiO_2 / 0.055 Al_2O_3 / 0.14 K^+ / 0.14 Na^+ / 15.6 H_2O. First, $Al(OH)_3$ (grade 0325, SPI Pharma) was added to a PFA jar (Savillex corp.). Next, potassium hydroxide pellets (KOH, 99%, Macron Fine Chemicals) were dissolved in half of the total DI water then added to the $Al(OH)_3$ and stirred for 0.25 h under ambient conditions. Next, NaOH pellets (99%, Macron Fine Chemicals) were dissolved in the remaining half of the DI water and added to the synthesis solution, and the synthesis solution was stirred for 24 h. Fumed silica (Cab-O-Sil, Cabot Corporation) was added to the solution and stirred mechanically until homogeneous. The synthesis solution was then transferred to a 45 mL Teflon-lined stainless-steel autoclave and placed in a forced convection oven at 453 K for 6 days.

As-synthesized zeolites were washed with four alternating DI water and acetone (99.9%, Sigma Aldrich) wash cycles, centrifuged to recover the solids, then dried in a static oven at 353 K for 24 hours. After drying, the zeolites were treated in flowing air (1.67 cm^3 s^{-1} g_{cat}^{-1}, Zero grade, Indiana Oxygen) to 853 K (0.0167 K s^{-1}) for 10 h. The zeolites were converted to the NH_4-form by aqueous-phase ion-exchange with a 1.0 M NH_4NO_3 solution (8.0 wt% in H_2O, 99.9 wt%, Sigma Aldrich), followed by four wash cycles with DI water. The solids, recovered via centrifugation, were then dried in a static oven at 353 K for 24 hours. To convert the NH_4-form zeolites to the H-form, the zeolites were then treated in flowing air (1.67 cm^3 s^{-1} g_{cat}^{-1}, Zero grade, Indiana Oxygen) to 773 K (0.0167 K s^{-1}) for 4 h.

Cu-form zeolites were obtained via aqueous phase ion-exchange of either the NH_4 or H-form zeolites in 0.003–0.2 M solutions of copper nitrate (99 wt%, Sigma Aldrich) for 24 h under ambient conditions. After the ion-exchange, the solids were recovered from the supernatant solution and were washed four times with DI water, then dried in a static oven at 353 K for 24 hours. The Cu-form zeolites were then treated in flowing air (1.67 cm^3 s^{-1} g_{cat}^{-1}, Zero grade, Indiana Oxygen) to 773 K (0.0167 K s^{-1}) for 4 h.

Zeolite characterization

The framework topology of as-synthesized zeolites was characterized using powder X-ray diffraction (XRD) on a Rigaku SmartLab X-ray diffractometer (Cu Kα radiation source, XRD patterns in Section S1, SI). Diffraction patterns were obtained by pressing a sample (~0.01 g) onto a low dead-volume sample holder (Rigaku) and scanning over a range of 4–40 ° 2θ at a rate of 0.0167 ° s^{-1}. To identify the dominant crystal phases, XRD patterns were compared to references of known topology. The micropore volumes of H-form zeolite samples were calculated from Ar adsorption isotherms measured at 87 K (isotherms in Section S1, SI) using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer as reported in our previous work.[17]

The elemental compositions of Cu and H-form zeolites was determined using atomic absorption spectroscopy (AAS) on a PerkinElmer PinAAcle 500 or using inductively coupled plasma optical emission spectrometry (ICP-OES) on a Thermo Scientific iCap 7000 Plus Series. Samples (0.01–0.05 g) were digested by first adding 2.5 g hydrofluoric acid (48 wt%, Alfa Aesar) for at least 2 days prior to dilution in an additional 50 g of DI water at ambient conditions. *Warning: use proper ventilation, engineering controls, and personal protective equipment when working with hydrofluoric acid.* For samples analyzed with ICP, nitric acid (70 wt%, Sigma Aldrich) was added to at least 2 wt% to acidify the solution. Quantitative elemental compositions of Al and Cu were done by generating calibration curves of known composition.

