Structure–activity relationships in NH₃-SCR over Cu-SSZ-13 as probed by reaction kinetics and EPR studies

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Cu-SSZ-13 catalysts with various Cu loadings were prepared via aqueous solution ion-exchange. The hydrated samples were characterized with Electron Paramagnetic Resonance (EPR). Cu²⁺ ion coordination numbers were obtained by analyzing the hyperfine structures, while Cu–Cu distances were estimated from line broadening of the EPR features. By examining EPR and temperature-programmed reduction (TPR) results, two Cu²⁺ ion locations are suggested. Standard NH₃-SCR, as well as non-selective NH₃ oxidation reaction with O₂, were carried out over these catalysts at high-space velocities. For the SCR reaction, intra-particle diffusion limitations are found. The kinetic data allow for reactant diffusivities to be estimated. However, clear structure–activity relationships for the SCR reaction cannot be derived due to this diffusion limitation. The slower NH₃ oxidation reaction, on the other hand, is kinetically limited at low temperatures, and, therefore allows for a correlation between Cu²⁺ ion location and reaction kinetics to be made.

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1. Introduction

The abatement of environmentally harmful NOₓ compounds (NO, NO₂, and N₂O) emitted from mobile or stationary power sources remains a challenging task for the catalysis community. In particular, conventional three-way catalysts used in the exhaust after-treatment technologies of internal combustion engines prove ineffective when the engine is operated under highly oxidizing conditions. However, in order to achieve better fuel efficiency and decrease CO₂ emission, operation under such fuel-lean conditions is a prerequisite for diesel engines and new-generation gasoline engines. The problem is daunting, since reduction chemistry (NOₓ to N₂) has to be carried out under highly oxidizing conditions. Hence, in order to achieve better fuel efficiency and decrease CO₂ emission, operation under such fuel-lean conditions is a prerequisite for diesel engines and new-generation gasoline engines. The problem is daunting, since reduction chemistry (NOₓ to N₂) has to be carried out under highly oxidizing conditions. Additionally, the engine is operated under highly oxidizing conditions. Therefore, in order to achieve better fuel efficiency and decrease CO₂ emission, operation under such fuel-lean conditions is a prerequisite for diesel engines and new-generation gasoline engines.

Later, Cu²⁺ ion-exchanged beta zeolite (Cu-beta) was shown to have excellent activity in the SCR of NOₓ with NH₃, and metal-exchanged beta zeolites are generally found to have greater hydrothermal stability than similar ZSM-5 catalysts [8]. Yet, none of these Cu-zeolite catalysts show durability sufficient for the automotive industry. Indeed, Cu²⁺-exchanged molecular sieves with Chabazite (CHA) structures, for example, Cu-SSZ-13 and Cu-SAPO-34, have been commercialized as NOx after-treatment catalysts in diesel-powered engines for transportation, due apparently to their much improved activity, selectivity, and durability [9–18].

We and other researchers compared SCR activities and hydrothermal stabilities of Cu-SSZ-13 with other Cu²⁺ ion-exchanged zeolites (especially Cu-ZSM-5 and Cu-beta) [10,13,15]. Indeed, Cu-SSZ-13 shows comparable or even higher activity, selectivity, and most impressively, much higher hydrothermal stability even under harsh treatment conditions; for example, extended hydrothermal treatments at 1073 K. There appears to be general consensus that these unique properties of Cu-SSZ-13 are due to its small-pore structure [10,13,15]. SSZ-13 adopts the R₃m space group with a hexagonal unit cell described via the following face symbol: [4⁶/2⁶] + [4²/2⁶/8₆]. The largest pore has an opening of 3.8 Å (8-membered ring). In contrast, ZSM-5 has medium size pore openings (~5.5 Å, 10-membered ring), while beta has the largest pores (~7 Å, 12-membered ring) [9]. This structural difference is significant in improving the stability of SSZ-13; (1) for zeolite materials, dealumination is the major cause of structural dealumination.
damage and activity loss. The dealumination product, Al(OH)$_3$, has a kinetic diameter of $\sim 5.03$ Å [15]. Thus, it is possible that aluminum cannot escape from the SSZ-13 pores during hydrothermal treatments; even if a dealumination reaction occurs it can insert back to the framework during cooling (i.e., reversible dealumination) to maintain the integrity of the zeolite structure [15]. (2) Medium- and large-pore zeolites adsorb large quantities of hydrocarbons at low temperatures. This is inevitable in vehicle emission treatments, since significant quantities of hydrocarbons are generated during cold-start. As the temperature rises, however, reaction heat generated via burning of these molecules can thermally destroy zeolites. Again, the small-pore SSZ-13 greatly eliminates this deactivation mechanism since hydrocarbons with kinetic diameters larger than methane (3.8 Å) have at most very limited diffusion into the pores [15].

Apart from the commercial success, detailed catalyst structures, reaction mechanisms, and structure–activity relationships are still lacking. For example, there are debates even regarding the location of Cu$^{2+}$, the catalytically active centers, within the SSZ-13 framework. Lobo and coworkers applied Rietveld refinement for TR-XRD data of their dehydrated Cu-SSZ-13 catalyst and proposed that Cu$^{2+}$ ions are located only in six-membered ring windows with a coordination number of 3 and average Cu–O distances of 2.2–2.3 Å [11]. In a more recent study, they used EXAFS to analyze Cu–SSZ-13 and concluded that, for a hydrated sample, four lattice oxygen atoms coordinate to the Cu$^{2+}$ ion with an average Cu–O distance of 2.02 Å, whereas for a dehydrated sample, the coordination number reduces to 3 at an average distance of 1.93 Å [16,19]. We, on the other hand, have recently commented that the copper locations within the SSZ-13 framework are affected by two factors: copper loading and moisture [14]. Both temperature-programmed reduction and FTIR coupled with CO and NO titrations reveal that there are two different Cu moieties in Cu-SSZ-13 as a function of Cu loading. For dehydrated samples and at low Cu loadings (at an ion-exchange (IE) level of $\sim 20$%), only a single type of Cu$^{2+}$ species exists which is rather hard to reduce to Cu$^+$ (at $\sim 653$ K). However, as the Cu loading increases, another Cu species develops, and the reduction temperatures are much lower ($\sim 503$ K). Furthermore, under wet-reducing conditions, the reduction temperatures for both species are significantly lower and are found at $\sim 523$ K and $\sim 483$ K, respectively. These findings are explained in the following way: at low Cu loading and under dehydrated conditions, Cu$^{2+}$ ions are located close to the face of the 6-membered rings via formation of Cu–O bonds with lattice oxygen as suggested by Lobo et al. [11,16,19]. When exposed to gases that strongly interact with Cu$^{2+}$ ions (e.g., NH$_3$), the Cu$^{2+}$ ions are pulled slightly into the large cages [19]. However, as the Cu loadings increase, some Cu$^{2+}$ ions also populate inside the large CHA cages next to 8-membered rings. Cu$^{2+}$ ions next to 8-membered rings have easier access to hydrogen (as they are closer to the pore openings) perhaps explaining, in part, their lower reduction temperatures. Moreover, under wet-reducing conditions, the interaction between water and Cu$^{2+}$ ions weakens interactions between Cu$^{2+}$ ions and lattice oxygen, allowing both types of Cu$^{2+}$ ions to move toward the large CHA cages and become more readily reducible. Note that this water-induced ion mobility is well known within the CHA cages [17,20].

