Understanding ammonia selective catalytic reduction kinetics over Cu/SSZ-13 from motion of the Cu ions

Feng Gao*, Eric D. Walter, Marton Kollar, Yilin Wang, János Szanyi*, Charles H.F. Peden*
Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, United States

Abstract

Cu/SSZ-13 catalysts with Si/Al = 6 and various Cu/Al ratios are synthesized with solution ion exchange. Catalysts are characterized with surface area/pore volume measurements, temperature programmed reduction (TPR), and electron paramagnetic resonance (EPR) spectroscopy. Catalytic properties are examined using NO oxidation, ammonia oxidation, and standard ammonia selective catalytic reduction (NH₃-SCR) reactions. Prior to full dehydration of the zeolite catalysts, hydrated Cu²⁺ ions are found to be very mobile as judged from EPR. NO oxidation is catalyzed by O-bridged Cu-dimer species that form at relatively high Cu loadings and in the presence of O₂. For NH₃ oxidation on samples with low to intermediate Cu loadings, transient Cu-dimers are the low-temperature (≤ 300 °C) active centers, while these dissociate to monomers at 350 °C and above and become active centers. For the much more complex standard SCR reaction, transient Cu-dimers are the active sites for reaction temperatures < 250 °C at very low Cu loadings (Cu/Al ≤ 0.016). Between ~ 250 and 350 °C, these Cu-dimers become less stable causing SCR reaction rates to decrease. At temperatures ≥ 350 °C, Cu²⁺ monomers that had migrated to faces of 6-membered rings are the active sites. At intermediate Cu loadings, monomeric Cu²⁺ ions are also active in SCR in the low-temperature regime; these are proposed to be located within CHA cages and next to 8-membered rings, likely in the form of [Cu(OH)]⁺. At high Cu loadings (i.e., more than one Cu²⁺ ion in each unit cell), stable Cu-dimers form and these do not dissociate at temperatures above 350 °C. These moieties effectively occupy CHA cage space and block pore openings causing decreased efficiency of the catalysts. Also these moieties are highly active in catalyzing the NH₃ oxidation reaction thus causing SCR selectivities to decrease above ~ 450 °C. Finally, our kinetics results strongly support a redox mechanism for standard SCR.

Keywords: selective catalytic reduction, Cu/SSZ-13, electron paramagnetic resonance, reaction kinetics, reaction mechanism.

*Corresponding authors – email addresses: feng.gao@pnnl.gov (F. Gao), janos.szanyi@pnnl.gov (J. Szanyi), chuck.peden@pnnl.gov (C.H.F. Peden).

1. Introduction

Selective catalytic reduction of NO_x by ammonia has received extensive research interest for over 20 years [1-3]. With the successful implementation of Cu/SSZ-13 (a small pore zeolite with Chabazite (CHA) structure) as part of the emission control systems for diesel passenger vehicles, and light- and medium-duty trucks in the U.S. and Europe [4, 5], there has been a new surge of research interest in NH_3 -SCR over Cu/Chabazite; as evidenced by the more than 40 open literature publications that have appeared in the past 3 years [6, 7 and references therein]. The commercial success of Cu/SSZ-13 as a diesel engine exhaust catalyst is due primarily to its exceptional hydrothermal stability [8-10]. One of the key attributes of Cu/SSZ-13 for fundamental research is its structural simplicity: The Chabazite structure is constructed by stacking double-6-rings (d6r) so that all tetrahedral sites (T-sites, Al and Si) are in equivalent structural positions. Cu ions have been initially suggested to be present only as isolated monomers (Cu^{2+} and Cu^+), and that they solely occupy one extra-frame site; that is, faces of 6-membered rings [11].

In view of this evident structural simplicity, we [7], and others [6, 11], have suggested that Cu/SSZ-13 offers an excellent opportunity to elucidate some long-standing questions regarding NH_3 -SCR, including the nature of the catalytically active centers and detailed reaction mechanism(s). With continuing research efforts, however, it has become evident that the situation is much more complicated than initially thought. First, it is an oversimplification to suggest one type and one location for the catalytic centers within Cu/SSZ-13 [12-15]. In line with studies on other Cu/zeolite SCR catalysts, the nature and location of Cu species are influenced by multiple factors including structure of the zeolites, Si/Al ratios, Cu loadings, and synthesis methods [3, 6, 16]. Second, oxidation states, locations and chemical nature of the Cu

catalytic centers are expected to vary as a function of reaction conditions; therefore, only operando spectroscopic techniques applicable to NH₃-SCR are, in principle, able to accurately monitor these dynamic variations allowing the establishment of proper structure-function relationships. Such techniques may include X-ray Absorption (XAS), UV-Vis, Diffuse Reflectance Infrared Fourier Transform Infrared (DRIFTS), Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopies. However, no technique at the present time has the satisfactory spatial and time scale resolution to allow the construction of such relationships. On the other hand, the relevance of results obtained by *ex situ* techniques can always be questioned. For example, Rietveld refinement of XRD has been well-established to study extra-framework metal ion locations on *dehydrated* zeolites. For Cu/SSZ-13 in particular, a few groups utilized this method and established that isolated Cu²⁺ ions prefer locations in the faces of 6-membered rings [11, 17]. This assignment also received support from DFT calculations [18, 19]. This is not surprising since after dehydration, Cu²⁺ ions require lattice oxygens as ligands for stabilization; and 5- and 6-membered rings in zeolites are the obvious choices for optimizing Cu-O coordination numbers and bond distances, as well as providing negative charge required to balance the Cu ion charge. However, under typical NH₃-SCR reaction conditions, that is, in the presence of large amounts of NH₃ and H₂O which both bind strongly with Cu ions as ligands at low to moderate temperatures, and an excess amount of O₂ which may interact with isolated Cu ion centers to generate Cu₂O_x complexes, it should not be expected that these ions remain in their dehydrated locations and forms, especially at relatively low temperatures.

The mechanism for SCR over Cu ion exchanged zeolite catalysts is still widely debated. The key points of disagreement are the following: (1) Whether the catalytically relevant Cu

species are monomeric or dimeric (even, perhaps very small Cu ion clusters). (2) Whether NO_2 plays a significant role in the mechanism. While some researchers suggest it is important and its formation could even be the rate-limiting step [3], others argue against this [20, 21]. (3) Whether Cu^+ plays an important role in standard NH_3 -SCR. If so $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling is important, otherwise it is likely not. (4) Whether Cu/CHA are dual functional in SCR; that is, whether both Cu ion sites and Brönsted acid sites collectively provide the catalytic functionality. Moreover, industrial researchers have discovered an interesting light-off behavior with commercial Cu/CHA catalysts in standard NH_3 -SCR, which is generally recognized as the “seagull shape” light-off curve. A typical “seagull shape” curve is displayed in Fig. 1 replotted using data published by Cummins, Inc. [22]. Interestingly, at a reaction temperature of 400 °C, NO_x conversion appears to be somewhat lower than those at 350 and 450 °C. One of the focuses of the present study is to understand this rather unusual behavior, and to confirm that it can be understood from kinetic reasons. In this study we also show that our kinetic data are fully consistent with a redox SCR reaction mechanism, and that most of the interesting SCR and NH_3/NO oxidation kinetic behaviors over Cu/SSZ-13 can be explained by motion of the Cu ions, especially formation and breaking of metastable oxygen-bridged dicopper active centers.

2. Experimental

2.1 Catalyst Synthesis

Na/SSZ-13 ($\text{Si}/\text{Al} = 6$) was synthesized using a method published elsewhere [8, 11]. Results from routine characterizations, including powder X-ray Diffraction (XRD), N_2 adsorption-desorption isotherms and Scanning Electron Microscopy (SEM) imaging, are displayed in Fig. S1. These results confirm formation of a highly crystallized microporous material with primary particles $< 3\mu\text{m}$. Cu/SSZ-13 samples were prepared using a standard two-

step solution ion exchange protocol reported previously, first with NH_4NO_3 followed by CuSO_4 solutions at 80 °C [13]. In our previous study, samples with Cu loadings at $\text{Cu}/\text{Al} > 0.1$ were used [13]. In the present study, a number of Cu/SSZ-13 samples were prepared with considerably lower Cu loadings ($\text{Cu}/\text{Al} < 0.05$). This was done by using diluted CuSO_4 solutions at 0.001M during ion exchange.

