



Effects of dioxygen pressure on rates of NO_x selective catalytic reduction with NH₃ on Cu-CHA zeolites



Casey B. Jones^{a,1}, Ishant Khurana^{a,1}, Siddarth H. Krishna^a, Arthur J. Shih^a, W. Nicholas Delgass^a, Jeffrey T. Miller^a, Fabio H. Ribeiro^a, William F. Schneider^b, Rajamani Gounder^{a,*}

^a Charles D. Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA

^b Department of Chemical and Biomolecular Engineering, University of Notre Dame, 250 Nieuwland Science Hall, Notre Dame, IN 46556, USA

ARTICLE INFO

Article history:

Received 9 April 2020

Revised 28 April 2020

Accepted 16 May 2020

Available online 28 May 2020

Keywords:

Cu-CHA zeolites

NO_x selective catalytic reduction

Oxidation-limited kinetics

Reduction-limited kinetics

In operando spectroscopy

ABSTRACT

At low temperatures (<523 K), the selective catalytic reduction (SCR) of NO with NH₃ on Cu-exchanged zeolites occurs via elementary steps catalyzed by NH₃-solvated Cu ions, which are reactive intermediates in a Cu^{II}/Cu^I redox cycle. SCR rates are typically measured under “standard” reaction conditions, in which O₂ is the oxidant and present at partial pressures (~10 kPa O₂) that cause both single-site Cu^{II} reduction and dual-site Cu^I oxidation to behave as kinetically relevant steps. As a result, “standard” SCR rates (per g) transition from a second-order to a first-order dependence on isolated Cu content (per g) among Cu-CHA zeolites with increasing Cu content and thus spatial density (Si/Al = 15, Cu/Al = 0.08–0.37), as dual-site Cu^I oxidation steps limit SCR rates to lesser extents. On a given Cu-CHA catalyst, SCR rates (per Cu, 473 K) show a Langmuirian dependence on dioxygen pressure when varied widely (0–60 kPa O₂), enabling the isolation of first-order or zero-order kinetic regimes with respect to O₂. These kinetic regimes respectively correspond to limiting conditions in which either Cu^I oxidation or Cu^{II} reduction becomes the dominant kinetically relevant step, consistent with *in operando* X-ray absorption spectra. First-order rate constants (per Cu) increase approximately linearly with Cu density, reflecting the dual-site requirement of O₂-assisted Cu^I-oxidation steps. Zero-order rate constants (per Cu) increase more gradually with Cu density, in part reflecting the increasing fraction of isolated Cu ions that are able to form binuclear intermediates and thus participate in SCR turnovers. Combining steady-state and transient kinetic data with *in operando* spectra provides a methodology to quantitatively describe the rate dependences of SCR reduction and oxidation processes on Cu-zeolite properties such as Cu ion density as shown here, and others including the zeolite framework topology and its density and distribution of Al atoms.

© 2020 Elsevier Inc. All rights reserved.

1. Introduction

Selective catalytic reduction (SCR) with ammonia is a strategy used to abate nitrogen oxide (NO_x, x = 1,2) emissions from diesel and lean-burn engines, and was implemented commercially about a decade ago with the advent of Cu-CHA zeolite catalysts that have sufficient hydrothermal stability to withstand the harsh environments encountered in automotive exhaust applications [1–3]. Typical protocols to evaluate catalysts for practical application have focused on the measurement of NO_x conversion profiles as a function of temperature [4], including identifying the onset of the rapid increase in NO_x conversion with increasing temperature (i.e.,

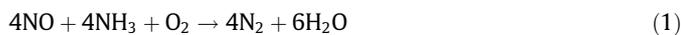
“light-off”) observed at low temperatures (<473 K) and the decrease in NO_x conversion with increasing temperature (i.e., “seagull”-shaped dip) observed at intermediate temperatures (523–623 K) [5–8]. Such macroscopic observations are manifestations of the underlying kinetic and mechanistic details of the SCR reaction on Cu-zeolites; they depend on the microscopic details of catalyst composition and active site arrangement. On Cu-CHA zeolites, these details include the number and spatial distribution of Cu cations exchanged at anionic framework sites introduced by Al substitution, and the fraction of Cu present nominally as monovalent [Cu^{II}OH]⁺ (i.e., ZCuOH) and divalent Cu^{II} (i.e., Z₂Cu) sites that respectively charge-compensate one and two framework Al centers [4,9–11].

The stoichiometry of the SCR reaction using molecular oxygen as the oxidant, which is also referred to as the “standard” SCR reaction, is:

* Corresponding author.

E-mail address: rgounder@purdue.edu (R. Gounder).

¹ C. B. J. and I. K. contributed equally to this work.



Rates of “standard” SCR are typically measured at ambient pressures with NO and NH₃ present in equimolar quantities (e.g., 0.03 kPa each), and O₂ is present in large stoichiometric excess (e.g., 10 kPa), to resemble the concentrations present in lean-burn exhaust. The observed coexistence of both Cu^I and Cu^{II} species under “standard” SCR reaction conditions, and the sensitivity of their proportions to catalyst composition and structure and to the specific reaction conditions used, points to a mechanism involving a redox cycle between these two Cu states [12]. At temperatures below ~ 523 K and under SCR-relevant conditions, exchanged Cu ions in Cu-CHA zeolites are fully solvated by NH₃ ligands, as evidenced by phase diagrams constructed from first-principles thermodynamic analyses of density functional theory (DFT)-based free energies of Cu-ligand complexes [9], by *in situ* X-ray emission spectra (XES) that show Cu-N coordination in their oxidized (Cu^{II}) and reduced (Cu^I) states [7,13], and by *in situ* X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of their oxidized and reduced states that are indistinguishable from those for four-fold and two-fold Cu-amine coordination complexes [9,14], respectively. The coordination of Cu ions to ammonia ligands and not to zeolite framework oxygen atoms is further evidenced by the absence of second-shell Cu-T atom (T = Si, Al) scattering in EXAFS spectra collected *in operando* [9] and the absence of perturbed zeolite framework T-O-T vibrations in diffuse reflectance IR (DRIFTS) spectra collected *in situ* [15]. Thus, during low temperature NO_x SCR on Cu-CHA zeolites, ammonia-solvated Cu ions are present as cationic complexes that are ionically bonded to anionic zeolite framework centers.

The preponderance of evidence is consistent with a reduction half-cycle that consumes both NO and NH₃, which proceeds by NO attack on Cu^{II}-amine complexes to form nitrosamine (H₂NNO)-like intermediates that decompose to yield N₂, H₂O, Cu^I-amine complexes, and an excess proton [16]. The excess proton formed upon reduction of Z₂Cu sites resides on the zeolite lattice at framework oxygen adjacent to an Al site, while that formed upon reduction of ZCuOH is rejected as H₂O [9]. Evidence for the reduction mechanism of mononuclear Cu^{II}-amine complexes includes DFT calculations of plausible Cu^{II} reduction pathways [9,14,16,17], transient XAS [14,16] and TPR measurements [18] that detect complete and stoichiometric reduction of Cu^{II} to Cu^I only when both NO and NH₃ are present, and NH₃ titrations that quantify the zeolitic H⁺ sites formed upon reduction of Z₂Cu sites [9]. The details of the oxidation half-cycle are less well understood [6,14,19,20], although O₂ must be consumed to balance stoichiometry. The oxidation of pairs of Cu^I complexes with O₂ is well-known in the homogeneous Cu literature [21–23]. Mononuclear Cu^I(NH₃)₂ complexes can react with O₂ to form NH₃-solvated binuclear Cu^{II} di-oxo complexes (e.g., (NH₃)₂Cu^{II}(O₂)Cu^{II}(NH₃)₂) [6,19], consistent with DFT calculations of plausible dual-site Cu^I oxidation pathways with O₂ [6,19,24,25] and with EXAFS spectra of Cu-CHA zeolites after their NH₃-solvated Cu^I ions are oxidized by O₂ that show second-shell Cu-Cu scattering at distances characteristic of binuclear Cu^{II} di-oxo complexes [19]. NH₃-solvated binuclear Cu^{II} di-oxo complexes can be reduced to two Cu^I sites while consuming two equivalents of NO and NH₃ to balance stoichiometry [19], via a sequence of elementary steps whose precise details have yet to be clarified.

Under low temperature “standard” SCR conditions, reaction rates on Cu-CHA (per mass or per pore volume catalyst) increase monotonically with the spatial density of isolated Cu ions (per mass or per pore volume catalyst), transitioning from a second-order dependence on Cu density in the dilute Cu limit to a first-order dependence on Cu density at higher Cu densities [9,19,26,27]. *In operando* X-ray absorption spectra (XAS) provide

direct evidence that Cu^I(NH₃)₂ is the most abundant reactive intermediate (MARI) at low Cu densities under “standard” SCR conditions [19], implying that Cu^I(NH₃)₂ oxidation with O₂ is the dominant kinetically-relevant process in the kinetic regime characterized by SCR rates that show a second-order dependence on Cu density. This interpretation is consistent with transient XAS experiments performed to measure O₂-assisted oxidation rates of Cu^I(-NH₃)₂ complexes in Cu-CHA, which are best described by rate equations that are second-order in Cu^I(NH₃)₂ concentration [19]. Transient XAS experiments were also used to quantify the fraction of Cu^I(NH₃)₂ complexes that were oxidized by O₂ in the asymptotic limit of long reaction times, and this fraction was found to increase monotonically with Cu spatial density [19]. These findings indicate that O₂-assisted oxidation steps require two Cu^I(NH₃)₂ complexes, nominally isolated from one another, to co-locate within a single CHA cage to form a binuclear Cu^{II} di-oxo complex. DFT calculations indicate that transport of Cu^I(NH₃)₂ through an 8-MR window into an adjacent CHA cage that already contains a Cu^I(NH₃)₂ complex occurs with lower barriers (~35 kJ mol⁻¹) [19] than the measured range of apparent SCR activation barriers (~40–80 kJ mol⁻¹) [6,14,19], and that subsequent reaction steps to form binuclear Cu^{II} di-oxo complexes are even more facile [19,24,28].