We note that understanding the Cu locations within SSZ-13 under wet conditions is more relevant to practical NH$_3$-SCR since engine exhausts typically contain $\sim 10$% moisture. In the current study, we use Electron Paramagnetic Resonance (EPR), a technique ideally suited for studying Cu$^{2+}$ exchanged zeolites, to study hydrated Cu-SSZ-13 catalysts at various Cu loadings in order to gain further insights into their locations. Also, NH$_3$-SCR and NH$_3$ oxidation kinetics are investigated over these catalysts at high-space velocity conditions for the development of structure–activity relationships.

2. Experimental

SSZ-13 was synthesized using a procedure first developed by Zones [21] and recently slightly modified by others [9–12,14–17]. The synthesis method is detailed in Ref. [11]. Briefly, following Na-SSZ-13 formation, an ion-exchange step was applied using excess amount of 0.1 M NH$_4$NO$_3$ at 353 K for 8 h to generate NH$_4$-SSZ-13. ICP analysis of the calcined sample gave a Si/Al ratio of 6. For a hexagonal unit cell containing 36 tetrahedral (T) atoms and 72 lattice oxygen atoms, the stoichiometry is H$_{3.14}$Al$_{1.43}$Si$_{30.86}$O$_{72}$. Based on this stoichiometry, five different CuSO$_4$ solutions were prepared by dissolving various weights of CuSO$_4$ in 100 mL of deionized water. The pH of the solutions was adjusted to $\sim 3.5$ by adding dilute HNO$_3$ solutions. Following which, 0.7 g of NH$_4$-SSZ-13 sample was added to each solution, and ion-exchange was conducted at 353 K for 1 h. After centrifugation separation and thorough washing, the samples were dried at 373 K for 12 h and calcined at 823 K for 8 h. ICP analysis gave Cu loadings for these samples, in a loading increasing manner, 1.31, 2.59, 3.43, 4.67, and 5.15 wt.%, respectively. Based also on ICP analysis of Al content within these samples, the ion-exchange (IE) levels were determined as 23%, 45%, 60%, 80%, and 90%, respectively, for the five Cu-SSZ-13 samples prepared, where IE level is defined as IE% = mass fraction of Cu / mass fraction of Cu$^+$ × 100.

EPR experiments were conducted on a Bruker E580 X-band spectrometer equipped with a SHQE resonator and a continuous flow cryostat. Powder samples (10 mg) were contained in 4 mm OD quartz tubes and sealed with a rubber septa. For the hydrated samples (i.e., samples saturated with moisture in air), no special treatments were applied other than purging with dry N$_2$ at ambient temperature. Spectra were recorded at both ambient ($\sim 294$ K) and 155 K temperatures. Microwave power was 200 microwatts, and the frequency was 9.86 GHz. The field was swept 1500 G in 84 s and modulated at 100 kHz with 5 G amplitude. A time constant of 20 ms was used.

Temperature-programmed reduction (TPR) was performed on a Micromeritics AutoChem II analyzer. After purging the hydrated samples (50 mg) with pure N$_2$ at 10 mL/min at room temperature for 30 min, TPR was carried out in 5% H$_2$/Ar at a flow rate of 30 mL/min. Temperature was ramped linearly from ambient to 1323 K at 10 K/min, and H$_2$ consumption was monitored with a TCD detector. Note that we have reported similar TPR results recently [14]. In this study, we extended the reduction temperatures in order to observe both Cu$^{2+}$ reduction to Cu$^+$ and Cu$^+$ reduction to Cu$^0$. To our knowledge, such measurements have not been reported before for the Cu-SSZ-13 system. Reaction kinetics were measured using a plug-flow reaction system described elsewhere [9]. Catalyst samples (15–120 mg, 0.251–0.422 mm sizes) were loaded in a 1 cm OD quartz tube and placed inside an electric tube furnace. Temperature control and measurements were achieved by two thermocouples, one inserted into the catalyst bed, and one placed between the quartz tube and the inner wall of the furnace. The feed gas contained 350 ppm NO, 350 ppm NH$_3$, 14% O$_2$, 2.5% H$_2$O and balance N$_2$. NH$_3$ oxidation reaction was conducted in the same manner without NO$_x$. Stoichiometries for these reactions are shown below:

Standard SCR reaction: $4\text{NH}_3 + 4\text{NO} + 2\text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$

Non-selective NH$_3$ oxidation reaction: $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$

All of the gas lines were heated to over 373 K to avoid water condensation. The total gas flow was 300 sccm, and the gas hourly space velocity (GHSV) was estimated to be $\sim 800,000$ h$^{-1}$ for a catalyst amount of 15 mg. Concentrations of reactants and products.
were measured by an online Nicolet Magna 560 FTIR spectrometer with a 2 m gas cell maintained at 423 K.

For temperature-dependent steady-state reaction measurements, the catalysts were first activated in 14% O2/N2 flow for 1 h at 873 K. Following which, NO, NH3, and H2O were added to the feed to start the SCR reaction. At each target temperature, a minimum waiting time of ~45 min was applied to reach a steady state. NOx and NH3 conversions were calculated based on the following equations:

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

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

Turnover frequencies (TOF) were estimated by dividing the moles of NOx (or NH3) molecules converted per second by the moles of Cu atoms in the catalysts.

### 3. Results

Fig. 1 presents EPR results of the Cu-SSZ-13 samples at room temperature. These samples were cooled to room temperature in air after calcination during which they adsorbed moisture and, therefore, are defined as hydrated samples. In these samples, Cu species should all be present as EPR active Cu2+ ions. Monotonic signal intensity increases with increasing Cu loading further confirming this. Rather unexpectedly, two (instead of one) features are found at high field at 3334 and 3407 G. The much narrower 3407-G feature dominates at low Cu loadings (IE 23%) but becomes a shoulder peak at higher Cu loadings (IE ≥ 60%). For all samples, however, hyperfine features at low field are barely detectable. Presumably, this behavior is caused by a combination of (1) facile Cu2+ ion mobility and (2) strong dipolar interactions between Cu2+ ions.