2.2 Catalyst Characterization

Cu contents of the Cu/SSZ-13 samples were determined with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at Galbraith Laboratories (Knoxville, TN, USA). Prior to measurements, the samples were dehydrated at 150 °C for 2 h in vacuum to remove adsorbed moisture. Table 1 presents Cu weight percentages, and the corresponding Cu/Al ratios and ion exchange levels for all Cu/SSZ-13 samples used in the present study. In the following text, in cases where only one measure of Cu loading is provided, the others can be readily found in this table. BET surface areas and micropore volumes of the samples were measured with a Quantachrome Autosorb-6 analyzer. Prior to analysis, the samples were dehydrated under vacuum overnight at 250 °C. For all the samples studied here, BET surface areas were 500-550 m^2/g and micropore volumes were $\sim 0.25 \text{ cm}^3/\text{g}$. Powder X-ray diffraction (XRD) measurements were performed on a Philips PW3040/00 X'Pert powder X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected with 2θ ranging from 5° to 50° with a step size of 0.02°. All of the samples showed perfect crystallinity.

EPR experiments were conducted on a Bruker E580 X-band spectrometer equipped with a SHQE resonator and a continuous flow cryostat. Powder samples ($\sim 10 \text{ mg}$) were contained in 4 mm OD quartz tubes that can be purged/treated with various gases, cooled with liquid N_2 and helium, and heated to $\sim 300 \text{ °C}$. During spectral acquisition, microwave power was 200

microwatts, and the frequency was 9.86 GHz. The field was swept by 1500 G in 84 seconds and modulated at 100 kHz with 5 G amplitude. A time constant of 20 ms was used.

2.3 SCR and NO/NH₃ oxidation reaction tests

NH₃-SCR reaction kinetics measurements were carried out in a plug-flow reaction system described elsewhere [11]. Powder samples were pressed, crushed and sieved (60-80 mesh) prior to use. For standard SCR, the feed gas contained 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O and balance N₂. NO and NH₃ oxidation reactions were conducted under identical conditions except that, in NO oxidation, the NH₃ feed was stopped, and vice versa. Stoichiometries for these reactions are shown below:

All of the gas lines were heated to over 100 °C to avoid water condensation. The total gas flow was 300 sccm, and the gas hourly space velocity (GHSV) was estimated to be ~400,000 h⁻¹ for a catalyst amount of 30 mg. Concentrations of reactants and products were measured by an online Nicolet Magna 560 FTIR spectrometer with a 2 m gas cell maintained at 150 °C.

Prior to temperature-dependent steady-state reaction measurements, the catalysts were activated in 14% O₂/N₂ flow for 1 h at 550 °C. At each target temperature, a minimum waiting time of ~45 min was applied to reach a steady-state. For standard SCR, NO_x and NH₃ conversions were calculated based on the following equations:

$$\text{NO}_x \text{ Conversion \%} = \frac{(\text{NO} + \text{NO}_2)_{\text{inlet}} - (\text{NO} + \text{NO}_2 + \text{N}_2\text{O})_{\text{outlet}}}{(\text{NO} + \text{NO}_2)_{\text{inlet}}} \times 100$$

$$\text{NH}_3 \text{ Conversion \%} = \frac{(\text{NH}_3)_{\text{inlet}} - (\text{NH}_3)_{\text{outlet}}}{(\text{NH}_3)_{\text{inlet}}} \times 100$$

For NH₃ oxidation reaction, the same NH₃ conversion equation was used. For NO oxidation reaction, the following equation was used:

$$NO \text{ Conversion } \% = \frac{(NO)_{inlet} - (NO)_{outlet}}{(NO)_{inlet}} \times 100$$

For NO and NH₃ oxidation reactions, reaction rates were normalized on a per sample weight basis, using conversions below ~20% (i.e., differential conversions). For standard SCR, previous studies have shown that under typical low-temperature conditions, this reaction can be treated as a first-order reaction [23-26]. Therefore, reaction rates were normalized using the first-order kinetic equation, i.e., $r = \frac{F}{W} (-\ln(1 - x))$, where F is the NO flow rate (moles of NO per s), w the mass of the catalyst (g), and x the NO conversion. Turnover frequencies (TOFs) were calculated using the first-order kinetic equation on a per mole of Cu basis (i.e., mol NO mol Cu⁻¹ s⁻¹). The Arrhenius equation, $k = \frac{r}{[NO]_0} = Ae^{\frac{-E_a}{RT}}$, was used for the calculations of preexponential factors (A) and apparent activation energies (E_a), where k is the rate constant and [NO]₀ the molar concentration of NO in the feed [23].

3 Results

3.1 Electron paramagnetic resonance (EPR) results

EPR was performed on the fully hydrated low Cu loading samples (Cu/Al < 0.05) for the purpose of investigating potential interactions between Cu ions. Fig. 2(a) presents the spectra collected at 120 K where all Cu²⁺ ions should remain immobilized at this temperature. Although all of the Cu²⁺ ions were fully hydrated in this case, spectra from the low field still indicated differences in their local environments (see the enlarged section). This suggests that some Cu²⁺ ions have stronger interactions with the CHA framework than others. When all spectra were normalized to the same high-field signal intensity (Fig. 2(b)), they almost completely overlapped

except the small deviation for the sample with the highest Cu loading. These results demonstrate that the hydrated Cu^{2+} ions are far apart in the low loading samples at such a low temperature and, therefore, no dipolar interactions between Cu^{2+} ions that cause line-broadening of the EPR signal.

Fig. 3 presents EPR spectra for one of the low Cu loading samples ($\text{Cu}/\text{Al} = 0.032$) during dehydration in dry N_2 . At ambient temperature (black curve), multiple features were found at high field and the low-field hyperfine structures were partially shielded by a large broad signal (“lump”). These spectral features are caused by rapid Cu^{2+} ion mobility and dipolar interactions between Cu^{2+} ions as we discussed previously [13]. At 250 °C (blue curve), in contrast, only one sharp feature was detected at high field, and the low-field hyperfine structures became well-defined indicating a loss of mobility for Cu^{2+} ions via strong interaction with the CHA framework. Clearly, this can only happen after H_2O ligands from the first coordination sphere surrounding Cu^{2+} ions have been removed via dehydration. Interestingly, at intermediate temperatures, especially at 150 °C (red curve), intensity for the high-field feature decreases dramatically, and the low-field hyperfine structures are completely absent. It is important to note that this considerable signal intensity loss at ~150 °C is not caused by formation of EPR silent species (Cu^+ ions, and/or Cu ion dimers). The real measure of the amount of Cu^{2+} ions, i.e., the double-integral spectra, did not show an intensity drop at this temperature more than that due to the Boltzmann distribution (data not shown). For Cu ions in SSZ-13 cationic positions, NO titration with FTIR has been shown to be extremely sensitive to oxidation states of Cu ions [27, 28]. NO FTIR spectra shown in Figs. S2(a) and (b) on samples ($\text{Cu}/\text{Al} = 0.032$) annealed in high vacuum ($\sim 1 \times 10^{-7}$ Torr) at 150 and 550 °C, respectively, clearly demonstrate that Cu^+ ions do not form during dehydration at 150 °C even in high vacuum. More likely, the signal loss in EPR is

caused by dipolar interactions between Cu^{2+} ions, demonstrating that the Cu^{2+} ions are still highly mobile at 150 °C. Since the Cu loading for this sample is so low (roughly one Cu^{2+} ion in every eight hexagonal unit cells), such dipolar interactions below 250 °C demonstrate that Cu^{2+} ions can travel between unit cells facilely at relatively low temperatures. This notion is very important for understanding low-temperature SCR kinetics and will be addressed further below.

