New insights into Cu/SSZ-13 SCR catalyst acidity.

Part I: Nature of Acidic Sites probed by NH₃ titration

Jinyong Luo^{1,*}, Feng Gao², Krishna Kamasamudram¹, Neal Currier¹, Charles H. F. Peden²,
Aleksey Yezerets^{1,*}

¹ Cummins Inc, Columbus, IN 47201 USA

² Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, United States

Abstract

In this work we investigated an unusual acidity feature of a Cu/SSZ-13 catalyst used in selective catalytic reduction of NO_x with NH₃ (NH₃-SCR). In particular, this catalyst showed two distinct NH₃ desorption peaks in NH₃-TPD measurements, in contrast to single, unresolved desorption peaks observed for other Cu-exchanged zeolites conventionally used in the SCR studies, including its isostructural but chemically different analogue Cu/SAPO-34. We further observed that the intensities of the two TPD peaks, which represented the amount of stored NH₃, changed in opposite directions in response to progressive mild hydrothermal aging, while the total storage capacity was preserved. We proposed an explanation for this remarkable behavior, by using model reference samples and additional characterization techniques. At least three NH₃ storage sites were identified: two distinct populations of Cu sites responsible for low-temperature NH₃ storage, and Brønsted acid sites responsible for high-temperature NH₃ storage. Contrary to the commonly accepted mechanism that Brønsted acid site loss during hydrothermal aging is driven by dealumination, we concluded that the decline in the number of Brønsted acid sites upon *mild* hydrothermal aging for Cu/SSZ-13 was not due to dealumination, but rather transformation of Cu sites, i.e., gradual conversion of ZCuOH (Cu²⁺ singly coordinated with Zeolite) to Z₂Cu (Cu²⁺ doubly coordinated with Zeolite). This transformation was responsible for the increased low-temperature desorption peak in NH₃-TPD since each ZCuOH adsorbed ~1 NH₃ molecule while each Z₂Cu adsorbed ~2 NH₃ molecules under the conditions used here. These findings were used in Part II of this series of studies to develop a method for quantifying hydrothermal ageing of industrial Cu/SSZ-13 SCR catalysts.

Key words: Zeolite, SCR, SSZ-13, NH₃-TPD, hydrothermal aging, DRIFTS

* Corresponding authors.

Email: jinyong.luo@cummins.com (J. Luo), aleksey.yezerets@cummins.com (A. Yezerets)

1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH_3 derived from urea solution has evolved in recent years into the primary technology in order to meet the rapidly evolving environmental regulations worldwide. Cu-zeolite catalysts with a CHA structure, such as Cu/SAPO-34 and Cu/SSZ-13, gained particular popularity due to their unparalleled hydrothermal stability, high activity and high resistance to hydrocarbon poisoning, as compared with traditional metal-zeolite based catalysts, such as Fe- or Cu-Beta, ZSM-5, etc. [1-10].

Under real-world applications, two major degradation mechanisms exist for Cu/SSZ-13 SCR catalysts: sulfur poisoning and hydrothermal aging [11]. Sulfur poisoning originates from the cumulative exposure of the catalyst to sub-ppm levels of SO_x , in the form of SO_2 or $\text{SO}_3/\text{H}_2\text{SO}_4$. These SO_x species bind strongly to the Cu sites, leading to decreased interaction of Cu species with zeolite sites, decreased redox function of Cu sites and, therefore, decreased activity for NO_x reduction. Sulfur poisoning is typically reversible; adsorbed SO_x could be desorbed during active regeneration events, which are performed periodically to regenerate or de-contaminate the other components of the aftertreatment system, most notably combustion of soot accumulated in Diesel Particulate Filter. However, during these regeneration events conditions for hydrothermal aging are simultaneously created, since the catalysts are exposed to high temperatures, typically in excess of 500°C in the presence of water vapor. In this paper, we will exclusively focus on hydrothermal aging effects to Cu/SSZ-13, so that any references to aging are specific to this mechanism. Hydrothermal aging is typically irreversible due to permanent structural changes, such as the loss of zeolite Brønsted acid sites, and the corresponding changes in Cu site positioning. In turn, such structural changes can impact the performance of the catalyst, including suppressed NO_x reduction activity, oxidation functions, and NH_3 storage capacity [11-13].