In order to decrease Cu2+ ion mobility and allow only dipole-dipole interactions to be monitored, additional EPR measurements were performed at 155 K. As shown in Fig. 2, in this case, only a single spectral feature is found at high field (3334 and 3407 G). The much narrower 3407-G feature dominates at low Cu loadings (IE 23%) but becomes a shoulder peak at higher Cu loadings (IE ≥ 60%). For all samples, however, hyperfine features at low field are barely detectable. Presumably, this behavior is caused by a combination of (1) facile Cu2+ ion mobility and (2) strong dipolar interactions between Cu2+ ions.

Fig. 2. EPR spectra of hydrated Cu-SSZ-13 samples measured at 155 K. Samples with different ion-exchange levels are displayed with different colors. The insert displays integrated signal areas versus ion-exchange levels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 1. EPR spectra of hydrated Cu-SSZ-13 samples measured at 294 K. Samples with different ion-exchange levels are displayed with different colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)

Fig. 4a depicts TPR curves for the hydrated Cu-SSZ-13 samples. Although these samples are initially hydrated, during ramping, both dehydration and Cu ion reduction are expected. Based on our previous study [14] and TPR spectra for dehydrated samples (heated to 823 K for 30 min in dry N2 before TPR measurements, shown in Fig. S2), the low-temperature reduction features (Cu2+ to Cu+, below ~800 K) are assigned as the following: the 640-K feature is attributed to reduction in dehydrated Cu2+ ions close to 6-membered rings; the 488-K feature is assigned to reduction in hydrated Cu2+ ions; and the ~530-K feature is assigned to reduction in dehydrated Cu2+ ions within the large CHA cages close to 8-membered rings. Note that this feature only occurs at IE levels of 60% and higher. Note also that all Cu2+ ions are hydrid prior to the TPR experiments. For the 530- and 640-K reduction states, dehydration occurs prior to reduction. For all the samples, full reduction from Cu2+ to Cu0 occurs at much higher temperatures (1157 K). Interestingly, however, for the IE 80% and 90% samples, a weak and broad reduction feature is also found (centered at ~886 K). We note also that, if the reduction experiments...
are stopped at 933 K, samples at IE levels of 60% and lower display a white color demonstrating the existence of Cu\(^+\) moieties. However, for the IE 80% and 90% samples, the slight purplish color means formation of a small amount of Cu\(^0\), although the majority of Cu\(^+\) is fully reduced at much higher temperatures.

For these TPR data, the integral H\(_2\) consumption peak areas below 800 K, above 800 K and the total areas are plotted in Fig. 4b as a function of Cu loading. First of all, the total H\(_2\) consumption areas vary linearly with Cu loadings as one would expect. For samples at IE levels \(\leq 60\%\), the integrated peak areas for low- and high-temperature reduction states are equal. However, for the IE 80% and 90% samples, the high-temperature peak areas are measurably smaller than the low-temperature peak areas. Since isolated Cu\(^{2+}\) ions have two reduction states (Cu\(^{2+}\) to Cu\(^+\) at lower temperatures and Cu\(^+\) to Cu\(^0\) at higher temperatures), and both states consume identical amount of H\(_2\) during TPR [25], it is concluded that for samples at IE levels \(\leq 60\%\), no Cu\(^6\) formation occurs below 800 K. However, for IE 80% and 90% samples, ~7.9% and \(~\sim 11\%) of Cu species, respectively, are reduced to Cu\(^6\) even below 800 K. Based on this analysis, the weak 860-K reduction state found for IE 80% and 90% samples is best assigned to reduction from Cu\(^+\) to Cu\(^0\). The nature of the readily reducible Cu species below 800 K is discussed in more detail below. In any case, extensive reduction from Cu\(^+\) to Cu\(^0\) is only expected when the Chabazite structure begins to degrade. The extremely high reduction temperature (~1157 K) found here is consistent with the excellent hydrothermal stability of the Cu-SSZ-13 catalysts.

Since Cu-SSZ-13 catalysts have smaller pore openings than other relevant NH\(_3\)-SCR zeolites, and since typical reactant mixtures contain very low concentrations of NO\(_x\) and NH\(_3\), SCR reactions were first conducted to search for kinetically benign (i.e., mass-transfer limitation free) regimes. Fig. S3a and c presents standard SCR reaction results for IE 23% and 90% Cu-SSZ-13 catalysts at various space velocities. In the absence of inter-particle mass-transfer limitations, NO\(_x\) conversion is expected to increase \(n\)-fold as the space velocity decreases \(n\)-fold. Based on this criterion, NO\(_x\) conversion ratio data displayed in Fig. S3b and d suggest that, for Cu-SSZ-13 samples at low Cu loadings (e.g., IE 23%), inter-particle mass-transfer limitation is more than 95% free under GHSV \(\geq 400,000 \text{ h}^{-1}\) and temperature \(\leq 448\) K conditions. For Cu-SSZ-13 samples at high Cu loadings (e.g., IE 90%), inter-particle mass-transfer limitation is more than 90% free under GHSV \(\geq 400,000 \text{ h}^{-1}\) and temperature \(\leq 423\) K conditions.

Fig. S4 presents reaction results of standard SCR at a high-space velocity (~800,000 h\(^{-1}\)) over Cu-SSZ-13 samples with the same weight (15 mg) but various Cu loadings. Reaction data on an H-SSZ-13 sample are also included. At reaction temperatures below \(~450\) K, these data clearly demonstrate that the SCR reaction is essentially only carried out on Cu sites, while the zeolite framework itself does not directly contribute to the activity. Note that in the differential regime (NO\(_x\) conversion \(\leq 15\%) and temperature \(\leq 423\) K, marked gray in Fig. S4), NO\(_x\) conversions over the IE 23% sample are lower than the higher Cu loading sample. For the latter samples, there are only slight differences in NO\(_x\) conversions as a function of Cu loadings at the same reduction temperatures. It is important to note, however, that inter-particle mass-transfer limitations can be safely ruled out in this regime based on the results displayed in Fig. S3. NO\(_x\) conversions level off at reaction temperatures higher than \(~500\) K. In this regime, NO\(_x\) conversions increase with Cu loadings up to IE 60%. For samples with Cu loadings higher than IE 23%, NO\(_x\) conversions slightly decrease at \(~650\) K and above; this is due to non-selective NH\(_3\) combustion as shown previously [9,10,12,15]. In this case, NO\(_x\) conversions are adversely affected by the availability of NH\(_3\).

