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Combining Kinetics and *Operando* Spectroscopy to Interrogate the Mechanism and Active Site Requirements of NO_x Selective Catalytic Reduction with NH_3 on Cu-Zeolites

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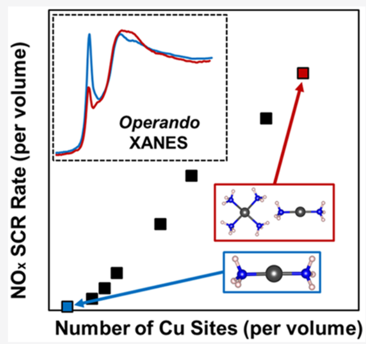
ABSTRACT: NO_x selective catalytic reduction (SCR) with NH_3 on Cu-zeolites is a commercial emissions control technology for diesel and lean-burn engines. Mitigating low-temperature emissions remains an outstanding challenge, motivating an improved understanding of the reaction mechanism, active site requirements, and rate-determining processes at low temperatures (<523 K). In this Perspective, we discuss how *operando* spectroscopy provides crucial information about how the structures, coordination environments, and oxidation states of Cu active sites depend on reaction conditions and sample composition; when combined with kinetic measurements, such *operando* data provide insights into the Cu site and spatial density requirements for reduction and oxidation steps relevant to the Cu(II)/Cu(I) SCR redox cycle. Isolated Cu ions coordinated to zeolite oxygen atoms *ex situ* become coordinated to NH_3 *in situ* and dynamically interconvert between mononuclear and binuclear NH_3-solvated Cu complexes to catalyze SCR turnovers. We conclude with future research directions that can benefit from combining quantitative kinetic measurements with *operando* spectroscopy.



Cu-CHA zeolites (e.g., Cu-SSZ-13) are used as catalysts for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x, $x = 1, 2$) with NH_3, commercially implemented a decade ago as the preferred technology for NO_x emissions abatement in diesel and lean-burn engines.[1−4] The majority of NO_x emissions from diesel engine exhaust occur at the low temperatures (<523 K) experienced during "cold-start" conditions and "low-load" operation; thus, mitigating NO_x emissions at low temperatures remains an outstanding challenge to meet future emissions regulations.[2,4] As such, basic research efforts in the scientific community have focused on understanding the NO_x SCR reaction mechanism, the Cu active site requirements, and the nature of the rate-determining processes at low temperatures.

These research questions have been studied using a diverse range of scientific tools and methodologies common to the heterogeneous catalysis and inorganic materials communities. SCR reactivity is typically assessed by measuring the dependence of NO conversion on temperature (i.e., "light-off curves") in reactant pressure and reactor hydrodynamic regimes resembling those of practical operation. The temperature corresponding to a specific NO conversion (i.e., T_{50} or T_{90}, corresponding to 50% or 90% conversion) is often used as a figure of merit for the onset of reactivity at low temperature (i.e., the "light-off" temperature). Yet, such figures of merit convolute the effects of properties that are extrinsic (e.g., gas composition, residence time) and intrinsic (e.g., framework topology, elemental composition, atomic arrangement) to Cu-zeolites, each of which influences the microscopic kinetic and mechanistic details that underpin the observed catalytic behavior. Kinetic and mechanistic details are interrogated more directly through reaction rate measurements, rigorously normalized to the number of catalytically active sites,[5] in differential hydrodynamic regimes that result in uniform temperature and concentration profiles throughout catalyst beds and within zeolite crystallites; such hydrodynamic regimes are not guaranteed solely by operating under differential reactant conversion. The implementation of differential (i.e., gradient-less) reactor hydrodynamics ensures that spectroscopic measurements made on any portion of the catalyst bed are representative of the entire bed, validating the use of *operando* measurements to directly link kinetic and spectral data.

As evidenced by a growing body of literature,[6−12] *operando* characterization is critical to obtain accurate descriptions of the working state of Cu-zeolite catalysts during low-temperature NO_x SCR with NH_3, because the oxidation state, coordination