Ammonia titration, e.g., NH_3 -TPD and NH_3 -FTIR, are commonly used to probe acidity changes of Cu/SSZ-13 catalysts caused by hydrothermal aging [14-20]. First, NH_3 is one of the SCR reactants, thus NH_3 storage/release properties probed by NH_3 -TPD are relevant for real-world NO_x reduction and NH_3 slip control; Second, NH_3 shows advantages over other basic probe molecules such as pyridine and n-propylamine for Cu/SSZ-13; this is due to the fact that pyridine and n-propylamine could not readily access to the CHA pores without appreciable mass-transfer limitations [17]; In terms of NH_3 -TPD on Cu/SSZ-13, I. Lezcano-Gonzalez reported three types of NH_3 desorption states, ascribed to NH_3 adsorbed on extra-framework Al species (below 200°C), Cu sites ($\sim 300^\circ\text{C}$) and Brønsted acid sites (above 400°C), respectively [15]; Gao et al. identified similar NH_3 desorption peaks [14], and discovered that the relative intensities of these peaks change as a function of hydrothermal aging [16]; NH_3 -TPD coupled with purging with wet carrier gas was successfully used by Gounder and coworkers to selectively probe Brønsted acid sites of Cu/SSZ-13 [17, 18], and to probe specific Cu sites (i.e., Cu^{2+} sites balanced by two framework Al atoms) through reduction treatment [19]. Efforts have also been made by Olsson and coworkers to model NH_3 -TPD profile of Cu/SSZ-13 catalysts. At least three sites are required for satisfactory simulations, including (i) Cu sites in six-member ring, (ii) Cu sites in large cages or CuOx sites, and (iii) weak physisorbed NH_3 at low temperatures [20].

Even though NH_3 titration has been extensively utilized to study Cu/SSZ-13 in the literature, the nature of the NH_3 adsorption sites, especially how they change during hydrothermal aging, is still not fully understood. As shown in this paper, alternative interpretations to the commonly accepted physical models are possible, allowing one to reconcile the results of various characterization techniques, applied to industrial catalysts with progressive hydrothermal aging history, or to model samples with tailored types of Cu species.

2. Experimental

2.1. Catalyst samples

A state-of-the-art Cu/SSZ-13 catalyst, coated on cordierite substrate with a cell density of 300 cells per square inch (cpsi), used in this work was purchased from market and the measured Si/Al and Cu/Al ratio were ~ 9.5 and 0.3 respectively. This translates to the Cu loading of $484 \mu\text{mol/g}$ (or $3.1 \text{ wt. } \%$) of washcoat material. Cylindrical catalyst samples with 1" diameter and 3" length ($2.54 \text{ cm} \times 7.62 \text{ cm}$) were used for evaluation in a laboratory reactor. The samples were aged at constant temperatures for different durations in humidified gas feed ($10\% \text{ O}_2$, $8\% \text{ CO}_2$, $7\% \text{ H}_2\text{O}$ with the balance of N_2). An H/SSZ-13 sample with the same Si/Al ratio and a Cu/SAPO-34 sample were also provided by the same provider from market.

