Dynamic multinuclear sites formed by mobilized copper ions in NO\textsubscript{x} selective catalytic reduction


Copper ions exchanged into zeolites are active for the selective catalytic reduction (SCR) of nitrogen oxides (NO\textsubscript{x}) with ammonia (NH\textsubscript{3}), but the low-temperature rate dependence on copper (Cu) volumetric density is inconsistent with reaction at single sites. We combine two-dimensional and transient kinetic measurements, x-ray absorption spectroscopy, and first-principles calculations to demonstrate that under reaction conditions, mobilized Cu ions can travel through zeolite windows and form transient ion pairs that participate in an oxygen (O\textsubscript{2})–mediated Cu\textsuperscript{II}–Cu\textsuperscript{I} redox step integral to SCR. Electrostatic tethering to framework aluminum centers limits the volume that each ion can explore and thus its capacity to form an ion pair. The dynamic, reversible formation of multinuclear sites from mobilized single atoms represents a distinct phenomenon that falls outside the conventional boundaries of a heterogeneous or homogeneous catalyst.

Single-site heterogeneous catalysts promise to combine the attractive features of homogeneous and heterogeneous catalysts: active sites of regular and tunable architecture that provide precise catalytic function, integrated into a thermally stable, porous, solid host that facilitates access of substrates to those sites and separation of products from the catalyst (1). In the conventional definition, a single-site catalyst contains functionally isolated active sites, such that reaction rates per active site are independent of their spatial proximity (2). Single metal atoms incorporated into solid oxide supports are reported to follow this conventional single-site behavior in catalytic CO oxidation to CO\textsubscript{2} (3–5), selective hydrogenation (6, 7), and water-gas shift (8, 9). Here we report that a nominally single-site catalyst (10) operates by dynamic, reversible, and density-dependent (non-mean field) interaction of multiple ionically tethered single sites, a behavior that lies outside the canonical definition of a single-site heterogeneous catalyst (11).

We discovered this phenomenon in the quest for a molecularly detailed model to unify the seemingly disparate observations of the catalytic function of copper-exchanged chabazite (Cu-CHA) zeolites, materials used in emissions control for the standard selective catalytic reduction (SCR) of nitrogen oxides (NO\textsubscript{x}, \(x = 1, 2\)) with ammonia (12)

\[
4\text{NO} + 2\text{O}_2 + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\]

Chabazite is a small-pore zeolite composed of cages (8 Å by 8 Å by 12 Å) interconnected by six-membered ring (6-MR) prisms and eight-membered ring (8-MR) windows (Fig. 1A). Substitution of Si\textsuperscript{+} by Al\textsuperscript{3+} within the framework introduces an anionic charge that is balanced by extra-lattice cations. After Cu ion exchange and high-temperature oxidation treatment, two isolated Cu site motifs are present: discrete Cu\textsuperscript{II} ions that balance two proximal Al centers and [Cu\textsuperscript{IV}OH]\textsuperscript{+} ions that balance single Al centers (10, 13, 14). Under low-temperature (<523 K) standard SCR conditions, ammonia coordinates to and liberates Cu ions from direct association with the zeolite support, and these solvated Cu ions act as the redox-active catalytic sites (15). At typical Cu ion volumetric densities, standard SCR rates increase linearly with Cu density, as expected for a single-site catalyst. As shown here, however, experimental observations in the low–Cu density limit reveal a portion of the catalytic cycle in which O\textsubscript{2} activation by transiently formed Cu pairs becomes rate limiting. These Cu pairs form from NH\textsubscript{3}-solvated Cu ions with mobilities restricted by electrostatic attraction to charge-compensating framework Al centers, leading to catalytic function that is neither single site nor homogeneous.

Recognizing the intermediacy of this distinct catalytic state reconciles a number of controversies in Cu-zeolite SCR catalysis, including the role of the zeolite support in the catalytic mechanism, the sensitivity of SCR rates to Cu density under different conditions of observation, the extent to which standard and the closely related fast SCR cycles (16) are connected through common intermediates, the chemical processes that limit low-temperature NO\textsubscript{x} SCR reactivity, and the origins of the apparent change in mechanism at elevated temperatures. These observations provide insight into the design of improved catalysts for SCR. More broadly, they reveal a distinct class of catalytic materials characterized by partially mobile ions that dynamically and reversibly form multinuclear active sites, a concept that may be exploited for a wide variety of reactions.