3.2 NO oxidation, NH_3 oxidation and standard NH_3 -SCR kinetics

3.2.1 NO oxidation

NO oxidation ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$) kinetics over Cu/SSZ-13 are first presented in this section. To mimic practical SCR reaction conditions, ~2.5% of H_2O was added to the reactant. Fig. S3 displays NO conversion as a function of reaction temperature over 5 Cu/SSZ-13 samples with Cu/Al ratios > 0.1. Note that “background” NO_2 , that is, small amounts of NO_2 formed in the gas phase and catalytically by the H/SSZ-13 substrate has been subtracted using NO conversions obtained from a blank experiment with H/SSZ-13. The normalized NO oxidation rates ($\text{mol NO g}^{-1} \text{ s}^{-1}$) are plotted in Fig. 4. Interestingly, NO oxidation activity was essentially absent below ~400 °C on samples with Cu/Al < 0.3. At even higher temperatures, these samples still displayed very limited activity. In contrast, the two higher Cu loading samples displayed NO oxidation activities over the entire temperature range investigated. Especially for the sample with Cu/Al = 0.44, NO conversions even approached thermodynamic limits above ~500 °C. We have shown previously that, in their hydrated form, Cu species within these samples were fully detectable with EPR, allowing us to rule out the presence of CuO_x clusters (which are highly active in NO oxidation yet EPR silent) in any of our samples [13]. Therefore, the dramatic difference in NO oxidation activity as a function of Cu loading can only be rationalized either by

activity differences for different Cu^{2+} ion monomers, or the formation of Cu ion dimers at higher Cu loadings.

3.2.2 NH_3 oxidation

Next, NH_3 oxidation ($4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$) kinetics are reported. Again, $\sim 2.5\%$ H_2O was added to the feed to simulate realistic reaction conditions. Note first that the H/SSZ-13 substrate did not have any activity for this reaction; therefore, no background subtraction was necessary during data analysis. Note also that all catalysts used in the present study were highly selective in N_2 formation. Even for samples with high Cu loadings, N_2O formation was very limited (no more than 4 ppm under any steady-state condition). Fig. S4 presents light-off curves on samples at five Cu/Al ratios. Fig. 5 displays normalized reaction rates (the dashed horizontal line represents 20% NH_3 conversion, below which differential reaction conditions maintain). For samples with Cu/Al ratios ≤ 0.11 , activity was rather low and NH_3 conversion was found to increase monotonically with increasing temperature. However for the two samples with higher Cu loadings, reaction rates were found to increase with temperature much more rapidly.

3.2.3 Standard NH_3 -SCR

Fig. S5(a) presents standard SCR light-off curves for samples with Cu/Al ratios > 0.1 . Note that we previously reported SCR activities for this series of samples at higher space velocities [13]. In the present study, a moderate GHSV of $\sim 400,000 \text{ h}^{-1}$ was used for all standard SCR measurements. Basically, very similar kinetic behavior is reproduced here. SCR was also conducted on samples with much lower Cu loadings, and the light-off curves are plotted in Fig. S4(b). Note that at such low Cu loadings, the “background” NO conversion catalyzed by H-SSZ-13 becomes non-negligible and Fig. S5(b) is plotted using data after a “background” reactivity subtraction. The most interesting finding from Fig S5 is that the “seagull shape” light-off

behavior found for the commercial Cu/CHA catalysts (Fig. 1) is reproduced on our model catalysts at $\text{Cu}/\text{Al} \leq 0.11$. Under typical standard NH_3 -SCR reaction conditions at steady-state, there is general consensus that the reaction follows first-order kinetics [23-26]; that is, reactions rates have a first order dependence on NO pressure and a zero order dependence on NH_3 . Since O_2 is typically in considerable excess, very small changes in its concentrations during reactions do not alter reaction rates. Therefore, the NH_3 -SCR reaction rate can be expressed as $r = \frac{F}{w}(-\ln(1 - x))$, where F is the NO feeding rate (moles of NO per s), w the catalyst weight (g) and x the NO conversion. Note that at reaction temperatures above $\sim 400^\circ\text{C}$, the first-order assumption is perhaps questionable since the NH_3 pressure dependence may become higher than zero order. Using this rate expression, SCR rates are normalized and the results are displayed in Fig. 6. The dashed horizontal line represents an NO conversion of 20% so that below this line, data points are within the differential regime. As will be shown below, the kinetically meaningful regime extends to NO conversions substantially higher than 20%. From this graph, the existence of multiple kinetic regimes is obvious for samples with $\text{Cu}/\text{Al} \leq 0.11$. From 100 to $\sim 250^\circ\text{C}$, reaction rates increase with increasing temperature and Cu loading, while from ~ 250 to $\sim 350^\circ\text{C}$, reaction rates *decrease* with increasing temperature. Above $\sim 350^\circ\text{C}$, reaction rates increase again very rapidly with increasing temperature. Since the “seagull shape” extends to samples at the lowest Cu loadings where NO conversions fall safely within the differential regime, it is clearly a kinetic behavior.

In the low-temperature regime (~ 100 - 250°C), one prominent finding from Fig. 6 is the non-linear increase in NO conversions as a function of Cu loading. In the following, more detailed analysis is given for all samples at reaction temperatures of 140, 155, 170 and 185°C . The results are plotted in Fig. 7 (a)–(d). At each temperature, the upper panel displays

normalized SCR rates ($\text{mol NO g}^{-1} \text{ s}^{-1}$) while the lower panel displays TOFs ($\text{mol NO mol Cu}^{-1} \text{ s}^{-1}$), both as a function of Cu loading. From the upper panels, it is seen that SCR rates increase reasonably linearly with increasing Cu loading up to 2.59 wt% ($\text{Cu/Al} = 0.22$). At higher Cu loadings, reaction rates become relatively unchanged. According to the Koros–Nowak criterion, this linear relationship rules out transport limitations and indicates that the samples run in the kinetic regime [29, 30]. Somewhat surprisingly, the kinetic regime appears to extend to NO conversions much higher than 20% (for example from Fig. S5, NO conversion reaches ~50% at 185 °C on the sample with $\text{Cu/Al} = 0.11$). However, closer examination of the normalized rates in the upper panels of Fig. 7 indicates that at the lowest Cu loadings (≤ 0.378 wt%, $\text{Cu/Al} \leq 0.032$), reaction rates are below the straight lines at all temperatures (i.e., non-linear increase in NO conversions as a function of Cu loading). This is more clearly evident in the TOF data plotted in the lower panels where TOFs raise sharply with increasing Cu loading up to 0.378 wt%. We note that, in a very recent study by Bates et al [25], the authors also found that their lowest Cu loading sample ($\text{Cu/Al} = 0.02$) is substantially less active than higher Cu loaded ones, thus emphasizing the reproducibility of this phenomenon where we demonstrate this clearly with multiple low Cu-loaded samples here. Within a wide Cu loading range from 0.516 to 2.59 wt%, consistent with the upper panels, TOFs maintain roughly unchanged at 140 °C, while they seem to marginally increase at reaction temperatures of 155, 170 and 185 °C. At even higher Cu loadings, since reaction rates no longer increase, expectedly, TOFs decrease with increasing Cu loading. Overall, the Koros–Nowak criterion is only obeyed at intermediate Cu loadings while at very low (< 0.516 wt%) and very high (> 2.59 wt%) Cu loading conditions, deviation is found. Such a deviation is due either to mass-transfer limitations, or to variations in the nature of Cu species. More detailed discussion of these issues will be given below.

As displayed in Fig. 6, from ~250 to ~350 °C, the decrease in NO conversions with increasing temperature on samples with low Cu loadings ($\text{Cu}/\text{Al} \leq 0.11$), is clearly evident and unusual. There could be a number of causes; for example, (1) reactants and/or products poisoning; (2) a change in reaction mechanism; and/or (3) a change in the nature of catalytically active centers in this temperature range. For deciding among these possibilities, we first note that the decrease in reaction rates from 250 to 350 °C cannot be explained by poisoning effects from NH_3 , H_2O or other reaction intermediates (e.g., NH_4NO_3) because such effects are expected to become less serious with increasing temperatures. Hydrocarbon poisoning, on the other hand, has recently been shown to cause a similar kinetic behavior [31] as also discussed in more detail below. However, hydrocarbons are absent in our reactant feed so cannot be playing a role in these experiments. Therefore, changes in the reaction mechanism or the nature of catalytically active centers appear to be more likely. In order to fully understand the complex SCR kinetics shown in Fig. 6, it is important to first find a situation where Cu ion locations can be unambiguously determined. For this, maintaining low Cu loading is critical since we have shown that as Cu loading rises, Cu^{2+} ions occupy different cationic sites in dehydrated catalysts [12, 13]. Furthermore, maintaining high reaction temperatures (≥ 350 °C) is important since, at such high temperatures [15], Cu^{2+} ions almost certainly locate in the most stable cationic positions; i.e., near the faces of 6-membered rings with two Al sites [11, 17].