Quantitative measurements that distinguish between the number of Cu sites that participate in SCR redox cycles, and the kinetics of reduction and oxidation processes catalyzed by such Cu sites, are difficult to extract from SCR rates measured under “standard” conditions that invariably convolute the kinetic contributions of both the oxidation and reduction half-cycles [12,14,16,19,29]. Here, we interrogate the catalytic function of Cu-CHA zeolites under reaction conditions perturbed far from those typical of “standard” SCR, in order to isolate either Cu^{II} reduction or Cu^I oxidation as the dominant kinetically-relevant process. Given that O₂ is only involved as a reactant in the oxidation half-cycle, we hypothesize that dual-site Cu^I oxidation becomes the dominant kinetically-relevant step at dilute O₂ pressures and becomes kinetically-irrelevant at higher O₂ pressures. We use *in operando* XAS measurements to quantify the prevalent Cu^{II} and Cu^I fractions as a function of reaction conditions and Cu density. Apparent Cu^{II} reduction and Cu^I oxidation rate constants are determined from regression of rate data to an empirical model that captures the observed Langmuirian dependence of SCR rates on O₂ pressure, which allows extracting kinetic parameters that describe the effects of Cu ion spatial density on SCR oxidation and reduction processes.

2. Experimental methods

2.1. Zeolite synthesis

The parent CHA zeolites (SSZ-13, Si/Al = 15) were synthesized using previously reported procedures [9]. Briefly, a molar ratio of 1 SiO₂/ 0.033 Al₂O₃/ 0.25 TMAdaOH/ 0.25 Na₂O/ 44 H₂O was used in the synthesis solution. An aqueous TMAdaOH solution (25 wt%, Sachem) was first added to deionized H₂O (18.2 MΩ·cm) in a perfluoroalkoxy alkane jar (PFA, Saville Corp.), followed by stirring the solution under ambient conditions for 0.25 h. Next, aluminum hydroxide (Al(OH)₃, grade O325, SPI Pharma) was added to the aqueous TMAdaOH solution. Then, a 5 M NaOH solution (16.7 wt % NaOH in deionized water; NaOH pellets 98 wt%, Alfa Aesar) was added dropwise to the solution and stirred under ambient conditions for 0.25 h. Lastly, fumed silica (SiO₂, 99 wt%, Cabot) was added, and the mixture was stirred for 2 h under ambient conditions. The obtained synthesis solution was then transferred 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 at 40 RPM for 6 days.

Cu-form zeolites were prepared via aqueous-phase Cu ion exchange of H-form zeolites using a $\text{Cu}^{\text{II}}(\text{NO}_3)_2$ solution (0.001–0.1 M, $100 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1}$; 99.999 wt%, Sigma-Aldrich) for 4 h and 300 RPM at ambient conditions, during which dropwise addition of 1.0 M NH_4OH (Sigma-Aldrich) was used to control the pH at 4.9 ± 0.1 , as reported previously [9]. The resulting Cu-form zeolites were recovered by centrifugation and washed six times with deionized water ($70 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1}$ per wash), dried in an oven at 373 K, and then treated in flowing dry air ($1.67 \text{ cm}^3 \text{ s}^{-1} \text{ g}_{\text{cat}}^{-1}$; Zero Grade, Indiana Oxygen) to 773 K (0.0167 K s^{-1}) for 4 h.

2.2. Characterization of H-form and Cu-form CHA zeolites

X-ray diffraction (XRD) patterns (Fig. S1, SI) of the synthesized CHA samples were used to confirm crystal topology, and were collected using a Rigaku SmartLab X-ray diffractometer equipped with a Cu $K\alpha$ X-ray source (40 kV, 44 mA) from 4 to $40^\circ 2\theta$ with a scan rate of $0.00833^\circ \text{ s}^{-1}$ and a step size of 0.01° . The micropore volumes of the H-CHA samples were calculated from Ar adsorption isotherms measured at 87 K (Fig. S2, SI) using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer; micropore volumes ($0.20 \text{ cm}^3 \text{ g}^{-1}$) were consistent with previously reported values for the CHA framework [9].

Elemental analysis of the Cu and H-form zeolites (Si, Al, Cu) was performed using atomic absorption spectroscopy (AAS) on a Perkin-Elmer AAnalyst 300. Samples were digested for AAS by adding 0.01 g of zeolite to 2 g of hydrofluoric acid (48 wt%, Sigma Aldrich) and allowing to sit at ambient conditions for 72 h, followed by dilution in 50 g of water ($18 \text{ M}\Omega\cdot\text{cm}$). *Warning: when using HF acid, always use adequate personal protective equipment and ventilation.* The absorbances of Al and Si were measured using a reducing nitrous oxide-acetylene flame at wavelengths of 309.3 and 251.6 nm, respectively. The absorbance of Cu was measured using an oxidizing air-acetylene flame at a wavelength of 324.8 nm. Absorbances were converted into concentrations using calibration solutions of known concentrations for each element.

The total number of H^+ sites on H-form zeolites and the residual number of H^+ sites on Cu-form zeolites were quantified by NH_3 titration (Table S1, SI) after zeolite samples were treated in an oxidative environment (10 kPa O_2 , balance N_2 , 773 K, 4 h) using previously reported methods [30,31]. Zeolite samples (0.03–0.05 g) were first saturated with gas-phase NH_3 (0.050 kPa in He, Indiana Oxygen) at 433 K for 2 h (0.05 kPa NH_3 , balance He, $5.8 \text{ cm}^3 \text{ s}^{-1}$), followed by selective removal of Lewis acid-bound and physisorbed NH_3 by treatment in a flowing wet helium stream at 433 K for 8 h (2.5–3.0 kPa H_2O in balance He, $5.8 \text{ cm}^3 \text{ s}^{-1}$), in order to selectively retain surface NH_4^+ species [31]. NH_3 was then desorbed in a subsequent temperature-programmed desorption (TPD) in flowing He (UHP, 99.999%, Indiana Oxygen, $5.8 \text{ cm}^3 \text{ s}^{-1}$) to 823 K (0.083 K s^{-1}), and quantified using on-board calibrations in a gas-phase FTIR spectrometer (MKS MultigasTM 2030). The speciation of Cu between sites that are nominally either Cu^{II} or $\text{Cu}^{\text{II}}\text{OH}$ was determined from a site balance that considered total Cu content, the difference in H^+ sites titrated on H-form and Cu-form samples, and the expected 2:1 and 1:1 $\text{H}^+:\text{Cu}$ exchange stoichiometry, respectively (Table S1, SI).

2.3. In operando and transient X-ray absorption spectroscopic characterization of Cu-CHA

X-ray absorption spectroscopy (XAS) experiments were carried out at the Advanced Photon Source (APS) at Argonne National Laboratory on the insertion device (ID) beam line of the Materials Research Collaborative Access Team (MRCAT, Sector 10) [32]. A

cryogenically cooled double-crystal Si(111) monochromator with an uncoated glass mirror was used to minimize the presence of harmonics. Spectra were recorded in transmission mode with the ionization chambers optimized for the maximum current with a linear response ($\sim 10^{10}$ photons s^{-1}) using gas mixtures to give 10% absorption in the incident X-ray detector and 70% absorption in the transmission X-ray detector. Calibration of the Cu K-edge to 8979 eV was performed by simultaneously collecting a Cu metal foil spectrum while collecting sample spectra. Spectra were collected under isothermal conditions and normalized using a first-order polynomial in the pre-edge region and a third-order polynomial in the post-edge region. Linear combination fitting of the XANES spectra was performed using standards for 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 measured at 473 K) [16] to determine the fractions of Cu^{I} and Cu^{II} species present.

In operando experiments were performed in a glassy carbon tube reactor described previously [12], in which steady-state SCR rate measurements (reaction conditions given in Section 2.4) were collected simultaneously with XAS spectra to verify that rates were identical to those measured in separate differential plug-flow reactor experiments. Multiple spectra were taken to confirm the absence of beam damage to the sample or any other time-dependent changes. Transient NO and NH_3 reduction experiments were carried out by first oxidizing the sample in flowing O_2 (20 kPa O_2 in balance N_2 , Airgas, $13.3 \text{ cm}^3 \text{ s}^{-1}$) at 673 K for 0.5 h, after which the sample was cooled to 473 K. After purging for 0.08 h in flowing N_2 ($13.3 \text{ cm}^3 \text{ s}^{-1}$, Airgas), flowing NH_3 (0.03 kPa in balance N_2 , Airgas, $13.3 \text{ cm}^3 \text{ s}^{-1}$) was introduced to the sample. Shortly thereafter (approximately 0.01–0.08 h), flowing NO was added to the gas stream (0.03 kPa NO, 0.03 kPa NH_3 , Airgas, balance N_2 , $13.3 \text{ cm}^3 \text{ s}^{-1}$) concurrently with the start of collecting XAS spectra. Transient O_2 oxidation experiments were then carried out, starting with the catalyst in the state at the end of the NO and NH_3 reduction. After purging in flowing N_2 ($13.3 \text{ cm}^3 \text{ s}^{-1}$) for 0.08 h, flowing O_2 (20 kPa in N_2 , Airgas, $13.3 \text{ cm}^3 \text{ s}^{-1}$) was introduced concurrently with the start of collecting XAS spectra. For both of the reduction and oxidation experiments, spectra were collected until changes were no longer detectable.

2.4. Measurement of standard SCR kinetics under differential conditions

Selective catalytic reduction (SCR) kinetics were measured using a bench-top tubular quartz reactor system described previously [33]. Zeolite samples were sieved to obtain aggregate particle sizes between 125 and 250 μm in diameter. A bed height of approximately 1 cm was obtained by dilution with silica gel (Davisil, 250–500 μm in diameter). NO conversions were kept below 20% for all steady-state kinetic measurements to ensure that the entire catalyst bed was exposed to approximately the same gas concentrations, using a reactant gas mixture of 0.03 kPa NO (3.5% NO/Ar, Praxair), 0.03 kPa NH_3 (3.0% NH_3/Ar , Praxair), 7 kPa CO_2 (liquid, Indiana Oxygen), 1–60 kPa O_2 (99.5%, Indiana Oxygen), 1 kPa H_2O (deionized, $18.2 \text{ M}\Omega\cdot\text{cm}$, introduced through a 24" Perma Pure MH NafionTM Series Humidifier), and balance N_2 (boil-off from a liquid N_2 dewar) at 473 K and ambient total pressure. The balance N_2 was composed of two independent streams, one which passed through the humidifier and was used as a carrier to maintain gas-phase water partial pressures at 1 kPa ("wet" N_2) and the other which was used as a diluent carrier for the other gas-phase reactants ("dry" N_2). The gas mixing pattern was designed such that the 3.5% NO/Ar stream was pre-diluted by the "wet" N_2 carrier stream and CO_2 prior to mixing with the "dry" N_2 and O_2 stream, in order to mitigate background NO_2 formation that occurs upon mixing of concentrated NO and O_2 streams. The

total gas flow rate was 16.7–33.3 cm³ s⁻¹ (at ambient temperature and pressure) and selected to maintain differential NO conversion. Outlet NO, NO₂, NH₃, CO₂, and H₂O concentrations were measured every 0.95 s using on-board gas calibrations on a gas-phase Fourier Transform Infrared (FTIR) spectrometer (MKS Multigas™ 2030).