**Turnover rates depend on the spatial density of single Cu sites**

To assess the catalytic consequences of Cu ion density, we prepared a series of Cu-CHA samples with fixed framework Al composition (Si/Al = 15) and Cu/Al content ranging from 0.04 to 0.44 (for synthesis methods and characterization data, see supplementary materials [SM] section S1, figs. S1 to S4, and tables S1 and S2), corresponding to Cu volumetric densities (\(\rho_{\text{Cu}}\)) from (0.3 to 4.2) \(\times 10^{-4} \text{ Cu Å}^{-3}\). We denote samples as Cu-CHA-X, where X indicates the mean Cu-Cu distance (in Å), assuming a homogeneous Cu distribution (table S2). Mean Cu-Cu distances vary from 40.7 to 16.6 Å from the least to most heavily Cu-exchanged samples, and the highest Cu loading corresponds to approximately one Cu ion per three chabazite cages (Fig. 1A).

We observed that SCR rates increased linearly with Cu density at \(\rho_{\text{Cu}} > 1.9 \times 10^{-4} \text{ Å}^{-3}\) (Fig. 1B), as would be expected for a reaction catalyzed by isolated Cu sites. Turnover rates, apparent reaction orders, and apparent activation energies (table S3) are consistent with values reported for high–Cu density Cu-CHA samples (17, 18). By contrast, standard SCR rates vary quadratically with Cu density below \(\rho_{\text{Cu}} < 1.13 \times 10^{-4} \text{ Å}^{-3}\). All kinetic quantities are consistent with those reported for Cu-dilute Cu-CHA samples (Si/Al = 4.5, Cu/Al < 0.02 (17); Si/Al = 6, Cu/Al < 0.03 (18)). We show that these two kinetic regimes, characterized by distinct kinetic parameters, reflect different rate-controlling elementary steps and prevalent reactive intermediates during steady-state NO\textsubscript{x} SCR.

To probe the mechanistic origins of this change in kinetic behavior, we used x-ray absorption near-edge structure (XANES) spectroscopy to quantify Cu oxidation state during steady-state standard SCR in operando. Figure 2 and table S4 report the steady-state Cu\textsuperscript{II} fraction obtained by XANES fitting (procedure detailed in SM section S3) as a function of Cu density for three samples in Fig. 1 (Si/Al = 15) and seven other Cu-CHA zeolites (Si/Al = 4.5, 16, and 25; table S4). Consistent with prior observation, the site-isolated Cu\textsuperscript{II} ions observed ex situ evolve into a mixture of Cu\textsuperscript{I} and Cu\textsuperscript{II} ions during standard SCR catalysis, indicative of redox cycling between Cu\textsuperscript{II} and Cu\textsuperscript{I} oxidation states coupled with the SCR catalytic cycle (19). The Cu\textsuperscript{I}–Cu\textsuperscript{II} half-cycle (Fig. 2, inset) is accepted to occur on site-isolated Cu\textsuperscript{I}, to consume one equivalent of NO and NH\textsubscript{3} per Cu\textsuperscript{II}, and to produce N\textsubscript{2} and H\textsubscript{2}O (15, 16).

The inverse relationship between steady-state Cu\textsuperscript{II} fraction and Cu volumetric density (Fig. 2) is inconsistent with the behavior expected of a single-site catalyst, for which the active-site oxidation state should depend only on the reaction...
conditions and temperature. The XANES data show that Cu\textsuperscript{II} is the minority oxidation state at the highest Cu density and smallest mean Cu-Cu separations (\textless; 15 Å) during steady-state catalytic operation but that its proportion increases with decreasing Cu density to the point that it becomes the majority oxidation state in the most dilute sample (mean Cu-Cu distance \sim 29 Å).

In this dilute limit, the operando XANES and extended x-ray absorption fine structure (EXAFS) spectra become indistinguishable from those of a Cu\textsuperscript{I}-CHA sample reduced in situ or of Cu\textsuperscript{II}(NH\textsubscript{3})\textsubscript{2} in aqueous solution (fig. S5 and table S4) (10). This observation suggests that Cu\textsuperscript{I}--Cu\textsuperscript{II} oxidation rates increase with Cu ion density and implies non-single-site behavior in the oxidation half-cycle, a process that is not well understood mechanistically beyond the observation that it consumes O\textsubscript{2} (12).