From Fig. 6, even at the lowest Cu loadings, reaction rates increase very rapidly with increasing temperatures above 350 °C making it hard to maintain differential NO conversions. To overcome this, in the following we describe high-temperature reactions that were carried out at a much higher GHSV of $\sim 1,200,000 \text{ h}^{-1}$ on the low Cu loading samples, and the light-off curves are shown in Fig. S6. Note again that a "background" subtraction was performed to

remove the small portion of NO conversion from the H/SSZ-13 substrate. For the two higher Cu loading samples in this data, it was still not possible to maintain differential NO conversions even at 350 °C. However for the lower three Cu loading samples, differential NO conversions were managed below ~400 °C. Fig. 8(a) presents normalized rates using the first-order kinetics equation shown above. Again, a horizontal dashed line defines the differential regime. Fig. 8(b) plots these rates versus Cu loading at 350, 365 and 380 °C for the three lowest Cu loading samples, and the Koros–Nowak criterion is nicely obeyed. This demonstrates that no mass transfer limitations of any kind are present for these particular samples and reaction conditions; moreover, this also strongly indicates that the catalytically active centers are identical and almost certainly isolated Cu ion monomers in faces of 6-membered rings. Fig. 8(c) displays Arrhenius plots for the three lowest Cu loading samples where reaction rates are normalized as TOFs (mol NO mol Cu⁻¹s⁻¹). As expected, TOFs remain constant as a function of Cu loading under differential reaction conditions. Note also that a rather high apparent reaction activation energy of ~140 kJ/mol is obtained for the linear Arrhenius regime, indicating the existence of rather demanding rate-limiting step(s). It is also seen from this figure that SCR TOFs roll over beyond differential NO conversions and, therefore, the linear Arrhenius regimes extend to higher temperatures as Cu loading decreases.

4 Discussion

At the outset of this discussion section, it is important to note that the presence or absence of coordinating water and/or ammonia on various Cu-ion species will play critical roles in determining the availability of the catalytically active forms. Furthermore, the stability of coordinating water/ammonia will delineate a specific temperature range (~250 – 350 °C) where such molecules will desorb from Cu-ion species and, thereby, alter their location and reactivity.

4.1 Nature of the catalytically active Cu centers

Isolated Cu^{2+} ions in the vicinity of the faces of double 6-membered rings in Cu/CHA have been proposed by a few research groups as the sole active centers for SCR [6,8,11,17,32]. Deka et al [17], based on their synchrotron-based XRD and XAS studies, even suggested that they remain in these positions under low-temperature SCR reaction conditions. The requirement of charge neutrality dictates that three types of isolated Cu ions can exist in Cu/zeolites: Cu^{2+} ions that balance 2 negative framework charges, and $[\text{Cu}^{\text{II}}(\text{OH})]^+$ and Cu^+ species that balance 1 negative charge [33]. The three Cu species are schematically shown below. Note that configuration (A) is only drawn for the sake of simplicity here: two Al sites can, in fact, be separated by more than one Si sites yet still charge balance a single Cu^{2+} ion [18].

Scheme 1: Three isolated ionic Cu species in Cu/zeolites

The binding strength of Cu^{2+} ions with the CHA framework can be readily probed with temperature-programmed reduction with H_2 (H_2 -TPR). In our previous studies [12, 13], it was discovered that under dehydrated conditions, Cu^{2+} ions first occupy sites that are more difficult to reduce to Cu^+ , while as Cu loading increases, some Cu^{2+} ions occupy sites that are more readily reducible. We have also shown that if TPR is performed in the presence of moisture, all Cu^{2+} ions become readily reducible [12]. Based also on FTIR studies of changes in Chabazite framework vibrations caused by the migration of Cu^{2+} ions during dehydration [15], we concluded that, for dehydrated samples, Cu^{2+} ions only occupy sites next to faces of 6-membered

rings (species (A)) at low loadings. These results also suggested that, at higher Cu loadings, some Cu^{2+} ions also occupy sites within the CHA cages, likely next to 8-membered rings. Due to spatial constraints, Cu^{2+} ions next to 8-membered rings may not be able to interact efficiently with two Al sites. In this case, a $[\text{Cu}^{\text{II}}(\text{OH})]^+$ species (species (B)) interacting with only one Al site becomes more likely. In the presence of H_2O , species (A) can hydrolyze to species (B) according to Scheme 2.

Scheme 2: Reversible hydrolysis of isolated Cu^{2+} species (A)

The fact that all Cu^{2+} ions become more readily reducible in the presence of moisture [12,13] can then be due, in part, to hydrolysis of isolated Cu^{2+} ions (the equilibrium in Scheme 2 is shifted to the right during TPR). Assuming this to be the case, it follows that Cu^{2+} ion monomer (B) has much lower redox barrier than the more strongly bound (A). In further support of this, our most recent study on Cu^{2+} ion locations in SSZ-13 from first principles and from NO titration FTIR, the stabilization of Cu^{2+} ions in 8-membered rings by H_2O and $-\text{OH}$ ligands is demonstrated [28].

We have shown previously that, for hydrated samples at high Cu loadings, EPR can be used to estimate Cu-Cu distances based on line-broadening of EPR signals originating from dipolar interactions [13]. In the present study, we further used EPR to study hydrated, yet very low Cu-loading samples (Fig. 2). As shown in Fig. 2(a), at such low Cu loadings (Cu/Al ratios <

0.05), hyperfine structures indicate more than one Cu^{2+} species. This suggests that not all Cu^{2+} ions are completely free from interactions with the CHA framework. For hydrated samples at much higher Cu loadings, such subtle differences could not be observed, and all spectra could be fit reasonably well with one set of g and A values [13]. From Fig. 2(b), no line-broadening is detectable in normalized spectra at such low Cu loadings, indicating that Cu^{2+} ions are far enough apart to eliminate dipolar interactions when they are “frozen” at 120 K. However, as shown in Fig. 3, Cu^{2+} ions become highly mobile from ambient temperature to $\sim 200^\circ\text{C}$, and only become immobile again upon extensive dehydration (at 250°C). The lack of hyperfine structures and the loss of high-field signal between ~ 100 to 200°C are due mainly to dipolar interactions between Cu^{2+} ions, and not to the formation of EPR silent species. For example, the NO titration FTIR results presented in Fig. S2 clearly demonstrate that Cu^{2+} ions are not reduced to EPR silent Cu^+ during dehydration at 150°C . It is conceivable that, under typical NH_3 -SCR conditions (that is, in the presence of H_2O and NH_3 that can strongly interact with Cu^{2+} ion centers), the mobility of copper ions will extend to even higher temperatures, since interactions between Cu^{2+} ion centers and the CHA framework are further weakened by the presence of these ligands. These mobile hydrated (and/or ammoniated) ions may also be more readily reducible and, therefore, also perhaps at least partially responsible for lower temperature $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction features in TPR experiments [12,13].

In the following we show that neither the NO/NH_3 oxidation reactions nor NH_3 -SCR kinetics can be reasonably understood by only considering isolated Cu^{2+} ions (species A and B in Schemes 1 and 2) as active sites, contrary to the current understandings of the nature of Cu species in Cu/CHA SCR catalysts [6,8,11,17,32]. NO oxidation kinetics are discussed first.

The lack of NO oxidation activity for samples with Cu/Al ratios < 0.3 , and the fact that little, if any, reaction is observed at temperatures below 300 °C (i.e., when Cu ions can be mobilized by water) (Fig. 4), suggests that both isolated Cu^{2+} species (A) and (B) are rather inert in NO oxidation, at least below ~ 400 °C.