Using reaction data shown in Fig. S4, Arrhenius plots in the differential regime are created by calculating NO\(_x\) turnover
frequencies (TOF) on a per mole of Cu basis. As displayed in Fig. 5, all five samples give similar apparent activation energies of ~62 kJ/mol suggesting identical rate determining mechanisms irrespective of Cu loading. The decrease in TOF with increasing Cu loading (i.e., inefficient utilization of Cu\(^{2+}\) ion catalytic centers) could be explained in two ways: (1) some Cu\(^{2+}\) ions are much more active than the others; or (2) the SCR reaction is controlled by intra-particle diffusion limitations (again from Fig. S3, inter-particle diffusion limitations can be safely ruled out). This will be discussed in more detail below.

Non-selective NH\(_3\) oxidation is the major side reaction in NH\(_3\)-SCR that affects NO\(_x\) conversions. In the following, this reaction is probed over the five Cu-SSZ-13 samples. Again, reactions were first conducted to search for kinetically benign regimes by using catalysts at different Cu loadings and various space velocities. As shown in Fig. S5 for the IE 23% sample, no inter-particle limitations are evident at GHSV \(\geq\) 200,000 h\(^{-1}\) and reaction temperatures \(\leq 623\) K. Even for the IE 90% sample (which is much more active in NH\(_3\) oxidation), inter-particle limitations can be ruled out at GHSV \(\geq 400,000\) h\(^{-1}\) and reaction temperatures \(\leq 523\) K. Fig. S6 plots NH\(_3\) conversions as a function of reaction temperature at GHSV \(= 400,000\) h\(^{-1}\) for the five catalysts. It is important to note that NH\(_3\) conversions increase with increasing Cu loading in contrast to the data for SCR reaction. For the SCR reaction, as shown in Fig. S4, NO\(_x\) conversions are relatively unchanged with Cu loading (except the IE 23% sample) in the differential regime at the same reaction temperature. Furthermore, H-SSZ-13 does not have any activity in NH\(_3\) oxidation (data not shown), meaning that this reaction occurs exclusively on Cu sites.

Using data within the differential regime (for the high Cu loading samples, a few data points at somewhat higher conversions were also used) displayed in Fig. S6, NH\(_3\) TOFs were calculated on a per mole of Cu basis and shown in Fig. 6 in the form of Arrhenius plots. We note that, especially for samples at IE levels \(\leq 45\%\), all data points used for the Arrhenius plots are strictly within the kinetically benign regime (NH\(_3\) conversion <15% and free of external mass-transfer limitations). Interestingly, for all samples, two well-defined kinetic regimes are found below and above 523 K.

Apparent reaction activation energies are also tabulated in Fig. 6. For each sample, \(E_a\) values at 448–523 K (\(~130\) kJ/mol) are roughly two times higher than those at 523–573 K (\(~60\) kJ/mol).

Over ion-exchanged zeolite catalysts, the standard NH\(_3\)-SCR rate can be presented using the following power-law model [26,27] at steady state:

\[
-R_{\text{SCR}} = A \exp \left( \frac{-E_a}{RT} \right) (\text{NO})^a (\text{NH}_3)^b (\text{O}_2)^c
\]

Since O\(_2\) used in this study (as well as in all realistic standard SCR conditions) is in considerable excess, the above equation can be simplified as:

\[
-R_{\text{SCR}} = k(\text{NO})^a (\text{NH}_3)^b
\]

In the following, power-law dependences on NO and NH\(_3\) are probed over the Cu-SSZ-13 sample at an IE level of 90%, and the results are plotted in Fig. 7a and b, respectively. In this case, NO conversions are presented as NO\(_x\) TOFs; that is, moles of NO\(_x\) converted on a per mole of Cu basis. As shown in Fig. 7a, at three reaction temperatures within the differential regime (393, 423, and 473 K), \(x = 1.0 \pm 0.1\). Fig. 7b depicts the power-law dependence in NH\(_3\) partial pressure at 423 K. In this case, \(\beta = 0\). The same dependence is found at 393 and 473 K (data are not shown). Also, these same power-law dependences are found for other Cu-SSZ-13 samples. Overall, in the differential regime, the standard NH\(_3\)-SCR rate can be presented as the following:

\[
-R_{\text{SCR}} = k_a (\text{NO})^1
\]

where \(k_a\) is the apparent rate constant.

4. Discussion

4.1. Nature of Cu species in Cu-SSZ-13

To understand structure–activity relationships in Cu-SSZ-13 catalyzed SCR reactions, the nature of Cu-containing species within the SSZ-13 framework is first discussed. Three types of Cu species

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**Fig. 5.** Arrhenius plots of NO\(_x\) conversion (in TOF, mol NO\(_x\)/mol Cu/s) over Cu-SSZ-13 catalysts with different ion-exchange levels. TOFs were calculated using reaction data shown in Fig. S4 within the differential regime. Samples with different ion-exchange levels are displayed with different colors and symbols. Reaction mixtures contain 350 ppm NO, 350 ppm NH\(_3\), 14% O\(_2\), 2.5% H\(_2\)O balanced with N\(_2\), at a GHSV \(= 800,000\) h\(^{-1}\).

**Fig. 6.** Arrhenius plots of NH\(_3\) conversion (in TOF, mol NH\(_3\)/mol Cu/s) during non-selective NH\(_3\) oxidation over Cu-SSZ-13 catalysts with different ion-exchange levels. TOFs were calculated using reaction data shown in Fig. S6. Samples with different ion-exchange levels are displayed with different colors and symbols. Reaction mixtures contain 350 ppm NH\(_3\), 14% O\(_2\), 2.5% H\(_2\)O balanced with N\(_2\), at a GHSV \(= 400,000\) h\(^{-1}\).
are common for Cu-zeolites: charge-balancing extra-framework Cu$^{2+}$ monomers, charge-balancing [Cu–O–Cu]$^{2+}$ dimers and CuO$_x$ clusters [28]. Fickel and Lobo applied Rietveld refinement for TR-XRD data of their dehydrated Cu-SSZ-13 catalyst at an ion-exchange level of 70% (4.39 wt.% Cu, Si/Al = 6 and Cu/Al = 0.35) [11] and did not suggest any Cu species other than Cu$^{2+}$ monomers. In another study by Korhonen et al. [16], absence of Cu-dimers was again confirmed on their Cu-SSZ-13 sample (Si/Al = 9 and 2.9 wt.% Cu). In the present study, the linear relationship between Cu loading and EPR signal intensity shown in Fig. 2 clearly rules out [Cu–O–Cu]$^{2+}$ dimers and CuO$_x$ clusters as these species are well known to be EPR silent [22–24]. However, this conclusion is drawn on fully hydrated samples at (sub)-ambient temperatures. According to the hexagonal unit cell stoichiometry of H-SSZ-13 used in this study (H$_{0.14}$Al$_{1.45}$Si$_{30.86}$O$_{72}$), an average IE = 39% corresponds to one Cu$^{2+}$ ion in one unit cell, and IE 78% corresponds to two Cu$^{2+}$ ions in one unit cell. Thus, for the IE 80% and 90% samples, Cu-dimer formation is possible during dehydration according to the following reaction pathway [28, and references therein]:

\[-\text{Al}–\text{O}–\text{Cu}$^{2+}$–\text{OH} + \text{–Al}–\text{O}–\text{Cu}$^{2+}$–\text{OH} \rightarrow \text{–Al}–\text{O}–\text{Cu}–\text{O}–\text{Cu}$^{2+}$–\text{–O}–\text{Al}– + \text{H}_2\text{O}\]

