Graphic Abstract

Low-temperature

High-temperature

Effects of Si/Al Ratio on Cu/SSZ-13 NH₃-SCR Catalysts: Implications for the active Cu species and the Roles of Brønsted Acidity

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Abstract

Cu/SSZ-13 catalysts with three Si/Al ratios of 6, 12 and 35 were synthesized with Cu incorporation via solution ion exchange. The implications of varying Si/Al ratios on the nature of the multiple Cu species that can be present in the SSZ-13 zeolite are a major focus of this work, as highlighted by the results of a variety of catalyst characterization and reaction kinetics measurements. Specifically, catalysts were characterized with surface area/pore volume measurements, temperature programmed reduction by H₂ (H₂-TPR), NH₃ temperature programmed desorption (NH₃-TPD), and DRIFTS and solid-state nuclear magnetic resonance (NMR) spectroscopies. Catalytic properties were examined using NO oxidation, ammonia oxidation, and standard ammonia selective catalytic reduction (NH₃-SCR) reactions on selected catalysts under differential conditions. Besides indicating the possibility of multiple active Cu species for these reactions, the measurements are also used to untangle some of the complexities caused by the interplay between redox of Cu ion centers and Brønsted acidity. All three reactions appear to follow a redox reaction mechanism, yet the roles of Brønsted acidity are quite different. For NO oxidation, increasing Si/Al ratio lowers Cu redox barriers, thus enhancing reaction rates. Brønsted acidity appears to play essentially no role for this reaction. For standard NH₃-SCR, residual Brønsted acidity plays a significant beneficial role at both low- and high-temperature regimes. For NH₃ oxidation, no clear trend is observed suggesting both Cu ion center redox and Brønsted acidity play important and perhaps competing roles.

Keywords: selective catalytic reduction, Cu/SSZ-13, Si/Al Ratio, NMR, temperature-programmed desorption, reaction kinetics.

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1. Introduction

The mechanism for ammonia selective catalytic reduction (NH₃-SCR) over Cu ion exchanged zeolite catalysts is still widely debated. Some 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) [1-3]. (2) Which NO_x and NH_x species are most relevant in the formation of key reaction intermediates? Specifically, whether NO oxidation to NO₂ is an indispensable step in standard SCR [2, 4-6], and which NH_x species, NH₄⁺, molecular NH₃, or even NH_{2(a)}, is the most relevant reductant? (3) Which reaction mechanism best describes NH₃-SCR? In particular, Langmuir-Hinshelwood, Eley-Rideal, and Mars van Krevelen (redox) mechanisms have been previously proposed for NH₃-SCR [7]. Note specifically that most prior mechanistic understanding for NH₃-SCR has been derived from the exhaustively studied VO_x/TiO₂ system. However, the applicability of such knowledge to the zeolite system is questionable since the latter has different catalytically active centers, much higher NH₃ storage capabilities and unique structural characteristics (confinement at a nanometer scale that also gives rise to electrostatic field effects). Most recently, the involvement of redox of metal ions as part of the reaction mechanism, seems to gain common agreement for zeolite-based catalysts [8-10]. (4) Whether Cu/CHA are dual functional in SCR; that is, whether both Cu ion sites and Brønsted acid sites collectively provide the catalytic functionality.

There have been numerous recent studies on the nature of Cu catalytic centers in Cu/SSZ-13 [9-20]. Cu has been suggested to stay predominately as isolated Cu²⁺ ions in SSZ-13; and under dehydrated conditions they prefer windows of 6MR as noted above. However, depending on the Al content/distribution and Cu loading, even when only isolated Cu²⁺ ions are considered, there is still a high degree of complexity regarding their locations [10, 13-15]. For example, at

relatively low Si/Al ratios and low Cu loadings, one expects that (again, in dehydrated form) the majority of isolated Cu^{2+} ions to reside near the windows of 6MR and bind with 2 Al T-sites [11, 16]. In contrast, at very high Si/Al ratios where the possibility for finding 2 Al sites in one 6MR is highly unlikely, it is possible that isolated Cu^{2+} ions will interact with 2 Al sites that are farther apart (e.g., 2 Al sites in one 8MR). Alternatively, Cu ions at high Si/Al ratios may charge-balance only one Al site. In this latter case, $[\text{Cu}^{\text{II}}(\text{OH})]^+$ or Cu^+ species are required in order to appropriately balance the negative framework charge [21]. Recently, Andersen et al. [22] studied the location of Cu^{2+} in CHA zeolite by X-ray diffraction using the Rietveld/maximum entropy method. These authors confirmed the presence of $[\text{Cu}^{\text{II}}(\text{OH})]^+$ located in windows of 8MRs for high Cu-loaded Cu/SSZ-13, a notion fully consistent with theoretical studies [23].

Very recently, we conducted a detailed kinetic study of NH_3 -SCR and two relevant reactions – i.e., NO and NH_3 oxidation – on a series of Cu/SSZ-13 catalysts with Si/Al = 6 and various Cu/Al ratios [10]. In terms of the nature of catalytically active Cu species, our results suggested the following key findings: (1) below a reaction temperature of $\sim 300^\circ\text{C}$, strong solvation effects from H_2O and NH_3 render high mobility for isolated Cu^{2+} ions such that transient Cu-ion dimers form (in equilibrium with monomers) at low to intermediate Cu loadings. These transient dimeric species are catalytically relevant for standard NH_3 -SCR and NH_3 oxidation reactions. (2) For standard NH_3 -SCR, Cu-ion monomers are also catalytically active and even become the dominant catalytic centers at intermediate Cu loadings below $\sim 300^\circ\text{C}$. However, low-temperature active monomers are not located at windows of 6-membered rings (6MR). (3) Cu-ion monomers migrate to windows of 6MR at elevated reaction temperatures ($> 350^\circ\text{C}$) and become the high-temperature catalytically relevant species. Because of the high redox barriers for Cu ion monomers in these locations, NH_3 -SCR is characterized by high

apparent reaction activation energies (~140 kJ/mol), much higher than typical **apparent** activation energies obtained on Cu/SSZ-13 zeolites at lower temperatures [9, 15]. (4) At high Cu loadings (more than one Cu^{2+} ion per unit cell), permanent Cu-ion dimers form under SCR reaction conditions. While these moieties are active in NO oxidation to NO_2 and are believed to be (even highly) active for NH_3 -SCR, they do not appear to improve catalyst performance. This can be rationalized by internal mass transfer limitations induced by these species since they both block pore openings and occupy space within CHA cages.

Overall, the interplay between Cu ion loading, Cu ion mobility and reaction temperature makes the entire NH_3 -SCR reaction network quite complicated. Indeed, SCR catalysis is further influenced by CHA zeolite Si/Al ratios, and the effects are at least two-fold: Si/Al ratios affect Cu ion locations as briefly discussed above, as well as significantly altering Brønsted acidity and, therefore, NH_3 storage of the catalysts. With regard to the roles of Brønsted acidity in SCR, the literature has been rather controversial. For V_2O_5 -based SCR catalysts, reactive NH_3 in the form of NH_4^+ has been frequently proposed [7, 24-27]. In explaining the beneficial effects of low Si/Al ratio to SCR on zeolite-based SCR catalysts, Yang and coworkers adapted the same argument and proposed that this is because more NH_4^+ species are formed at lower Si/Al ratios (i.e., more Brønsted acid sites) [28, 29]. However, titration experiments in a few recent studies on Cu/CHA catalysts demonstrate that NH_4^+ species are far less reactive toward NO_x than molecular NH_3 adsorbed on Cu sites [30-32]. Interestingly, in V_2O_5 -based catalysts, NH_4^+ binds to the catalysts more weakly than **NH_3 adsorbed on** Lewis acid sites [7], while it is the opposite for zeolite-based catalysts. Therefore, if one makes the reasonable argument that more weakly bound NH_x species are more reactive, consistency still maintains for the two classes of catalysts. In any case, for zeolite-based SCR catalysts, Brønsted acidity may be expected to influence the

reaction by affecting Cu ion location and NH₃ storage (the latter plays a more significant role under transient rather than steady-state reaction conditions), rather than the formation of reactive NH₄⁺. Indeed, in recent studies by Bates et al. [9, 33] on a series of Cu/SSZ-13 SCR catalysts with Si/Al = 4.5 and a narrow range of Cu/Al ratios, the authors found an apparent zero-order dependence of SCR rates on the number of residual Brønsted acid sites measured from NH₃ titration. In our recent study, TOFs were also found to be largely insensitive to Cu/Al ratios under certain reaction conditions [10]. Note, however, that this zero-order dependence on Brønsted acidity may not be general: using samples with the same Si/Al ratio and a narrow range of low Cu/Al ratios (< 0.2), the numbers of residual Brønsted acid sites in different samples are not expected to vary dramatically to allow reliable correlations between SCR rate and Brønsted acid density.