Note, again, that we are able to completely rule out the existence of Cu_xO_y ($x > 2$) clusters in our fully hydrated samples based on the results obtained from both H_2 TPR and EPR studies (the existence of such moieties would give H_2/Cu ratios different from reduction of isolated Cu^{2+} to Cu^+ in TPR measurements, and non-linear relationships in EPR signals versus Cu loading curves since Cu ions in Cu_xO_y clusters are EPR silent) [13]. As such, the Cu species active in NO oxidation are most likely Cu ion dimers that begin to form in our samples at Cu/Al ratios > 0.3 . The CHA cage can readily accommodate a Cu-dimer species; for example, a single O-bridged dicopper $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$, double O-bridged dicopper (e.g., bis(μ -oxo)-dicopper or (μ - η^2 : η^2 -peroxo)-dicopper), or even bis(μ -hydroxo)-dicopper [33, 34]. In a recent study by Giordanino, et al., UV-Vis spectroscopy was used to study Cu/SSZ-13 ($\text{Si}/\text{Al} = 13.1$, $\text{Cu}/\text{Al} = 0.444$) under "dry" O_2 activation and "dry" SCR conditions [35]. In both cases, these authors observe charge transfer (CT) transition features at ~ 32000 and ~ 29000 cm^{-1} which, albeit only appearing as weak shoulders, can reasonably be assigned to double O-bridged dicopper moieties mentioned above. Interestingly, they did not observe a single O-bridged dicopper CT feature at 22700 cm^{-1} for their Cu/SSZ-13 catalyst, but did observe it for their Cu/ZSM-5 and Cu/beta samples. They also found that their Cu/SSZ-13 catalyst turned dark blue upon O_2 activation and only turned pale blue again upon full rehydration. Inspired by this discovery, we also visually examined our samples after high-temperature O_2 activation. Interestingly, $\text{Cu}/\text{Al} \geq 0.4$ samples that displayed good NO oxidation activities showed a dark blue color upon O_2 activation, while the inert ones

remained light blue in color. We suggest, therefore, that the dark blue color is due to double O-bridged dicopper formation while its disappearance in the presence of moisture is caused by hydrolysis; i.e., regeneration of hydrated isolated Cu^{2+} monomers, which are light blue in color.

In a more recent study by Guo, et al. [36], Raman spectroscopy was used to study high-temperature calcined Cu/SSZ-13 samples. At high Cu loading ($\text{Si/Al} = 4.3$, $\text{Cu/Al} \geq 0.259$), a number of bands were found in the $350\text{-}600\text{ cm}^{-1}$ range that were assigned to Cu-O-Cu vibrations. At lower Cu loadings, these bands were absent. In particular, for one of their samples, generated from solution ion exchange (just like all of our samples), a 610 cm^{-1} band was found that can be attributed to bis(μ -oxo)-dicopper. Note also that in an EXAFS study, Deka et al [17] indeed reported Cu-Cu distances of $3.76\text{ \AA}$ on their calcined Cu/SSZ-13 samples ($\text{Si/Al} \sim 12$, Cu loading 3.6 wt%). Although the authors suggested that this is the distance between two isolated Cu^{2+} ions located in the faces of 6-membered rings within one d6r, based on the more recent spectroscopic evidence, it is more likely the Cu-Cu distance of double O-bridged dicopper species, specifically (μ - η^2 : η^2 -peroxo)-dicopper [34]. Very recently, a careful and thorough study by Verma et al [37] on NO oxidation on Cu/SSZ-13 appeared in the open literature. This study confirms that under “dry” reaction conditions, NO oxidation is indeed only catalyzed by Cu dimers while monomers are completely inert at a reaction temperature of $270\text{ }^\circ\text{C}$. Their DFT calculations indicate exceedingly high O_2 activation barriers by “naked” Cu^{2+} ion monomers near 6-membered rings thus explaining why monomers cannot be active sites for NO oxidation. In this study, our kinetic data shown in Fig. 4 demonstrates that the same conclusion can be extended to a “wet” NO oxidation condition. Moreover, monomers may start to have limited activities above $400\text{ }^\circ\text{C}$. In summary, based on our reaction kinetics and kinetics/spectroscopic studies by others, it is reasonable to suggest that under both “wet” and “dry” NO oxidation

conditions, the majority of activity is provided by O-bridged dicopper centers, although we are not in a position to determine which type. Our NO oxidation results indicate that such centers only form above certain Cu loadings (i.e., more than one Cu^{2+} ions within each hexagonal CHA unit cell).

Low-temperature NH_3 oxidation and SCR kinetics cannot be understood by the general picture on the nature of Cu ion species we derived for the NO oxidation kinetics; notably for NO oxidation, that they stay as isolated ions at low loadings and convert to O-bridged dimers in oxygen at high loadings. Next, kinetic data displayed in Fig. 5 for NH_3 oxidation are analyzed in more detail.

NH_3 oxidation essentially does not commence at 200 °C for all samples. At 250 and 300 °C, it is apparent that NH_3 conversions increase significantly (greater than linearly) with increasing Cu loading. Interestingly, as shown in Fig. 9(a), a clear linear relationship is found when normalized NH_3 oxidation rates are plotted against *the square of Cu loading* at these two temperatures. We note that this is strong evidence suggesting that the *low-temperature* (i.e., $< \sim 300$ °C) active sites for NH_3 oxidation are also Cu dimers and, rather surprisingly, they appear to exist even at fairly low Cu loadings. However, as shown in Fig. 9(b), at reaction temperatures of 350 and 400 °C, a completely different linear relationship is found. In this case, NH_3 oxidation rates increase linearly with Cu loading for samples with $\text{Cu}/\text{Al} \leq 0.11$ (at higher Cu loadings, NH_3 conversions are too far above differential regime) suggesting at such elevated temperatures, Cu ion monomers become the active centers. We explain this dramatic temperature-dependent transition as follows: at relatively low reaction temperatures (i.e., ≤ 300 °C), the high mobility of Cu^{2+} ions under reaction conditions (also demonstrated by the results of EPR measurements in

Fig. 3) allows the formation of *transient* Cu ion dimers which function as the catalytically active centers. Note that this behavior even extends to low Cu loadings. Notable from our discussion above, even if transient Cu dimers form during NO oxidation at very low Cu loadings when water is present, reaction rates at these temperatures are still very low as evidenced by the results shown in Fig. 4. Thus, we propose that the formation of transient dimeric centers during NH₃ oxidation is facilitated by the presence of NH₃ and/or H₂O; that is, interaction between Cu²⁺ ion monomers and the CHA framework is further weakened when these molecules are present. Note that in a Cu-dimer model provided by Kieger et al [38], NH₃ ligands were indeed included. At even higher reaction temperatures (350 °C and above), these transient dimers become unstable due, in part, to loss of ammonia and/or water ligands, and dissociate into monomers that bind strongly with the 6-membered rings. In this case, Cu ion monomers serve as the catalytically active centers as demonstrated from Fig. 9(b).

Next, the even more complicated standard SCR kinetics are discussed. We begin by noting that the current general understanding is that Cu²⁺ ion monomers next to faces of 6-membered rings are the primary (even sole) active sites in Cu/CHA [6,8,11,17,32]. However, without rigorous reaction kinetics studies, evidence for the existence of isolated Cu²⁺ ions in an active Cu/SSZ-13 catalyst, especially from *ex situ* methods, is insufficient to justify such a conclusion. Unfortunately, the current general understanding has largely been reached in this way. An obvious argument against such a proposal is that isolated Cu²⁺ ions have the highest redox barriers when located in faces of 6-membered rings; as such, why would these sites be the preferred ones for a redox reaction? Notably, in view of our recent study on Cu/SSZ-13 dehydration using XANES and FTIR [15], and with the EPR results in the present study (Fig. 3), full dehydration of Cu/SSZ-13 at low loading in vacuum or an inert flow occurs at ~250 °C, at

which point Cu^{2+} ions will migrate to locations near faces of 6-membered rings. Under typical SCR reaction conditions, strong interactions between Cu^{2+} ions and ligands including $-\text{OH}$, H_2O and NH_3 will definitely “delay” this Cu^{2+} ion migration process. Therefore, the final siting of Cu^{2+} ions near faces of 6-membered rings should occur at temperatures somewhat higher than 250 °C. Therefore, as pointed out above, in order to study SCR on Cu^{2+} ions near faces of 6-membered rings with two Al sites, high reaction temperatures and low Cu loadings are the two prerequisites that must be met. Our kinetic data shown in Fig. 9 demonstrate that these monomeric Cu^{2+} ions are indeed active in NH_3 -SCR. However, SCR in this regime is characterized by a quite high apparent activation energy of ~140 kJ/mol, much higher than values found in the lower temperature regime on Cu/CHA catalysts [13, 25].