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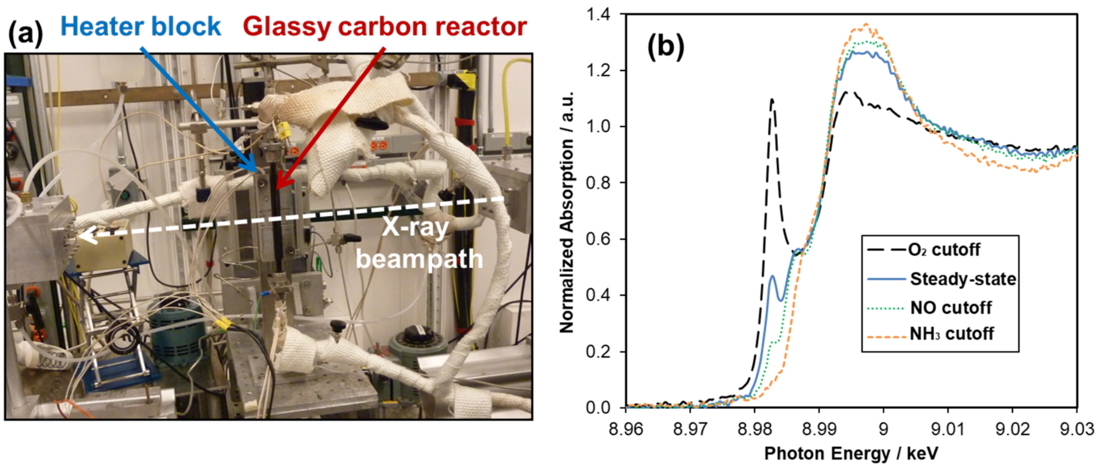

Figure 1. (a) Reactor apparatus for *operando* XAS measurements including gas lines, heater block, and glassy carbon reactor, as originally described by Kispersky et al.[15] The front plate of the heater block has been removed to show the position of the glassy carbon reactor. (b) *Operando* XANES spectra of Cu-SSZ-13 during low-temperature NO_x SCR with NH_3 ("steady-state") and after cutoff of O_2, NO, or NH_3 from the SCR reactant stream. Adapted from Paolucci et al.[9] with permission from John Wiley and Sons. Copyright 2014.

environment, and nuclearity of Cu active sites change in response to the reaction temperature and gas composition. To this end, X-ray absorption techniques are particularly useful, because the X-ray absorption near-edge structure (XANES) region can provide information about metal coordination environments and oxidation states, while the extended X-ray absorption fine structure (EXAFS) region can provide information about the identity, number, and distance of other atoms in surrounding coordination spheres. A broader commentary on the role of *operando* spectroscopy in active site elucidation is provided by Weckhuysen,[13] and a more extensive review of how kinetic measurements can be combined with *operando* and transient X-ray absorption spectroscopy (XAS) to investigate the nature of active sites in heterogeneous catalysts is provided by Kondrat and van Bokhoven.[14] This Perspective will highlight research efforts to combine quantitative kinetic measurements and *operando* spectroscopic data to probe the structure and function of Cu-zeolites during low-temperature NO_x SCR with NH_3, in order to study the following scientific questions regarding the mechanism, kinetics, and Cu active site requirements for different elementary steps in the SCR reaction:

(i) What are the prevalent Cu oxidation states during SCR, and how do their relative proportions respond to changes in reaction conditions?

(ii) How does the Cu coordination environment evolve with reaction conditions and temperature, and what are the resulting implications for the low-temperature SCR reaction mechanism?

(iii) What are the Cu active site requirements for the different Cu(II) reduction and Cu(I) oxidation processes that may occur during low-temperature SCR?

The measurement of X-ray spectra under *operando* conditions requires a synchrotron X-ray source in order to obtain high-quality spectra under the temperature and pressure conditions relevant for reaction and a reactor capable of maintaining differential hydrodynamic regimes while being able to transmit X-rays, such as a vitreous (i.e., glassy) carbon reactor. Such an apparatus (Figure 1a) was originally used by Kispersky et al.[15] to show that Cu-exchanged zeolites and silicoaluminophosphates (ZSM-5, SSZ-13, and SAPO-34, containing ~2−3 wt % Cu) prepared to contain solely Cu(II) ions after oxidative pretreatments evolve to a mixture of Cu(I) and Cu(II) under low-temperature SCR conditions (473 K; 0.03 kPa NO, 0.03 kPa NH_3, 5 kPa O_2, 5 kPa H_2O, 5 kPa CO_2, balance He). SCR rates did not correlate solely with the amount of either Cu(II) or Cu(I) present under *operando* conditions, implying that a Cu(II)/Cu(I) redox cycle is involved in the SCR reaction mechanism.[15] The mixture of Cu(I) and Cu(II) oxidation states observed under *operando* conditions further indicates that both Cu(I) oxidation and Cu(II) reduction half-cycles are kinetically relevant under typical SCR reaction conditions. In contrast, XANES spectra collected *in situ* on catalyst wafers exposed to SCR reactant gases show only minority amounts of Cu(I), likely because of non-differential hydrodynamic (e.g., gas bypassing) and transport (e.g., intracrystalline concentration gradients) artifacts.[15] These data demonstrate the necessity of *operando* measurements in obtaining accurate kinetic and mechanistic insights on the working state of Cu-zeolite catalysts.