The rate of NO consumption was calculated according to:

$$-r_{\text{NO}} = \frac{(y_{\text{NO,in}} - y_{\text{NO,out}}) P \dot{V}_{\text{total}}}{10^6 RT} \quad (2)$$

where y is the volume fraction of NO in ppm, \dot{V}_{total} is the total volumetric flow rate, P is the ambient pressure, T is the ambient temperature, and R is the gas constant. The SCR rate was determined by correcting the overall rate of NO consumption in each experiment for contributions to NO consumption resulting from “fast” SCR reactions with NO₂, present both as an impurity in NO reactant cylinders and formed as a product from homogeneous NO oxidation reactions within the reactor unit (details in Section S.3, SI). These methods were validated by measuring identical SCR rates independently in two different reactor units, with different rates of background NO₂ formation and, in turn, contributions from “fast” SCR reactions (details in Section S.3, SI). Measured SCR rates were independent of space velocity (Fig. S6, SI) and thus insensitive to external transport phenomena (details in Section S.4, SI) [9,33,34]. Measured SCR rates were also found not to be corrupted by intracrystallite transport phenomena according to the Weisz-Prater criterion (details in Section S.4, SI) [35]. In addition, SCR rates were independent of H₂O (0.2–4 kPa) [19,36] and CO₂ (0–16 kPa) [33,36] pressures as reported in our prior work.

Apparent NO and NH₃ reaction orders on Cu-CHA zeolites were measured at three different O₂ pressures (1, 10, 60 kPa O₂) at 473 K, holding the concentration of other gases fixed (1 kPa H₂O, 7 kPa CO₂, balance N₂, 0.030 kPa NO or NH₃) while maintaining differential conversion. The NO concentration was varied between 0.015 and 0.060 kPa for the NO reaction order measurement, while the NH₃ concentration was varied between 0.015 and 0.090 kPa for the NH₃ reaction order measurement (all partial pressure changes were made in random order). Similarly, the apparent reaction orders in O₂ in the low, “standard”, and high O₂ pressure limits were measured by varying dioxygen pressure from 1 to 4 kPa (a range of 2–5 kPa was used for Cu-CHA-0.078, Cu-CHA-0.084, and Cu-CHA-0.10; details in Section S.5, SI), 5–15 kPa and 40–60 kPa, respectively, while maintaining differential conversion and holding other gas pressures constant (0.030 kPa NO, 0.030 kPa NH₃, 1 kPa H₂O, 7 kPa CO₂ in balance N₂ at 473 K). The logarithm of SCR reaction rates was plotted against the logarithm of reactant concentration and regressed to a linear function, whose slope was taken as the apparent reaction order (Figs. S9–S11, SI).

3. Results and discussion

3.1. Both Cu^I oxidation and Cu^{II} reduction steps are kinetically relevant during “standard” SCR

In order to study the effects of Cu ion density on the Cu^I oxidation and Cu^{II} reduction processes that occur during steady-state SCR turnover, a series of Cu-CHA samples was prepared by starting with H-form zeolites of fixed framework Al content (Si/Al = 15) and performing Cu ion exchange to varying extents (Cu/Al = 0.08–0.37, Table 1; additional characterization data reported in Table S1, SI and in our prior study [19]). Cu-CHA samples are denoted as Cu-CHA-X, where X denotes the mean Cu volumetric density (number of Cu atoms per 1000 Å³) assuming a homogeneous Cu distribution throughout the crystallite volume (details in our prior study [19]). Mean Cu volumetric densities vary from 0.078 to 0.35 Cu atoms per 10³ Å³ from the least to most heavily Cu-exchanged samples,

respectively corresponding to approximately one Cu ion per seventeen to four CHA cages (Table 1).

SCR rates (per 10³ Å³, 473 K) were measured at 1, 10 and 60 kPa O₂ on these Cu-CHA samples and are plotted as a function of Cu volumetric density (per 10³ Å³) in Fig. 1a. The corresponding fraction of total Cu (Cu_{tot}) present in the Cu^{II} state (Cu^{II}/Cu_{tot}), as measured *in operando* by XAS, at these three O₂ pressures is shown in Fig. 1b. SCR rates measured at 10 kPa O₂ (Fig. 1a, circles), which are representative of “standard” SCR conditions, increase with a second-order dependence on Cu density at low values of Cu density (<0.2 Cu per 10³ Å³) and gradually transition to increasing with a first-order dependence on Cu density at high values of Cu density (>0.3 Cu per 10³ Å³), consistent with prior reports [19,26]. At dilute values of Cu density (<0.1 Cu per 10³ Å³), *in operando* XAS spectra reveal that Cu^I(NH₃)₂ is the MARI (<0.30 Cu^{II}/Cu_{tot}, Fig. 1b) under “standard” SCR conditions. These data indicate that Cu^I oxidation with O₂ becomes the dominant kinetically relevant step when measured SCR rates show a second-order dependence on Cu density, consistent with mechanistic proposals for the involvement of two Cu(NH₃)₂ complexes in O₂-assisted oxidation steps [19]. With increasing Cu density, the fraction of Cu^{II} present during steady-state SCR at 10 kPa O₂ increases (Fig. 1b, circles) as single-site Cu^{II} reduction processes increase in kinetic relevance, as also reported previously [19].

Apparent reaction orders in O₂ measured in pressure ranges characteristic of the low (1–5 kPa O₂), “standard” (5–15 kPa O₂) and high (40–60 kPa O₂) pressure regimes are shown in Table 2. With increasing Cu density, apparent reaction orders in O₂ at “standard” SCR conditions decrease systematically from 0.8 to 0.3 (Table 2), as single-site Cu^{II} reduction increases in kinetic relevance. These data reveal that both Cu^{II} reduction and Cu^I oxidation are kinetically relevant steps when low-temperature SCR rates (473 K) are measured under “standard” reaction conditions (10 kPa O₂), for Cu-CHA composition ranges similar to those typically used in practice (Si/Al ~ 15, Cu/Al ~ 0.5) [37]. These data also indicate that measured SCR rates become more sensitive to the kinetics of Cu^I oxidation steps as the Cu density becomes more dilute, given the dual-site requirements of O₂-assisted oxidation of NH₃-solvated Cu^I ions and the single-site requirements of NO + NH₃-assisted reduction of NH₃-solvated Cu^{II} ions.

The net rates of Cu^{II} reduction and Cu^I oxidation steps in the SCR redox cycle must be equal during steady-state catalytic turnover; yet, the rates of such steps depend on the apparent rate constants and the pressures of reactants involved in them. Current mechanistic proposals involve dioxygen as a reactant only in the Cu^I oxidation step, suggesting that varying the O₂ pressure should change the rates of Cu^I oxidation processes, but not of Cu^{II} reduction processes. In turn, varying the O₂ pressure should not change the extent to which each step limits the rates of the overall SCR redox cycle, and lower O₂ pressures should cause Cu^I oxidation rates to become increasingly rate-limiting. Insights into the kinetically-relevant processes at varying O₂ pressure are also relevant to practical SCR implementation, as transient excursions to low O₂ pressures (e.g., 2 kPa O₂) occur during operation of diesel vehicles (e.g., rapid acceleration), and have been observed to cause decreases in NO_x conversion [38]. In the range of Cu density values studied, SCR rates (per 10³ Å³, 473 K) on Cu-CHA are systematically higher at 60 kPa O₂ than at 10 kPa O₂ (Fig. 1a), and the fraction of Cu^I present *in operando* is systematically lower at 60 kPa O₂ than at 10 kPa O₂ (Fig. 1b). Conversely, SCR rates (per 10³ Å³, 473 K) are systematically lower at 1 kPa O₂ than at 10 kPa O₂ (Fig. 1a), and the fraction of Cu^I present *in operando* is systematically higher at 1 kPa O₂ than at 10 kPa O₂ (Fig. 1b). Additionally, apparent reaction orders in O₂ approach unity at low pressures (<5 kPa O₂), decrease systematically with increasing pressure, and approach zero at high pressures (>50 kPa O₂), as listed in Table 2 (additional details in Section S.5,

Table 1
Characterization data of the Cu-CHA samples studied.