Additional model Cu/SSZ-13 catalysts were prepared in-house using methodologies described elsewhere [14], in an attempt to provide reference samples that contain Cu species that are balanced by 1 or 2 negative framework charges, commonly referred to as ZCuOH or Z2Cu, respectively [14, 21]. One sample was prepared by using a SSZ-13 material with a high Si/Al ratio of 35 to minimize the population of Z2Cu species. The catalyst has a Cu/Al ratio of 0.62 . This catalyst is referenced here as Model_35. A second sample was prepared using a low Si/Al ratio zeolite of 6 in order to maximize Z2Cu population. This sample was ion-exchanged to a Cu/Al ratio of only 0.04 to guarantee a single population of Z2Cu sites. This catalyst is referenced in this paper as Model_6. To mimic the state-of-the-art catalyst for ^{27}Al NMR study and to avoid potential complexities caused by the cordierite support and other unknown additives/binders, a third model catalyst was prepared that has a Si/Al ratio of 12 and a Cu/Al ratio of 0.27 . This sample is referenced in this paper as Model_12.

2.2. Experimental Setup and Conditions

Experimental data were collected using a bench-flow reactor system described in detail previously [11-13]. Simulated exhaust gases (200 ppm NO , 200 ppm NH_3 , $10\% \text{ O}_2$, $8\% \text{ CO}_2$, $7\% \text{ H}_2\text{O}$, balance N_2) were fed to the catalyst sample at a total flow rate of 26 SLPM , corresponding to a gas hourly space velocity (GHSV) of approximately $40,000 \text{ h}^{-1}$. The effluent gas composition was analyzed by a high-speed MKS MultiGas 2030 FTIR. Hydrothermal aging was carried out at 600°C for varying durations in a base feed containing $10\% \text{ O}_2$, $8\% \text{ CO}_2$, $7\% \text{ H}_2\text{O}$, balance N_2 .

2.3. NH_3 Temperature programmed desorption (NH_3 -TPD)

Quantity and distribution of acid sites were probed by temperature-programmed desorption of ammonia (NH₃-TPD). Prior to NH₃-TPD, the catalyst was hydrothermally aged as described above, then saturated using 200 ppm NH₃ at a desired temperature, typically 200°C. The NH₃-TPD experiment was performed by ramping from 200 to 550°C, under a gas mixture of 8% CO₂, 7% H₂O and balance N₂, at a rate of 10°C/min. Note that oxygen was excluded from the TPD gas mixture, to avoid oxidation of ammonia at elevated temperatures.

2.4 DRIFTS characterization of Cu/SSZ-13

DRIFTS spectroscopy was used to characterize the Cu species in the samples at 35°C and to capture the surface adsorbed NH₃ species during NH₃-TPD. Cu/SSZ-13 powders, either the model samples or the commercial samples scraped from the cores, were examined in a DRIFTS setup (Nicolet 6700 spectrometer equipped with Praying Mantis DRIFTS cell and gas manifold). The samples were pretreated at 500°C in 10% O₂/Ar for 30 min prior to other measurements. i) For the characterization of Cu species, the samples were cooled to 35°C in 10% O₂/Ar, and then exposed to pure Ar before reference spectra acquisition. Afterwards, probe molecule NH₃ (200ppm/Ar) was introduced to the sample for ~2hrs, during which time DRIFTS spectra were continuously collected until they no longer change with time. ii) For capturing surface adsorbed NH₃ species during TPD, the pretreated samples were cooled to 50°C in the same gas feed, then exposed to 200 ppm NH₃/Ar until saturation. Then NH₃ was switched off, and the sample temperature was ramped up at 10°C/min. At 200°C and 350°C, DRIFTS spectra were collected while holding the temperatures constant for 5 mins.

2.5 H₂-TPR of Cu/SSZ-13

Temperature-programmed reduction by H₂ (H₂-TPR) was performed using a Micromeritics AutoChem II analyzer. Catalyst powders (85mg upon dehydration) were pretreated at 300°C for 30min in 5% O₂/He, followed by cooling down to room temperature under the same gas feed, then purged with He for 15 min prior to TPR. The TPR experiment was performed by ramping the temperature to 650°C at a heating rate of 10°C/min in 5% H₂/Ar. The total gas flow rate was kept at 30 ml/min. H₂ consumption was monitored with a TCD detector. The quantification of H₂ consumption was based on a calibration derived using set of reference Cu-containing samples with known amounts of Cu, derived using ICP analysis.