From the H$_2$ consumption peak area analysis shown in Fig. 4b, we indeed cannot completely rule out this possibility since the IE 80% and 90% samples contain up to ~10% of Cu species that are apparently reduced to Cu$^0$ below 800 K. In particular, one possible explanation for this result is that during TPR, up to ~10% [Cu–O–Cu]$^{2+}$ dimers do form, and these are readily reduced to metallic Cu below 800 K. The more facile reduction in Cu-dimers compared to Cu ion monomers has been confirmed previously [29]. For samples with lower Cu loadings, Cu$^0$ formation occurs exclusively above 800 K; therefore, dimer formation is safely excluded. We note that this Cu-dimer formation reaction, even if it occurs, must be reversible as evidenced from the EPR spectra area analysis of the fully hydrated samples (Fig. 2). Since diesel engine after-treatment catalytic convertors inevitably operate under humid conditions with light-off temperatures typically as low as 473 K, Cu-dimers are not expected to play a significant role for the Cu-SSZ-13 catalysts even at high Cu loadings. In the following, only the dominant and more relevant Cu$^{2+}$ ion monomers are considered.

### 4.2. Cu$^{2+}$ monomer locations in hydrated Cu-SSZ-13

To visually aid the understanding of Cu ion monomer locations, a schematic of the hexagonal unit cell is illustrated in Fig. 8 (double 6-membered ring prism on top and large cage on the bottom). Note that the unit cell dimensions are the following: $a = b = 13.461$ Å and $c = 15.044$ Å [11]. We emphasize that only under dehydrated conditions and at low Cu loadings, can Cu$^{2+}$ ions be located within the face of 6-membered rings (position A, Fig. 8) [11,19]. Under wet reaction conditions, specifically at relatively low temperatures
where H₂O and NH₃ strongly bond to the Cu²⁺ ion centers, they no longer occupy these positions due to their weaker interactions with lattice oxygens. For example, as displayed in Fig. 1, the lack of hyperfine structure and the appearance of double high-field features for EPR spectra of the hydrated samples at ambient temperature clearly demonstrate Cu²⁺ ion mobility. In the presence of H₂O and/or NH₃, several scenarios are expected: (1) At low Cu loading (no more than one Cu²⁺ ion in one unit cell), Cu²⁺ ions will move slightly into the large cage and relocate at position A (Fig. 8) as recently suggested by Deka et al. [19]. (We note that it is not possible to precisely locate Cu²⁺ ion positions under dynamic reaction conditions; therefore, this, and the following positions are only reasonable speculations.) For a structurally similar material, Cu-SAPO-34, a Cu²⁺ ion location at A was also suggested for low exchange levels and hydrated conditions [30]. (2) As the Cu loadings increase to such an extent that two Cu²⁺ ions are located in one unit cell, we propose that the second Cu²⁺ will be located in position B (equivalent to position C in the neighbor unit cell) if it stays close to a 6-membered ring or, instead, inside the large cage close to an 8-membered ring (for example, positions D, E or their equivalents). Our recent temperature-programmed reduction and FTIR studies provide good evidence that some Cu²⁺ ions must be located inside the large cages and close to 8-membered rings at high Cu loadings. Notably, positions A–C shown in Fig. 8 are equivalent positions; therefore, two TPR Cu reduction features with rather different temperatures found experimentally are inconsistent with all Cu²⁺ ions being positioned close to 6-membered rings [14]. TPR results displayed in Figs. 4 and S2 in the present study further corroborate this argument. Specifically, the ~530 K reduction features at IE levels of 60% and higher clearly demonstrate the existence of more easily reducible Cu²⁺ ions within the large CHA cages. Furthermore, Cu–Cu distances of 5–10 Å (Fig. 3) are best assigned such that two Cu²⁺ ions are located within one unit cell; one is close to a 6-membered ring while the other being close to an 8-membered ring. For example, Cu²⁺ ions at positions A and E in Fig. 8 meet these criteria. A Cu–Cu distance of 4–5 Å can be assigned in a similar way, with locations A and D being consistent with these smaller Cu–Cu distances. Alternatively, these short Cu–Cu distances could be assigned to two Cu²⁺ ions in mirror positions of two unit cells (for example, positions A and C in Fig. 8). We note that CuO₄ cluster formation is safely excluded since in that case, much shorter Cu–Cu distances are expected. Indeed, the inset shown in Fig. 2 rather convincingly rules out EPR silent CuO₄.

Despite the Cu²⁺ location differences, in the fully hydrated form, only a single hyperfine structure is found with δ|| = 2.394 and η|| = 131 G for samples with various ion-exchange levels (Fig. 2). Previous studies with Cu-ZSM-5 [22,23] revealed relationships between δ|| values and Cu²⁺ ion coordination. Briefly, δ|| = 2.27 indicates square planar coordination; δ|| = 2.33 corresponds to square pyramidal coordination; and δ|| = 2.38 is assigned to octahedral coordination. Recently, Sultana et al. [24] suggested that these assignments can be used on other types of Cu²⁺-exchanged zeolites. Accordingly, for the hydrated Cu-SSZ-13 samples used in this study, Cu²⁺ ion coordinations are best described as [CuO₄]⁶⁺, where O(1) are lattice oxygen atoms that coordinate with Cu²⁺. In a recent study by Ribeiro and coworkers [17], hydrated Cu-SSZ-13 at ambient temperatures was found to display identical XANES spectra as [Cu(H₂O)₆]²⁺. Therefore, both EPR and XANES measurements demonstrate octahedral coordination of Cu²⁺ ions in a fully hydrated form. The single set of hyperfine structure shown in Fig. 2, however, suggests that EPR is unable to differentiate hydrated Cu²⁺ ions at different locations. As is expected, even in the presence of moisture, as the temperature rises, gradual dehydration should occur and Cu²⁺ ions will move closer to the face of 6- or 8-membered rings where they coordinate stronger with lattice oxygen atoms. Unfortunately, for hydrated samples, the hyperfine structures tend to disappear even at ambient temperature (see, for example, Fig. 1) so that g-value analysis from EPR cannot be used to capture such changes. In contrast, Fickel and Lobo were able to obtain such changes via XRD simulations [11]. They found that the average Cu–O bond length gradually decreases as the temperature rises and becomes unchanged above ~673 K. This temperature can be deemed as the temperature at which complete dehydration occurs.