Importantly, correlation between SCR rates and residual Brønsted acid density requires the latter to be quantified *in situ* (i.e., under SCR reaction conditions). This is experimentally challenging. Recently, Gounder and coworkers developed protocols for *ex situ* quantification of Brønsted acid sites using NH₃-TPD [33, 34]. These authors showed that, for Cu/SSZ-13 samples with high Al content and low Cu/Al ratios, Brønsted acid sites are exchanged by Cu²⁺ ions stoichiometrically (i.e., 2H⁺ per Cu²⁺). However, this trend does not extend to high Cu loadings and is suggested to be due to the formation of Cu_xO_y clusters that do not play a charge-balancing role [34]. Recent studies by others also revealed the presence of substantial residual Brønsted acid sites in Cu/SSZ-13 at high Cu loadings. For example, one study by Giordanino et al. [35] determined that Brønsted sites are still present even if the Cu/Al ratio is not far from the stoichiometric exchange level. They suggested that some of the Brønsted sites are exchanged by monovalent copper complexes [CuOH]⁺. In another study, Lezcano-Gonzalez et al. [31] showed

that the intensity of ν_{OH} vibrations (bands at 3605 and 3585 cm^{-1} assigned to Brønsted acid sites) in their Cu/SSZ-13 sample at a 100% ion exchange level (i.e., Cu/Al = 0.5), was still comparable to their parent H/SSZ-13.

Clearly, from the recent publications described above, there is still much to learn about the nature of Cu ion species and the roles of Brønsted acidity in Cu/SSZ-13 SCR catalysts. For example, a catalytic property comparison between Cu^{2+} and $[\text{Cu}(\text{OH})]^+$ active sites has not yet been established; and SCR performance between catalysts with vastly different Brønsted acid site densities has not yet been studied. In the present study, we aim to obtain a more general picture on the roles of Cu ion location and Brønsted acidity in NH_3 -SCR by using a relatively large number of samples with various Si/Al and Cu/Al ratios.

2. Experimental

2.1 Catalyst Synthesis

Based on the above considerations, three SSZ-13 substrates with different Si/Al ratios were synthesized and used in the present study. The synthesis for SSZ-13 with Si/Al = 6 via a static hydrothermal method has been described in detail elsewhere [11, 12] and will not be repeated here. For the two higher Si/Al ratio samples, synthesis was conducted hydrothermally under stirring using a method modified from a protocol developed recently by Deka, et al. [16]. Composition of the gel is the following: 10SDA : 10NaOH : $x\text{Al}_2\text{O}_3$: 100SiO_2 : $2200\text{H}_2\text{O}$, where x varies to allow preparation of samples with different Si/Al ratios. The gel is prepared by first dissolving NaOH (99.95%, Aldrich) in water and adding the SDA (TMAda-OH, Sachem ZeoGen 2825). Following which, $\text{Al}(\text{OH})_3$ (contains ~54% Al_2O_3 , Aldrich) and fumed silica (0.007 μm average particle size, Aldrich) were added sequentially under vigorous stirring until the gel was homogenized. The gel was then sealed into a 125 ml Teflon-lined stainless steel

autoclave with a stir bar in. Thereafter, the autoclave was placed in a salt bath on top of a hot plate stirrer to carry out hydrothermal synthesis at 160 °C for 96 h under stirring. Note that continuous stirring during hydrothermal synthesis was very critical for the formation of uniform and highly crystallized SSZ-13 in this method. After synthesis, Na/SSZ-13 was separated from the mother liquid via centrifugation and washed with deionized water 3 times. Finally, the zeolite powders were dried at 120 °C under flowing N₂, and calcined in air for 8 h to remove the SDA (calcination temperatures detailed below). Si and Al contents of the product powders were measured with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at Galbraith Laboratories (Knoxville, TN, USA). Prior to these composition measurements, the samples were dehydrated at 150 °C for 2 h in vacuum to remove adsorbed moisture. The Si and Al **weight** contents, as well as the Si/Al **molar** ratios thus derived, are listed in Table 1. For the Si/Al = 6 and 12 samples, a calcination temperature of 550 °C is sufficient to completely burn off the SDA. However, for the Si/Al = 35 sample, a calcination temperature of 650 °C is required. One likely explanation is that sodium promotes SDA combustion, and this sample contains much less Na than the lower Si/Al samples. XRD patterns and SEM images of the calcined samples are shown in Supplementary Information (SI-1 and SI-2, respectively). Solid-state nuclear magnetic resonance (NMR) analysis of the calcined samples was conducted on a Varian VNMRS system. Experimental details can be found elsewhere [36]. Cu/SSZ-13 samples were prepared using a standard two-step solution ion exchange protocol reported previously, first with NH₄NO₃ followed by CuSO₄ solutions at 80 °C [15].

2.2 Catalyst Characterization

Cu contents of the Cu/SSZ-13 samples were also determined with ICP-AES. Table 2 presents Cu weight percentages, and the corresponding Cu/Al **molar** 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 of the samples studied here, BET surface areas are 500-550 m²/g and micropore volumes are ~0.25 cm³/g. Temperature-programmed reduction (TPR) was performed on a Micromeritics AutoChem II analyzer. TPR was carried out on both hydrated samples (samples stored in air and saturated with moisture) and fully dehydrated samples (samples calcined at 550 °C in 5% O₂/He flow for 30 min and cooled to ambient temperature in the same flow). Typically ~50 mg of sample was used for each measurement. TPR was carried out in 5% H₂/Ar at a flow rate of 30 mL/min. Temperature was ramped linearly from ambient to 650 °C at 10 °C/min and H₂ consumption was monitored with a TCD detector. A water condenser was applied in front of the TCD detector to trap H₂O within the outlet stream. 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 2 θ ranging from 5° to 50° using a step size of 0.02°. Scanning Electron Microscopy (SEM) was conducted on a FEI Helios 600 FIB-SEM instrument. Samples were mounted on a carbon tape and 5nm of carbon was deposited onto the samples for conductivity. Imaging was done at 5 keV.

NH₃ temperature programmed desorption (NH₃-TPD) was used to quantify Brønsted acid sites in the H/SSZ-13 samples, as well as to describe NH₃ adsorption on Lewis and Brønsted acid sites in the Cu/SSZ-13 catalysts. NH₃-TPD was carried out using our SCR reaction system, with NH₃ detection via gas-phase FTIR. 60mg catalyst (60-80 mesh) were used for each measurement and the following experimental steps were followed: (1) Heat the sample to 550 °C in O₂/N₂

(300 sccm, 14% O₂) and keep at 550 °C for 30 min; (2) Stop O₂ flow, maintain N₂ flow, cool sample to NH₃ adsorption temperatures (defined below); (3) Adsorb NH₃ (~500 ppm in N₂) until outlet NH₃ concentration stays constant for 1 h; (4) Turn off the NH₃ flow and purge with N₂ for 1 h at the adsorption temperature; (5) Ramp from the adsorption temperature to 600 °C at 10 °C/min, and maintain at 600 °C until NH₃ desorption is complete. For the quantification of Brønsted acid sites in the H/SSZ-13 samples, the NH₃ adsorption and purging temperature was set at 200 °C to avoid weakly-bound NH₃. For the Lewis/Brønsted site titrations in Cu/SSZ-13 catalysts, the NH₃ adsorption and purging temperature was set at 100 °C. Stretching vibrations of Brønsted acid sites (ν_{OH}) were probed with DRIFT spectroscopy as described previously [30]. After the sample was loaded into the ceramic sample holder cup of a high temperature/high pressure cell, it was dehydrated at 550 °C for 1 h in flowing helium (10 ml/min). After that, the sample was cooled to 227 °C under flowing helium prior to spectrum acquisition. Spectra were ratioed to a background spectrum collected of KBr at the same temperature.

2.3 SCR and NO/NH₃ oxidation reaction tests

NH₃-SCR and NO/NH₃ oxidation kinetics measurements were carried out in a plug-flow reaction system. Experimental details and mathematic equations used for data analysis are given elsewhere [10, 15]. Specifically, all kinetic data for detailed analyses were judged kinetically benign using the Koros-Nowak criterion [9, 10], and the NH₃-SCR data were further corrected assuming first-order kinetics.