2.6 In-situ XRD

In-situ XRD was performed on a Philips PANalytical X'Pert MPD system with a vertical Θ - Θ goniometer (220 mm radius). The X-ray source was a long-fine-focus, ceramic X-ray tube with a Cu anode, operating at 45 kV and 40 mA. The sample was placed on a sample stage (Anton Paar HTK 1200, temperature range 25–1000 °C) and heated to and maintained at 600 °C in wet air flow (1L/min, containing ~2.5% water vapor by flowing through a bubble generator). At this temperature, scanning was conducted for 1 h each from 10 to 80° with a step size of 0.04°, and repeated for 16 times. Lattice parameters were calculated from whole-pattern fitting (Rietveld refinement) using TOPAS v4.2 (Bruker AXS GmbH, Germany).

2.7 ²⁷Al solid-state NMR

²⁷Al direct polarization (DP) experiments were conducted on a 20 Tesla Agilent VNMRs system utilizing a 1.6 mm HXY probe in DR mode tuned to 221.4119 MHz. A calibrated p/20 pulse of 0.30 ms with a recycle delay of 0.5 s was used to collect 32000 transients. Samples were spun at 34 kHz under a constant 20°C temperature. Time domain free induction decays were apodized with 150 Hz of Lorentzian broadening after zero filling twice.

3. Results and Discussion

3.1. *NH₃ release feature uniquely changes with aging state of Cu/SSZ-13*

NH₃-TPD profiles for Cu/SSZ-13 upon progressive aging at 600°C with different time durations are shown in Fig.1 (a). Two distinct NH₃ release peaks could be clearly observed, likely corresponding to two energetically distinct populations of acidic sites. Upon progressive aging, the low-temperature NH₃ peak intensifies with a concurrent decrease in the high-temperature peak. Remarkably, the overall NH₃ storage remained nearly constant with aging. The impact of hydrothermal aging on SCR performance of this catalyst can be found in our previous papers [11, 12].

Such well-resolved bi-modal NH₃ release profiles appear to be a unique feature for Cu/SSZ-13 catalysts, as compared to other Cu-SCR catalysts, such as Cu/Beta, Cu/ZSM-5, Cu/SAPO-34, etc [22, 23]. For example, as shown in Fig. 1(b), for a commercial Cu/SAPO-34 catalyst, iso-structural to Cu/SSZ-13, only one broad NH₃ desorption peak centered around 300°C was observed. Interestingly, the intensity and lineshape of the peaks do not change with aging durations. Other popular Cu/Zeolite SCR catalysts such as Cu/Beta and Cu/ZSM-5 also exhibit single, unresolved NH₃ desorption peaks.

Figure 1. NH₃-TPD profiles of Cu/SSZ-13 (a) and Cu/SAPO-34 (b) upon progressive aging at 600°C

3.2. *Physical significance of the bi-modal NH₃ desorption peaks*

In order to fully understand the physical nature of the two desorption peaks, we employed three approaches, aiming to provide further insights into the underlying adsorption sites. The first approach was utilizing DRIFTS to probe Cu/SSZ-13 at different stages of the TPD process. The second was comparing the NH₃-TPD profiles of Cu/SSZ-13 and H/SSZ-13. The third approach was based on examining samples with removed Brønsted sites through severe aging.

DRIFTS spectroscopy is suitable for differentiating surface NH₃ adsorption sites, namely Lewis and Brønsted acid sites: IR vibrational band at 1620 cm⁻¹ is attributed to NH₃ adsorbed on Lewis acid sites (such as Cu²⁺ sites) in the molecular form, while IR band at 1450 cm⁻¹ is assigned to NH₃ adsorbed on Brønsted acid sites, in the form of NH₄⁺ [24, 25]. Over a Cu/SSZ-13 sample degreened at 550°C for 4h, two snapshots of IR spectra were captured at 200 and 350°C during NH₃-TPD, as shown in Fig.2. At 200°C, where NH₃ was adsorbed on both weak and strong acid sites according to TPD, bands of NH₃ adsorbed on both Lewis and Brønsted acid sites could be spectroscopically identified; at 350°C where NH₃ was only adsorbed on strong acid sites according to the TPD, NH₄⁺ dominated in the IR spectrum. On this basis, we assign the low-temperature NH₃ desorption peak shown in Fig.1a to NH₃ released from Lewis acid sites, and the high-temperature peak to NH₃ desorption from Brønsted acid sites.