The implication of both Cu(I) and Cu(II) species in the SCR redox mechanism motivates questions regarding which Cu structures present in Cu-SSZ-13 *ex situ* are able to evolve to the active Cu(I) and Cu(II) states under *operando* conditions and how the relative proportions of active Cu(I) and Cu(II) states vary in response to changes in the reaction environment.[3] Bates et al. performed spectroscopic (UV−visible, XAS) measurements on Cu-SSZ-13 zeolites (Si/Al = 4.5, Cu/Al = 0−0.35) to show that initially hydrated, isolated Cu(II) ions (but not bulk Cu-oxide clusters[16]) convert to a mixture of Cu(II) or Cu(I) states under low-temperature SCR conditions (473 K; 0.032 kPa NO, 0.032 kPa NH_3, 10 kPa O_2, 6 kPa H_2O, 8 kPa CO_2, balance He),[8] consistent with the *ex situ* and *in situ* characterization data (XAS and XRD) reported by Deka et al.[17,18] A subsequent report by Paolucci et al. showed that different isolated Cu(II) site motifs in Cu-SSZ-13 present *ex situ* (Cu(II) or Cu(II)OH, for sample compositions containing Si/Al = 4.5−25, Cu/Al = 0−0.45) were able to evolve to similar Cu(II) and Cu(I) structures under low-temperature SCR conditions.[6] Starting from steady-state SCR catalysis on Cu-SSZ-13 samples that contained a mixture of Cu(I) (~30%) and Cu(II) (~70%) under *operando* conditions (Cu-SSZ-13,

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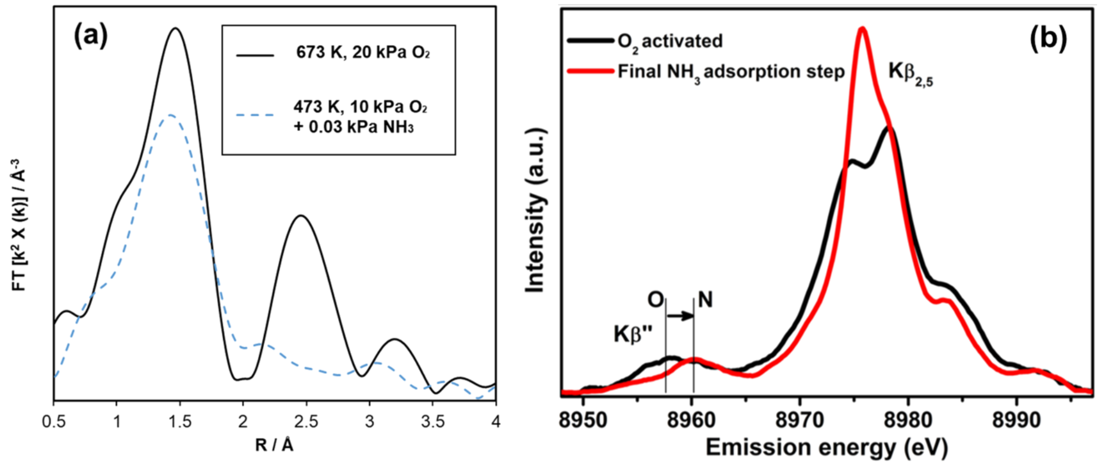

Figure 2. (a) EXAFS spectra of Cu-SSZ-13 (Si/Al = 4.5, Cu/Al = 0.09) measured at 298 K after high-temperature oxidative treatment (673 K, 20 kPa O_2), and measured at 473 K after subsequent low-temperature exposure to NH_3 (473 K, 0.03 kPa NH_3, 10 kPa O_2). Adapted from Paolucci et al.[6] Copyright 2016 American Chemical Society. (b) Background-subtracted vtc-XES spectra of Cu-SSZ-13 (Si/Al = 13, Cu/Al = 0.44) following high-temperature oxidative treatment (673 K, 50 kPa O_2 in He) and after subsequent low-temperature exposure to NH_3 (393 K, 0.13 kPa NH_3 in He). Reprinted from Giordanino et al.[19] Copyright 2014 American Chemical Society.

Si/Al = 5, Cu/Al = 0.11–0.16; 473 K; 0.032 kPa NO, 0.032 kPa NH_3, 10 kPa O_2, 5 kPa H_2O, balance He), Paolucci et al. showed that removing either NH_3 or NO from SCR reactant streams resulted in the transient oxidation of the majority of the Cu to its Cu(II) state (Figure 1b), indicating that both NO and NH_3 are required for complete Cu(II) reduction,[9] as also observed by Janssens et al.[11] Analogous experiments that instead removed O_2 from SCR reactant streams resulted in the transient reduction of the majority of the Cu to its Cu(I) state (Figure 1b), indicating that O_2 is required for Cu(I) oxidation.