Steady-state and transient SCR kinetic measurements

Steady-state SCR kinetic measurements were performed in a benchtop tubular reactor system described in our previous work.[14,17] Zeolite samples were pelletized, crushed, and sieved to particle diameters of 125 to 250 μm. Bed lengths of approximately 1 cm were obtained by dilution of the catalyst in silica gel (Davisil, 250-500 μm diameter). Rates were measured using a reactant gas mixture of 0.03 kPa NO (3.5% NO/Ar, Indiana Oxygen), 0.03 kPa NH_3 (3.0% NH_3/Ar, Indiana Oxygen) 1–60 kPa O_2 (99.5%, Indiana Oxygen), 2 kPa H_2O (deionized, 18.2 MΩ cm, introduced through a 24" Perma Pure MH Nafion^{TM} Series Humidifier), 7 kPa CO_2 (liquid, commercial grade, Indiana Oxygen), and balance N_2 (boil-off from a liquid N_2 dewar) at 473 K and ambient total pressure. The water pressure was kept constant at varied O_2 pressures by using two N_2 streams, one passing through the humidifier ("wet" N_2) and one bypassing the humidifier ("dry" N_2), and the "dry" N_2 flow rate was adjusted to compensate for changes in the O_2 flowrate. Background gas-phase NO oxidation was minimized by mixing the 3.5% NO stream with the "wet" N_2 and CO_2 prior to mixing with the "dry" N_2 and O_2. Total gas flow rates were between 16.7–33.3 $cm^3\ s^{-1}$ (at ambient temperature and pressure) and were chosen to keep conversions differential in NO. Outlet concentrations of NO, NH_3, NO_2, CO_2, and H_2O were monitored using a gas-phase Fourier Transform Infrared (FTIR) spectrometer (MKS Multigas^{TM} 2030). Any net NO_2 consumption (when compared to a blank reactor) was assumed to be consumed via the "fast" SCR reaction (equimolar NO and NO_2 consumption) and was corrected for according to methods detailed previously.[17]

X-ray absorption spectroscopy (XAS) experiments were performed at the Advanced Photon Source (APS) at Argonne National Laboratory on the insertion device (ID) line of the Materials Research Collaborative Access Team (MRCAT, Sector 10).[47] Spectra were collected in transmission mode, and calibration of the Cu K-edge to 8979 eV was done by collecting a Cu metal foil spectrum simultaneously with Cu-zeolite sample spectra. *In situ* and *operando* experiments were performed using a glassy-carbon reactor system described previously.[48] Three sequential transient experiments were performed at the beamline: initial reduction, oxidation, and second reduction. Samples were treated in 10% O_2 and 673 K until spectra were no longer changing, then cooled to 473 K. Initial reduction transient experiments were performed at 473 K and ambient pressures; first, 0.03 kPa NH_3 was introduced and, upon NH_3 breakthrough, 0.03 kPa NO was introduced via a switching valve until spectra stopped changing. The sample was then purged in flowing N_2 (13.3 $cm^3\ s^{-1}$) for 0.08 h. Transient O_2 oxidation experiments were performed by introducing flowing O_2 (10 kPa O_2 in N_2, 13.3 $cm^3\ s^{-1}$) while XAS spectra were taken until the spectra were no longer changing. Samples were purged in flowing N_2 (13.3 $cm^3\ s^{-1}$) for 0.08 h. The second transient reduction was measured following the procedure described above (0.03 kPa NH_3, 0.03 kPa NO, balance N_2, 473 K) and XAS spectra were collected until the spectra were no longer changing. XAS spectra were normalized using a first-order polynomial in the pre-edge region and a third-order polynomial in the post-edge region.