Figure 2. DRIFTS spectra upon NH₃ desorption at 200°C (black) and at 350°C (red).

To further confirm these assignments, NH₃-TPD was performed on a Cu-free, H/SSZ-13 sample, and the results are presented in Fig.3. In this case, only one NH₃ desorption peak centered at ~400°C was observed, ascribed to NH₃ released from Brønsted acid sites. With progressive aging, the desorption peak decreased in its intensity, indicative of zeolite dealumination. Comparing NH₃-TPD profiles with and without Cu, it is clear that the low-temperature desorption peak is related to NH₃ adsorbed on Cu sites, i.e., Cu ions are predominant Lewis acid sites in Cu/SSZ-13. Note that NH₃ can also adsorb on other Lewis acid sites (e.g., extra-lattice Al sites). However, such adsorption is typically very weak and is not expected at the NH₃ adsorption temperature used here (200 °C) [15].

Figure 3. NH_3 -TPD profiles of an H/SSZ-13 catalyst upon progressive aging at 600°C

Finally, on a severely aged Cu/SSZ-13 sample where the majority of the Brønsted acid sites were lost, as confirmed by DRIFTS [12], only one NH_3 desorption peak at $\sim 300^\circ\text{C}$ could be observed, corresponding to NH_3 desorption from Cu sites. Thus, all three pieces of evidence reported in this section confirm the attribution of low-temperature desorption peak to Cu-related sites, and high-temperature desorption peak to Brønsted acid sites.

It is important to point out again that for the state-of-the-art Cu/SSZ-13 catalyst, despite the fact that substantial changes occurred in the NH_3 adsorption characteristics with progressive aging at 600°C , virtually no change was found in the total NH_3 storage capacity. For the H/SSZ-13 sample, continuous storage capacity decline was noticed following the same aging procedure. A direct comparison is displayed in Fig. 4.

Figure 4. Normalized total NH_3 storage capacity of H/SSZ-13 and Cu/SSZ-13 as a function of aging time at 600°C (data from Fig.1 and 3)

3.3. Interpretation of the progressive changes in the ratio of two NH_3 -TPD peaks

In this section possible interpretations of the observed changes in the NH₃-TPD profiles with respect to aging are discussed, based on several complementary characterization techniques. As mentioned above, the low-temperature NH₃ desorption peak is related to Cu sites. This peak intensifies upon aging. In principle, such an increase can be accounted for by an increase in the total number of adsorbing sites and/or the numbers of NH₃ adsorbents on each site. As shown below, our data strongly favor the latter scenario, i.e., the total Cu sites keep constant, but the population of sites capable of adsorbing two instead of one NH₃ molecules increases with aging.

Let us first examine the evidence which suggests that the increase in the low-temperature peak is unlikely to be caused by an increase in the number of adsorbing Cu sites capable for NH₃ adsorption. This situation only occurs if some Cu species incapable of NH₃ adsorption in the freshly prepared catalysts become accessible in aged ones. For example, if a fraction of Cu in the as-prepared catalyst existed in the form of CuO, during aging it could disperse into isolated Cu²⁺ sites in charge-balancing positions via solid-state ion-exchange, thus acquiring NH₃ adsorption capacity. In practice, this scenario appears highly unlikely, given the state-of-the-art nature of this catalyst (i.e., optimized dispersion of the active isolated Cu ions), and its under-stoichiometric ion-exchange level (i.e., a Cu/Al ratio of 0.3). Furthermore, it is important to note that aging resulted in no enhancement in catalytic activities, which would have been expected if the number of exchanged (isolated) Cu sites increased [25-27]. Second, the increase is not related to changes in oxidation states of Cu ions, i.e. reduction of Cu²⁺ to Cu⁺. This is because such a reduction is highly unlikely under our sample pretreatment/adsorption conditions prior to NH₃-TPD [9]; Also, reduction of Cu²⁺ to Cu⁺ during desorption at ~300 °C is less likely, considering the identical low-temperature NH₃ desorption peak regardless of whether the desorption was performed in inert condition or in oxidizing environment [13].