Cu-CHA-X	Cu/Al	Cu wt%	Cu volumetric density (per 10^3 \AA^3)	Cu per CHA cage	Number of cages per Cu
Cu-CHA-0.078	0.08	0.55	0.078	0.06	16.7
Cu-CHA-0.084	0.09	0.59	0.084	0.06	15.4
Cu-CHA-0.10	0.10	0.69	0.10	0.08	13.3
Cu-CHA-0.17	0.18	1.21	0.17	0.13	7.5
Cu-CHA-0.23	0.24	1.60	0.23	0.18	5.7
Cu-CHA-0.29	0.31	2.04	0.29	0.22	4.5
Cu-CHA-0.31	0.33	2.16	0.31	0.24	4.2
Cu-CHA-0.35	0.37	2.47	0.35	0.27	3.7

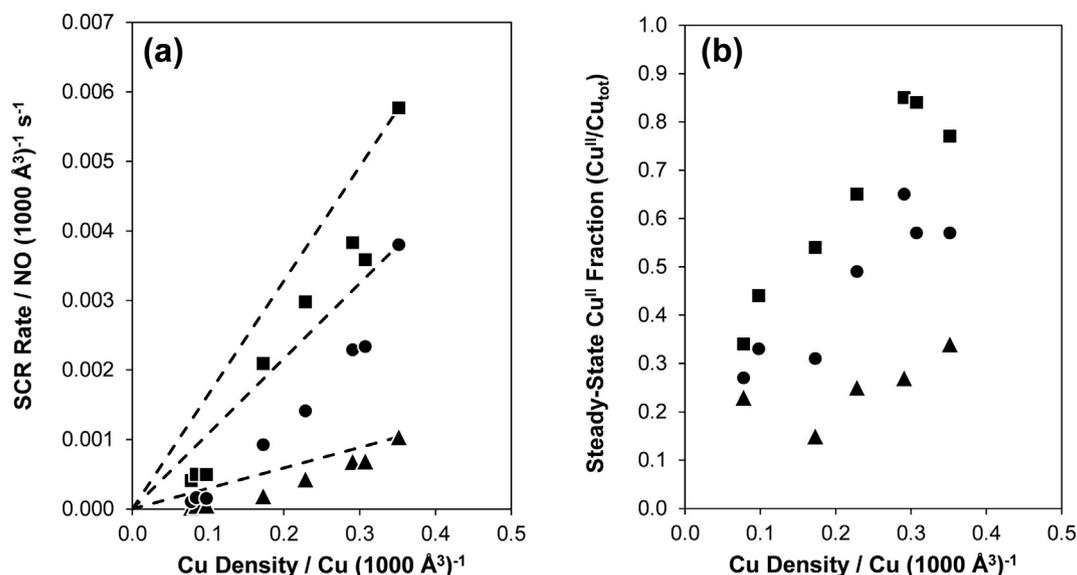


Fig. 1. (a) SCR rates (per 10^3 \AA^3 , 473 K) measured on Cu-CHA-X samples at 1 (▲), 10 (●), and 60 kPa (■) O₂ (other reaction conditions: 0.030 kPa NO, 0.030 kPa NH₃, 7 kPa CO₂, 1 kPa H₂O, balance N₂). Dashed lines are drawn through the origin and the rate on Cu-CHA-0.35 for each data series to guide the eye, illustrating that SCR rates deviate from a first-order dependence at dilute Cu density. (b) Steady-state Cu^{II} fraction (Cu^{II}/Cu_{tot}) at 1 (▲), 10 (●), and 60 kPa (■) O₂ measured *in operando* by XAS as a function of Cu density on Cu-CHA-X samples.

Table 2
Apparent O₂ reaction orders measured on Cu-CHA samples near low (1 kPa O₂), “standard” (10 kPa O₂) and high (60 kPa O₂) dioxygen pressures.

Sample	Apparent O ₂ Order ^a		
	1 kPa O ₂	10 kPa O ₂	60 kPa O ₂
Cu-CHA-0.078	0.6	0.8	0.4
Cu-CHA-0.084	1.0	0.7	0.6
Cu-CHA-0.10	0.9 ^b	0.7	0.4
Cu-CHA-0.17	0.8	0.6	0.2
Cu-CHA-0.23	0.7	0.5	0.2
Cu-CHA-0.29	0.5	0.4	0.0
Cu-CHA-0.31	0.5	0.3	0.0
Cu-CHA-0.35	0.5	0.3	0.1

^a Other conditions: 0.030 kPa NO, 0.030 kPa NH₃, 7 kPa CO₂, 1 kPa H₂O and balance N₂ at 473 K. Uncertainties are ± 0.1 , unless otherwise noted.

^b Uncertainty is ± 0.3 .

SI). These trends are consistent with the preferential decrease in intrinsic Cu^I oxidation rates relative to intrinsic Cu^{II} reduction rates at lower O₂ pressures.

These data serve as yet another reminder that the extent to which Cu^I oxidation steps limit SCR rates depends both on the sample composition and the reaction conditions used, given the different kinetic and active site requirements of Cu^I oxidation and Cu^{II} reduction processes in the SCR redox cycle. The kinetic relevance of Cu^I oxidation steps increases both with decreasing Cu ion density and with decreasing O₂ pressure. Yet, even at low but fixed O₂ pressure (1 kPa), SCR rates are not solely limited by the rates

of Cu^I oxidation steps, as evident by the finite Cu^{II} fractions (0.15–0.35) quantified *in operando* by XANES. Thus, we next systematically investigate the steady-state catalytic behavior of Cu-CHA zeolites under widely varying O₂ pressures, in order to isolate limiting kinetic behavior that allows deconvoluting the influence of Cu^I oxidation and Cu^{II} reduction steps on overall rates of SCR redox cycles.

3.2. Effects of O₂ pressure on SCR rates and the Cu^{II}/Cu^I redox balance

SCR rates (per Cu_{tot}, 473 K) measured on a representative Cu-CHA sample (Cu-CHA-0.23) as a function of O₂ pressure are shown in Fig. 2a. SCR rates (per Cu_{tot}) show a Langmuirian dependence on O₂ pressure when varied over a wide range (1–60 kPa O₂), according to the following empirical rate expression:

$$\frac{-r_{\text{NO}}}{[\text{Cu}_{\text{tot}}]} = \frac{k_{\text{first}}k_{\text{zero}}P_{\text{O}_2}}{k_{\text{zero}} + k_{\text{first}}P_{\text{O}_2}} \quad (3)$$

where k_{first} is the apparent rate constant in the limiting kinetic regime that is first-order in O₂ pressure, and k_{zero} is the apparent rate constant in the limiting kinetic regime that is zero-order in O₂ pressure (additional details of the kinetic fitting in Section S.5, SI). The corresponding steady-state fraction of Cu present in the Cu^{II} state (Cu^{II}/Cu_{tot}), measured *in operando* by XANES, is shown on the secondary ordinate in Fig. 2a (*in operando* XANES spectra of Cu-CHA-0.23 shown in Fig. S12, SI). In the first-order dioxygen pressure limit, Cu ions are predominantly in their Cu^I state (Cu^{II}/Cu_{tot} = 0.25,

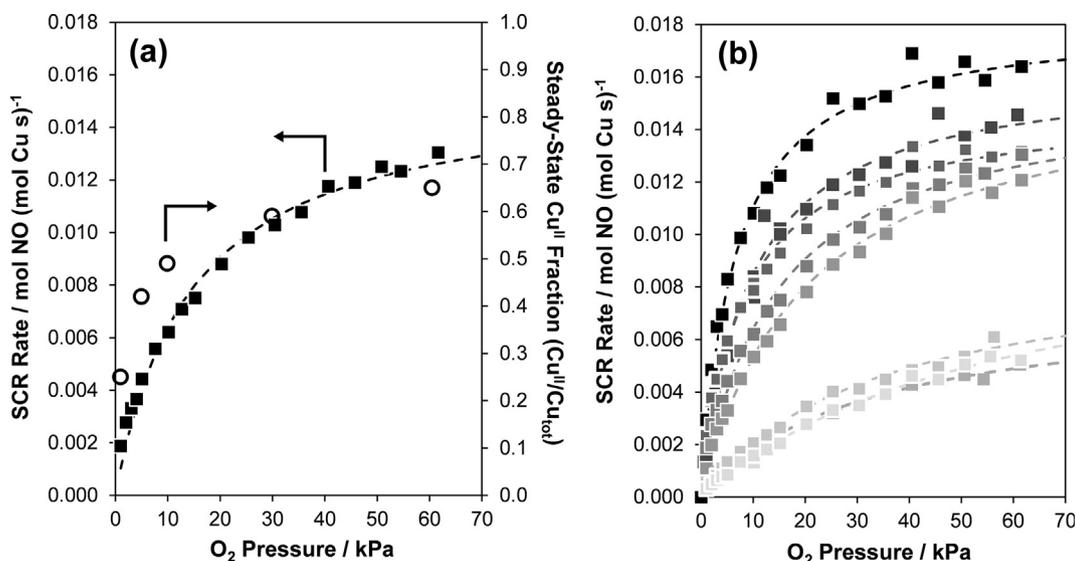


Fig. 2. (a) Steady-state SCR rate (per Cu_{tot}, 473 K, ■) and Cu^{II} fraction (Cu^{II}/Cu_{tot}) (○) as a function of O₂ pressure on Cu-CHA-0.23; dashed line represents the best-fit regressions of rates to Eq. (3). (b) Steady-state SCR rate (per Cu, 473 K) as a function of O₂ pressure on all Cu-CHA-X samples (X increases with light-to-dark shading); dashed lines represent best-fit regressions of rates to Eq. (3).

Fig. 2a), consistent with dual-site oxidation of Cu^I(NH₃)₂ with O₂ becoming the dominant kinetically relevant step in this regime. The steady-state Cu^{II} fraction increases systematically with increasing O₂ pressure (Fig. 2a), as Cu^{II} reduction steps increase in kinetic relevance. These findings are also consistent with a recent report by Liu et al. that the steady-state Cu^{II} fraction increased systematically with O₂ pressures (0–10 kPa; other conditions: 473 K, 0.1 kPa NO, 0.1 kPa NH₃, balance He) for Cu-CHA compositions (Si/Al = 15, Cu/Al = 0.03 and 0.29) similar to those studied here [39].

Importantly, the steady-state Cu^{II} fraction asymptotically approaches a non-unity value (Cu^{II}/Cu_{tot} = 0.65, Fig. 2a) under conditions (60 kPa O₂) that nearly approach the zero-order dioxygen pressure limit (apparent O₂ order = 0.2). This limiting condition should correspond to a kinetic regime in which Cu^{II} reduction becomes the sole kinetically-relevant step, and should have resulted in Cu^{II} as the sole MARI (Cu^{II}/Cu_{tot} = 1) if every Cu ion were able to participate in the SCR redox cycle. The presence of a finite fraction of Cu^I in the zero-order dioxygen pressure limit would therefore suggest that some Cu^I ions are unable to participate in SCR turnovers, which can be rationalized from data reported in our prior study [19]. Reduction of Cu-CHA samples to their Cu^I(NH₃)₂ states in flowing NO and NH₃ (473 K), followed by exposure to flowing O₂ (473 K) resulted in the transient oxidation of only a fraction of the Cu^I(NH₃)₂ species present [19]. A recalcitrant fraction of Cu^I(NH₃)₂ remained unoxidized at long O₂ exposure times, either because they were physically or functionally isolated from other Cu^I(NH₃)₂ complexes and thus unable to oxidize via the dual-site mechanism to form a binuclear Cu^{II} di-oxo intermediate. In turn, any such recalcitrant Cu^I(NH₃)₂ complexes would not contribute to measured SCR rates, and thus persist as the Cu^I fraction measured on Cu-CHA zeolites at high O₂ pressures when SCR rates are limited predominantly by Cu^{II} reduction steps.