The X-ray absorption near edge structure (XANES) spectra was analyzed using Athena program in the package iFeffit.[49] Spectra were normalized from 20–300 eV above the edge energy. Linear combination fitting of transients was performed using known Cu^I (Cu-CHA zeolite reduced in NO and NH_3 at 473 K) and Cu^{II} (Cu-CHA zeolite oxidized in 20 kPa O_2 to 673 K, spectra taken at 473 K) standards.[20] The extended X-ray absorption fine structure (EXAFS) was analyzed using the WinXAS program.[50] The EXAFS coordination parameters were obtained by a least square fit in q- and r-space of the isolated nearest neighbor, k^2-weighted Fourier transform (FT) data.

FT-EXAFS provides critical structural information for Cu ions; however, second-shell scattering paths between Cu–(Si/Al) framework atoms and Cu–Cu overlap in the R space and thus are indistinguishable. Instead, the k^2-weighted EXAFS signal and its FT representation can be combined with a wavelet transform to visualize different atomic elements in the k and R spaces. This is particularly useful for distinguishing second-shell scattering paths because the single scattering contributions are localized differently in k-space for Cu–Cu (~7 $Å^{-1}$) and Cu–(Si/Al) framework atoms (4 $Å^{-1}$). The wavelet transforms were performed from ~3–10 $Å^{-1}$ in k-space and 0.5–3.5 Å in R-space. The waveforms were computed using the Morlet transform, expressed as:

$$\psi(k) = \frac{1}{\sqrt{2\pi}\sigma} e^{i\eta k} e^{\frac{-k^I}{2\sigma^2}} \tag{1}$$

where i denotes the complex unit and η and σ govern the wavelet resolution in R-space and k-space. Here, σ = 1 and η = 7 were used for all wavelet transformations; these values are obtained from the relationship $\eta_{opt} \approx 2r_{opt}$ where r_{opt} is the backscattering distance,[51] and consistent with prior reports on Cu–Cu scatter.[16,19,35]

UV-Visible Spectroscopy Experiments

The effects of NH_3-solvation on Cu^{II} reduction rates were examined with diffuse reflectance UV-Visible experiments. Spectra were recorded using a Varian Cary 5000 UV-vis-NIR spectrophotometer attached with a Praying Mantis diffuse reflectance accessory. Baseline spectra were recorded using $BaSO_4$ as a 100% reflectance material. The sieved Cu-FER-0.19 sample was first oxidized to Cu^{II} by holding in dry air (Indiana Oxygen, 5.6 cm s^{-1} g^{-1}) while increasing the temperature to 723 K (0.167 K s^{-1}) and holding for 2 h. The sample was then cooled to 473 K in the oxidizing atmosphere and spectra were recorded at the fully oxidized state.

Two treatments were performed the study the effects of NH_3-solvation on Cu^{II} reduction rates. The first method involved exposing the catalyst (after high temperature oxidation) to 0.042 kPa NH_3 until spectra stopped changing (~1 h). Upon full solvation of Cu sites by NH_3, 0.042 kPa of NO was introduced to monitor the transient reduction of Cu^{II}. The second method involved exposing the catalyst (after high temperature oxidation) to 0.042 kPa of NH_3 and 0.042 kPa of NO simultaneously, while collecting spectra to monitor transient Cu^{II} reduction.

Assessments of Zeolite Framework Pore Size Distribution

The pore size distribution, described in depth elsewhere,[52] is used to compare and contrast the distribution and fraction of void space in CHA, AFX, AEI, LEV, FER, and MOR. Structure files of each framework were obtained from the International Zeolite Association (IZA) database.[33] Pore size distributions were calculated using the Zeo++ program with 100,000 samples in the Monte Carlo algorithms and bin sizes of 0.1 Å. The radii of oxygen and silicon were set to 1.35 Å and a probe radius of 1.3 Å was used in all PSD calculations. The derivative distribution for each framework is reported in Figure 1, wherein the relative heights of each peak correspond to the fraction of void space occupied by each pore size. Scatter plots of the pore size distribution are reported in Section S2 of the Supplemental Information.