3 Results

3.1 Solid-state nuclear magnetic resonance (NMR) results

Fig. 1(a) presents ^{27}Al NMR spectra for the calcined H/SSZ-13 samples. For the sample with $\text{Si}/\text{Al} = 6$, the feature at ~ 60 ppm is assigned to framework, tetrahedral Al (Al_f) and the much weaker feature at ~ 0 ppm is attributed to extra-framework, octahedral Al. A simple peak area analysis gives $\text{Al}_f/\text{Al}_{\text{total}} = 0.88$. For the $\text{Si}/\text{Al} = 12$ sample, framework Al becomes more dominant with $\text{Al}_f/\text{Al}_{\text{total}} = 0.98$. For the $\text{Si}/\text{Al} = 35$ sample, essentially all Al stays as Al_f . Fig. 1(b) presents the corresponding ^{29}Si NMR results. For the $\text{Si}/\text{Al} = 6$ sample, features at -110, -104 and -99 ppm are attributed to $\text{Si}(4\text{Si}, 0\text{Al})$, $\text{Si}(3\text{Si}, 1\text{Al})$ and $\text{Si}(2\text{Si}, 2\text{Al})$, respectively [37, 38]. For the $\text{Si}/\text{Al} = 12$ sample, no -Al-O-Si-O-Al- linkages exist and tetrahedral Si in $\text{Si}(4\text{Si}, 0\text{Al})$ and $\text{Si}(3\text{Si}, 1\text{Al})$ are observed at -111 and -105 ppm, where the former is more dominant as expected from the Si/Al ratio of 12. For the $\text{Si}/\text{Al} = 35$ sample, feature at -112 ppm assigned to $\text{Si}(4\text{Si}, 0\text{Al})$ becomes even more dominant, as compared to the $\text{Si}(3\text{Si}, 1\text{Al})$ feature at -105 ppm. Note that this sample also has a new feature at -101 ppm. This belongs to a Q3 SiO_2 impurity phase [37]. At such a high Si/Al ratio, the appearance of a SiO_2 phase is not unexpected. The XRD pattern for this sample shown in Fig. SI-1, however, indicates that the SiO_2 impurity does not possess a long range order.

3.2 H_2 temperature programmed reduction (H_2 -TPR) results

Cu^{2+} ions located at different cationic sites have different binding energies with the framework; H_2 -TPR provides a simple and direct measure of such differences. In our previous study, it was found that reduction of isolated Cu^{2+} to Cu^+ in Cu/CHA catalysts occurs below ~ 600 °C while Cu^+ reduction to Cu^0 occurs at much higher temperatures [15]. In the present study, H_2 -TPR experiments were conducted only up to 650 °C to gain insight into the reduction behavior of Cu^{2+} as a function of Si/Al and Cu/Al ratios, and the results are plotted in Fig. 2. Experiments were conducted on both hydrated and dehydrated samples. Note that for the fully

hydrated samples (samples stored at ambient conditions long enough to saturate with moisture), no other treatment was applied prior to TPR, except purging with helium at ambient temperature. For fully dehydrated samples, on the other hand, the samples were heated to 550 °C in dry 5% O₂/He, maintained at 550 °C for 30 min, and then cooled to ambient temperature in the same gas mixture prior to TPR.

Fig. 2(a) presents results for the series of Cu/SSZ-13 samples with Si/Al = 6. As shown in the lower panel for the hydrated samples, no reduction is found below ~300 °C for samples with very low Cu loadings ($\text{Cu/Al} \leq 0.044$), and a single, rather symmetric peak is found centered at ~380 °C. As Cu loading rises, a lower-temperature reduction peak develops at ~230 °C, and its intensity increases with increasing Cu loading. In the meantime, the high-temperature state shifts gradually to lower temperatures. This is especially the case for the two samples with the highest Cu loadings. Note also that, for samples displaying two reduction states, the low-temperature reduction state starts commonly at ~160 °C irrespective of Cu loadings. From the upper panel (for samples dehydrated in O₂ prior to TPR), no noticeable difference is found as compared to their hydrated counterparts for samples with the lowest Cu loadings ($\text{Cu/Al} \leq 0.044$). However for samples at intermediate Cu loadings ($0.11 \leq \text{Cu/Al} \leq 0.29$), the low-temperature state shifts to higher temperatures and partially converts to the high-temperature one. For the two highest Cu loading samples, one prominent finding is that the total H₂ consumption (as determined from the H₂ consumption peak areas) becomes substantially less for the dehydrated samples. This indicates that some Cu²⁺ species have already converted to Cu⁺ during dehydration via a so-called “autoreduction” even in flowing O₂ atmospheres. This is important for our understanding of the relative stabilities of different Cu ion species as Si/Al ratios and Cu loading vary; and more details will be given below. Note also that the onset of reduction for the

dehydrated samples with the highest Cu loadings is as low as ~ 100 °C, considerably lower than that for the hydrated samples (~ 160 °C).

Figs. 2(b) and 2(c) presents TPR results for samples with Si/Al = 12 and 35, respectively. The hydrated Si/Al = 12 samples display two reduction states centered at ~ 240 and ~ 380 °C, resembling the Si/Al = 6 samples. However, the Si/Al = 35 samples only display one dominant reduction state at ~ 240 °C. TPR for dehydrated samples is more complicated. For the dehydrated Si/Al = 12 samples, as displayed in the upper panel of Fig. 2(b), the ~ 380 °C reduction state is similar to the corresponding hydrated samples, while for the Cu/Al = 0.13 and 0.23 samples, H_2 consumption at lower temperatures is apparently less than the corresponding hydrated samples. This again demonstrates that, during the dehydration process, a portion of Cu^{2+} converts to Cu^+ even in the oxygen flow. Meanwhile, reduction peak temperatures also vary. For example, on the dehydrated sample with Cu/Al = 0.23, the predominant low-temperature reduction state is found at ~ 280 °C while a lower temperature state (seen as a shoulder) is also apparent at ~ 180 °C. For the dehydrated Si/Al = 35 samples (Fig. 2(c), upper panel), the sample with the lowest Cu loading (Cu/Al = 0.10) yields one weak reduction peak at ~ 180 °C. For the two samples with higher Cu loadings, the 180 °C reduction state also dominates. However, weaker but clear reduction states are also evident at ~ 240 and ~ 300 °C. Furthermore, it is important to note that for the latter samples, reduction starts as low as ~ 100 °C.

Fig. 3 presents H_2 consumption as a function of Cu loading for all *hydrated* samples (normalized to the same sample weight used in the TPR experiments). An excellent linear relationship is obtained in this case. Using CuO TPR as a calibration, H_2 consumption corresponds to $H_2/Cu = 0.5$ for all of the hydrated samples demonstrating that reduction below ~ 600 °C is due to the following reactions:

Importantly, the good linear relationship rules out the existence of appreciable amounts of CuO clusters in any of our samples even at the highest Cu loadings. This follows since CuO is reduced directly to Cu⁰ at ~300 °C, consuming two times the quantity of H₂ compared to reactions (1) and (2). This is consistent with our previous Electron Paramagnetic Resonance (EPR) spectroscopy analysis of these samples, where it was found that the majority of Cu species within our hydrated samples are EPR active (note that CuO clusters are EPR silent) [15]. For dehydrated samples, H₂ consumption is also determined in order to quantify the amounts of Cu⁺ formed during dehydration via autoreduction. As shown in Table 3, for the Si/Al = 6 samples, no apparent autoreduction is found for samples with Cu/Al ≤ 0.29. For the two higher Cu loading samples, more than 20% of Cu²⁺ is reduced to Cu⁺ during dehydration. For the Si/Al = 12 samples, as with the Si/Al = 6 samples, the extent of autoreduction increases as Cu loading rises. Note that autoreduction becomes more facile for the Si/Al = 12 samples. For example, even the Cu/Al = 0.13 sample has 18% of Cu²⁺ autoreduced to Cu⁺ during dehydration. The Si/Al = 35 samples behave considerably different. First, autoreduction appears to be even more facile for these samples. Second, the percentage of autoreduction decreases as Cu loading rises perhaps suggesting a limitation for total Cu⁺ amounts. In any case, results shown in Table 3 appear to be consistent with an expected general picture that as the binding energy between Cu²⁺ and the CHA framework decreases either by increasing Cu loading or by increasing the Si/Al ratio, Cu⁺ formation via autoreduction increases. The unusual behavior for the Si/Al = 35 samples will be discussed in more detail below.

3.3 NH₃ temperature programmed desorption (NH₃-TPD) and DRIFTS results

NH₃-TPD was used to titrate Brønsted acid sites in H/SSZ-13, and both Lewis and Brønsted acid sites in Cu/SSZ-13 samples, in order to gain insights into the relationships between Al_f and H⁺, as well as chemisorbed NH₃/NH₄⁺ and SCR kinetics. Note that NH₃-TPD has been successfully used by Gounder and coworkers recently to quantify Brønsted acid sites in their MFI- and CHA-based SCR catalysts [9, 33, 34]. Fig. 4 depicts NH₃-TPD profiles for the three H/SSZ-13 samples. To eliminate weakly-bound NH₃ species in this data, adsorption and purging were carried out at 200 °C. Expectedly, the amounts of NH₃ storage increase with decreasing Si/Al ratios. It is also found that the desorption peak maximum for the Si/Al = 35 sample (~450 °C) is slightly lower than the lower Si/Al ratio samples (at ~480 °C). Based on NH₃ desorption yields and ²⁷Al NMR results shown in Fig. 1(a), Table 4 presents the quantified titration results. For the Si/Al = 35 sample, an NH₃/Al_f ratio of unity is found. This demonstrates that our experimental procedure indeed allows all Brønsted acid sites to be probed by NH₃. However, for the Si/Al = 6 and 12 samples, NH₃/Al_f ratios are only found to be 0.70 and 0.87, respectively. This could mean that not all Al_f sites are associated with H⁺ as also evident in the results of Bates et al. for their H/SSZ-13 samples [33].