SCR rates (per Cu, 473 K) as a function of O₂ pressure are shown in Fig. 2b for Cu-CHA samples of increasing Cu volumetric density (Table 1). For each Cu-CHA sample, SCR rates show a Langmuirian dependence on O₂ pressure, according to Equation (3). In the entire range of Cu density values studied (0.078–0.35 Cu per 1000 Å³), SCR rates (per Cu_{tot}) at a fixed O₂ pressure increase systematically with Cu volumetric density (Fig. 2b). These trends include rates that are measured at low (1 kPa O₂) and high (60 kPa O₂) dioxygen

pressures, which begin to approach the first-order and zero-order kinetic regimes, albeit to different extents on Cu-CHA samples of different Cu density (Table 2). The first-order kinetic regime in which Cu^I oxidation is the sole kinetically-relevant step is nearly approached at 1 kPa O₂ on the lowest Cu density samples, while the zero-order kinetic regime in which Cu^{II} reduction is the sole kinetically-relevant step is nearly approached at 60 kPa O₂ on the highest density samples (Table 2). These data again remind that rates of Cu^I oxidation and Cu^{II} reduction steps depend both on the pressures of gaseous reactants involved and on Cu volumetric density in a manner that reflects the specific Cu site requirements of such steps. As a result, apparent rate constants that strictly correspond to first-order and zero-order kinetic regimes on a given Cu-CHA sample must be estimated by extrapolating measured rate data using a rate equation, as discussed next.

3.3. Dependence of apparent first-order rate constants on Cu volumetric density

Values of apparent first-order (k_{first}) and zero-order (k_{zero}) rate constants, determined by regressing the steady-state SCR rate data in Fig. 2b to Equation (3), are listed for each sample in Table 3. The dependence of k_{first} on Cu volumetric density in Cu-CHA (Si/Al = 15) is shown in Fig. 3. Values of k_{first} increase systematically with Cu volumetric density in the entire range of Cu density values studied (0.078–0.35 Cu per 1000 Å³). A strictly linear dependence of k_{first} (per Cu) on Cu density is equivalent to a strictly second-order dependence of the SCR rate on Cu concentration, as would be expected for a mean-field rate expression for a homogeneous reaction involving two Cu sites. Yet, the oxidation of Cu^I sites in Cu-CHA by O₂ is not mean-field in nature; only a fraction of Cu^I(NH₃)₂ species are able to be oxidized by O₂ to form a binuclear Cu^{II} di-oxo complex, and the fraction of such oxidizable Cu^I sites increases with total Cu volumetric density [19]. Thus, we surmise that values of k_{first} deviate from a linear dependence on Cu density, especially apparent at low values of Cu density (Fig. 3), because of the non-mean-field kinetic behavior of O₂-assisted oxidation of Cu^I(NH₃)₂ species in Cu-CHA.

To investigate this behavior further, we performed transient XAS experiments during O₂-assisted oxidation of pre-reduced Cu-

Table 3
Measured first and zero order rate constants from steady-state SCR kinetics and intrinsic reduction and oxidation rate constants from transient kinetic experiments.

Sample	Steady-state measurements		Transient measurements		
	$k_{\text{zero}} / 10^{-3} \text{ mol NO mol Cu}^{-1} \text{ s}^{-1}$	$k_{\text{first}} / 10^{-3} \text{ mol NO mol Cu}^{-1} \text{ kPa O}_2^{-1} \text{ s}^{-1}$	$k_{\text{red}} / 10^{-3} \text{ s}^{-1}$	$k_{\text{ox}} / 10^{-5} \text{ m}^3 \text{ mol Cu}^{-1} \text{ s}^{-1}$	Final Cu ^{II} fraction after O ₂ oxidation transient
Cu-CHA-0.078	10.7	0.18	20.4	14.1	0.67
Cu-CHA-0.084	9.1	0.27	18.4	–	–
Cu-CHA-0.10	7.5	0.24	–	7.9	0.77
Cu-CHA-0.17	16.1	0.80	10.2	8.1	0.78
Cu-CHA-0.23	15.6	1.09	7.4	7.1	0.85
Cu-CHA-0.29	14.8	1.87	–	7.8	0.83
Cu-CHA-0.31	16.4	1.76	–	14.5	0.85
Cu-CHA-0.35	18.2	2.80	21.1	12.4	0.81

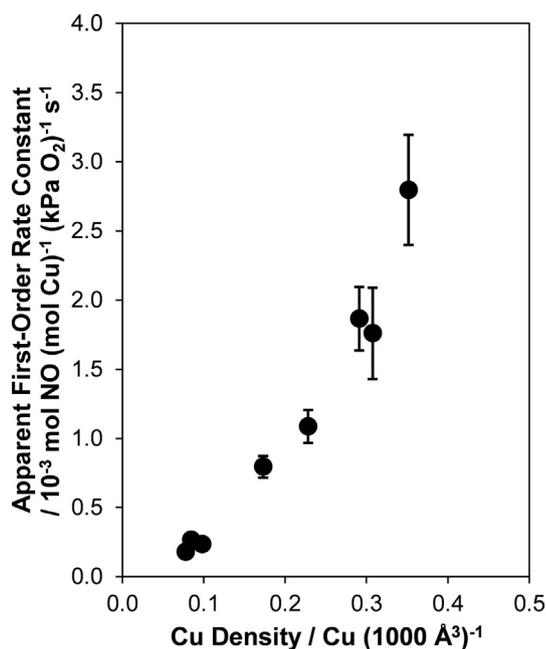


Fig. 3. Apparent first-order SCR rate constants (k_{first} , 473 K) as a function of Cu density.

CHA-X samples (seven samples of varying Cu density), analogous to such experiments reported in our prior study (on three Cu-CHA samples of varying Cu density) [19]. Cu-CHA samples were first reduced in flowing NO and NH₃ (0.030 kPa NO, 0.030 kPa NH₃, 473 K) to convert all Cu ions to Cu^I(NH₃)₂ species, followed by exposure to flowing O₂ (10 kPa O₂, 473 K) while monitoring time-resolved XAS spectra (XANES spectra in Figs. S13–S19, SI). Linear-combination fitting of XANES spectra were used to determine the fraction of Cu present in the Cu^I(NH₃)₂ state (Cu^I/Cu_{tot}) as a function of reaction time, as shown in Fig. 4.

For each Cu-CHA sample, regardless of Cu content, the transient Cu^I oxidation rate was best modeled using a rate law with a second-order dependence on Cu concentration that accounts for a recalcitrant fraction of un-oxidized Cu^I in the limit of long reaction time (details in Section S.7, SI) [19]. The fitted value for the intrinsic second-order rate constant for O₂-assisted oxidation (k_{ox}) of Cu^I(NH₃)₂ species is listed in Table 3. Values of k_{ox} are essentially invariant (within 2×, 473 K) for the range of Cu volumetric densities studied (0.078–0.35 Cu per 1000 Å³). The fraction of Cu sites that were oxidized to the Cu^{II} state at the end of the transient O₂-oxidation experiment is also shown in Table 3; this fraction increased (0.67–0.85) with Cu volumetric density (0.078–0.35 Cu per 1000 Å³), consistent with our prior work [19]. These findings are also consistent with data reported recently by

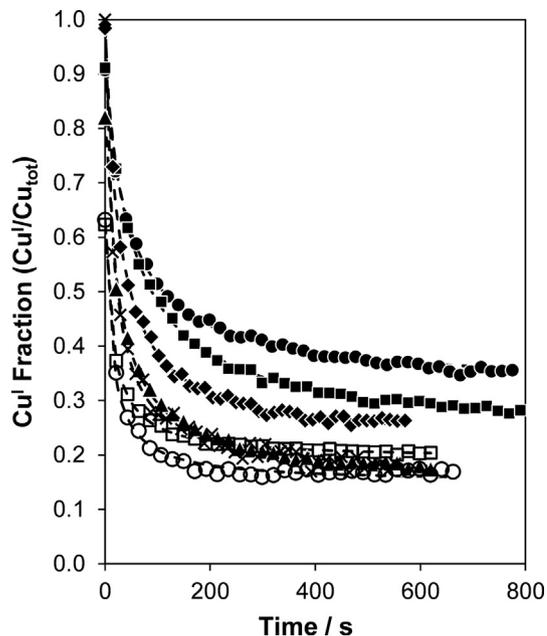


Fig. 4. Cu^I fraction (Cu^I/Cu_{tot}) from XAS experiments during transient O₂-assisted oxidation (10 kPa O₂, 473 K) of pre-reduced Cu-CHA-X samples (0.030 kPa NO, 0.030 kPa NH₃, 473 K): Cu-CHA-0.078 (●), Cu-CHA-0.10 (■), Cu-CHA-0.17 (◆), Cu-CHA-0.23 (▲), Cu-CHA-0.29 (×), Cu-CHA-0.31 (○), Cu-CHA-0.35 (□). Dotted lines represent least-squares regression of the data to a rate model second-order in Cu (details in Section S.7, SI).

Liu et al., in which O₂-assisted oxidation (473 K, 10 kPa O₂) of pre-reduced Cu-CHA (Si/Al = 15) resulted in higher fractions of oxidizable Cu(I) on a sample with higher Cu content (0.95, Cu/Al = 0.29) than on a sample of lower Cu content (0.53, Cu/Al = 0.03) [39].