4.3. NH₃ oxidation over Cu-SSZ-13, structure–activity relationships

From the reaction data shown in Fig. 55, kinetic regimes free from inter-particle mass-transfer limitations can be readily obtained for the NH₃ oxidation reaction. This allows for the determination of the kinetically benign reaction data points (NH₃ conversion <15% as well as free from external limitations) displayed in Fig. S56. Using these data (and a few data points somewhat outside of the differential regime), Arrhenius plots shown in Fig. 6 clearly define two kinetic regimes: below 523 K with Eₚ ~ 130 kJ/mol and above 523 K with Eₚ ~ 60 kJ/mol.

Importantly, by comparing Figs. 4 and 6, a clear correlation can be made between the reducibility of Cu²⁺ ions and the NH₃ oxidation activities, where the easier Cu²⁺ ions are reduced, the higher the average oxidation activities are. This most certainly demonstrates that NH₃ oxidation over Cu-SSZ-13 follows a redox mechanism. There are two possible explanations for the NH₃ oxidation activity enhancement with increasing Cu loadings. First, the electrostatic interaction between Cu²⁺ ions and the SSZ-13 framework decreases as the Cu loading increases. This renders redox cycling between Cu²⁺ and Cu⁺ more facile at higher Cu loadings thus facilitating NH₃ oxidation. Second, as the Cu loading increases, more Cu²⁺ ions are placed closer to the pore openings and become more accessible to NH₃ and O₂. Moreover, for the IE 80% and 90% samples, NH₃ oxidation activity increases dramatically above ~548 K (see, for example, Fig. S55c). Possibly, the (reversible) formation of Cu-dimers is responsible for this enhancement.

The reason for the appearance of two distinct kinetic regimes below and above 523 K even within the differential conditions as shown in Fig. 6 is less clear. There are a few possibilities. First, it is possible that NH₃ oxidation below 523 K is kinetically limited but becomes intra-particle diffusion (also called configurational diffusion) limited above 523 K. Under intra-particle diffusion limitations, reaction kinetics are affected by both reaction and mass-transfer limitations. Correspondingly, the apparent activation energies within the differential regime are given by [31]:

\[ E_a = \frac{E_k + E_0}{2} \]  

where \( E_a \) is the apparent activation energy, \( E_k \) is the intrinsic activation energy, and \( E_d \) is the diffusion activation energy of reactants within the zeolite channels. Note that under kinetic control, \( E_a = E_k \). The apparent activation energies displayed in Fig. 6 can be understood in the following way: below 523 K, the measured activation energies are intrinsic activation energies. Above 523 K, the measured activation energies are determined by Eq. (4). This indicates that ammonia diffusion within the channels of Cu-SSZ-13 is non-or weakly-activated (i.e., \( E_d \sim 0 \text{ kJ/mol} \)) above ~523 K.

Alternatively, the appearance of the two kinetic regimes below and above 523 K might reflect coordination changes of the catalytic center. By examining TPR curves of hydrated (Fig. 4a) and dehydrated (Fig. S2) Cu-SSZ-13 samples, the largest difference is the 488 K feature that is assigned to reduction in hydrated Cu²⁺ ions. Since this feature is only detected on hydrated samples, this allows one to roughly estimate the dehydration temperatures for Cu-SSZ-13 to be ~488–530 K. Fig. S7 displays a series of NH₃ temperature-programmed desorption (TPD) spectra on
Cu-SSZ-13, demonstrating that NH₃ begins to desorb from the Cu²⁺ ion centers at ~500 K. Note that these desorption temperatures are rather close to 523 K where the two kinetic regimes are separated (Fig. 6). As H₂O and NH₃ desorb from the Cu²⁺ ion centers, one expects that the coordination of these centers with the zeolite framework also changes. Presumably, this can cause changes of their catalytic properties and might be reflected by the apparent activation energy change displayed in Fig. 6.

4.4. NH₃-SCR over Cu-SSZ-13, mass-transfer limited kinetics

In the introduction section, we addressed the significance of the small-pore opening structure of Cu-SSZ-13 (3.8 Å) for the success of this material as an NH₃-SCR catalyst. This structure, however, brings extra complexities for understanding the SCR kinetics. Table 1 presents kinetic diameters of molecules most relevant to NH₃-SCR [32]. Clearly, these molecules have kinetic diameters very close to the openings of the Chabazite structures indicating that intra-particle diffusion limitations are possible for rapid reactions like NH₃-SCR. Recently, Metkar et al. systematically studied mass-transfer limitations for NH₃-SCR for layered Cu(Fe)-ZSM-5 catalysts. They observed washcoat limitations for the standard SCR reaction on both Fe-zeolite (>623 K) and Cu-zeolite (>523 K) catalysts, whereas for fast SCR and NO₂-SCR, diffusion limitations (both external and internal) were observed throughout the temperature range explored (473–823 K) [33].

Arrhenius plots displayed in Fig. 5 show that NOx TOFs decrease as the Cu loading increases. However, all five catalysts show similar apparent reaction activation energies suggesting an identical rate-controlling mechanism. In the following, we demonstrate that the reaction kinetics are intra-particle diffusion limitation controlled. First, in this temperature range (400–440 K), reaction rates fall safely within the differential regime, and inter-particle diffusion limitations can be ruled out (Figs. S3 and S4). Secondly, it seems highly unlikely that as the Cu loading increases, the SCR activity for individual Cu²⁺ ions decrease. This follows since (1) at high Cu loadings, more Cu ions are populated closer to pore openings (i.e., more readily accessible to reactants); and (2) redox cycling between Cu²⁺ and Cu⁺ becomes more facile at higher Cu loadings due to the weaker interactions between Cu and the zeolite framework. Indeed, for the much slower NH₃ oxidation reaction, activity increases with increasing Cu loadings (Fig. 6). Intra-particle limitation, on the other hand, nicely explains the NOx TOF decrease with increasing Cu loading due to the inefficient utilization of Cu active centers. In this case, the apparent activation energy is determined by Eq. (3). For Cu(Fe)-zeolite materials with larger pores where intra-particle diffusion may be less of an issue, activation energies typically fall in the range of 40–60 kJ/mol [8,7,34–36]. Assuming that these are intrinsic activation energies and noting the standard NH₃-SCR Eₚ for Cu-SSZ-13 of ~62 kJ/mol (Fig. 5) gives an estimated E₀ of 60–80 kJ/mol according to Eq. (3). This high reactant diffusion activation energy is not surprising. Since it is known that zeolite NH₃-SCR catalysts store large amounts of NH₃ but little NO, it is reasonable to assume that NH₃ is the major diffusion-limited reactant. Note also that typical SCR reactants contain large amounts of H₂O (in the present study, NH₃/H₂O ratios are ~1/70).