Using the Arrhenius equation, $k = \frac{r}{[\text{NO}]_0} = Ae^{\frac{-E_a}{RT}}$, and normalized SCR rates shown in Fig. 6, Arrhenius plots are presented in Fig. 10 in the temperature region from 110 to 200 °C. The preexponential factors (in $\ln(A)$) and the apparent activation energies (E_a) are shown in Table 2. It is interesting to note that the three lowest Cu loading samples have the lowest E_a and quite small values of A. Starting from a Cu/Al ratio of 0.032, $\ln(A)$ and E_a values increase significantly suggesting a considerable change in the nature of active sites at this Cu/Al ratio. Still, these kinetics ($\ln(A)$ and E_a values) are significantly different from those obtained at low Cu loading and higher reaction temperatures (Fig. 8). From Fig. 7, note also that TOFs increase sharply with increasing Cu/Al ratios at the lowest Cu loadings. From these results, we propose that, in the low-temperature regime (< 300 °C), even if SCR is catalyzed by isolated Cu^{2+} ions as previously suggested, the active Cu^{2+} ions must not be located in faces of 6-membered rings. Because of the high redox barriers for such species, they are only active above ~350 °C (Fig. 8).

From Fig. 7 (upper panels), the Koros-Nowak criterion does not hold at very low (≤ 0.378 wt%, $\text{Cu/Al} \leq 0.032$) and very high (≥ 3.43 wt%, $\text{Cu/Al} \geq 0.29$) Cu loadings. Since no mass transfer limitations are obvious at intermediate Cu loadings, the lower efficiency for Cu ions at the lowest Cu loadings cannot be due to mass transfer limitations. More detailed SCR rate dependence on Cu loading at the lowest Cu concentrations is presented in Fig. 11. As shown in Fig. 11(a), up to a reaction temperature of 250 °C, SCR rates clearly increase nonlinearly as a function of Cu loading. However, as displayed in Fig. 11(b), very good SCR rate dependence on $[\text{Cu loading}]^2$ is found at such low Cu loadings. As was also the case for low-temperature NH_3 oxidation, this again demonstrates that the catalytically active centers are transient Cu dimers. Yet there is a dramatic difference between the two reactions: for low-temperature NH_3 oxidation, this dependence extends to a Cu loading of 2.59 wt% (Fig. 9(a)); however for standard SCR (Fig. 7, lower panels), TOFs maintain constant or increase slightly in the Cu loading range from 0.516 to 2.59 wt% at reaction temperatures ≤ 185 °C suggesting that all Cu ions in this loading range have similar activities. This likely means that, above the threshold of $\text{Cu/Al} = 0.016$, monomeric Cu ion species start to become SCR active in this temperature regime. This notion is consistent with the dramatic changes in $\ln(A)$ and E_a values above this threshold shown in Table 2. We note again that these cannot be Cu^{2+} ions next to 6-membered rings which are active only at much higher temperatures (Fig. 8). Overall, we propose that low-temperature NH_3 oxidation and NH_3 -SCR over Cu/CHA catalysts at low to medium Cu loadings can be viewed as “quasi” homogeneous catalytic processes where Cu ion monomer and dimer species are in equilibrium in the dynamic reaction environment. NH_3 oxidation, being a more difficult reaction, can only be catalyzed by the transient Cu dimers. The much more facile NH_3 -SCR reaction, on the other hand, is exclusively catalyzed by transient Cu dimers only at the lowest Cu loadings ($\text{Cu/Al} \leq$

0.016). At higher Cu loadings, the results suggest that monomers also become active. Up to a Cu loading of 2.59 wt% (Cu/Al = 0.22), the TOF versus Cu loading plots shown in Fig. 7 for NH₃-SCR are fully consistent with a redox mechanism suggested recently by Kispersky et al [39]. That is, as Cu loading rises, electrostatic interactions between Cu ions and the CHA framework weaken, resulting in more facile Cu²⁺/Cu⁺ redox cycling. The nature of the low-temperature active Cu ion monomer species, however, will be addressed in the next section together with reaction mechanism discussions.

At the highest Cu loadings (≥ 3.43 wt%), the Koros-Nowak criterion once again does not hold. Reaction rates no longer increase with increasing Cu loadings and accordingly, TOFs decrease monotonically with increasing Cu loading (Fig. 7). In our previous study [13], this was suggested to be caused by mass-transfer limitations. Very recently, Bates et al, based on the detection of Cu_xO_y ($x, y \geq 1$) species from ambient XAS measurements on their high Cu loading samples, suggested instead that this is because the Cu_xO_y species are not active in standard SCR [25]. However, a recent review article by Deka, et. al summarized that Cu dimers are the SCR active centers in Cu-exchanged Y, ZSM-5 and beta catalysts [6]. While this issue is far from settled, it is not clear to us why Cu dimers in SSZ-13 would not be SCR active as they apparently are in other zeolites. In any case, we believe that mass-transfer limitations are the major cause of inefficiency of Cu ions at high loadings where the Koros-Nowak criterion (Fig. 7) is not met. Since Cu dimers are not associated with 6-membered rings [37], they instead likely locate near 8-membered rings (i.e., pore openings) of the CHA structure. At Si/Al = 6 and Cu/Al = 0.29, 0.40 and 0.44, each hexagonal unit cell (ideal stoichiometry H_{5.14-2x}Cu_xAl_{5.14}Si_{30.86}O₇₂) contains 1.5, 2.0 and 2.3 Cu ions, respectively. Therefore, even at Cu/Al = 0.29, at least half of the unit cells can readily contain oxygen-bridged dimeric species at low temperatures which both occupy

CHA cage spaces and block pore openings, factors that are expected to cause mass-transfer limitations.

In Fig. 8 we have shown that, at low Cu loadings and in the *high-temperature* ($> 350\text{ }^{\circ}\text{C}$) kinetic regime, standard SCR TOFs become independent of Cu loadings suggesting that Cu^{2+} ion monomers are the active centers. As just discussed, transient Cu ion dimers are apparently the active centers at low loadings for lower ($< 300\text{ }^{\circ}\text{C}$) temperatures (Fig. 11(b)). Clearly, there must be a transition in the nature of catalytically active species from ~ 250 to $\sim 350\text{ }^{\circ}\text{C}$. This is rationalized by the instability of Cu-complexed H_2O and NH_3 species which ‘desorb’ at temperatures higher than $\sim 250\text{ }^{\circ}\text{C}$, causing Cu^{2+} ions to migrate closer to 6-membered rings. Thus, this argument explains the unusual NO conversion decrease for the low Cu loading samples as shown in Fig. 6. Although from ~ 250 to $\sim 350\text{ }^{\circ}\text{C}$, differential NO conversions only maintain at the lowest Cu loadings, the consistency of this behavior suggests that reaction rate decreases within this temperature range for higher Cu loading samples (up to $\text{Cu}/\text{Al} = 0.11$) are due to the same kinetic causes. Thus, this behavior is key to understanding the “seagull shape” light-off kinetics. From Fig. 6, this phenomenon is only seen at relatively low Cu loadings. At high Cu loadings, due to the fact that a portion of catalytically active Cu^{2+} ions do not migrate to 6-membered rings, and to possible mass-transfer limitations, this phenomenon is no longer observed.

A recent study by Ye, et al. [31], with and without propylene in the reactant feed, seems to convincingly show that “seagull shape” performance curves can be caused by hydrocarbon poisoning; i.e., by coke formation within this temperature window that blocks reactive sites. However, this process is clearly different from the seemingly similar kinetic behavior we describe in the present study (Fig. 6) for low Cu loading samples that, as we have shown above,

is due to migration of, and correspondingly altered reactivity for Cu^{2+} ions. Furthermore, we note that the NO_x light-off curve shown in Fig. 1 was measured without the presence of hydrocarbons. Therefore, the “seagull shape” is better understood via Cu^{2+} ion migrations.