Stochastic simulations

Stochastic simulations were performed to predict the oxidizable ("SCR-active") fraction of Cu as a function of Cu content on CHA, AEI, AFX, FER, and MOR. Zeolite frameworks were represented as graphs that incorporated Cu ion density and spatial distribution as dictated by the zeolite framework topology. The influence of topology on Cu^I-Cu^I accessibility was assessed by seeding Cu^I into the frameworks assuming Cu ions are randomly associated with anchoring Al sites, and then titrating Cu^I-Cu^I pairs sequentially, starting from randomly selected site pairs that satisfy the shortest separation criterion, followed by the next shortest separation, and so on. Further details are in Section S.9 of the Supplemental Information.

AIMD simulations

Ab initio molecular dynamics (AIMD) were performed using CP2K.[53] Supercell calculations were performed on the FER framework, selected to explore the consequences of channel structure on $Cu^I(NH_3)_2$ mobility. Core states were represented using norm-conserving GTH pseudopotentials, valence states represented using double-zeta plus polarization (DZVP) basis functions, densities expanded in plane waves up to 400 Rydberg, and exchange and correlation represented using the PBE functional. Dynamics simulations were performed in the NVT ensemble at 473 K using a Nosé-Hoover thermostat and a 1 fs timestep. Consistent with prior work,[3] the free energy landscape for $Cu^I(NH_3)_2$ ions to migrate from anchoring Al sites was explored using metadynamics.[54] The Cu-Al distance was used as a collective variable with further constraints introduced as described below (additional details in Section S10, SI).

SUPPLEMENTAL INFORMATION

Supplemental information includes details of catalyst characterization, EXAFS and XANES spectra, formulas and fits for transient oxidation and reduction experiments, details of calculations of Cu_{active} for each framework, and details of AIMD calculations, and can be found online at:

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AUTHOR CONTRIBUTIONS

R. G., W. F. S., S. P., and A. M. supervised the project. [†]M. D. and C. B. J. contributed equally to this work. M. D., C. B. J., S. H. K. and R. G. acquired and analyzed the experimental data in this work. A. G., R. S., S. L. and W. F. S. acquired and analyzed the computational data in this work. M. D., C. B. J. and R. G. led the writing of the manuscript. All authors participated in discussion of the results and assisted in the writing and revision of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

INCLUSION AND DIVERSITY

We support inclusive, diverse and equitable conduct of research.

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FIGURE AND SCHEME TITLES

Figure 1. Pore size distribution of zeolite catalysts calculated with 1.2 Å probe (additional details reported in Section S.3, SI).

Figure 2. SCR rates (0.03 kPa NO, 0.03 kPa NH_3, 473 K) on (a) Cu-AFX-0.27 (🟩) and Cu-CHA-0.29 (○) and (b) Cu-AFX-0.32 (■) and Cu-CHA-0.31 (○), and (c) ratio of k_{first} (red) and k_{zero} (blue) on Cu-AFX samples relative to Cu-CHA samples of quantitatively comparable (± 10%) volumetric Cu density (adapted from Jones et al.[17]). Values and uncertainties are also reported in Table 2.

Figure 3. Transient changes to the Cu^{II} fraction during first reduction (0.03 kPa NO, 0.03 kPa NH_3), oxidation (10% O_2), and second reduction (0.03 kPa NO, 0.03 kPa NH_3) treatments (473 K) of Cu-AFX-0.32.

Figure 4. SCR rates (0.03 kPa NO, 0.03 kPa NH_3, 473 K) on (a) Cu-AEI-0.10 (🟩) and Cu-CHA-0.10 (○), (b) Cu-AEI-0.21 (■) and Cu-CHA, 0.23 (○), and (c) Cu-AEI-0.25 (■) and Cu-CHA-0.23 (○), (d) Cu^{II} fraction measured by *operando* XANES on Cu-AEI-0.25 (■) and Cu-CHA-0.23 (□), and (e) ratio of k_{first} (red) and k_{zero} (blue) on Cu-AEI samples relative to Cu-CHA samples of quantitatively comparable (±10%) volumetric Cu density (adapted from Jones et al.[17]). Values and uncertainties are also reported in Table 2.