NH₃-TPD was also performed on selected Cu/SSZ-13 samples with different Si/Al but similar Cu/Al ratios. In this case, NH₃ adsorption was conducted at 100 °C to allow saturation of both Brønsted acid and Lewis acid (including Cu ion and extra-framework Al) sites. Note that the relatively short purging time only drives off the most weakly bound NH₃; therefore, the desorption features contain adsorption from Lewis and Brønsted acid sites, even possibly NH₃ complexed with NH₄⁺ [35]. As shown in Fig. 5, each sample displays two NH₃ desorption states: desorption above ~400 °C assigned to desorption from Brønsted acid sites and desorption at

lower temperature due to molecularly adsorbed NH_3 . The considerable overlap of the two states precludes reliable quantification. However, it is important to note that higher framework charge density (i.e., lower Si/Al ratios) plays a significant role in attracting weakly bound NH_3 . For example, low-temperature NH_3 desorption yields from the Si/Al = 35 sample is only ~10% of that from the Si/Al = 6 sample despite the fact that Cu loading of the former sample is ~30% of the latter. It will be shown below that this difference profoundly affects SCR rates.

DRIFT spectroscopy was also used to probe Brønsted acidity of the samples by analyzing OH vibrations (ν_{OH}). Fig. 6(a) presents results for selected Si/Al = 6 samples (after dehydration at 550 °C, with spectra acquired at 227 °C). The H/SSZ-13 samples display 4 ν_{OH} bands. The band at 3731 cm^{-1} is assigned to silanol (Si-OH) while the bands at 3604/3564 cm^{-1} are assigned to Brønsted acid sites (Al-O(H)-Si) [20, 31, 35]. This band also possesses a weak shoulder feature at 3644 cm^{-1} whose origin is not clear but may be assigned to Al-OH. For the Cu/SSZ-13 samples, the intensities for the Brønsted acid bands decrease with increasing Cu loading and a new band at ~3658 cm^{-1} appears. Note that this latter feature is distinct from the 3644 cm^{-1} band and, therefore, can be reasonably assigned to $[\text{CuOH}]^+$ species as also suggested recently [20, 31, 35]. Fig. 6(b) plots the intensity of the 3604 cm^{-1} Brønsted acid band as a function of Cu/Al ratio. The intensity drop of this feature decreases with increasing Cu loading, consistent with the notion that Cu-ions balance 2 Brønsted acid sites at low loadings and only one site at high loadings [22, 31, 35].

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

As described in the introduction, NH_3 -SCR and NH_3 oxidation kinetics are influenced by Si/Al ratios, Cu/Al ratios and reaction conditions in a rather complicated fashion. NO oxidation kinetics, on the other hand, are expected to be controlled by redox of Cu ion sites but not

influenced by Brønsted acid sites. Therefore, detailed kinetic studies of these three reactions allow simplification and isolation of at least part of the complex structure-function relationships.

3.4.1 NO oxidation

From the recent studies by Verma et al. [39] and by us [10], there appears to be a general agreement that NO oxidation ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$) cannot be catalyzed by monomeric Cu ion centers. Therefore, only Cu/SSZ-13 samples at high ion-exchange levels display activity. Three such samples with different Si/Al ratios are chosen here for this reaction. To mimic practical SCR reaction conditions, ~2.5% of H_2O was added to the reactant feed. NO conversion versus reaction temperature curves (collected at GHSV = 200,000 h^{-1}) are shown in SI-3. Note that “background” NO_2 formation (i.e., NO_2 formation by passing the reactants through the empty quartz reactor under reaction conditions) has been subtracted. However, because of the presence of the reverse reaction (i.e., $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$) [39] and the potential $\text{NO}_2\text{-H}_2\text{O}$ interactions (e.g., $4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 4\text{HNO}_3$), detailed kinetics analysis of the reaction data becomes nontrivial. Fig. 7 simply presents normalized overall reaction rates ($\text{mol NO mol Cu}^{-1} \text{ s}^{-1}$) in the form of Arrhenius plots. Adjacent to each plot, Si/Al and Cu/Al ratios are displayed. Apparent activation energies are not shown here; in the presence of multiple reactions, their physical meaning is ambiguous. Importantly, however, reaction rates are markedly different for the three samples, where they increase with increasing Si/Al ratios. These results are fully consistent with a redox reaction mechanism; i.e., as Si/Al ratios rise, redox barriers for Cu ion centers decrease. It is also worth emphasizing that Brønsted acidity plays no direct role in this reaction.

3.4.2 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. In our most recent study using samples at Si/Al = 6, a dramatic temperature-dependent transition in catalytic

centers for this reaction was discovered at low to intermediate Cu loadings. That is, at reaction temperatures of 300 °C and lower, ‘transient’ Cu-ion dimers appear to be the catalytic centers and at reaction temperatures of 350 °C and above, dimeric Cu centers become unstable and dissociate into catalytically active monomeric centers [10]. Here we report results using samples with different Si/Al ratios. In order to maintain differential NH₃ conversions, three low Cu loading samples with similar Cu/Al ratios are chosen for high-temperature NH₃ oxidation and the three high Cu loading samples (same as those used for NO oxidation shown above) are chosen for low-temperature NH₃ oxidation. All reactions are carried out at GHSV = 400,000 h⁻¹. Again, ~2.5% H₂O is added to the feed to simulate realistic reaction conditions.

High-temperature (400 to 550 °C) NH₃ conversion versus temperature curves are displayed in SI-4. NH₃ conversions remain sufficiently low to facilitate the following kinetics analyses. Fig. 8 presents normalized reaction rates (mol NH₃ mol Cu⁻¹ s⁻¹) in the form of Arrhenius plots. Adjacent to each plot, Si/Al and Cu/Al ratios and apparent activation energies are also displayed. Si/Al = 6 and 12 samples display rather similar rates and apparent activation energies (~70 kJ/mol) suggesting identical catalytic centers in both samples. At such high reaction temperature and low Cu loading, it is almost certain that the catalytic centers are isolated Cu²⁺ ions in windows of 6MRs. However, the Si/Al = 35 sample displays higher rates and a high apparent activation energy of 150 kJ/mol. Interestingly, above a reaction temperature of ~460 °C, a clear transition in kinetics is observed and the apparent activation energy decreases to 61.9 kJ/mol, similar to those of the lower Si/Al samples. The likely origin for this transition will be discussed in more detail below.

SI-5 presents NH_3 light-off curves in the low-temperature regime for samples with high Cu/Al ratios. Again, only data at low conversions are used for further analysis. Fig. 9 presents normalized rates ($\text{mol NH}_3 \text{ mol Cu}^{-1} \text{ s}^{-1}$) in the form of Arrhenius plots. Adjacent to each plot, Si/Al and Cu/Al ratios and apparent activation energies are also displayed. This graph shows a high degree of complexity indicating that both Cu ion redox and Brønsted acidity play important roles in determining reaction rates and activation energies. Again, these will be discussed in more detail below.

3.4.3 Standard NH_3 -SCR

In our recent publication, detailed NH_3 -SCR kinetics analyses were described on a series of Cu/SSZ-13 catalysts with Si/Al = 6 [10]. Briefly NO conversions were normalized based on sample weights and further corrected with a first-order rate equation. Then the Arrhenius equation was used to calculate pre-exponential factors and apparent activation energies. Similar to the NH_3 oxidation reaction, standard SCR also undergoes a transition in the nature/position of active centers as a function of temperature. Therefore, two kinetic regimes, i.e., below $\sim 200^\circ\text{C}$ and above $\sim 350^\circ\text{C}$, are chosen to compare kinetics for samples with different Si/Al ratios. Reaction conditions, i.e., space velocities and sample Cu loadings insure collection of data within kinetically relevant regimes for fair comparisons.