The coordination states of site-isolated Cu\textsuperscript{I} and Cu\textsuperscript{II} ions under standard SCR conditions at 473 K have been explored previously in detail (10). X-ray absorption spectroscopy (10), x-ray emission spectroscopy (19, 20), and density functional theory (DFT)-based models (10) (including ab initio thermodynamic phase diagrams in figs. S17 and S18) show that NH\textsubscript{3} competes with other gases present under standard SCR conditions, including H\textsubscript{2}O, for binding at both Cu\textsuperscript{I} and Cu\textsuperscript{II} ions, which are respectively two- and four-fold coordinated. Consistent with these findings, the standard SCR reaction rate is zero order with respect to water pressure (1 to 10% atm; fig. S19). Schematic illustrations of the most probable coordination states of Cu\textsuperscript{I} and Cu\textsuperscript{II} ions under these conditions are shown in the inset of Fig. 2.

In the high-Cu density samples (Fig. 2, samples c to g), the first-shell Cu coordination number (CN) derived from operando EXAFS is three, consistent with the expectation for a nearly equimolar mixture of Cu\textsuperscript{I} and Cu\textsuperscript{II} (10), table S4). The CN decreases to two in the fully reduced (Fig. 2, samples a to b), lowest-Cu density samples, consistent with site-isolated Cu\textsuperscript{II}(NH\textsubscript{3})\textsubscript{2} as the most abundant reactive intermediate present during steady-state standard SCR. In this limit, the SCR turnover rate is solely limited by the Cu\textsuperscript{I}--Cu\textsuperscript{II} half-reaction. The increase in apparent O\textsubscript{2} reaction order from 0.3 to 0.8 with decreasing Cu density reinforces the increasing kinetic relevance of the Cu\textsuperscript{I}--Cu\textsuperscript{II} half-cycle as Cu becomes more dilute (Fig. 1). This change also corresponds with the transition from a first-order to a second-order dependence of SCR rate on Cu ion density [Fig. 1, (18)]. From these observations, we conclude that the kinetically relevant O\textsubscript{2}-consuming step in the oxidation half-cycle is sensitive to Cu density.

Cu\textsuperscript{I} site density requirements differ for oxidation with O\textsubscript{2} and NO\textsubscript{2}

To probe the coupled roles of O\textsubscript{2} and Cu density in the oxidation half-cycle, Cu-CHA-29, Cu-CHA-20, and Cu-CHA-15 (Fig. 2, labels a, c, and h, respectively) were first reduced to the Cu\textsuperscript{I} state in flowing NO and NH\textsubscript{3} (details in SM section S3, figs. S6 to S8) (10). Then, samples were held under flowing O\textsubscript{2} and the transient evolution of the Cu oxidation state was monitored by using XANES. The Cu\textsuperscript{I} fraction decayed...
in the presence of O₂ at different rates on the three samples (Fig. 3A), and different fractions of Cu²⁺ (0.05 to 0.30) persisted at steady state (table S6).

The dependence of the transient oxidation state response on Cu density suggests some underlying spatial requirements for Cu₃(NH₃)₂ ions to react with O₂. After exploring various rate laws, we found that an expression that is second order in total Cu density [Cu¹] and offset by a recalcitrant fraction of Cu¹, [Cu¹]ₙ₉₉, fits the data most satisfactorily [coefficient of determination (R²) = 0.99 (a), 0.98 (c), and 0.99 (h), Fig. 2; details in SM section S4]. Normalizing to the initial Cu density, [Cu¹]₀, the integrated rate law becomes

\[
\text{Cu}^1\text{fraction} = \frac{[\text{Cu}^1(t)]}{[\text{Cu}^1]_0} = \frac{1 - ([\text{Cu}^1]_0 - [\text{Cu}^1]_\infty)}{1 + 2k([\text{Cu}^1]_0 - [\text{Cu}^1]_\infty)t} + \frac{[\text{Cu}^1]_\infty}{[\text{Cu}^1]_0}
\]

(2)

where \(t\) is time and \(k\) is a pseudohomogeneous second-order rate constant for disappearance of Cu¹. Solid lines in Fig. 3A denote best-fit regressions of the data to Eq. 2. Fitted \(k\) values of (10, 17, and 8.2) × 10⁻⁴ m³ mol⁻¹ s⁻¹ for Cu-CHA-29, Cu-CHA-20 and Cu-CHA-15, respectively, increased systematically with Cu density. The variation in \(k\) demonstrates that all the reaction sites are not kinetically equivalent. Further analysis below suggests that the oxidation kinetics cannot be faithfully captured by a mean-field model.