We next sought to compare the rate measurements from transient Cu^I oxidation experiments performed at 10 kPa O₂ to the steady-state SCR rates measured in the first-order (i.e., “low” O₂ pressure) kinetic regime. The steady-state Cu^I oxidation rate expected at 10 kPa O₂ was estimated by multiplying k_{first} by this dioxygen pressure (10 kPa O₂), and these values are plotted on the primary ordinate of Fig. 5. Initial rates of Cu^I oxidation from the transient XAS experiments (at 10 kPa O₂) were estimated by extrapolating the fitted second-order rate models to initial time (details in Section S.7, SI), and these values are plotted on the secondary ordinate of Fig. 5. Both of these rates systematically increase with a similar functional dependence on Cu volumetric density (Fig. 5); the deviation from a strictly linear dependence on Cu volumetric density, as would have otherwise been expected for a mean-field rate expression for a dual-site Cu^I oxidation step, reflects the non-mean-field nature of this process.

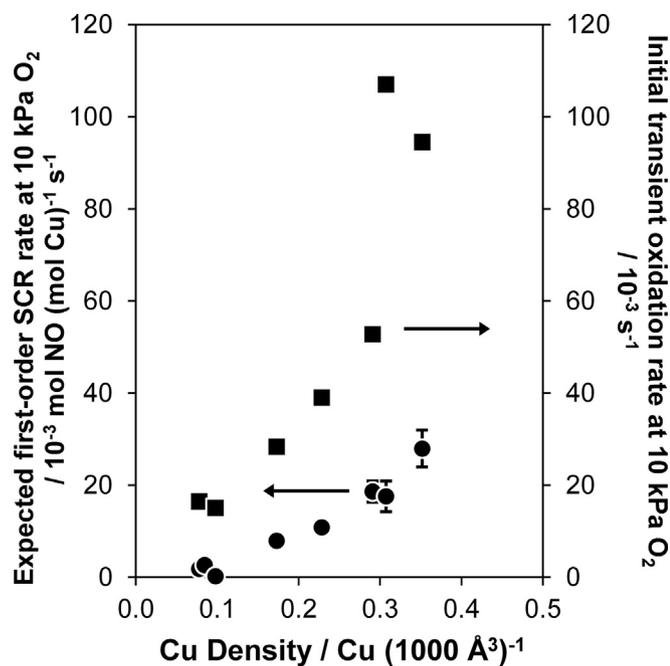


Fig. 5. Estimated Cu^{I} -oxidation-limited steady-state SCR rates (473 K) at 10 kPa O_2 (●) plotted along with initial Cu^{I} oxidation rates measured from transient XAS experiments (■), as a function of Cu density.

3.4. Dependence of apparent zero-order rate constants on Cu spatial density

The dependence of k_{zero} on Cu volumetric density in Cu-CHA (Si/Al = 15) is shown in Fig. 6. In the entire range of Cu densities studied (0.078–0.35 Cu per 1000 \AA^3), values of k_{zero} show a much weaker dependence on Cu density than k_{first} (Fig. 3). Values of k_{zero} are lower among the three samples of lowest Cu density ($7.5\text{--}10.7 \times 10^{-3}$ mol NO mol Cu^{-1} s^{-1} , Table 3) than among the five samples of higher Cu density ($14.8\text{--}18.2 \times 10^{-3}$ mol NO mol Cu^{-1} s^{-1} , Table 3). Values of k_{zero} also appear to become invariant of Cu density above the threshold value of 0.17 Cu per 1000 \AA^3 in the sample composition studied. Such variations in k_{zero} with Cu density could, in principle, reflect changes in either the intrinsic rate constant for Cu^{II} reduction, or the fraction of Cu sites that participate in steady-state SCR turnovers.

To investigate the intrinsic reduction behavior of NH_3 -solvated Cu^{II} sites in Cu-CHA, and its dependence on Cu volumetric density, we performed transient XAS experiments during NO + NH_3 -assisted co-reduction of oxidized Cu-CHA-X samples (five samples of varying Cu density). Cu-CHA samples were first oxidized in flowing O_2 (20 kPa O_2 , 673 K) to convert all Cu ions to zeolite-bound Cu^{II} species, followed by exposure to flowing NO and NH_3 (0.030 kPa NO, 0.030 kPa NH_3 , 473 K) to solvate Cu^{II} ions with NH_3 to form $\text{Cu}^{\text{II}}(\text{NH}_3)_4$ or $\text{Cu}^{\text{II}}(\text{OH})(\text{NH}_3)_3$ complexes and to subsequently reduce them to $\text{Cu}^{\text{I}}(\text{NH}_3)_2$, while monitoring time-resolved XAS spectra (XANES spectra in Figs. S20–S24, SI). Linear-combination fitting of XANES spectra were used to determine the fraction of Cu present in the NH_3 -solvated Cu^{II} state ($\text{Cu}^{\text{II}}/\text{Cu}_{\text{tot}}$) as a function of reaction time, as shown in Fig. 7.

On all Cu-CHA samples, the transient Cu^{II} reduction rate showed a first-order dependence on Cu density (Fig. 7). In some samples, XANES spectra at the end of the transient NO + NH_3 -assisted reduction experiments (Figs. S20–S24, SI) showed small percentages ($\leq 10\%$) of Cu^{II} that were not reduced; these values are within the uncertainty of the linear combination XANES fitting procedure, but were explicitly accounted for when fitting the transient data

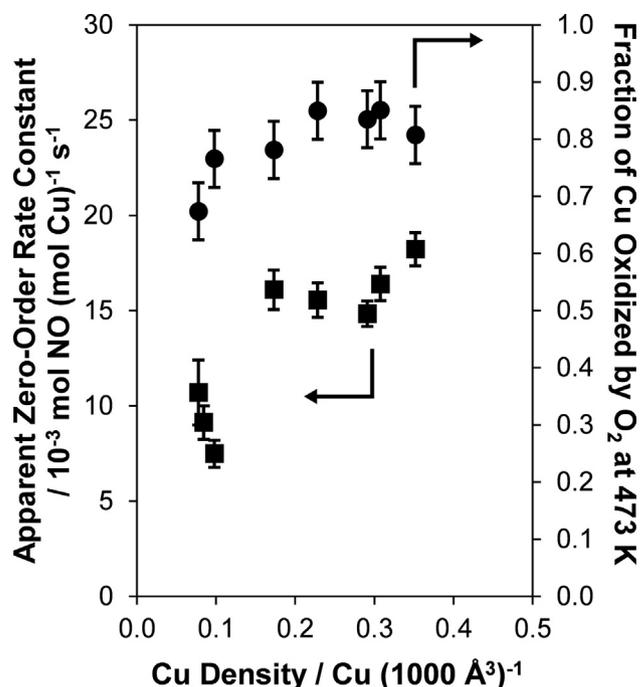


Fig. 6. Cu volumetric density dependence of apparent zero-order SCR rate constants (k_{zero}) at 473 K (■) and the fraction Cu^{I} that is oxidized to Cu^{II} after treatment in 10 kPa O_2 at 473 K (●) from the transient XAS experiments shown in Fig. 5.

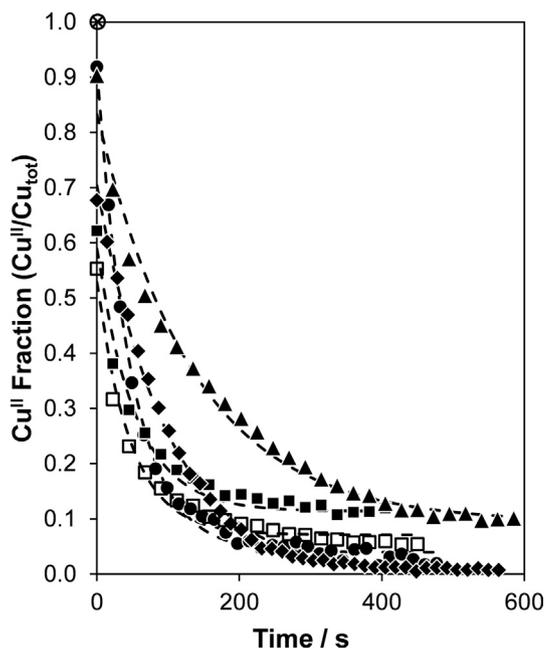


Fig. 7. Cu^{II} fraction ($\text{Cu}^{\text{II}}/\text{Cu}_{\text{tot}}$) from XAS experiments during transient NO + NH_3 -assisted reduction (0.030 kPa NO, 0.030 kPa NH_3 , 473 K) of oxidized Cu-CHA-X samples (20 kPa O_2 , 673 K): Cu-CHA-0.078 (●), Cu-CHA-0.084 (■), Cu-CHA-0.17 (◆), Cu-CHA-0.23 (▲), and Cu-CHA-0.35 (□). Dotted lines are best fits to a rate equation that is first-order in Cu concentration (details in Section S.8, SI).

to a first-order rate equation (details in Section S.8, SI). Values of k_{red} were similar (within $3\times$ at 473 K, $7.4\text{--}21.1 \times 10^{-3}$ s^{-1} ; Table 3) and did not vary systematically with Cu density. These values are quantitatively consistent with the initial rate of Cu^{II} reduction (1.7 mmol NO $\text{g}^{-1}\text{h}^{-1}$ at 0.05 kPa NO and 423 K) reported recently

on a Cu-CHA sample of similar composition (2 wt% Cu) [39], assuming a first-order dependence on NO pressure and an activation energy consistent with those reported for reduction-limited SCR kinetics (full calculation in Section S.8, SI) [6,19]. Similar Cu^{II} reduction rate constants measured among Cu-CHA samples of different Cu density would also be consistent with the proposed single-site mechanism of NO and NH₃-assisted co-reduction of mononuclear NH₃-solvated Cu^{II} sites [9,16].

Thus, we considered the alternate possibility that k_{zero} values are influenced by the fraction of Cu sites that participate in steady-state SCR turnover. This fraction of active Cu was estimated to be the fraction of Cu^I(NH₃)₂ that was oxidized by O₂ at the end of transient XAS experiments shown in Fig. 4; as listed in Table 3, they increase (0.67–0.85) with Cu density (0.078–0.35 Cu per 1000 Å³). These values are plotted on the secondary ordinate of Fig. 6, and show a similar functional dependence on Cu density as k_{zero} . This indicates that the dependence of k_{zero} (normalized per Cu_{tot}) on Cu volumetric density primarily reflects changes in the fraction of Cu sites that participate in steady-state SCR redox cycles, specifically in the dual-site O₂-assisted oxidation half-cycle.