SI-6 presents light-off curves (low temperature reactivity) for a large number of Cu/SSZ-13 samples at various Si/Al and Cu/Al ratios. Among these, three samples (Si/Al = 6, Cu/Al = 0.044; Si/Al = 12, Cu/Al = 0.13; Si/Al = 35, Cu/Al = 0.31) are chosen for a direct comparison of low-temperature kinetics, and the results are displayed in SI-7. Fig. 10 presents normalized reaction rates ($\text{mol NH}_3 \text{ mol Cu}^{-1} \text{ s}^{-1}$) in the form of Arrhenius plots. Adjacent to each plot, Si/Al and Cu/Al ratios, and pre-factors ($\ln A$) and E_a values (obtained from SI-7) are also displayed.

For the Si/Al = 6 and 12 samples, $\ln A$ and E_a values appear to be rather similar indicating identical catalytic centers and rate-limiting steps. For the Si/Al = 35 sample, both $\ln A$ and E_a values are considerably lower indicating either the catalytic centers, or rate-limiting steps, or both, are somewhat different. It is important to note that **reaction rates** appear to increase as Si/Al ratio decreases suggesting that Brønsted acidity does promote reaction rates.

To compare kinetics in the high-temperature regime, three samples with much lower Cu loadings (Si/Al = 6, Cu/Al = 0.016; Si/Al = 12, Cu/Al = 0.06; Si/Al = 35, Cu/Al = 0.1) are chosen and reactions are carried out at a much higher GHSV of 1200,000 h⁻¹ to collect kinetically relevant data. Following an identical data analysis procedure as in SI-6 and SI-7 to obtain $\ln A$ and E_a values (data not shown for the sake of brevity), Fig. 11 presents **reaction rates** in the form of Arrhenius plots where the corresponding parameters are listed adjacent each plot. It is quite interesting that, in this case, all three samples have very similar $\ln A$ and E_a values suggesting similar reaction mechanism and rate-limiting steps. Again, **reaction rates** increase with decreasing Si/Al ratios suggesting Brønsted acidity promotes reaction at such high temperatures.

4 Discussion

To investigate the roles of Brønsted acidity in Cu/SSZ-13 SCR catalysts, using samples with various Si/Al ratios is an illuminating approach. However, Si/Al ratios affect not only acid site density, but also the location and coordination of Cu ion centers. We have shown recently that Cu ion positioning, especially whether they are located in the CHA cages or in windows of 6MRs, profoundly influences SCR kinetics [10, 15]. In this study, we have used H₂-TPR to probe the redox properties of Cu ions, and NH₃-TPD and DRIFTS to study the Brønsted acidity of the catalysts. To untangle some of the complexities caused by the interplay between Cu ion

redox and Brønsted acidity, besides SCR, NO and NH₃ oxidation reactions were also investigated. Especially for NO oxidation, Brønsted acidity is not expected to directly influence its kinetics.

First, we discuss the types of Cu ion species that are possibly present in our experiments. Much work has been done to investigate the nature of Cu ion species in Cu/SSZ-13. In the fully hydrated form, an extreme situation is that Cu²⁺ ions are fully coordinated to H₂O ligands to form [Cu(H₂O)₆]²⁺. Indeed, XANES spectra between hydrated Cu/SSZ-13 and a hexa-aqua Cu(II) solution appear to be very similar [17]. However, Cu²⁺ ions can also hydrolyze in the presence of H₂O according the following reaction:

Equilibrium for reaction (2) shifts to the right side as pH rises; yet pH inside zeolite cages is not readily determined or controllable as in an aqueous solution. Therefore, reaction (2) cannot be disregarded unless in a highly acidic environment, which, however, is not expected under low-temperature NH₃-SCR conditions. In this sense, one can also not rule out the existence of [Cu(OH)(H₂O)₅]⁺ in fully hydrated samples. Furthermore, one even cannot rule out the possibility that, in fully hydrated samples, Cu²⁺ ion and lattice O interactions are present; i.e., the formation of [Cu(H₂O)_x(O_L)_{6-x}]²⁺ and [Cu(OH)(H₂O)_x(O_L)_{5-x}]⁺ moieties. XANES is not expected to be precise enough to distinguish these species, and neither are EPR and UV-Vis spectroscopies. In our recent EPR studies, hydrated Cu²⁺ ions in the low Cu-loaded samples do seem to display more than one type of hyperfine characteristics [10], yet detailed assignments are not possible to give.

Upon full dehydration, Cu ions will lose most if not all coordinated water molecules and migrate to the most stable cationic sites. Numerous experimental and theoretical studies have agreed that the windows of 6MRs with two Al T-sites are the most stable site for ‘naked’ Cu^{2+} [9-20]. Even in this case, complexity still exists since there are two possible framework configurations: -Al-O-Si-O-Al- and -Al-O-Si-O-Si-O-Al-. According to DFT calculations, the latter confirmation stabilizes Cu^{2+} more than the former [23]. Densities of these linkages are determined by Si/Al ratios if one assumes a random distribution of T sites in SSZ-13. From Fig. 1, it is clear that -Al-O-Si-O-Al- linkages only exist in our Si/Al = 6 samples. The existence of -Al-O-Si-O-Si-O-Al- linkages cannot be directly probed using ^{29}Si NMR. However, one expects that when the density of Si(3Si, 1Al) sites (-105 ppm) is sufficiently low, for example in the Si/Al = 35 sample, the formation of -Al-O-Si-O-Si-O-Al- linkages is unlikely. Considering their stability, one expects that windows of 6MRs with 2 Al will be saturated by Cu^{2+} first. However, one should be aware that, in the presence spatial confinements typical for zeolites, it is possible that Cu^{2+} ions populate in less-stable sites even before the most stable sites are saturated. In any case, it becomes complicated when Cu loading continues to increase above that required to fill the most stable cationic sites. When only Cu^{2+} ions are considered, they can either reside next to 8MRs with 2 Al sites in the ‘naked’ form, or next to 6- or 8-MRs with 1 Al site in the hydrolyzed form, i.e., $[\text{Cu}(\text{OH})]^+$. Note that the formation of $[\text{Cu}(\text{OH})]^+$ in Cu/SSZ-13 has been demonstrated using infrared spectroscopy by a few studies [20, 31, 35], and further confirmed by DRIFTS measurements shown in Fig. 6 here. In a more recent study, Andersen et al. [22] further confirmed the presence of $[\text{Cu}^{\text{II}}(\text{OH})]^+$ located in windows of 8MRs for high Cu-loaded Cu/SSZ-13. Our recent theoretical study has also shown that $[\text{Cu}(\text{OH})]^+$ species next to 8MRs are particularly stable [23].

With these considerations, next we aim to better understand the H₂-TPR results described in Figs. 2 and 3. The results shown in Fig. 3 provide two pieces of important information: (1) all Cu ions at ambient conditions remain as Cu²⁺ and all of these are reduced to Cu⁺ before 600 °C; (2) no measureable amounts of CuO clusters are present in our samples. Two key points are worth addressing regarding the TPR curves for hydrated samples shown in the lower panels of Fig. 2. First, during the TPR process, some Cu²⁺ species are reduced in a partially hydrated form and some are reduced after full dehydration. Therefore, the ~230 °C (~250 °C for the Si/Al = 35 samples) reduction state is due to reduction of partially hydrated Cu²⁺ and [Cu(OH)]⁺ ions within CHA cages, and the ~380 °C reduction state is due to reduction of the portion of now dehydrated Cu²⁺ ions that migrate to windows of 6MRs prior to reduction. Second, as shown in the lower panel of Fig. 2(c), this high-temperature reduction state is absent for the Si/Al = 35 samples indicating that the configuration of having two Al sites within one 6MR is essentially impossible at such a high Si/Al ratio. It is also interesting to note that, regardless of the Si/Al and Cu/Al ratios, there appears to be a common onset temperature of ~160 °C for the low-temperature reduction state. This likely means that the coordinated H₂O surrounding Cu ions starts to desorb at this temperature to create space for H₂ adsorption and activation. This temperature corresponds very well with the onset of H₂O desorption monitored with FTIR [20].