This second-order Cu dependence suggests a pseudobimolecular reaction between two Cu₃(NH₃)₂ ions and O₂ during the transient experiment

\[
2\text{Cu}^1(\text{NH}_3)_2 + O_2 \rightarrow \left[NH_3\right]_2\text{Cu}^{II}\text{O}_2\text{Cu}^{II}(\text{NH}_3)_2
\]

(3)

Oxygen-bridged Cu dimers are well known in Cu-zeolate chemistry (21–23) and find analogies in the biological chemistry of Cu that prevails at lower temperatures (24–29). These dimers can adopt various oxygen-bridging configurations (25, 30). To probe the plausibility of this reaction between two caged Cu₃(NH₃)₂ centers, we turned to DFT (computational details in SM section S5).

We first considered the energy landscape for two Cu₃(NH₃)₂ ions to occupy the same CHA cage. Starting from two Cu₃(NH₃)₂ ions in adjacent cages that share an A₁ T-site vertex (Fig. 4, structure A), the computed barrier for one Cu₃(NH₃)₂ to diffuse through an 8-MR window into the adjacent Cu₃(NH₃)₂-containing cage (structure B) is 35 kJ mol⁻¹, consistent with prior estimates of Cu₃(NH₃)₂ diffusion barriers into an empty cage (10, S1). The net pairing cost is 23 kJ mol⁻¹. Thus, transport between adjacent Al-sharing cages is expected to be facile at temperatures of catalytic interest. Two Cu₃(NH₃)₂ ions bind O₂ more effectively (~59 kJ mol⁻¹) than does an isolated Cu₃(NH₃)₂ (~26 kJ mol⁻¹) (table S10 and fig. S14), and the O₂ binding energy more than offsets the energy cost for two Cu²⁺(NH₃)₂ to cohabit the same cage. Initial reaction likely generates the end-on spin-triplet species shown in Fig. 4 (structure C), and further rearrangement and dissociation of O₂ across two Cu²⁺ centers ultimately leads to the di-oxo structure E, containing two four-fold-coordinated Cu²⁺ centers. Conversion of structure C into D is spin forbidden; the effective barrier in similar ligand environments is estimated to be 20 kJ mol⁻¹ (24). Subsequent conversion of structure D into E occurs with a modest barrier. The rate-limiting process across this entire cascade (A to E, table S9) is the migration of Cu¹ through the 8-MR; beyond that point, reaction energies are computed to be independent of the zeolite cage. Thus, the primary role of the zeolite support in this oxidation process is to regulate Cu¹ mobility.

Structure E is consistent both with XANES-observed Cu¹ oxidation state and with the first- and second-shell features extracted from EXAFS (Fig. 3A, inset, and figs. S9 to S11) at the end of the transient O₂ oxidation experiment. Thus, experiment and computation both reveal a second Cu²⁺ state of the catalyst, distinct from framework-bound Cu⁺ observed after oxidative treatments and from NH₃-solvated Cu²⁺ detected during low-temperature standard SCR (10, 20). Exposure of samples to NO and NH₃ at 473 K after the transient O₂ oxidation experiments reduces all sites to the original mononuclear Cu²⁺ state, demonstrating that the SCR redox cycle can be closed through sequential stoichiometric reactions.
Further, subsequent O2 treatment recovers the same transient response and the same fraction of CuI sites that are unresponsive to O2 exposure (table S7), indicating that CuI ions do not irreversibly aggregate during O2 exposure, but return to their original site-isolated state after each reduction step.

To verify that the residual CuI fraction did not represent a physically inaccessible or chemically distinct site, transient O2 experiments were compared with an analogous transient NO3 experiment (details in SM section S3) on reduced forms of the same three samples (figs. S6 to S8). After NO3 exposure at 473 K, the CuI fraction decayed with time as in the O2 experiment, but the CuI absorption edges disappeared completely after ~300 s. Further, the decrease in CuI fraction with time is best described ($R^2 = 0.98$ (a), 0.98 (c), and 0.89 (b); details in SM section S4) by a pseudo-first-order rate expression with apparent rate constants (0.030 s$^{-1}$) that are independent of Cu density (SM section S4, fig. S13). Thus, all CuI sites are equivalently susceptible to oxidation by NO3. We compute the reaction energy for NO3 binding to CuI(NH3)$_2$ to be ~46 kJ mol$^{-1}$ and to generate a CuII center (SM section S5, fig. S14, and table S10).