In the differential regime for NH₃-SCR (400–440 K), H₂O and NH₃ are not expected to be very mobile and highly activated diffusion is very reasonable. Interestingly, NH₃ diffusion may become non-activated at temperatures ≥523 K if one assumes, as displayed in Fig. 6, that the apparent activation energy decrease above 523 K is due to intra-particle limitations.

The extent to which diffusion transport limits the reaction rate can be quantified using the Thiele relationship, giving the catalyst effectiveness factor (η), as a function of Thiele modulus ϕ [31,38]. The functional relationship between the effectiveness factor and the parameter ϕ depends on the geometry of the crystal and the kinetic order of the reaction. For the Cu-SSZ-13 powder catalysts used in this study, the crystal geometry can be approximated as spheres with a radius of 1 µm (1 × 10⁻⁶ m) [11]. Since both O₂ and H₂O are in considerable excess, the power-law dependence in the differential regime is simplified as a first-order reaction: –R_SCR = kₐ(NO), where kₐ is the apparent rate constant. The validity of this treatment is clearly demonstrated by data shown in Fig. 7. Note that this simplification is generally accepted in SCR reactions over other ion-exchanged zeolites [26]. With both assumptions, that is, spherical catalyst particles and first-order reaction, the effectiveness factor (η) is given as follows [39]:

\[
\eta = \frac{3}{\phi} \left( \frac{1}{\tan h \phi} - \frac{1}{\phi} \right)
\]

The Thiele modulus is defined by

\[
\phi = r \sqrt{\frac{k}{D}}
\]

where r is the average radius of the catalyst particles crystals (m), k is an intrinsic reaction rate constant (s⁻¹), and D is an effective diffusivity (m² s⁻¹). The intrinsic and apparent reaction rate constants follow a very simple relationship [36]:

\[
k = \frac{k_o}{\eta}
\]

For zeolite catalysts, mass-transfer limitations for NH₃-SCR become negligible (i.e., effectiveness factor close to unity) below ~573 K for D values larger than ~1 × 10⁻⁸ m² s⁻¹ [36]. For zeolites in the powder form, inter-particle diffusivity generally falls in between 1 × 10⁻⁶ and 1 × 10⁻⁷ m² s⁻¹, while intra-particle diffusivity varies widely from 1 × 10⁻⁶ to 1 × 10⁻²⁰ m² s⁻¹ for hydrocarbons [40,41]. For NH₃-SCR, intra-particle diffusion limitations may also be the dominating limitation factor for zeolite powder catalysts. Results from the present study clearly indicate that this is the case for Cu-SSZ-13. In the following, effective diffusivities of the reaction gas molecules within the channels of Cu-SSZ-13 samples are estimated, using a reaction temperature of 423 K as the example.

Two assumptions are made in order to obtain numerical solutions for these estimations: (1) all Cu²⁺ ions within the catalysts are active in NH₃-SCR, and they have identical activities. As discussed above, there is no solid reason to assume that certain Cu ions are less active than the others; and (2) the effective diffusivity D decreases linearly with increasing Cu loading. This latter assumption is derived from our reaction data. As the Cu loading increases, more Cu²⁺ ions are populated near 8-membered rings (i.e., close to pore openings), it is rather conceivable that these species, especially when coordinating with H₂O/NH₃ molecules, effectively hinder pore diffusion at low temperatures. To start the estimation, η = 1 is arbitrarily chosen for the IE 23% sample. Based on reaction results shown in Fig. 4 and the first assumption described immediately above, effectiveness factors for the other four samples are obtained. Using Eq. (5), Thiele moduli for these samples are then

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinetic diameter (Å)</th>
<th>Molecule</th>
<th>Kinetic diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>2.6</td>
<td>O₂</td>
<td>3.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.7</td>
<td>N₂</td>
<td>3.6</td>
</tr>
<tr>
<td>NO</td>
<td>3.2</td>
<td>CO</td>
<td>3.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.3</td>
<td>CH₄</td>
<td>3.8</td>
</tr>
<tr>
<td>N₂O</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
calculated. Next, by using \( r = 1 \times 10^{-6} \text{ m} \) [11] and \( k_0 = 133 \text{ s}^{-1} \) that we recently obtained for the same reaction system at 423 K [12], as well as Eqs. (6) and (7), effective diffusivities for the 4 higher Cu loading samples are calculated. Then, by using the second assumption shown above, the effective diffusivity for the IE 23% sample is estimated via linear fitting and extrapolation of the effective diffusivities for the 4 higher Cu loading samples. By bringing this value back to Eq. (6), a new \( \phi \) is calculated. Using this new \( \phi \) to solve Eq. (5), a new effectiveness factor \( \eta \) is obtained for the IE 23% sample. Using this new \( \eta \), the next cycle of calculations is carried out. The process is repeated until effectiveness factors during two consecutive calculations differ by less than 2%. As shown in Fig. 9, eight cycles of calculations are sufficient to obtain the final \( \eta \) values.

Table 2 lists the catalyst effectiveness factors \( \eta \), Thiele moduli \( \phi \) and effective diffusivities \( D \) (m\(^2\) s\(^{-1}\)) in NH\(_3\)-SCR for the five Cu-SSZ-13 catalysts at 423 K. These values, especially \( \phi \geq 5 \) for all the samples, indeed, demonstrate significant intra-particle diffusion limitations [38].