H₂-TPR results for the dehydrated samples provide insights into Cu ion species within dehydrated and O₂-activated samples. First, it is interesting that some samples undergo autoreduction during dehydration even in the presence of O₂ (Table 3). This may a priori seem surprising. However, previous studies have revealed the same phenomenon on other Cu/zeolites. For example in a study by Bulanek et al. [40], Cu/zeolite samples with MFI, FER and ERI structures were treated in an oxygen flow up to 400 °C prior to H₂-TPR. Copper not oxidized to a

divalent state before the TPR experiment was found, and the amount increased with total Cu loading. These results are fully consistent with our TPR data. In recent studies using XANES to directly monitor oxidation states of Cu ions during Cu/SSZ-13 activation in oxygen, we [20] and Giordanino, et al. [35] also revealed Cu^+ formation at elevated temperatures. Especially, a very recent study by Godiksen, et al. [19] suggested a mechanism for Cu^{2+} autoreduction via cleavage of $[\text{Cu}(\text{OH})]^+$ that occurs in a He flow at $\sim 250^\circ\text{C}$. Results from the present study and the work by Bulanek et al. [40] demonstrate that this chemistry also occurs in an O_2 flow, albeit at higher temperatures. The key to understanding this phenomenon is the stability of Cu^{2+} ions in various zeolite locations under ‘dry’ conditions. As noted above, calculations have demonstrated that the windows of 6MRs containing 2 substituted Al ions are most favorable for Cu^{2+} ; a situation that is more probable as Si/Al ratios decrease (i.e., at higher Al content). For such a configuration, as discussed in more detail below, the reduction of Cu^{2+} to Cu^+ is difficult and only occurs at quite high ($\sim 380^\circ\text{C}$) temperatures. This explains why Cu^+ ions form during dehydration only at higher Cu loadings for Si/Al ratios of 6 and 12 (Table 3). Also consistent with this is the fact that the autoreduction of Cu^{2+} during dehydration occurs at lower Cu/Al ratios for samples with higher Si/Al ratios where the probability of finding 2 Al atoms in the same 6MR is reduced. Indeed, in the Si/Al = 35 samples, the configuration for ‘naked’ Cu^{2+} ions in faces of 6MRs with 2 Al is probably not possible so, Cu^{2+} must stay in other forms. In this case, substantial autoreduction occurs even at the lowest Cu loading. Note, however, from Fig. 2(c) and Table 3 for the three dehydrated Si/Al = 35 samples, $\text{Cu}^+/\text{Cu}_{\text{total}}$ ratios decrease with Cu loading; for these samples, Cu^+/Al ratios are 0.077, 0.108 and 0.118, gradually approaching saturation. While it seems clear that the reason autoreduction is so prevalent even at low Cu loading for this series of samples is the absence of sites for the most stable Cu^{2+} bonding configuration, why the $\text{Cu}^+/\text{Cu}_{\text{total}}$ ratios

decrease with Cu loading rather than increasing, as was the case for the Si/Al = 6 and 12 samples, is less obvious. We will address this issue after first proposing possible assignments for all of the Cu^{2+} reduction features in the TPR data.

Since unambiguous spectroscopic identification/quantification is not yet available, here we tentatively account for a semi-quantification of the H_2 -TPR for the dehydrated samples with respect to some possible Cu ion species. For the TPR curves displayed in upper panels in Fig. 2, the 350-450 °C peak is assigned to reduction of Cu^{2+} next to 6MR with 2 Al as we have previously proposed [13, 15]. Note that this reduction state is quite Cu loading dependent: the lower the Cu loading, the higher the reduction temperature. It is significant that this TPR feature is absent in the results for the Si/Al = 35 ratio sample; in this case, there is a very low probability that two Al ions will be located in the same 6MR (or even in the same zeolite cage). Thus, the formation of a highly stable Cu^{2+} ion with 2 Al in a 6MR is not possible, explaining the absence of the 350-450 °C TPR peak in Fig. 2c.

Because of the broadness of the TPR features in all of this data, strict assignment of lower temperature reduction features is more difficult; notably, it depends on the Si/Al ratio of the CHA zeolite, Cu loading, and the presence of water. Considering these various factors, in the following we suggest a number of likely structures to account for the lower temperature reduction features in the Fig. 2 TPR data. The reduction state at ~250-300 °C in Fig. 2(a) at high Cu loadings for the Si/Al = 6 sample is assigned primarily to reduction of Cu^{2+} next to 8MR with 2 Al. Cu^{2+} to Cu^+ reduction at somewhat lower (~200 °C) temperatures, most apparent for the Si/Al = 35 samples and the Si/Al = 12, Cu/Al = 0.23 sample, is assigned to reduction of $[\text{Cu}(\text{OH})]^+$ and Cu-dimer species. The especially broad lower temperature TPR feature for the

Si/Al = 12 sample in Fig. 2(b) is likely due to the presence of these species as well as Cu²⁺ coordinated to 2 Al in 8MRs. Specifically for the Si/Al = 35 samples, the onset of reduction for the dehydrated samples in Fig. 2(c) occurs as low as ~100 °C strongly indicating the existence of a readily reducible oxo-bridged dimeric species. The following equation gives an example for the formation of a possible Cu-dimer species:

According to the recent studies by Verma et al. [39] and by us [10], it seems clear that NO oxidation is catalyzed by Cu-ion dimers while Cu-ion monomers are completely inert. Reaction pathways can be presented as the following:

Note that reactions (5) and (6) are more or less illustrative since it is not yet clear whether Cu-dimers in Cu/SSZ-13 are single-oxygen bridged or double-oxygen bridged [41]. In any case, we show in Fig. 7 that overall NO oxidation rates increase with increasing Si/Al ratios. Although it is difficult to quantify the number of permanent dimers in different samples in order to compare their intrinsic rates, their propensity to form, assuming they involve [Cu(OH)]⁺ species, will be most likely for the Si/Al = 35 sample. It is also likely significant that these samples show the largest proportion of autoreduced Cu, another indication that Cu is generally more readily reducible when it is not able to coordinate to two Al-O-Si ion exchange sites. Finally, it is also clear that Brønsted acidity does not play a beneficial role in NO oxidation since samples with lower acidity (higher Si/Al ratios) give higher NO oxidation rates.

With respect to the TPR data obtained for hydrated samples (lower panels in Fig. 2), we generally find Cu^{2+} to Cu^+ reduction to occur in the 200-300 °C temperature range. It is also important to keep in mind that the Cu ion species that form in the presence of water are not susceptible to autoreduction under the conditions used in our studies. This may be a consequence of the ‘saturation’ of these Cu species with water ligands. Despite this, hydrated Cu species are more readily reducible than ‘naked’ Cu ions located in their most stable position; i.e., charge compensating 2 Al substituted ion exchange sites in a single 6MR. In this regard, note that the “hydrated” sample experiments in Fig. 2 (lower panels) result in some dehydration during the experiment. This is why there are still high temperature (~380 °C) peaks for the Si/Al = 6 and 12 samples. Indeed, we have previously reported [13] TPR measurements for Cu in Si/Al = 6 samples that were performed in the presence of water (rather than simply hydrated before the TPR measurements as reported here). In this case, all Cu^{2+} to Cu^+ reduction occurs below (~300 °C at all Cu loadings.

In the Brønsted acid site titration experiments, results shown in Fig. 4 and Table 4 suggest that our experimental procedures do allow all Brønsted acid sites in the H/SSZ-13 samples to be probed by NH_3 . The strongest evidence comes from the fact that an $\text{NH}_3/\text{Al}_{\text{total}}$ ratio of unity is obtained for the Si/Al = 35 sample. Note also that, for our Si/Al = 6 sample, an $\text{NH}_3/\text{Al}_{\text{total}}$ ratio of 0.62 is very close to a ratio of 0.65 obtained by Bates et al. [33] for a Si/Al = 4.5 sample using similar experimental procedures. However, our NH_3 -TPD procedure for the Cu/SSZ-13 samples does not allow such quantifications. Instead, we use results shown in Fig. 5 to qualitatively describe NH_3 desorption from Cu ion and weak Lewis acid sites during TPD. Since the Si/Al = 35 sample does not have any extra-framework Al sites (Fig. 1), from the bottom desorption curve shown in Fig. 5, the state centered at ~350 °C contains primarily NH_3

adsorbed on Cu sites, as well as possibly NH_3 complexed with NH_4^+ sites [35]. For the lower Si/Al ratio samples, the low-temperature state likely also contains NH_3 desorption from Lewis acidic extra-framework Al species. A key piece of information obtained from Fig. 5 is that low-temperature NH_3 desorption yield dramatically increases with decreasing Si/Al ratios. Recently, Giordanino et al. suggested $[\text{Cu}(\text{NH}_3)_2]^+$ complex formation during NH_3 adsorption on Cu/SSZ-13 from XANES and DFT simulations [35]. During TPD, such a complex releases NH_3 that contributes to the low-temperature NH_3 desorption state. These authors also identified $\text{NH}_4^+ \cdot n\text{NH}_3$ ($n \geq 1$) formation during NH_3 adsorption. Again, decomposition of such complexes also contributes to the low-temperature state. The following three facts, i.e., (1) $\text{Cu}(\text{OH})^+$ likely binds fewer NH_3 molecules than Cu^{2+} , (2) lower Si/Al samples contain higher densities of residual Brønsted acid sites, and (3) lower Si/Al samples contain higher quantities of extraframework Al sites seem to nicely account for low-temperature NH_3 desorption yield differences shown in Fig. 5.

In the following, we briefly discuss the NH_3 oxidation and NH_3 SCR kinetics with respect their possible dependence on Brønsted acidity. As noted above, however, the complexity (as compared to NO oxidation) caused by influences from Cu ion redox, Brønsted acidity and reaction temperature will make such a determination difficult. We also note here that, in our recent publication, a surprising transition in catalytic centers from Cu-dimers to Cu-monomers as a function of temperature was evident in ‘standard’ SCR kinetic studies using a series of Cu/SSZ-13 catalysts with Si/Al = 6 [10].