We conclude that the spatial proximity of isolated CuI ions, and not the presence of minority dimeric Cu species at low Cu densities, is responsible for the transition in the standard SCR turnover rate from a quadratic to a linear dependence on Cu ion density with increasing Cu density (Fig. 1B). The steady-state and transient experiments and DFT models are consistent with a CuI → CuII half-cycle that combines two CuI(NH3)$_2$ complexes with one O2 molecule to create a previously unobserved binuclear CuII intermediate (Eq. 3 and Fig. 4).

The available data exclude the possibility that O2 activation occurs on a persistent minority fraction of CuI ion pairs within single zeolite cages (22). First, the fraction of isolated CuI(NH3)$_2$ complexes that could be reversibly oxidized with O2 (Fig. 3A) exceeds by 10-fold the fraction of Cu pairs within a single cage if Cu were randomly dispersed on the zeolite support (SM section S7, fig. S15). Second, steady-state and transient rates of CuI oxidation with O2 would exhibit a first-order dependence on Cu density, as observed with NO3 as the oxidant. Rather, these results imply a pseudohomogeneous reaction between equivalent site-isolated CuI ions with mobilities constrained in a manner that limits the total fraction of sites reactive toward O2.

**Solvation by ammonia confers mobility to single Cu ions**

To assess the mobility of CuI(NH3)$_2$ complexes over time scales inaccessible to conventional ab initio molecular dynamics, we turned to ab initio metadynamics (SM section S8), taking Cu-Al coordination distance as the collective variable, using a supercell with a minimum image distance of >10 Å (SM section S8), and sampling at 473 K. Free energy was minimized at a Cu-Al distance of 4.7 Å and increased with Cu-Al separation until the Cu ion entered an 8-MR window separating two cages, at 6 Å (Fig. 5). Free energy decreased as the Cu ion moved into the adjacent cage, before increasing again as the Cu-Al distance exceeded 9 Å. Comparison with a point-charge model indicates that electrostatics dominate this distance-dependent free energy (SM section S9, Fig. 5). From the computed free-energy landscape, we estimate the hopping rate for a CuI(NH3)$_2$ to leave its resting cage to be $6 \times 10^8$ s$^{-1}$ at 473 K, much faster than steady-state SCR turnover rates (table S3), and the equilibrium fraction of Cu ions outside their resting cage to be $1.4 \times 10^{-3}$ at 473 K.

CuI(NH3)$_2$ migration is thus rapid at 473 K but constrained by electrostatic tethering to charge-compensating framework Al sites. We next use this concept to predict the unoxidized fraction of CuI(NH3)$_2$ in the transient O2 experiments (Fig. 3A), assuming that CuI ions are randomly associated with Al in the CHA lattice, that each Cu can access a limited diffusion volume, and that only CuI ions with overlapping diffusion volumes can form an O2-bridged Cu pair (Fig. 4). To exercise the model, we distributed Al onto a periodic supercell of the CHA lattice following Löwenstein’s rule (33), occupied sites with Cu following previously validated rules (10), counted the number of overlapping diffusion spheres at a given radius (Fig. 3B, t = 0) permitting each Cu to be counted only once, and repeated until the average unoxidized CuI fraction converged (SM section S10 and fig. S16). At the end of a single simulation, the unoxidized CuI fraction consisted of CuI ions that either were initially physically isolated from all other Cu (iso) or were functionally isolated because they shared overlapping diffusion volumes with Cu ions that had more than one potential partner, the losers in a molecular game of musical chairs (MC). Representative initial and final simulation snapshots are shown in Fig. 3B for Cu densities corresponding to Cu-CHA-15, Cu-CHA-20, and Cu-CHA-29, and the predicted fraction of unoxidized CuI assuming a diffusion radius of 9 Å are plotted as solid horizontal bars in Fig. 3A. Model results agree quantitatively with both experimental observation and the metadynamics observation of a ~9 Å maximum diffusion distance, implying that the Cu sites are neither conventionally heterogeneous (immobile) nor homogeneous (mobility governed by molecular diffusion) and demonstrating that the fraction of spectator [CuI]$_2$ sites is a consequence of regulated and localized mobility due to electrostatic tethering.

These observations resolve the outstanding issues regarding SCR catalysis raised in the introduction. NH3 solvates and mobilizes discrete Cu active sites under low-temperature SCR conditions. When the activation of O2 is not rate controlling, NH3-solvated CuI ions appear catalytically equivalent, such that rates increase linearly with their number density. In this regime, the zeolite framework itself has only a weak influence on the SCR turnover rate (10) because it functions primarily as an ionic host for homogeneous-like NH3-ligated CuII complexes. Experiments performed on samples with low Cu density revealed, however, that a homogeneous picture of the SCR mechanism is incomplete.