Figure 5. (a) Cu^{II} fraction during first reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K) and oxidation (10% O_2, 473 K) transients on Cu-AEI-0.25 and wavelet transform of the final state after (b) reduction and (c) oxidation.

Figure 6. Oxidizable Cu^{I} fraction as a function of Cu density in Cu/1000 Å^3, evaluated for (a) CHA (b) AEI (c) AFX and (d) LEV. Blue, red, yellow, green, and grey regions correspond to titrated Cu pairs within the same cage ($y = 0$) or separated by one ($y = 1$), two, three, four, and five cages, respectively. Data points and error bars indicate Cu_{active} measured experimentally. Schematics illustrate selected pairing rules (details in Section S.9, SI).

Figure 7. (a) SCR rates (per mol Cu, 0.03 kPa NO, 0.03 kPa NH_3, 473 K) as a function of O_2 pressure on Cu-LEV-0.18 (🟩) and Cu-CHA-0.17 (○), (b) ratio of k_{first} (red) and k_{zero} (blue) on Cu-LEV-0.18 relative to Cu-CHA-0.17, and (c) Cu^{II} fraction during first reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K), oxidation (10% O_2, 473 K), and second reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K) treatments.

Figure 8. SCR rates (0.03 kPa NO, 0.03 kPa NH_3, 473 K) on (a) Cu-FER-0.09 (🟩) and Cu-CHA-0.10 (○) and (b) Cu-FER-0.19 (■) and Cu-CHA-0.17 (○), and (c) ratio of k_{first} (red) and k_{zero} (blue) on Cu-FER samples relative to Cu-CHA samples of comparable (±10%) volumetric Cu density (adapted from Jones et al.[17]). Values and uncertainties are also reported in Table 3.

Figure 9. Oxidizable Cu^{I} fraction as a function of Cu density in Cu/1000 Å^3 for (a) FER and (b) MOR. Blue, orange, green, red, purple, brown, pink, grey, yellow and cyan colored regions correspond to titrated Cu pairs at physical separation of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 Å, respectively. Data points indicate Cu_{active} with error bars indicating uncertainties in measurement. Schematics illustrate assumed pairing pathways in each titration.

Figure 10. (a) SCR rates (per mol Cu, 0.03 kPa NO, 0.03 kPa NH_3, 473 K) as a function of O_2 pressure on Cu-FER-0.09 (□) and Cu-FER-0.19 (●), and Cu^{II} fraction on (b) Cu-FER-0.09 and (c) Cu-FER-0.19 during first reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K), oxidation (10% O_2, 473 K), and second reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K) treatments.

Figure 11. SCR rates (0.03 kPa NO, 0.03 kPa NH_3, 473 K) on (a) Cu-MOR-0.12 (🟩) and Cu-CHA-0.10 (○) and (b) Cu-MOR-0.27 (🟩) and Cu-CHA-0.29 (○), and (c) ratio of k_{first} (red) and k_{zero} (blue) on Cu-FER samples relative to Cu-CHA samples of quantitatively comparable (± 10%) volumetric Cu density (adapted from Jones et al.[17]). Values and errors are also reported in Table 3.

Figure 12. Cu^{II} fraction during first reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K), oxidation (10% O_2, 473 K), and second reduction (0.03 kPa NO, 0.03 kPa NH_3, 473 K) treatments.

Figure 13. Steady-state (a) k_{zero} and (b) k_{first} values on Cu-CHA (unfilled circles, adapted from Jones et al.[17]), Cu-AEI (light blue), Cu-AFX (green), Cu-LEV (yellow), Cu-FER (red), and Cu-MOR (blue) of varying Cu density.

Figure 14. (a) Fraction of Cu_{active} on CHA (open circles, adapted from Jones et al.[17]), AEI (light blue), AFX (green), LEV (yellow), FER (red), MOR (navy) and (b) rate ratio normalized by Cu_{total} (dark shading) and Cu_{active} (light shading).