Further kinetic and spectroscopic investigations showed that NH_3 not only acts as a co-reductant in NO_x SCR but also coordinates to and solvates isolated Cu(I) and Cu(II) ions under low-temperature SCR reaction conditions. Using *operando* XAS measurements of Cu-SSZ-13 at low temperatures (<523 K), Paolucci et al.,[6] Janssens et al.,[11] and Lomachenko et al.[10] independently demonstrated that the Cu(I) and Cu(II) species observed in XANES spectra are essentially identical to homogeneous $Cu(I)(NH_3)_2$ and $Cu(II)(NH_3)_4$ complexes. Moreover, the EXAFS region shows first-shell Cu–X coordination numbers of ~2 for Cu(I) and ~4 for Cu(II) species, while the second-shell region shows the absence of scattering to T atoms (T = Si and Al) in the zeolite lattice (Figure 2a). In agreement with these findings, Giordanino et al.[19] used valence-to-core X-ray emission spectroscopy (vtc-XES) to show that exposure of Cu-SSZ-13 (Si/Al = 13, Cu/Al = 0.44) to NH_3 (393 K, 0.13 kPa NH_3 in He) causes Cu ions to become ligated by N rather than O atoms (Figure 2b). Peden and co-workers used *in situ* diffuse reflectance IR spectroscopy (DRIFTS) to show that the perturbation of lattice T–O–T vibrations of Cu-SSZ-13 (Si/Al = 10, Cu/Al = 0.14), which results from coordination of metal ions within siloxane rings, decreases in the presence of NH_3 (523 K, 0.05 kPa NH_3).[20,21] These observations support the interpretation that Cu ions are coordinated to NH_3 ligands rather than to zeolitic oxygen atoms. In contrast, at higher temperatures, Deka et al. observed that Cu ions in Cu-SSZ-13 (Si/Al ≈ 18, Cu/Al ≈ 0.65) show XANES features indicative of dehydrated Cu ions (573 K; 0.1 kPa NO, 0.1 kPa NH_3, 5 kPa O_2, balance He).[17] Consistent with these findings, Paolucci et al. observed that Cu ions in Cu-SSZ-13 (Si/Al = 4.5, Cu/Al = 0.08) at high temperature in the presence of NH_3 and O_2 (673 K, 0.03 kPa NH_3, 10 kPa O_2) show second-shell scattering to T atoms in the zeolite lattice,[6] as also reported by Lomachenko et al.[10]

The preponderance of evidence indicates that isolated Cu ions in Cu-zeolites are solvated by NH_3 under low-temperature (<523 K) SCR-relevant reaction conditions. *Operando*

Operando structural characterization reveals signatures solely for homogeneous Cu–amine coordination complexes during low-temperature NO_x SCR; from these data alone, one could not determine that a solid zeolite powder was actually placed in the path of the X-ray beam.

structural characterization reveals signatures solely for homogeneous Cu–amine coordination complexes during low-temperature NO_x SCR; from these data alone, one could not determine that a solid zeolite powder was actually placed in the path of the X-ray beam. The fact that Cu ion active sites are NH_3-solvated under low-temperature conditions but zeolite-bound under high-temperature conditions suggests that there is a transition in the mechanism of NO_x SCR with temperature, which has been invoked as an explanation for the "seagull dip" in NO-conversion observed in light-off curves in an intermediate temperature range (523–623 K).[22]

Kinetic measurements on Cu-CHA samples with widely varying Cu content, combined with *operando* and transient XAS measurements, have been used to better understand the effects of Cu structure and coordination by NH_3 on the mechanism of low-temperature NO_x SCR. Low-temperature NO_x SCR rates (per mass, 473 K) were observed by Peden et al.[23] (Si/Al = 12, Cu/Al = 0–0.033; 473 K; 0.035 kPa NO, 0.035 kPa NH_3, 14 kPa O_2, 2.5 kPa H_2O, balance N_2) and Paolucci et al.[7] (Si/Al = 15, Cu/Al = 0–0.12; 473 K; 0.03 kPa