Simulations reveal that NH3-solvated CuI ions have sufficient mobility to travel through 8-MR CHA windows, visit adjacent cages, and form Cu site pairs that activate O2 via Eq. 3. Because of this requirement for dynamic Cu pairing, SCR rates scale approximately second order with Cu density under conditions in which the CuI → CuII oxidation by O2 is rate determining, consistent...
with quantitative analysis of the transient oxidation of Cu with O2. In contrast with previous assertions (34), binuclear CuII intermediates can be detected experimentally and are structurally distinct from the mononuclear NH3-solvated CuII observed in operando (10, 20), and the number of such binuclear sites that can form on a given Cu-CHA sample can be quantitatively predicted. These results motivate a revision of previous mechanisms to incorporate this dynamic coupling of isolated Cu ions, as illustrated in Fig. 6. Isolated, NH3-solvated CuII ions charge-compensating either one (left-hand cycle) or two (right-hand cycle) framework Al centers with constrained diffusion of CuII ions into single cages and oxidation by O2 (inner step). NH3+ is formed and consumed in the right-hand cycle to maintain stoichiometry and charge balance. Gray, Cu; green, Al; blue, N; and white, H.

A key aspect of our model is that Cu ions supported on the zeolite are neither mobile as prescribed by molecular diffusion processes, as in a homogeneous catalyst, nor segregated into separate ensembles of active and inactive sites, as in a heterogeneous catalyst. Rather, all Cu ions located within diffusion distances of other ions can potentially form Cu pairs dynamically and reversibly during the SCR cycle, at rates influenced by the mobility and effective diffusion distances of Cu ions. Thus, rates of O2-assisted oxidations are sensitive to Cu proximity and could also be sensitive to the zeolite support composition and topology. By contrast, all NH3-solvated CuII sites are equivalently susceptible to first-order oxidation by NO2, independent of Cu spatial density, and are subsequently reducible by NO and NH3. These observations demonstrate that fast SCR, in which oxidation capacity is provided by NO2 rather than O2

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (4)
\]

is not linked through a common intermediate to standard SCR under conditions in which Cu sites are solvated by NH3 (30). NO2 oxidants accelerate SCR rates both by accelerating CuI oxidation kinetics and by engaging a larger fraction of Cu sites in the catalyst.

At higher temperatures (>523 K), standard SCR rates are independent of Cu density (22, 38), the apparent activation energy increases to 140 kJ mol\(^{-1}\) (38), and Cu ions lose their NH3 solvation shell (22), implicating the involvement of different O2 activation steps that do not occur at the Cu ion pairs formed dynamically at lower temperatures (<523 K). Of greater practical importance to NOx emissions control is to increase SCR rates at even lower temperatures (<473 K) (12). The results here imply that standard SCR onset ("light-off") temperatures, which are observed to depend on zeolite composition, topology, and Cu distribution (35), are sensitive to changes in rate-determining O2 activation steps. Thus, optimization of Cu spatial distribution and promotion of Cu mobility are promising strategies for accelerating CuII oxidation rates and improving low-temperature SCR catalysts.

**Outlook**

Our results point to a previously unrecognized catalytic mechanism that embodies salient features of homogeneous and heterogeneous catalysts. This mechanism encompasses solvent mobilization of discrete active site precursors (e.g., single metal ions) and ionic bonds to the support that limit their mobility. The active site precursor has an effective diffusion distance and occupies a volumetric footprint that restricts its interactions only to other precursors within overlapping volumes; such catalytic behavior cannot be described by mean-field, Langmuir kinetics. The ionic tethering motif provides opportunities to confer catalytic benefits beyond immobilization strategies based on covalent anchors or tethers. This motif enables the in situ dynamic generation of multinuclear complexes implicated as active sites in O2 activation and therefore could also apply to other reactions, such as the partial oxidation of methane to methanol on Cu-zeolites. We expect that design parameters to regulate the mobility of active sites and their precursors would include the structure, composition and electronic conductivity of the support, and the molecules that solvate such sites to promote their mobility. Manipulating these variables could open approaches to catalyst design for a wide variety of reactions by combining knowledge from homogeneous and heterogeneous catalysis.

**REFERENCES AND NOTES**


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SUPPLEMENTARY MATERIALS
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Materials and Methods
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