4.2 Considerations in standard SCR mechanisms

While we are still not in a position to provide a complete mechanistic SCR reaction network for Cu/CHA catalysts, we next briefly discuss the relevance of our findings regarding such mechanisms. Based on the detection of both Cu^{2+} and Cu^+ species with operando XAS during standard SCR, Kispersky, et al. proposed that standard SCR over Cu/CHA follows a redox mechanism between these two species [39]. Note that a similar mechanism has been proposed before for other Cu/Fe-Zeolite SCR systems [20, 38]. In order for such a mechanism to work, understanding Cu^+ oxidation back to Cu^{2+} is critical, since Cu^{2+} reduction to Cu^+ is considered facile either by charge transfer between NO and Cu^{2+} [14], or by reduction with NH_3 . Note that in the text shown above, we only report NO kinetics for standard SCR reactions. It is also useful to directly compare both NO and NH_3 conversions during SCR in the Fig. 12 plots, where panel (a) displays results for the Cu/Al = 0.11 sample, and panel (b) for the Cu/Al = 0.44.

On the basis of the stoichiometry for the standard NH_3 -SCR reaction, NH_3 and NO react at a 1/1 molar ratio. However, typically above $\sim 400^\circ\text{C}$ and on samples very active in NH_3 oxidation, NH_3 overconsumption has frequently been observed. This is generally known as non-selective NH_3 oxidation, and occurs when NH_3 oxidation (by O_2) reaction rates become comparable to that of SCR. For the Cu/Al = 0.44 sample at temperatures above $\sim 450^\circ\text{C}$, NH_3 conversions clearly surpass NO conversions due to non-selective NH_3 oxidation, as shown in Fig. 12(b). However, the most significant observation from Fig. 12(a) is NO overconsumption under certain reaction conditions (e.g., $\sim 200\text{--}300^\circ\text{C}$ and above $\sim 400^\circ\text{C}$). Similar interesting

phenomena have been observed by Kieger, et al. for Cu/FAU NH₃-SCR catalysts, and were rationalized by a Cu⁺ oxidation (to Cu²⁺) mechanism that involves NO+O₂ [38]. Therefore, NO overconsumption during standard SCR strongly supports a Cu²⁺/Cu⁺ redox mechanism as further discussed next.

Under typical standard SCR reaction conditions, O₂ is in a considerable surplus; as such, it is reasonably regarded as the most likely reactant for the oxidation of Cu⁺ according to the following reaction:

However, since NO₂ is a stronger oxidant than O₂, the following reactions may also be considered:

In reaction (3), NO₂ is reduced to NO. The combination of reactions (2) and (3) gives (1). In both cases, NO_x overconsumption does not occur (that is, NO is consumed in (2) and reformed in (3)). However, if NO is directly involved in Cu⁺ oxidation (in this case, N₂ must form since in most cases we do not detect N₂O), then the following reaction stoichiometry can be written:

Although reaction (4) can account for NO overconsumption during standard NH₃-SCR, our results from this study indicate that both standard SCR and NH₃ oxidation are catalyzed by Cu-dimers at temperatures below ~350 °C. For Cu-dimers, the redox reactions can be written as the following. (According to Giordanino, et al [35], double O-bridged dimers more likely form for Cu/CHA catalysts):

If only reaction (5) occurs during Cu⁺ oxidation, no NO overconsumption is expected. However if reaction (6) also occurs, NO overconsumption becomes explainable. Interestingly, Fig. 12(a) indicates that reaction (6) must be much slower than (5) below ~200 °C, becomes competitive at ~250 °C, and then much slower than (5) again at ~350 °C. This might suggest that the Cu-Cu complexes are optimized (in terms of bond distance and angle) to accommodate NO molecules at ~250 °C. It is important to note that, although we observe NO overconsumption during NH₃-SCR, none of our Cu/SSZ-13 samples catalyze NO decomposition (i.e., without the presence of O₂ and NH₃). This provides additional evidence to suggest that Cu-dimers only form at low temperatures in the presence of O₂, and that their formation is facilitated by the presence of NH₃ and/or H₂O ligands which weaken Cu ion-CHA framework attractions.

Equations (5) and (6) provide a straightforward explanation why Cu-dimers are relevant as low-temperature catalytic centers at very low Cu loadings (Fig. 11(b)); notably, because Cu²⁺/Cu⁺ redox for dimers is much more facile than for monomers. Indeed, recent theoretical work has suggested that O₂ activation by Cu ion monomers is challenging [18, 37]. However, at intermediate Cu loadings and low reaction temperatures, results shown in Fig. 7 indicate that

Cu^{2+} ion monomers (albeit not in faces of 6-membered rings) are also active. Again, this conclusion comes from the Arrhenius plots shown in Fig. 10, and $\ln(A)$ and E_a values shown in Table 2. At $\text{Cu}/\text{Al} \leq 0.016$, transient Cu dimers are the only active centers (Fig. 11(b)). From Table 2, these samples are characterized by the lowest apparent activation energies, and the lowest preexponential factors, as compared with samples with higher Cu loadings. As Cu loading increases, the changes in apparent activation energies and preexponential factors up to $\text{Cu}/\text{Al} = 0.22$ (Table 2) demonstrate that monomeric Cu species with higher redox barriers and much more frequent accessibility to reactants as compared with Cu-dimers, become the catalytically active centers. The key to understanding this complex transition in catalytically active centers is from the generally accepted redox reaction mechanism. Notably, at exceedingly low Cu loadings, interactions between Cu^{2+} monomers and negative framework charges are strong enough such that redox barriers of Cu^{2+} monomers are not readily overcome. However, formation of transient dimers effectively lowers the redox barriers of Cu^{2+} ions. Still, formation of such transient dimers at such low Cu loadings is an inefficient way of generating active centers. Precisely because of this, our Arrhenius plot analysis gives much lower prefactors at the lowest Cu loadings as shown in Table 2. As such, at intermediate Cu loadings, the contribution from the transient dimers becomes insignificant to the overall SCR activities.

In terms of catalytically active Cu^{2+} ion monomers, at low reaction temperatures, it is important to consider the Cu^{2+} ion monomers as being “delocalized”. Especially, these should not be considered as being next to faces of 6-membered rings where the redox barriers are apparently the highest. A $[\text{Cu}^{\text{II}}(\text{OH})]^+$ species next to 8-membered rings has been found to be specifically stable [28]; next we address the possibility that this is a likely low-temperature active Cu^{2+} ion monomer species.

Similar to oxygen-bridged Cu dimers, $[\text{Cu}^{\text{II}}(\text{OH})]^+$ also contains extra-lattice oxygen (ELO), which has been suggested to be critical to oxidize NO [16]. For standard SCR, N-atoms in the +3 oxidation state is required. Possible intermediates with this oxidation state are NO^+ , N_2O_3 and HNO_2 . Formation of N_2O_3 requires some NO to be oxidized first to NO_2 , which, according to our NO oxidation results shown in Fig. 4, and from recently published results by Verma et al. [37], does not occur below $\sim 350^\circ\text{C}$ for Cu/SSZ-13 samples with low to intermediate Cu loadings. To explain the apparent discrepancy that Cu/zeolites are inert in NO oxidation but highly active in NH_3 -SCR, some have argued that NO_2 formation via NO oxidation, being a possible rate-limiting step in standard NH_3 -SCR, is limited by $\text{NO}_{2(\text{ads})}$ desorption. As such, NO oxidation is presumed to be promoted by the consumption of $\text{NO}_{2(\text{ads})}$ via the NH_3 -SCR reactions [3]. A recent careful study by Ellmers et al [21], casts doubt on this argument and, therefore, NO_2 is likely not an intermediate of the reaction mechanism for standard SCR. An HNO_2 intermediate, on the other hand, has been detected and proved reactive with NH_3 to form N_2 even at 120°C by Ruggeri et al. [40] using an elegant chemical trapping method.