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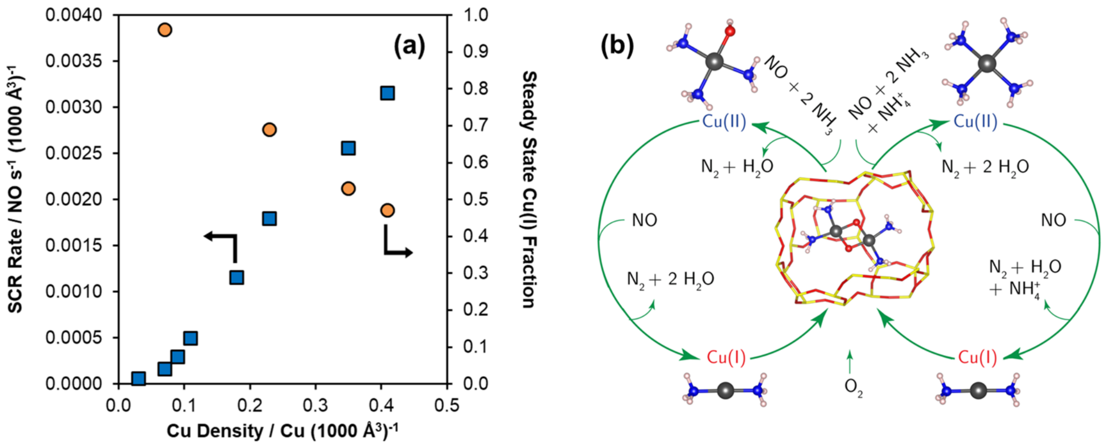

Figure 3. (a) SCR rate (per pore volume) and steady-state Cu(I) fraction versus Cu density (per pore volume) for Cu-SSZ-13 (Si/Al = 15, Cu/Al = 0–0.44; 473 K; 0.03 kPa NO, 0.03 kPa NH_3, 10 kPa O_2, 2.5 kPa H_2O, 5 kPa CO_2, balance N_2). Adapted from Paolucci et al.[7] Reprinted with permission from AAAS. Copyright 2017. (b) Proposed mechanism of low-temperature NO_x-SCR. The reduction half-cycle proceeds on NH_3-solvated Cu(II) ions residing near one (left-hand cycle) or two (right-hand cycle) framework Al atoms, while the O_2-oxidation half-cycle proceeds via restricted diffusion of two NH_3-solvated Cu(I) ions into single cages to form binuclear intermediates. Gray, Cu; yellow, Si; red, O; blue, N; and white, H. From Paolucci et al.[7] Reprinted with permission from AAAS. Copyright 2017.

NO, 0.03 kPa NH_3, 10 kPa O_2, 2.5 kPa H_2O, 5 kPa CO_2, balance N_2) to increase with a second-order dependence on Cu content for Cu-SSZ-13 samples with low Cu content (Figure 3a). In contrast, Gao et al. reported that high-temperature NO_x SCR rates (per mass, 623 K) increase linearly with Cu content even for Cu-SSZ-13 samples with low Cu content (Si/Al = 6, Cu/Al = 0–0.016; 0.035 kPa NO, 0.035 kPa NH_3, 14 kPa O_2, 2.5 kPa H_2O, balance N_2),[24] suggesting that different active site requirements and mechanisms prevail in low- and high-temperature regimes. *Operando* XAS measurements were used by Paolucci et al. to provide insights into the mechanistic origin of the non-single site kinetic regime observed at low temperature.[7] With decreasing Cu content on Cu-SSZ-13 samples, the fraction of Cu(I) under low-temperature SCR conditions increases systematically and approaches unity, indicating that Cu(I) oxidation becomes increasingly rate-limiting at lower Cu content. These *operando* XAS measurements provide a direct link between the observed second-order dependence of SCR rates on Cu concentration and the rates of SCR-relevant Cu(I) oxidation processes (Figure 3a).

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Transient XAS measurements have been used by Paolucci et al. to further isolate the kinetic behavior of the Cu(I) oxidation half-cycle, after first fully reducing Cu-SSZ-13 samples of different Cu content (0.5–3.7 wt %) to the Cu(I) state in an NO and NH_3 environment (473 K, 0.03 kPa NH_3, 0.03 kPa NO).[7] Transient changes to the Cu oxidation state were monitored during subsequent O_2-assisted oxidation (473 K, 10 kPa O_2) to show that rates of Cu(I) oxidation are best described by a rate equation that is second-order in Cu concentration (Figure 4a).[7] This kinetic behavior implies that two mononuclear Cu(I) complexes, which were nominally isolated after the NO + NH_3 reduction step, are able to react with O_2 and become oxidized to the Cu(II) state. This proposal is supported by a combination of density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations by Paolucci et al. which showed that NH_3-solvated Cu ions are bound ionically to anionic (i.e., framework Al) centers in the zeolite lattice, and that NH_3 solvation endows mobility to Cu ions that is sufficient to enable their diffusion between adjacent cages in the CHA structure and formation of binuclear O_2-bridged Cu complexes within a single cage.[7] Furthermore, a fraction of Cu(I) remains unoxidized at the end of the transient O_2-assisted oxidation of Cu-SSZ-13 (Figure 4a). This fraction of unoxidizable Cu(I) decreases systematically with increasing Cu density, implying that a fraction of Cu(I) ions are isolated from other Cu(I) ions and thus unable to pair and become oxidized by O_2.[7] Similarly, Liu et al. reported that O_2-assisted oxidation (473 K, 10 kPa O_2) of prereduced Cu-CHA (Si/Al = 15) resulted in a higher percentage of unoxidizable Cu(I) on a sample of lower Cu content (47% Cu(I), Cu/Al = 0.03) than on a sample with a higher Cu content (5% Cu(I), Cu/Al = 0.29).[25] XANES and EXAFS measurements of the final state of Cu(II) in the O_2-oxidation transient experiments by Paolucci et al. were consistent with a binuclear O_2-bridged Cu complex, such as that shown in Figure 3b, which contains Cu in oxidation states of +2.1 according to DFT-computed Bader charge analysis.[7]