Scheme 1. Salient details of void shape, size, and pore dimensionality for CHA, AEI, AFX, LEV, FER, and MOR. Distance measurements are taken from the IZA database[33] assuming a Si and O radius of 1.35 Å.

Scheme 2. Proposed low-temperature SCR cycle, adapted from Paolucci et al.[3], also depicting the direct reduction from the binuclear Cu^{II} state to $Cu^{I}(NH_3)_2$ (green pathway). Cycle shown for the mononuclear Cu^{II} site for brevity, an analogous cycle can be drawn for the mononuclear $Cu^{II}(OH)$ site.

TABLES

Table 1. Composition and characterization of zeolite materials.

Sample[a]	Si/Al	Cu/Al	Cu wt%	Cu volumetric density (per 10^3 Å^3)
Cu-CHA-0.10[b]	15	0.10	0.69	0.10
Cu-CHA-0.17[b]	15	0.18	1.21	0.17
Cu-CHA-0.23[b]	15	0.24	1.60	0.23
Cu-CHA-0.29[b]	15	0.31	2.04	0.29
Cu-CHA-0.31[b]	15	0.33	2.16	0.31
Cu-AEI-0.10	10	0.07	0.71	0.10
Cu-AEI-0.21	10	0.15	1.47	0.21
Cu-AEI-0.25	10	0.18	1.74	0.25
Cu-AFX-0.27	9	0.18	1.87	0.27
Cu-AFX-0.32	9	0.21	2.20	0.32
Cu-LEV-0.18	19	0.22	1.17	0.18
Cu-FER-0.09	10	0.05	0.58	0.09
Cu-FER-0.19	10	0.11	1.20	0.19
Cu-MOR-0.12	13	0.10	0.76	0.12
Cu-MOR-0.27	13	0.22	1.67	0.27

[a] Sample code: Cu-ZZZ-X; ZZZ = three-letter IZA framework code, X = Cu volumetric density per 10^3 Å^3.

[b] Cu-CHA data are adapted from Jones et al.[17]

Table 2. Measured first and zero-order SCR rate constants (473 K) from steady-state kinetic data, oxidation and reduction constants and fraction of SCR-active Cu from transient XAS data, on 8-MR window-cage zeolites.

Sample	k_{first} [a,b]	k_{zero} [a,b]	k_{ox} [a,b]	$k_{red,1}$ [a]	$k_{red,2}$ [a]	Cu_{active}[c]
	10^{-3} mol NO (mol Cu)$^{-1}$ (kPa O_2)$^{-1}$ s^{-1}	*10^{-3} mol NO (mol Cu)$^{-1}$ s^{-1}*	*10^{-5} m^3 (mol Cu)$^{-1}$ s^{-1}*	*10^{-3} s^{-1}*	*10^{-3} s^{-1}*	
Cu-CHA-0.10[d]	0.24 ± 0.02	7.48 ± 0.70	7.89 ± 0.30	–	–	0.77 ± 0.05
Cu-CHA-0.23[d]	1.09 ± 0.12	15.56 ± 0.86	7.14 ± 0.40	7.44 ± 0.64	–	0.85 ± 0.05
Cu-CHA-0.29[d]	1.87 ± 0.20	14.84 ± 0.59	7.80 ± 0.65	–	–	0.83 ± 0.05
Cu-CHA-0.31[d]	1.76 ± 0.25	16.40 ± 0.99	14.50 ± 1.80	–	–	0.85 ± 0.05
Cu-AFX-0.27	0.72 ± 0.07	9.40 ± 0.50	–	–	–	–
Cu-AFX-0.32	1.00 ± 0.11	11.09 ± 0.63	3.96 ± 0.43	–	16.18 ± 2.52	0.84 ± 0.10
Cu-AEI-0.10	0.13 ± 0.02	7.01 ± 1.21	–	–	–	–
Cu-AEI-0.21	0.58 ± 0.04	19.82 ± 1.28	–	–	–	–
Cu-AEI-0.25	0.65 ± 0.05	12.35 ± 0.69	7.60 ± 1.75	–	–	0.75 ± 0.10

[a] Errors in rate constant fits are reported as 95% confidence intervals (twice the standard deviation).