4. Conclusions

The selective catalytic reduction (SCR) of NO with NH₃ on Cu-CHA zeolites is mediated by NH₃-solvated Cu^{II} and Cu^I ions at low temperatures (<523 K), and occurs via a Cu^{II}/Cu^I redox cycle involving single-site Cu^{II} reduction assisted by NO and NH₃ and dual-site Cu^I oxidation assisted by O₂. When low-temperature SCR rates are measured at fixed reaction conditions (e.g., “standard” SCR conditions), they depend on the rates of both Cu^{II} reduction and Cu^I oxidation processes. With increasing Cu density, SCR rates (per Cu) transition from a second-order to first-order dependence on Cu density, Cu^{II} fractions measured *in operando* by XAS systematically increase, and apparent reaction orders in O₂ systematically decrease. The kinetic influences of Cu^I oxidation and Cu^{II} reduction processes are convoluted in apparent kinetic parameters measured under “standard” SCR conditions, obfuscating the individual influences of Cu-zeolite structure and composition on the fraction of Cu sites that participate in SCR turnovers and on the rate constants for Cu^I oxidation and Cu^{II} reduction processes.

Low-temperature (473 K) SCR rates on Cu-CHA show a Langmuirian dependence on dioxygen pressure when varied widely (1–60 kPa O₂), and approach a first-order dependence in the “low O₂ pressure” limit and a zero-order dependence in the “high O₂ pressure” limit. Yet, even when SCR rates are measured at fixed pressure in the “low O₂ pressure” limit (e.g., 1 kPa O₂), *in operando* characterization reveals that a fraction of Cu in Cu-CHA is present in the Cu^{II} state, and this fraction increases systematically with increasing Cu density. This serves as yet another reminder that differences in kinetic behavior among catalysts of varying composition are more accurately evaluated through comparisons of rate constants, not turnover rates measured at fixed reaction conditions. This is especially pertinent for catalytic cycles comprised of elementary steps that have different active site density requirements, for which changes in catalyst composition will change the kinetic relevance of each step.

Steady-state SCR rates measured over widely varying dioxygen pressures enable estimating apparent first-order (k_{first}) and zero-order (k_{zero}) rate constants that reflect SCR redox cycles limited by dual-site Cu^I oxidation with O₂ and by single-site Cu^{II} reduction with NO and NH₃, respectively. On Cu-CHA zeolites, values of k_{first} (per Cu, 473 K) increase with Cu density, according to a functional dependence consistent with the dual-site and non-mean-field nature of O₂-assisted Cu^I oxidation steps. Values of k_{zero} (per Cu, 473 K) show a weaker dependence on Cu density, a consequence of its

underlying dependence on the fraction of Cu sites that can participate in SCR redox cycles and specifically in O₂-assisted Cu^I oxidation steps. Importantly, among Cu-CHA samples of varying composition that are comprised nominally of isolated Cu ions, the mechanisms of Cu^I oxidation and Cu^{II} reduction do not appear to change; rather the relative intrinsic rates of these processes change with reaction conditions due to their differing kinetic and site requirements, and neither one solely limits the rates of the SCR redox cycle.

As illustrated here for low-temperature NO_x SCR with NH₃ on Cu-CHA zeolites, such phenomena can be identified by measuring reaction rates under varying reaction conditions to isolate kinetic regimes wherein rates of certain elementary steps limit rates of the overall catalytic cycle. Such rate measurements facilitate precise mechanistic interpretation, when complemented with measurements of transient rates of stoichiometric reactions that are proposed facsimiles of the elementary steps that prevail during steady-state catalytic turnover, and *in operando* spectroscopy to determine the structures of the relevant MARI [40]. The measurement of steady-state SCR rates over widely varying dioxygen pressures, in order to estimate apparent first-order and zero-order rate constants in O₂ pressure, enables quantitative comparisons of reactivity among Cu-zeolite catalysts of different Cu content. We expect these conclusions will apply for low-temperature NO_x SCR catalysis on other Cu-based materials, under conditions wherein the reactive intermediates are NH₃-solvated Cu ions and O₂ is the oxidant used in Cu^I oxidation half-cycles. The approach used here can also quantitatively describe how other catalyst properties, such as zeolite framework topology and framework Al density and arrangement, influence the fraction of Cu sites that participate in SCR redox cycles and the rates at which they catalyze relevant Cu^I oxidation and Cu^{II} reduction processes.

Declaration of Competing Interest

None.

Acknowledgements

We acknowledge financial support provided by the National Science Foundation CAREER program under award number 1552517-CBET. Use of the Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract no. DE-AC02-06CH11357. MRCAT operations and beamline 10-BM are supported by the Department of Energy and the MRCAT member institutions. We thank Prof. Christopher Paolucci (Virginia), Trevor M. Lardinois (Purdue), Dr. John Di Iorio (Purdue) and Dr. Atish Parekh (Purdue) for helpful technical discussions. We also thank Sachem, Inc. for providing the organic structure-directing agent used to synthesize SSZ-13.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2020.05.022>.

References

- [1] C.H.F. Peden, Cu/Chabazite Catalysts for ‘Lean-Burn’ Vehicle Emission Control, *J. Catal.* 373 (2019) 384–389, <https://doi.org/10.1016/j.jcat.2019.04.046>.
- [2] I. Bull, R.S. Boorse, W.M. Jaglowski, G.S. Koermer, A. Moini, J.A. Patchett, W.-M. Xue, P. Burk, J.C. Dettling, M.T. Caudle, Copper CHA Zeolite Catalysts, US20080226545A1, 2008.
- [3] P.J. Andersen, J.E. Bailie, J.L. Casci, H.-Y. Chen, J.M. Fedeyko, R.K.S. Foo, R.R. Rajaram, Transition Metal/Zeolite SCR Catalysts, WO2008132452A2, (2008).
- [4] C. Paolucci, J.R. Di Iorio, F.H. Ribeiro, R. Gounder, W.F. Schneider, Chapter One - Catalysis Science of NO_x Selective Catalytic Reduction With Ammonia Over Cu-