In contrast to O_2-assisted oxidation, Paolucci et al. showed that NO_2-assisted oxidation (473 K, 0.01 kPa NO_2) of $Cu(I)(NH_3)_2$ complexes in Cu-SSZ-13 was best described by a rate model that is first-order in Cu concentration, and that all Cu(I) became oxidized to the Cu(II) state (Figure 4b).[7] These experimental findings are consistent with DFT calculations indicating that NO_2 can oxidize single Cu(I) sites to form $Cu(II)-NO_2^-$.[9] Ueda et al. used transient XAS measurements to study the reduction and oxidation half cycles for low-temperature (398 K) NO_x SCR on fully reduced Cu-ZSM-5 samples (Si/Al = 20, Cu/Al = 0.50; 0.1 kPa NO, 0.1 kPa NH_3),[26] finding that only a fraction (~0.50) of Cu(I) could be

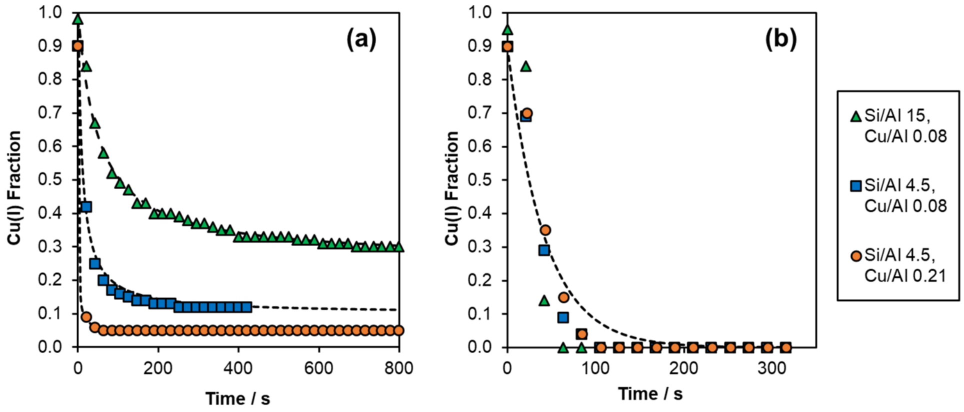

Figure 4. Transient oxidation (473 K) of pre-reduced Cu-SSZ-13 with varying Cu content using (a) 10 kPa O_2 or (b) 0.01 kPa NO_2 as the oxidant. Adapted from Paolucci et al.[7] Reprinted with permission from AAAS. Copyright 2017.

oxidized to Cu(II) in O_2 (10 kPa), but that all Cu(I) could be oxidized in a mixture of NO and O_2 (0.1 kPa NO, 10 kPa O_2), potentially because of *in situ* NO oxidation to form NO_2. Taken together, the different kinetic behavior of O_2-assisted and NO_2-assisted oxidation of $Cu(I)(NH_3)_2$ complexes in Cu-SSZ-13 imply that the "standard" SCR reaction (eq 1; O_2 as the oxidant) has different active site requirements than the "fast" SCR reaction (eq 2; NO_2 as the oxidant):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

$$2NO_2 + 2NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{2}$$

Thus, the ratio of NO_2 and O_2 present in diesel exhaust streams, which depends on the reaction conditions of the combustion and oxidation processes located upstream of the SCR catalyst,[27] influences low-temperature SCR "light-off" behavior, given the prevalence of Cu(I) species at these conditions (Figure 3a) that implies Cu(I) oxidation processes are kinetically relevant.