[b] Rate constants are normalized per Cu_{total}. Rate constants normalized per Cu_{active} can be found in Table S6 of the SI.

[c] Cu_{active} is calculated as the difference between Cu^{II} reduced by NO and NH_3 (assumed to be 100% in Cu-CHA samples) and Cu^{I} un-oxidized by O_2, reported in Table S3 of the SI. Errors in Cu fraction are calculated from 5% absolute error from XANES LCF fitting.

[d] Cu-CHA data is adapted from Jones et al.[17]

Table 3. Measured first and zero-order SCR rate constants (473 K) from steady-state kinetic data, and fraction of SCR-active Cu and oxidation and reduction constants from transient XAS data, on 2D and 1D frameworks.

Sample	k_{first} [a,b]	k_{zero} [a,b]	k_{ox} [a,b]	$k_{red,1}$ [a]	$k_{red,2}$ [a]	Cu_{active} [c]
	10^{-3} mol NO (mol Cu)$^{-1}$ (kPa O_2)$^{-1}$ s^{-1}	10^{-3} mol NO (mol Cu)$^{-1}$ s^{-1}	10^{-5} m^3 (mol Cu)$^{-1}$ s^{-1}	10^{-3} s^{-1}	10^{-3} s^{-1}	
Cu-CHA-0.10[d]	0.24 ± 0.02	7.48 ± 0.70	7.89 ± 0.30	–	–	0.77 ± 0.05
Cu-CHA-0.17[d]	0.80 ± 0.03	16.10 ± 0.89	8.10 ± 0.38	10.20 ± 0.40	–	0.78 ± 0.05
Cu-CHA-0.23[d]	1.09 ± 0.12	15.56 ± 0.86	7.14 ± 0.40	7.44 ± 0.64	–	0.85 ± 0.05
Cu-CHA-0.29[d]	1.87 ± 0.20	14.84 ± 0.59	7.80 ± 0.65	–	–	0.83 ± 0.05
Cu-CHA-0.31[d]	1.76 ± 0.25	16.40 ± 0.99	14.50 ± 1.80	–	–	0.85 ± 0.05
Cu-CHA-0.35[d]	2.80 ± 0.29	18.18 ± 0.57	12.42 ± 0.45	21.06 ± 3.13	–	0.81 ± 0.05
Cu-LEV-0.18	0.06 ± 0.006	7.82 ± 2.14	8.92 ± 1.49	5.87 ± 0.54	14.49 ± 1.62	0.55 ± 0.10
Cu-FER-0.09	0.04 ± 0.002	2.66 ± 0.49	8.78 ± 2.25	4.61 ± 0.43	–	0.70 ± 0.10
Cu-FER-0.19	0.79 ± 0.13	6.33 ± 0.33	4.26 ± 0.59	–	13.92 ± 2.18	0.70 ± 0.10
Cu-MOR-0.12	0.05 ± 0.008	7.20 ± 4.24	–	–	–	–
Cu-MOR-0.27	0.34 ± 0.02	10.39 ± 0.64	3.17 ± 0.20	–	5.77 ± 0.36	0.71 ± 0.10

[a] Errors in rate constant fits are reported as 95% confidence intervals (twice the standard deviation).

[b] Rate constants are normalized per Cu_{total}. Rate constants normalized per Cu_{active} can be found in Table S6 of the SI.

[c] Cu_{active} is calculated as the difference between Cu^{II} reduced by NO and NH_3 (assumed to be 100% in Cu-CHA samples) and Cu^{I} un-oxidized by O_2, reported in Table S3 of the SI. Errors in Cu fraction are calculated from 5% absolute error from XANES LCF fitting.

[d] Cu-CHA data is adapted from Jones et al.[17]