- SSZ-13 and Cu-SAPO-34, in: C. Song (Ed.), *Adv. Catal.*, Academic Press, 2016: pp. 1–107. <https://doi.org/10.1016/bs.acat.2016.10.002>.
- [5] K. Kamasamudram, N. Currier, T. Szailer, A. Yezerets, Why Cu- and Fe-Zeolite SCR Catalysts Behave Differently at Low Temperatures, *SAE Int. J. Fuels Lubr.* 3 (2010) 664–672, <https://doi.org/10.4271/2010-01-1182>.
- [6] F. Gao, D. Mei, Y. Wang, J. Szanyi, C.H.F. Peden, Selective Catalytic Reduction over Cu/SSZ-13: Linking Homo- and Heterogeneous Catalysis, *J. Am. Chem. Soc.* 139 (2017) 4935–4942, <https://doi.org/10.1021/jacs.7b01128>.
- [7] K.A. Lomachenko, E. Borfecchia, C. Negri, G. Berlier, C. Lamberti, P. Beato, H. Falsig, S. Bordiga, The Cu-CHA deNO_x Catalyst in Action: Temperature-Dependent NH₃-Assisted Selective Catalytic Reduction Monitored by Operando XAS and XES, *J. Am. Chem. Soc.* 138 (2016) 12025–12028, <https://doi.org/10.1021/jacs.6b06809>.
- [8] A.R. Fahami, T. Günter, D.E. Doronkin, M. Casapu, D. Zengel, T.H. Vuong, M. Simon, F. Breher, A.V. Kucherov, A. Brückner, J.-D. Grunwaldt, The Dynamic Nature of Cu Sites in Cu-SSZ-13 and the Origin of the Seagull NO_x Conversion Profile During NH₃-SCR, *React. Chem. Eng.* 4 (2019) 1000–1018, <https://doi.org/10.1039/C8RE00290H>.
- [9] C. Paolucci, A.A. Parekh, I. Khurana, J.R. Di Iorio, H. Li, J.D. Albarracin Caballero, A.J. Shih, T. Anggara, W.N. Delgass, J.T. Miller, F.H. Ribeiro, R. Gounder, W.F. Schneider, Catalysis in a Cage: Condition-Dependent Speciation and Dynamics of Exchanged Cu Cations in SSZ-13 Zeolites, *J. Am. Chem. Soc.* 138 (2016) 6028–6048, <https://doi.org/10.1021/jacs.6b02651>.
- [10] E. Borfecchia, K.A. Lomachenko, F. Giordano, H. Falsig, P. Beato, A.V. Soldatov, S. Bordiga, C. Lamberti, Revisiting the Nature of Cu Sites in the Activated Cu-SSZ-13 Catalyst for SCR Reaction, *Chem. Sci.* 6 (2014) 548–563, <https://doi.org/10.1039/C4SC02907K>.
- [11] F. Giordano, P.N.R. Vennestrom, L.F. Lundegaard, F.N. Stappen, S. Mossin, P. Beato, S. Bordiga, C. Lamberti, Characterization of Cu-exchanged SSZ-13: A Comparative FTIR, UV-Vis, and EPR study with Cu-ZSM-5 and Cu-β with Similar Si/Al and Cu/Al Ratios, *Dalton Trans.* 42 (2013) 12741–12761, <https://doi.org/10.1039/C3DT50732G>.
- [12] V.F. Kispersky, A.J. Kropf, F.H. Ribeiro, J.T. Miller, Low Absorption Vitreous Carbon Reactors for Operando XAS: A Case Study on Cu/Zeolites for Selective Catalytic Reduction of NO_x by NH₃, *Phys. Chem. Chem. Phys.* 14 (2012) 2229–2238, <https://doi.org/10.1039/C1CP22992C>.
- [13] T. Günter, D.E. Doronkin, A. Boubnov, H.W.P. Carvalho, M. Casapu, J.-D. Grunwaldt, The SCR of NO_x with NH₃ Examined by Novel X-ray Emission and X-ray Absorption Methods, *Top. Catal.* 59 (2016) 866–874, <https://doi.org/10.1007/s11244-016-0561-7>.
- [14] T.V.W. Janssens, H. Falsig, L.F. Lundegaard, P.N.R. Vennestrom, S.B. Rasmussen, P.G. Moses, F. Giordano, E. Borfecchia, K.A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia, *ACS Catal.* 5 (2015) 2832–2845, <https://doi.org/10.1021/cs501673g>.
- [15] J. Luo, F. Gao, K. Kamasamudram, N. Currier, C.H.F. Peden, A. Yezerets, New Insights into Cu/SSZ-13 SCR Catalyst Acidity. Part I: Nature of Acidic Sites Probed by NH₃ Titration, *J. Catal.* 348 (2017) 291–299, <https://doi.org/10.1016/j.jcat.2017.02.025>.
- [16] C. Paolucci, A.A. Verma, S.A. Bates, V.F. Kispersky, J.T. Miller, R. Gounder, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, Isolation of the Copper Redox Steps in the Standard Selective Catalytic Reduction on Cu-SSZ-13, *Angew. Chem. Int. Ed.* 53 (2014) 11828–11833, <https://doi.org/10.1002/anie.201407030>.
- [17] F. Giordano, E. Borfecchia, K.A. Lomachenko, A. Lazzarini, G. Agostini, E. Gallo, A.V. Soldatov, P. Beato, S. Bordiga, C. Lamberti, Interaction of NH₃ with Cu-SSZ-13 Catalyst: A Complementary FTIR, XANES, and XES Study, *J. Phys. Chem. Lett.* 5 (2014) 1552–1559, <https://doi.org/10.1021/jz500241m>.
- [18] R. Villamaina, S. Liu, I. Nova, E. Tronconi, M.P. Ruggeri, J. Collier, A. York, D. Thompsett, Speciation of Cu Cations in Cu-CHA Catalysts for NH₃-SCR: Effects of SiO₂/AlO₃ Ratio and Cu-Loading Investigated by Transient Response Methods, *ACS Catal.* 9 (2019) 8916–8927, <https://doi.org/10.1021/acscatal.9b02578>.
- [19] C. Paolucci, I. Khurana, A.A. Parekh, S. Li, A.J. Shih, H. Li, J.R. Di Iorio, J.D. Albarracin-Caballero, A. Yezerets, J.T. Miller, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, R. Gounder, Dynamic Multinuclear Sites Formed by Mobilized Copper Ions in NO_x Selective Catalytic Reduction, *Science*. 357 (2017) 898–903, <https://doi.org/10.1126/science.aan5630>.
- [20] T. Sella, M.P. Ruggeri, I. Nova, E. Tronconi, The Low Temperature Interaction of NO + O₂ with a Commercial Cu-CHA Catalyst: A Chemical Trapping Study, *Top. Catal.* 59 (2016) 678–685, <https://doi.org/10.1007/s11244-016-0543-9>.
- [21] L.M. Mirica, X. Ottenwaelder, T.D.P. Stack, Structure and Spectroscopy of Copper–Dioxigen Complexes, *Chem. Rev.* 104 (2004) 1013–1046, <https://doi.org/10.1021/cr020632z>.
- [22] C.E. Elwell, N.L. Gagnon, B.D. Neisen, D. Dhar, A.D. Spaeth, G.M. Yee, W.B. Tolman, Copper–Oxygen Complexes Revisited: Structures, Spectroscopy, and Reactivity, *Chem. Rev.* 117 (2017) 2059–2107, <https://doi.org/10.1021/acs.chemrev.6b00636>.
- [23] E.A. Lewis, W.B. Tolman, Reactivity of Dioxigen–Copper Systems, *Chem. Rev.* 104 (2004) 1047–1076, <https://doi.org/10.1021/cr020633r>.
- [24] L. Chen, H. Falsig, T.V.W. Janssens, H. Grönbeck, Activation of Oxygen on (NH₃CuNH₃)⁺ in NH₃-SCR over Cu-CHA, *J. Catal.* 358 (2018) 179–186, <https://doi.org/10.1016/j.jcat.2017.12.009>.
- [25] L. Chen, T.V.W. Janssens, H. Grönbeck, A Comparative Test of Different Density Functionals for Calculations of NH₃-SCR over Cu-Chabazite, *Phys. Chem. Chem. Phys.* 21 (2019) 10923–10930, <https://doi.org/10.1039/C9CP01576K>.
- [26] F. Gao, E.D. Walter, M. Kollar, Y. Wang, J. Szanyi, C.H.F. Peden, Understanding Ammonia Selective Catalytic Reduction Kinetics over Cu/SSZ-13 from Motion of the Cu Ions, *J. Catal.* 319 (2014) 1–14, <https://doi.org/10.1016/j.jcat.2014.08.010>.
- [27] F. Gao, N.M. Washton, Y. Wang, M. Kollár, J. Szanyi, C.H.F. Peden, Effects of Si/Al Ratio on Cu/SSZ-13 NH₃-SCR Catalysts: Implications for the Active Cu Species and the Roles of Brønsted Acidity, *J. Catal.* 331 (2015) 25–38, <https://doi.org/10.1016/j.jcat.2015.08.004>.
- [28] L. Chen, H. Falsig, T.V.W. Janssens, J. Jansson, M. Skoglundh, H. Grönbeck, Effect of Al-Distribution on Oxygen Activation over Cu-CHA, *Catal. Sci. Technol.* 8 (2018) 2131–2136, <https://doi.org/10.1039/C8CY00083B>.
- [29] A. Marberger, A.W. Petrov, P. Steiger, M. Elsener, O. Kröcher, M. Nachtgeal, D. Ferri, Time-resolved Copper Speciation During Selective Catalytic Reduction of NO on Cu-SSZ-13, *Nat. Catal.* 1 (2018) 221–227, <https://doi.org/10.1038/s41929-018-0032-6>.
- [30] S.A. Bates, W.N. Delgass, F.H. Ribeiro, J.T. Miller, R. Gounder, Methods for NH₃ Titration of Brønsted Acid Sites in Cu-zeolites that Catalyze the Selective Catalytic Reduction of NO_x with NH₃, *J. Catal.* 312 (2014) 26–36, <https://doi.org/10.1016/j.jcat.2013.12.020>.
- [31] J.R. Di Iorio, S.A. Bates, A.A. Verma, W.N. Delgass, F.H. Ribeiro, J.T. Miller, R. Gounder, The Dynamic Nature of Brønsted Acid Sites in Cu-Zeolites During NO_x Selective Catalytic Reduction: Quantification by Gas-Phase Ammonia Titration, *Top. Catal.* 58 (2015) 424–434, <https://doi.org/10.1007/s11244-015-0387-8>.
- [32] A.J. Kropf, J. Katsoudas, S. Chattopadhyay, T. Shibata, E.A. Lang, V.N. Zyryanov, B. Ravel, K. McIvor, K.M. Kemner, K.G. Scheckel, S.R. Bare, J. Terry, S.D. Kelly, B. A. Bunker, C.U. Segre, The New MRCAT (Sector 10) Bending Magnet Beamline at the Advanced Photon Source, *AIP Conf. Proc.* 1234 (2010) 299–302, <https://doi.org/10.1063/1.3463194>.
- [33] S.A. Bates, A.A. Verma, C. Paolucci, A.A. Parekh, T. Anggara, A. Yezerets, W.F. Schneider, J.T. Miller, W.N. Delgass, F.H. Ribeiro, Identification of the Active Cu Site in Standard Selective Catalytic Reduction with Ammonia on Cu-SSZ-13, *J. Catal.* 312 (2014) 87–97, <https://doi.org/10.1016/j.jcat.2014.01.004>.
- [34] R.M. Koros, E.J. Nowak, A Diagnostic Test of the Kinetic Regime in a Packed Bed Reactor, *Chem. Eng. Sci.* 22 (1967) 470, [https://doi.org/10.1016/0009-2509\(67\)80134-9](https://doi.org/10.1016/0009-2509(67)80134-9).
- [35] P.B. Weisz, C.D. Prater, Interpretation of Measurements in Experimental Catalysis, in: W.G. Frankenburg, V.I. Komarewsky, E.K. Rideal (Eds.), *Adv. Catal.*, Academic Press, 1954: pp. 143–196. [https://doi.org/10.1016/S0360-0564\(08\)60390-9](https://doi.org/10.1016/S0360-0564(08)60390-9).
- [36] A.J. Shih, I. Khurana, H. Li, J. González, A. Kumar, C. Paolucci, T.M. Lardinois, C.B. Jones, J.D. Albarracin Caballero, K. Kamasamudram, A. Yezerets, W.N. Delgass, J.T. Miller, A.L. Villa, W.F. Schneider, R. Gounder, F.H. Ribeiro, Spectroscopic and Kinetic Responses of Cu-SSZ-13 to SO₂ Exposure and Implications for NO_x Selective Catalytic Reduction, *Appl. Catal. A* 574 (2019) 122–131, <https://doi.org/10.1016/j.apcata.2019.01.024>.
- [37] Y. Jangjou, C.S. Sampara, Y. Gu, D. Wang, A. Kumar, J. Li, W.S. Epling, Mechanism-based Kinetic Modeling of Cu-SSZ-13 Sulfation and Desulfation for NH₃-SCR Applications, *React. Chem. Eng.* 4 (2019) 1038–1049, <https://doi.org/10.1039/C8RE00210J>.
- [38] G. Cavataio, J. Girard, J.E. Patterson, C. Montreuil, Y. Cheng, C.K. Lambert, Laboratory Testing of Urea-SCR Formulations to Meet Tier 2 Bin 5 Emissions, in: 2007: pp. 2007-01–1575. <https://doi.org/10.4271/2007-01-1575>.
- [39] C. Liu, H. Kubota, T. Amada, K. Kon, T. Toyao, Z. Maeno, K. Ueda, J. Ohyama, A. Satsuma, T. Tanigawa, N. Tsunoi, T. Sano, K. Shimizu, In Situ Spectroscopic Studies on the Redox Cycle of NH₃-SCR over Cu-CHA Zeolites, *ChemCatChem* 12 (2020) 3050–3059, <https://doi.org/10.1002/cctc.202000024>.
- [40] S.H. Krishna, C.B. Jones, J.T. Miller, F.H. Ribeiro, R. Gounder, Combining Kinetics and Operando Spectroscopy to Interrogate the Mechanism and Active Site Requirements of NO_x Selective Catalytic Reduction with NH₃ on Cu-Zeolites, *J. Phys. Chem. Lett.* (2020), <https://doi.org/10.1021/acs.jpcclett.0c09093>.