These experimental kinetic and *operando* XAS measurements provide evidence that Cu-zeolites cannot be treated as conventional heterogeneous catalysts under low-temperature NO_x SCR reaction conditions, given that low-temperature (<523 K) SCR rates on Cu-SSZ-13 samples that nominally contain isolated Cu ions show both first-order and second-order dependences on Cu concentration for different oxidation and reduction processes in the SCR cycle. NH_3-solvation mobilizes Cu ions in a manner regulated by electrostatic interactions with anionic centers (i.e., framework Al) in the zeolite lattice, such that the spatial proximity of Cu ions influences rates of the O_2-assisted SCR oxidation half-cycle.[7] The mobility of ionic active sites regulated by electrostatic tethering to the support falls outside canonical descriptions of homogeneous or heterogeneous catalysis.

The mobility of ionic active sites regulated by electrostatic tethering to the support falls outside canonical descriptions of homogeneous or heterogeneous catalysis.

The combination of *operando* XAS and quantitative kinetic measurements has been instrumental in developing our current understanding of the reaction mechanism and active site and spatial density requirements of low-temperature NO_x SCR with NH_3. The currently proposed reaction mechanism involves reduction of NH_3-solvated Cu(II) ions by NO and NH_3 and O_2-assisted oxidation of two NH_3-solvated Cu(I) ions to form binuclear O_2-bridged Cu intermediates (Figure 3b). As we discuss next, investigations that combine kinetic measurements and *operando* spectroscopy can continue to provide new insights into the three research questions outlined earlier in our Perspective.

Concerning the first question regarding Cu oxidation states and the extent to which reduction and oxidation half-cycles determine overall SCR rates, we note that typically used SCR reaction conditions cause both half-cycles to behave as kinetically relevant, as evidenced by the mixture of Cu(I) and Cu(II) observed during steady-state turnover (Figure 3a). Yet, the intrinsic rates of the two half-cycles should depend on the specific reaction conditions used (e.g., gas pressures, temperatures). Doronkin et al. performed spatially resolved *operando* XANES measurements on Cu-SAPO-34 (3.48 wt % Cu) during NO_x SCR reactions (528 K; 0.1 kPa NO, 0.1 kPa NH_3, 10 kPa O_2, 1.5 kPa H_2O, balance He) and found that the Cu(II) fraction systematically increased down the length of the catalyst bed as NO conversions increased and led to higher oxidant (O_2) to reductant (NO and NH_3) ratios.[28] Greenaway et al. used modulation excitation of the inlet NO gas pressure during *operando* XANES, which caused oscillation in the Cu(I) and Cu(II) fractions (Cu-SSZ-13, Si/Al = 13, Cu/Al = 0.39; 523 K; 0.126 kPa NO, 0.126 kPa NH_3, 10 kPa O_2, balance N_2), indicating that the relative oxidant-to-reductant pressures affect the distribution of Cu oxidation states.[29] Furthermore, Liu et al. demonstrated that decreasing the O_2 pressure (0−10 kPa O_2) systematically increases the Cu(I) fraction observed using *operando* XANES of Cu-SSZ-13 (Si/Al = 15, Cu/Al = 0.03 or 0.29; 473 K; 0.1 kPa NO, 0.1 kPa NH_3, balance He). Thus, varying the reaction conditions (e.g., O_2 pressure) should perturb the redox cycle so as to allow the isolation of reduction-limited and oxidation-limited kinetic regimes. We recently showed that NO_x-SCR rates (per Cu) display a Langmuirian dependence on O_2 pressure, while *operando* XAS reveals that the prevalent Cu oxidation state transitions from Cu(I) to Cu(II) with increasing O_2 pressure.[30] Such measurements allow extracting rate constants in limiting kinetic regimes: oxidation-limited rate constants (per Cu) increase with an approximately linear dependence on Cu density, consistent with a non-mean field dual-site oxidation mechanism; reduction-limited rate constants increase more gradually Cu density, in part reflecting changes in the fraction of Cu ions that can form binuclear intermediates and thus participate in SCR turnovers. This approach enables interrogating how reaction conditions (e.g., temperature, gas composition) and catalyst composition (e.g., zeolite topology, active site density and arrangement) affect the kinetics of the oxidation and reduction half cycles separately, providing insights into the kinetic and mechanistic factors that determine low-temperature NO_x conversion and "light-off" behavior during practical operation.