Over oxide and zeolite catalysts, two NH_3 oxidation mechanisms have been suggested previously [7, 42-45]: (1) a portion of NH_3 is first oxidized to NO, followed by a standard NH_3 -SCR reaction with the remaining NH_3 ; and (2) $\text{NH}_{2(a)}$ formation by H abstraction from NH_3 ,

followed by N₂H₄ formation and oxidation. In any case, a common first step in these proposed mechanisms is H abstraction from NH₃. This can be done via two pathways:

The significant difference between reactions (7) and (8) is whether or not an active form of oxygen species is needed. In terms of zeolite based catalysts, this becomes whether extra lattice oxygen (ELO) is needed. Our recent study, therefore, may suggest that, in the low-temperature regime (< 300 °C), ELO provided by the oxo-bridged Cu-dimer active sites is indeed needed, while at elevated temperatures, such species are no longer required since Cu ion monomers become catalytically active [10].

From Fig. 8, it is clear that the Si/Al = 6, Cu/Al = 0.044 sample and Si/Al = 12, Cu/Al = 0.06 sample display rather similar apparent activation energies in the high (>400 °C) temperature regime. This indicates that both samples have identical active centers at the relatively low Cu loading for these catalysts; namely, isolated Cu²⁺ ions in windows of 6MR. Indeed, H₂-TPR results displayed in Fig. 2 for these two samples fully supports this assignment. The fact that **reaction rates** for the Si/Al = 6 sample are ~2 times higher than the Si/Al = 12 sample suggests that Brønsted acidity plays a positive role in this reaction. Interestingly, the Si/Al = 35, Cu/Al = 0.1 sample not only displays substantially higher activity, but also two distinct kinetic regimes below and above ~460 °C. Since this sample has the lowest Brønsted acidity, the higher activity can only be rationalized by the lower Cu²⁺/Cu⁺ redox barriers for this sample that is evident in the TPR results (Fig. 2(c)). The origin for the much higher apparent activation energy of ~150 kJ/mol in the temperature window of 400 to 460 °C is not clear, **yet** seems likely related to

differences in the nature and/or location of the catalytic centers for this sample as compared with those at lower Si/Al ratios. For example, one possibility is that the active centers for the Si/Al = 35 samples are $[\text{Cu}(\text{OH})]^+$ ions. Indeed, the transition in kinetics at $\sim 460^\circ\text{C}$ could then be due to partial decomposition of the $[\text{Cu}(\text{OH})]^+$ ion centers, consistent with FTIR analysis of the ν_{OH} region showing that a Cu-OH band diminishes above $\sim 425^\circ\text{C}$ (SI-8).

In the low ($< 300^\circ\text{C}$) temperature regime, NH_3 oxidation kinetics, shown in Fig. 9, do not appear to display any clear trends. This situation makes it more difficult to draw any meaningful conclusions regarding the specific nature of the active Cu species, and the relative importance of Cu ion redox and Brønsted acidity in determining reactivity. Still, a complex interplay between these three effects as a function of temperature is evident in the quite varied NH_3 oxidation kinetics at low reaction temperatures.

Finally, the roles of Brønsted acidity in low- and high-temperature kinetic regimes for the standard NH_3 -SCR reaction are discussed. All reaction mechanisms that involve an NH_4^+ intermediate favor the argument that Brønsted acidity is indispensable. For V_2O_5 -based SCR catalysts, reactive NH_3 in the form of NH_4^+ has been frequently proposed [7, 25, 27]. Under conditions that $\text{O}_2 > 1\text{-}2\%$ and $T > 280^\circ\text{C}$, standard SCR rates for V_2O_5 -based catalysts can be approximated as [46]:

$$r = k(T) \times [\text{NO}] \times \theta_{\text{NH}_3} \quad (9)$$

where the reaction order is equal to one with respect to NO pressure, and reaction rates are also approximately proportional to NH_3 coverage. With regard to the contribution of Brønsted acidity to SCR rates on Cu/zeolites, it is also useful to first consider the following power law model, where α , β , and γ represent the reaction orders for NO, NH_3 , and O_2 , respectively:

$$r = A \exp\left(\frac{-E_a}{RT}\right) [NO]^\alpha [NH_3]^\beta [O_2]^\gamma \quad (10)$$

Studies by numerous groups agree in general that, at relatively low temperatures (e.g., < 300 °C), $\alpha \approx 1$, $\beta \approx 0$ and $\gamma \approx 0.5$ over Cu/CHA catalysts [9, 15, 47]. Because under typical SCR reaction conditions, O_2 concentrations are in considerable surplus compared to both NO and NH_3 , the power-law equation can be simplified as:

$$r = A \exp\left(\frac{-E_a}{RT}\right) [NO] \quad (11)$$

Thus, from Eq. 11, were there any effects for Brønsted acidity to SCR rates, one expects that either the pre-exponential factor A, or apparent activation energy E_a , or both, varies with H^+ concentration. From the Arrhenius plots displayed in Fig. 10, it is notable that, for the Si/Al = 6 and 12 samples, $\ln A$ and E_a values are strikingly similar yet SCR rates for the Si/Al = 6 sample are clearly higher. As such, Eq. 11 seems unable to accurately describe low-temperature SCR rates. Next we show that Eq. 9, derived empirically from studies on V_2O_5 -based catalysts, better describes our kinetic results for Cu/SSZ-13 catalysts. As described earlier, it is non-trivial to quantify the density of Brønsted acid sites under SCR reaction conditions. However, Brønsted acid site density of the parent H/SSZ-13 (represented by numbers of NH_3 chemisorbed in each unit cell, Table 4) can be regarded as a first approximation. This approximation is especially valid for catalysts with relatively low Cu/Al ratios (Fig. 6). Using low-temperature kinetic data given in Fig. 10, Fig. 12 plots SCR rates as a function of Brønsted acid sites per hexagonal unit cell of the parent H/SSZ-13, for three selected Cu/SSZ-13 catalysts with different Si/Al ratios at 4 reaction temperatures from 125 to 170 °C. Indeed, at these low temperatures, SCR rates vary approximately linearly with Brønsted acid density. Combining Eq. 9 and 11, the following empirical equation can be used to describe standard SCR rates on Cu/zeolites more generally:

$$r \approx A \exp\left(\frac{-E_a}{RT}\right) [NO] \times \theta_{NH_3} \quad (12)$$

Here the θ_{NH_3} term is roughly defined as the coverage of NH_3 species that do not adsorb directly on Cu-ion active centers, but on sites with relatively weak binding energies such that they facilely diffuse to Cu-ion sites. Note that recent titration experiments in studies on Cu-CHA catalysts demonstrate that NH_4^+ species are far less reactive toward NO_x than molecular NH_3 adsorbed on Cu sites [30-32, 48]. Therefore, NH_4^+ species can be safely excluded as a contributor to θ_{NH_3} . NH_3 adsorbed on extraframework Al sites, on the other hand, can be regarded as contributing to θ_{NH_3} , as also suggested recently by Lezcano-Gonzalez et al. [31]. From a recent study by Giordanino et al., $NH_4^+ \cdot nNH_3$ complexes form during NH_3 adsorption on Cu/SSZ-13 and maintain up to ~ 300 °C [35]. Therefore, despite the low reactivity of NH_4^+ , it still benefits SCR by attracting more weakly bound NH_3 species (i.e., contributes to θ_{NH_3}). We note that equation 12 does not contradict the commonly measured zero order dependence on NH_3 pressure in low-temperature standard NH_3 -SCR. Notably, as long as the rate constant for the gas phase NH_3 adsorption on these weak sites is higher than the rate constant for adsorbed NH_3 diffusion to Cu sites, this zero order dependence maintains. In the higher temperature kinetic regime, Arrhenius plots shown in Fig. 11 are also fully consistent with Eq. 12. In this case, however, despite the fact that the redox properties for the active Cu species in the Si/Al = 35 sample is different from the lower Si/Al samples, $\ln A$ and E_a values are essentially identical. This strongly indicates that the rate-limiting step in this case is less likely redox of Cu active sites. The rather high E_a of ~ 140 kJ/mol indicates a demanding rate-limiting step, likely N–H bond cleavage by Cu sites. Recent theoretical work does demonstrate a high NH_3 dissociation energy of ~ 120 kJ/mol on isolated Cu^{2+} ions in windows of 6MR [49]. Even though still not

conclusive, the striking similarity between experimental activation energy and the theoretical NH_3 dissociation energy suggests the possibility that the high-temperature standard SCR catalyzed by isolated Cu^{2+} ions, occurs via an $\text{NH}_2\text{-Cu-NO}$ intermediate, where the rate limiting step is the formation of $\text{NH}_2\text{-Cu}$.