Diffusivities and diffusion activation energies for zeolite systems can be expressed as the following Arrhenius-type relationship:

\[
D = D_0 \exp \left( \frac{-E_u}{RT} \right)
\]

(8)

where \( D_0 \) is the pre-exponential term (i.e., diffusivity at infinite temperatures) [40,41]. In the following, this equation is used to test the reliability of the diffusivities we calculated. We are unaware of any published diffusivity values for small molecules in SSZ-13. The closest value that is useful to compare with is a \( D \) value for CH\(_4\) in 4A molecular sieves at 300 K, which is \( 1.2 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \) [42]. We have shown in Fig. 9 and Table 2 that diffusivity is heavily affected by Cu content in SSZ-13, so a direct comparison between 4A molecular sieve and the Cu-free H-SSZ-13 may be more meaningful. Bear in mind that (1) the pore openings for 4A and H-SSZ-13 are similar, and both materials have 3-dimensional channels, and (2) O\(_2\), N\(_2\), NO, NH\(_3\) and H\(_2\)O have kinetic diameters close to or smaller than CH\(_4\) (Table 1). Thus, it is assumed that the value \( 1.2 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \) can be judged as a lower diffusivity limit for the NH\(_3\)-SCR relevant gases in H-SSZ-13 at 300 K. Note that the same assumption has been suggested previously [36]. Using diffusivity numbers listed in Table 2 and a monotonic relationship between Cu content and diffusivities, a simple extrapolation allows for the \( D \) value at zero Cu loading (i.e., H-SSZ-13) to be estimated as \( D_{D_{300K}}=1.26 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \). Note that by using Eq. (4), \( E_u \) values are estimated between 60 and 80 kJ/mol. By using Eq. (9) derived from Eq. (8),

\[
D_1 \exp \left[ \frac{E_D}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right]
\]

(9)

\( D_{D_{300K}} \) for H-SSZ-13 are calculated, and the values are between \( 1.16 \times 10^{-14} \) and \( 1.13 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \). Apparently, values derived from our estimations are rather close to the literature value for CH\(_4\) in 4A molecular sieves (\( 1.2 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \)). This strongly suggests that our diffusivities and diffusion activation energy estimations are reasonable. We also note that the diffusivity of CH\(_4\) in ZSM-5 is \( (6.5 \pm 1.0) \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \) [43]. This value is consistent with the much lower diffusion limitations for standard SCR over ion-exchanged ZSM-5 powder catalysts [36].

The diffusion-limited kinetics for NH\(_3\)-SCR for Cu-SSZ-13 catalysts at low temperatures found in this study are technically important suggesting in SCR modeling, catalyst design and optimization of CHA-type catalysts, both washcoat and pore diffusion limitations, should be considered. From a more fundamental point of view, unfortunately, good structure–activity relationships are difficult to obtain for the CHA system because of the complex mass-transfer limitations. Still, important information regarding the catalytic centers can be obtained. From the calculated diffusivity results shown in Table 2, it is expected that, at least at relatively low temperatures, some Cu\(^{2+}\) ions are located close to pore openings and coordinated with H\(_2\)O and NH\(_3\) molecules such that these moieties effectively limit mass transfer. The higher the Cu loadings are, the more severe mass-transfer limitations become. We note again that only at low Cu loading and for dehydrated conditions are position A (Fig. 8) occupied; as these sites are not expected to adversely affect diffusivity of reactants inside the SSZ-13 channels. Therefore, we conclude that the EPR and TPR characterizations and reaction kinetics are consistent with one another in terms of Cu\(^{2+}\) locations at low temperatures and humid conditions.

Furthermore, it has been shown recently by us [10] and others [17] that, at relatively low temperatures (e.g., 473 K), SCR reaction rates (freshly prepared catalysts, on a per Cu atom basis) over Cu-ZSM-5 and Cu-Beta are a few times higher than over Cu-CHA catalysts. Based on results shown in the present study, this may be better explained by the more severe mass-transfer limitations for the Cu-CHA system, rather than intrinsic activity differences of Cu\(^{2+}\) centers within different zeolite frameworks. In a very recent SCR study over Cu-SSAPO-34 by Wang et al. [44], the authors were able to exclude external mass-transfer limitations yet could not explain the low reaction activation energy (9.8 kJ/mol) they obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IE 23%</th>
<th>IE 45%</th>
<th>IE 60%</th>
<th>IE 80%</th>
<th>IE 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effectiveness factor (( \eta ))</td>
<td>0.485</td>
<td>0.372</td>
<td>0.313</td>
<td>0.236</td>
<td>0.186</td>
</tr>
<tr>
<td>Thiele modulus (( \phi ))</td>
<td>4.93</td>
<td>6.89</td>
<td>8.45</td>
<td>11.6</td>
<td>15.1</td>
</tr>
<tr>
<td>Effective diffusivity ( D ) at 423 K (m(^2) s(^{-1}))</td>
<td>(1.02 \times 10^{-11})</td>
<td>(7.96 \times 10^{-12})</td>
<td>(6.33 \times 10^{-12})</td>
<td>(4.37 \times 10^{-12})</td>
<td>(3.32 \times 10^{-12})</td>
</tr>
</tbody>
</table>
Presumably, their results are better understood considering severe pore limitations for the CHA system.

5. Conclusions

(1) Cu-SSZ-13 powder catalysts with various ion-exchange levels were characterized with Electron Paramagnetic Resonance (EPR) and temperature-programmed reduction (TPR). At low ion-exchange levels (e.g. IE 23%), Cu²⁺ ions are in far apart suggesting one Cu²⁺ ion within one hexagonal unit cell. In this case, hydrated Cu²⁺ ions are octahedrally coordinated at ambient temperatures supporting these are located within the large CHA cages yet still coordinated to lattice oxygen atoms of the 6-membered rings. As the Cu loading increases, it is possible for two Cu²⁺ ions to sit in one unit cell. The estimated Cu-Cu distances from EPR, as well as TPR results suggest some Cu²⁺ ions are located in the CHA cages and close to 8-membered rings. For IE ≥ 80% samples, a small amount (≤10%) of Cu species become readily reducible to Cu⁰ below 800 K. This may be due to reversible Cu ion dimerization.

(2) Standard NH₃-SCR reaction kinetics were measured at high-space velocities. Within the differential kinetic regime where inter-particle diffusion limitations are safely ruled out, NOx/TOFs decrease with increasing Cu loading. This demonstrates that the reaction kinetics are controlled by intra-particle diffusion limitations. Catalyst effectiveness factors were estimated using the Thiele relationship. The estimated effective diffusivities of the reactants were very reasonable by comparing with CH₄ diffusivities within 4Å molecular sieves. These results suggest that for the CHA SCR system, both washcoat and pore diffusion limitations should be considered for optimum practical application.

(3) For the much slower Non-selective NH₃ oxidation, reaction rates increase with increasing Cu loadings. This is attributed to: (1) the weaker interactions between Cu ions and the zeolite framework at higher Cu loadings. This allows for more facile Cu²⁺ ↔ Cu⁰ redox cycling and, thus facilitating NH₃ oxidation. (2) At higher Cu loadings, the catalytic centers are located closer to pore openings and become more accessible to reactants. Even under differential reaction conditions free from inter-particle limitations, two kinetic regimes below and above 523 K were found with dramatically different apparent activation energies. This is either due to a change in rate limiting mechanism or, alternatively, a change in the coordination of the Cu ion catalytic centers that imparts different reactivity.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.02.020.

References