Regarding the second question about the coordination environment of Cu ions, although prior work has demonstrated that NH_3 participates as both a reactant and a solvent during low-temperature NO_x SCR, an NH_3 inhibition effect has also been reported in several studies.[22,31,32] After establishing steady-state NO_x SCR under predominantly oxidation-limited conditions (463−498 K; 0.1 kPa NO, 0.1 kPa NH_3, 6 kPa O_2, 2 kPa H_2O, balance N_2), Marberger et al. removed NH_3 from the reactant stream and monitored transient changes in the oxidation state of Cu-SSZ-13 (Si/Al = 14, Cu/Al = 0.17) and the gas composition of the product stream;[31] as NH_3 was depleted from the system with increasing time-on-stream, NO conversions increased to a maximum value and then subsequently decreased, although the mechanistic origin of such NH_3 inhibition effects remains unclear. Additionally, when a stoichiometric NO and NH_3 ratio is present in the feed stream, the coordination environment of Cu ions may change with increasing conversion and in turn increasing H_2O/NH_3 ratios, as it is plausible that H_2O progressively replaces NH_3 in the Cu ligand environment.[6] Such changes in the extent of NH_3 and H_2O coordination, which can be identified spectroscopically using vtc-XES (Figure 2b) to identify Cu coordination to N or O atoms,[19] could influence Cu ion mobility[6] and thus the rates of different elementary steps in the SCR redox cycle. A combination of kinetic and *operando* spectroscopic measurements under varying NH_3 and H_2O pressures would provide additional insights into the mechanism of NH_3 inhibition and the coordination environment of Cu ions under the integral (and near complete) NO and NH_3 conversions experienced during practical application.

Finally, regarding the third question about the active site requirements of low-temperature NO_x SCR and the dual Cu(I)-site dependence of the O_2-assisted oxidation process, we hypothesize that the rate of this half-cycle is influenced by the mobility and spatial distribution of Cu ions during Cu(I) ion pairing.[7,30] Even though Cu(II) reduction by NO + NH_3 is hypothesized to be a "single-site" process, reduction-limited rates also depend on Cu spatial density because not all Cu ions can participate in the full SCR redox cycle if some are isolated and thus unable to react in the Cu(I) oxidation half-cycle.[30] Kinetic parameters for both oxidation and reduction half-cycles, in turn, could be sensitive to the density and arrangement of cationic Cu sites and their charge-compensating anionic lattice sites, as well as the zeolite framework topology.[30] Chen et al. used a combination of DFT and AIMD methods to predict that the stability of two proximal $Cu(I)(NH_3)_2$ species in CHA is dependent on the framework Al arrangement.[33] EPR spectroscopic measurements by Godiksen et al. during transient oxidation (473 K; 0.1 kPa NO, 10 kPa O_2) of pre-reduced $Cu(I)(NH_3)_2$ (Cu-SSZ-13; Si/Al = 15, Cu/Al = 0.04 or 0.09) were reported to reveal distinct spectroscopic signatures for Al−O−Si−O−Al versus Al−O−Si−O−Si−O−Al within the six-membered ring (6-MR) of CHA,[34] and O_2-assisted oxidation of the (Al−O−Si−O−Al) site was reported to be an order of magnitude faster than oxidation of the (Al−O−Si−O−Si−O−Al) site. Synthetic strategies to vary the arrangement of Al atoms in the CHA framework[35−37] can be used to study such effects of Al arrangement on the kinetic behavior of different steps in SCR redox cycles. These hypotheses can be tested using steady-state and transient kinetic measurements combined with XAS, while varying the reaction conditions to probe oxidation-limited and reduction-limited kinetic regimes.

More broadly, while mean-field rate expressions have been able to describe a wide variety of catalytic processes and represent the standard approach in catalysis research, the mechanism of low-temperature NO_x SCR cannot strictly be described by traditional heterogeneous "single-site" kinetic models, nor by homogeneous "dual-site" oxidation kinetic models. As stated by Boudart, the turnover rate of a catalytic process, rigorously normalized to the number of (purported) active sites, is a quantitative measurement useful in interrogating the active site requirements for a catalytic reaction.[5] According to transition-state theory, turnover rate constants reflect Gibbs free energy differences between transition states and kinetically relevant intermediates, thus serving as a characterization tool of the reaction coordinate. Combining intrinsic kinetic measurements (rather than non-quantitative assessments such as "light-off" curves) with *operando* spectroscopy (rather than *ex situ* or *in situ* measurements) is critical to understanding the rate-limiting processes and most abundant reactive intermediates under reaction conditions. This approach led to the discovery of the dual-site and non-mean-field behavior of the O_2-assisted Cu(I) oxidation half-cycle of low-temperature NO_x SCR, and it will be necessary to further decouple the intrinsic reactivity of Cu active sites from the fraction of Cu sites that participate in steady-state turnover.

Combining intrinsic kinetic measurements (rather than non-quantitative assessments such as "light-off" curves) with *operando* spectroscopy (rather than *ex situ* or *in situ* measurements) is critical to understanding the rate-limiting processes and most abundant reactive intermediates under reaction conditions.

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