Overall, from the most recent kinetic studies on Cu/CHA, and from previous studies on other zeolite catalysts, it appears that a rather general conclusion can be made regarding the role of acidity as already pointed out by a few groups; notably, that acidity favors the reaction without being an essential ingredient of the active site and, correspondingly, the reaction mechanism [50, 51]. Rather, higher acidity may simply promote SCR by increasing NH_3 concentrations near active sites. Finally, we note that the use of Eq. 12 here only serves as an illustration of the possible roles that Brønsted acidity may play in standard SCR. We note that it is oversimplified for practical rate descriptions and prediction, especially at transient reaction conditions. For the latter uses, much more powerful rate equations can be found elsewhere [52-54].

5 Conclusions

Cu^{2+} ion locations and redox properties can be systemically tuned by varying Si/Al and Cu/Al ratios of the Cu/SSZ-13 catalysts. With increasing Si/Al and Cu/Al ratios, Cu^{2+} ions become more readily reducible indicative of reduction in redox barriers. While 6MR faces with 2 Al are the most favorable sites in stabilizing Cu^{2+} ions, in the absence of such sites, Cu^+ and $[\text{Cu}(\text{OH})]^+$ appear to be the most stable Cu ion species. Using $\text{H}_2\text{-TPR}$, all possible Cu^{2+} moieties can be semi-quantitatively identified. Specifically, for high Cu/Al ratio samples activated in O_2 , the onset of reduction as low as $\sim 100^\circ\text{C}$ is a strong indication for the formation of oxo-bridged Cu-dimer species. $\text{NH}_3\text{-TPD}$ and OH vibrational FTIR can both be used to titrate residual Brønsted

acid sites in Cu/SSZ-13. At low Si/Al ratios and low Cu loading conditions, each Cu^{2+} replaces two H^+ sites. However this trend does not extend to high Si/Al ratios and high Cu loading conditions due to the presence of $[\text{Cu}(\text{OH})]^+$ moieties. NH_3 -TPD can also be used to probe NH_3 chemisorbed on Lewis acid sites (Cu and extraframework Al sites) and complexed with NH_4^+ . Lower Si/Al ratios favor adsorption of these NH_3 species. NO oxidation follows a simple redox mechanism. With increasing Si/Al ratios, reaction rates greatly increase. NH_3 oxidation and NH_3 -SCR also involve redox of Cu active sites. However, reaction kinetics are greatly influenced by Brønsted acidity. The role of Brønsted acidity is not to provide a reactive NH_4^+ species, but to provide reactive NH_3 molecules to Cu sites as a reservoir. The extent of the Brønsted acidity contribution, however, is highly dependent on the catalysts used and the reaction conditions.

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Table 1: Si and Al contents and corresponding Si/Al ratios for the 3 SSZ-13 samples.

Sample	Si content (wt.%)	Al content (wt.%)	Si/Al Ratio
1	30.4	5.03	6
2	40.3	3.23	12
3	43.4	1.20	35

Table 2: Cu contents, and 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
Cu/SSZ-13 (Si/Al = 12)	0.48	0.06	13
	1.00	0.13	26
	1.74	0.23	46
Cu/SSZ-13 (Si/Al = 35)	0.28	0.10	20
	0.64	0.23	45
	0.87	0.31	62

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

Table 3: Quantification of Cu^+ formation during Cu/SSZ-13 sample dehydration in 5% O_2/He at 550 °C.

Si/Al	Cu/Al	$\text{Cu}^+/\text{Cu}_{\text{total}}$
6	0.006	≈ 0
	0.198	≈ 0
	0.044	≈ 0
	0.11	0.02
	0.22	0.03
	0.29	0.02
	0.40	0.21
	0.44	0.24
12	0.06	≈ 0
	0.13	0.18
	0.23	0.34
35	0.10	0.77
	0.23	0.47
	0.31	0.38

Table 4: Quantification of $\text{Al}_f/\text{Al}_{\text{total}}$, $\text{NH}_3/\text{Al}_{\text{total}}$ and NH_3/Al_f ratios based on NH_3 -TPD results shown in Fig. 4 and ^{27}Al NMR results shown in Fig. 1 for the three H/SSZ-13 samples.

Si/Al	Ideal Stoichiometry	$\text{Al}_f/\text{Al}_{\text{total}}$	$\text{NH}_3/\text{Al}_{\text{total}}$	NH_3/Al_f
6	$\text{H}_{5.1}\text{Al}_{5.1}\text{Si}_{30.9}\text{O}_{72}$	0.88	0.62	0.70
12	$\text{H}_{2.8}\text{Al}_{2.8}\text{Si}_{33.2}\text{O}_{72}$	0.98	0.85	0.87
35	$\text{H}_1\text{Al}_1\text{Si}_{35}\text{O}_{72}$	1.0	1.0	1.0

Figure Captions

Figure 1

Solid state (a) ^{27}Al - and (b) ^{31}Si -NMR spectra for the H/SSZ-13 samples with Si/Al ratio = 6, 12 and 35. Samples were prepared by ion-exchanging Na/SSZ-13 samples to NH_4 /SSZ-13 followed by a calcination in air at 550 °C. Note that small features in the ^{27}Al -NMR spectra at ~-17 and ~135 ppm, especially evident in the spectrum for the Si/Al = 6 sample, are spinning side bands.

Figure 2

Temperature-programmed reduction (TPR) data for Cu/SSZ-13 samples with various Cu loadings for (a) Si/Al = 6, (b) Si/Al = 12 and (c) Si/Al = 35. The upper panels show TPR for dehydrated samples while the lower panels show TPR for fully hydrated samples.

Figure 3

H_2 consumption peak areas as a function of Cu loading during TPR for hydrated samples shown in the lower panels of Fig. 2.

Figure 4

NH_3 -TPD curves for the three H/SSZ-13 samples. NH_3 adsorption and purging was carried out at 200 °C prior to TPD.

Figure 5

NH_3 -TPD curves for selected Cu/SSZ-13 samples with different Si/Al and Cu/Al ratios. NH_3 adsorption and purging was carried out at 100 °C prior to TPD.

Figure 6

(a) OH vibrational DRIFT spectra for the H/SSZ-13 and selected Cu/SSZ-13 samples with Si/Al = 6. Samples were dehydrated in flowing helium at 550 °C, and then cooled to 227 °C for spectra collection. (b) The signal intensity at 3604 cm^{-1} as a function of Cu/Al ratio.

Figure 7

Arrhenius plots for NO oxidation on three high Cu loading samples: (■) Si/Al = 6, Cu/Al = 0.44; (●) Si/Al = 12, Cu/Al = 0.23; (▲) Si/Al = 35, Cu/Al = 0.31. Reactant feed contains 350 ppm NO, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 8

Arrhenius plots for NH₃ oxidation in the high-temperature regime on three low Cu loading samples: (■) Si/Al = 6, Cu/Al = 0.044; (●) Si/Al = 12, Cu/Al = 0.06; (▲) Si/Al = 35, Cu/Al = 0.1. Reactant feed contains 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 400,000 h⁻¹.

Figure 9

Arrhenius plots for NH₃ oxidation in the low-temperature regime on three high Cu loading samples: (■) Si/Al = 6, Cu/Al = 0.44; (●) Si/Al = 12, Cu/Al = 0.23; (▲) Si/Al = 35, Cu/Al = 0.31. Reactant feed contains 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 400,000 h⁻¹.

Figure 10

Arrhenius plots for standard NH₃-SCR in the low-temperature regime on three samples that display similar catalytic performance: (■) Si/Al = 6, Cu/Al = 0.044; (●) Si/Al = 12, Cu/Al = 0.13; (▲) Si/Al = 35, Cu/Al = 0.31. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 400,000 h⁻¹.

Figure 11

Arrhenius plots for standard NH₃-SCR in the high-temperature regime on three low Cu loading samples: (■) Si/Al = 6, Cu/Al = 0.016; (●) Si/Al = 12, Cu/Al = 0.06; (▲) Si/Al = 35, Cu/Al = 0.1.

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.

Figure 12

SCR rates (s⁻¹), taken from Fig. 10) as a function of the number of Brønsted acid sites per unit cell of the parent H/SSZ-13 in the low-temperature regime (125 to 170 °C). The numbers of Brønsted acid sites per unit cell of the parent H/SSZ-13 were derived from NH₃ titration data given in Table 4.

Fig. 1, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 2, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 3, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 4, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 5, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 6, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 7, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 8, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 9, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 10, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 11, Gao, Kollar, Washton, Wang, Szanyi, Peden

Fig. 12, Gao, Kollar, Washton, Wang, Szanyi, Peden