Based on the above discussion, we propose the following SCR reaction pathways catalyzed by $[\text{Cu}^{\text{II}}(\text{OH})]^+$ species located next to 8-membered rings:

We note that reactions (8) and (9) have long been suggested to be part of the standard SCR mechanism where the instability of NH_4NO_2 making it a much more plausible intermediate than any nitrate moieties [1-3, 15]. For reaction (10), we note that partially reduced Cu/SSZ-13 quickly oxidizes in air at ambient conditions suggesting that this reaction should be facile under typical low-temperature SCR reaction conditions. Also, it is critical to have H_2O and/or NH_3 present in order for Cu^+ ions to have sufficient mobility. Indeed, the activation of O_2 may require transient dimeric Cu species (e.g., $[\text{Cu}-\square-\text{Cu}]^{2+}$, “ $\square$ ” is an oxygen vacancy).

5 Conclusions

(1) Prior to full dehydration, isolated Cu^{2+} ions are highly mobile. Even at very low Cu loadings, i.e., one Cu^{2+} ion for multiple unit cells, transient Cu-Cu interactions are evidenced by line-broadening and a signal intensity drop in EPR at temperatures below that required for dehydration.

(2) Isolated Cu^{2+} ions do not catalyze NO oxidation, at least below $\sim 400^\circ\text{C}$. NO oxidation only occurs above critical Cu loadings where relatively stable O-bridged Cu-dimers form.

(3) At low to intermediate Cu loadings ($\text{Cu}/\text{Al} \leq 0.22$), transient Cu-dimers are the relevant active sites at reaction temperatures $\leq 300^\circ\text{C}$ for standard SCR reactions. Although their detailed structures have not been determined yet, these dimer species are in equilibrium with two monomeric Cu ion complexes under reaction conditions. Between ~ 250 and 350°C , these moieties become less stable causing a decrease in reaction rates. At temperatures above 350°C and at low Cu loadings, Cu-dimers completely dissociate to regenerate isolated Cu^{2+} monomers; these are the high-temperature catalytic centers for NH_3 oxidation and standard SCR. At intermediate Cu loadings ($0.032 \leq \text{Cu}/\text{Al} \leq 0.22$), Cu^{2+} ion monomers located next to 8-

membered rings also become relevant active sites for standard SCR. At high Cu loadings (i.e., more than one Cu^{2+} ions in each unit cell), stable Cu-dimers form and these do not dissociate at temperatures above 350 °C. These moieties effectively occupy CHA cage space and block pore openings causing decreased efficiency of the catalysts. Also these moieties are highly active in catalyzing NO and NH_3 oxidation reactions. In the latter case, these stable Cu-dimers cause SCR selectivities to decrease above ~450 °C.

(4) Detailed reaction kinetics, especially from NO overconsumption under certain reaction conditions, are consistent with prior suggestions that standard SCR over Cu/CHA follows a $\text{Cu}^{2+}/\text{Cu}^+$ redox mechanism.

(5) Finally, we would like to emphasize the importance of considering the dynamic nature of catalytically active sites under reaction conditions. For this specific reaction system, without considering the strong ligand effects from $-\text{OH}$, H_2O and NH_3 which cause mobility and transient interactions among Cu^{2+} ions, it is not possible to elucidate the real nature of the catalytic centers and detailed reaction pathways.

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Appendix A. Supplementary material

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Table 1: Cu contents and the corresponding Cu/Al ratios and ion exchange levels for all of the Cu/SSZ-13 samples (in dehydrated form) used in this study

Sample	Cu content (wt.%)	Cu/Al Ratio	Ion exchange level (%) ^{a)}
Cu/SSZ-13 (Si/Al = 6)	0.065	0.006	1.1
	0.095	0.008	1.6
	0.188	0.016	3.2
	0.378	0.032	6.4
	0.516	0.044	8.7
	1.31	0.11	22
	2.59	0.22	44
	3.43	0.29	58
	4.67	0.40	79
	5.15	0.44	87

a): Ion exchange level = $\left(\frac{\text{mole content of Cu}}{\text{mole content of Al}} \right) \times 2 \times 100\%$

Table 2: Preexponential factors (ln(A)) and apparent activation energies (E_a) obtained from the Arrhenius plots show in Fig. 10 on samples with different Cu/Al ratios.

Cu/Al Ratio	0.006	0.008	0.016	0.032	0.044	0.11	0.22	0.29	0.40	0.44
ln(A)	0.16	0.70	0.82	11.2	11.7	11.9	15.9	16.1	17.7	16.9
E _a (kJ/mol)	43	41	40	65	68	65	79	80	84	84

Figure Captions

Figure 1

Steady-state NO_x conversion on a degreened commercial Cu/Chabazite catalyst, replotted using data taken from Ref. [22].

Figure 2

(a) Electron Paramagnetic Resonance (EPR) spectra of the low Cu-loading Cu/SSZ-13 samples. Spectra were collected at 120 K. The corresponding Cu loadings are also tabulated in this figure.

(b) The same spectra shown in Fig. 2(a) normalized to the same high-field signal intensity.

Figure 3

Electron Paramagnetic Resonance (EPR) spectra of a Cu/SSZ-13 sample ($\text{Cu}/\text{Al} = 0.032$) during dehydration.

Figure 4

NO oxidation rates as a function of temperature for the various Cu/SSZ-13 samples. Reactant feed contains 350 ppm NO , 14% O_2 , 2.5% H_2O balanced with N_2 at a GHSV of $100,000 \text{ h}^{-1}$. Different symbols represent samples with different Cu loadings as indicated in the figure.

Figure 5

NH_3 oxidation rates as a function of temperature for the various Cu/SSZ-13 samples. Reactant feed contains 350 ppm NH_3 , 14% O_2 , 2.5% H_2O balanced with N_2 at a GHSV of $400,000 \text{ h}^{-1}$. Different symbols represent samples with different Cu loadings. The dashed horizontal line represents an NH_3 conversion of 20%.

Figure 6

Standard SCR rates as a function of temperature for Cu/SSZ-13 samples with various Cu-loadings. Reactant feed contains 350 ppm NO , 350 ppm NH_3 , 14% O_2 , 2.5% H_2O balanced with N_2 at a GHSV of $400,000 \text{ h}^{-1}$. Different symbols represent samples with different Cu loadings. The dashed horizontal line represents NO and NH_3 conversions of 20%.

Figure 7

SCR rates (upper panels) and SCR turnover frequencies (lower panels) as a function of Cu loading in the low temperature kinetic regime. Reaction temperatures are (a) 140 °C, (b) 155 °C, (c) 170 °C, and (d) 180 °C.

Figure 8

(a) SCR rate as a function of temperature on low Cu-loading Cu/SSZ-13 samples. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 1,200,000 h⁻¹. Different symbols represent samples with different Cu loadings. The dashed horizontal line represents NO and NH₃ conversions of 20%.

(b) SCR rates within the differential regime shown in (a) plotted as a function of the Cu loading.

(c) Turnover frequencies (TOFs, mol NO mol Cu⁻¹ s⁻¹) calculated using SCR rates shown in (a) for the three lowest Cu loading samples.

Figure 9

(a) NH₃ oxidation rates at 250 and 300 °C shown in Fig. 5 plotted as a function of the square of the Cu loading.

(b) NH₃ oxidation rates at 350 and 400 °C shown in Fig. 5 plotted as a function of the Cu loading.

Figure 10

Arrhenius plots for standard SCR in the low-temperature regime (< 200 °C) on samples with different Cu loadings. Rate constants (k) were calculated using the first-order kinetic equation shown in the main text. Note that ln(A) and E_a values obtained from these plots were shown in Table 2.

Figure 11

(a) Standard SCR rates shown in Fig. 6 plotted as a function of the Cu loading on samples with the lowest Cu loadings. Note the clear non-linear relationships at reaction temperatures from 170 to 250 °C.

(b) Standard SCR rates shown in Fig. 6 plotted as a function of the square of the Cu loading on samples with the lowest Cu loadings. Note the linear relationships extend up to a reaction temperature of 250 °C.

Figure 12

Comparison between NO and NH₃ conversions during standard SCR on two Cu/SSZ-13 samples: (a) Cu/Al = 0.11; (b) Cu/Al = 0.44. Reactant feeds contained 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 400,000 h⁻¹.

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 1

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 2

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 3

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 4

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 5

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 6

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 7

(a)

(b)

(c)

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 8

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 9

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 10

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 11

(a)

(b)

Gao, Walter, Kollar, Wang, Szanyi and Peden, Figure 12

TOC