Rather, we believe that the increase in low-temperature NH₃ desorption peak with aging time is related to changes in the population of the two different types of isolated Cu sites with different NH₃ storage capacities. In the following sub-sections, we will first show the identification of the two types of Cu sites by DRIFTS, followed by their quantification through H₂-TPR, and finally the estimation of their different NH₃ storage capacities based on NH₃-TPD.

3.3.1 DRIFTS analysis

It has been realized in recent years that, based on their perturbation to the T-O-T vibrations of the zeolite frameworks, different types of Cu sites can be identified. As described above, there exist two isolated Cu ions in Cu/SSZ-13, i.e., Z₂Cu and ZCuOH. When these ions interact strongly with the SSZ-13 framework, i.e., via Cu-O bond formation, two perturbed T-O-T perturbation peaks form at ~900 and ~940cm⁻¹, respectively [7]. The former peak is typically much stronger. These perturbed features disappear when Cu ions are fully solvated, for example by H₂O in fully hydrated samples. Applying the same methodology, DRIFTS spectra of the state-of-the-art Cu/SSZ-13 samples at different stages of aging were obtained using KBr spectrum as a background and the results are shown in Fig. 5(a). IR bands at 1040 and 814cm⁻¹ correspond to intrinsic asymmetric and symmetric T-O-T vibrational modes of SSZ-13 [7]. IR bands at 900 and 950cm⁻¹ are attributed to, as described above, the asymmetric T-O-T vibrations that are perturbed by Cu ions.

These perturbed bands can be better resolved using NH_3 as a Cu ion solvation agent, i.e., by comparing spectra in NH_3 -saturated against NH_3 -free dehydrated forms. When saturated with NH_3 , framework O ligands are replaced by NH_3 molecules to interact with Cu, generating better-resolved, negative perturbed T-O-T vibrations. The differential IR spectra in Fig. 5(b) were produced by subtracting spectra of NH_3 -free samples from their NH_3 -saturated counterparts. In this case, bands at 900 and 950 cm^{-1} are very well resolved; their evolution with aging is also clearly seen. In particular, upon progressive aging, intensity of the 950 cm^{-1} band decreases with concomitant increase of the band at 900 cm^{-1} , indicating gradual ZCuOH transformation to Z_2Cu as will be discussed in more detail below. Time-resolved spectra with progressive catalyst exposure to NH_3 , referenced against KBr (Fig S1a) and NH_3 -free samples (Fig S1b) are provided in the supporting information, to further illustrate the solvation effect.

Figure 5. DRIFTS spectra of Cu/SSZ-13 samples upon aging at different temperatures: (a) using KBr as a background, (b) difference spectra between NH_3 -saturated and NH_3 -free spectra.

3.3.2 H_2 -TPR

Besides the qualitative description of Cu sites shown above, quantitative analysis of the Cu sites were also performed using H_2 -TPR, based on reducibility difference of the two types of Cu sites as reported previously [11]. Figure 6(a) shows H_2 -TPR profiles of the Cu/SSZ-13 catalysts upon progressive aging at 550, 650 and 750°C for 4h. Two reduction peaks could be observed at approximately 250°C and 350°C, corresponding to the reduction of the two types of Cu^{2+} species to Cu^+ . Upon aging, the total amount of reducible Cu species does not change, as confirmed by the same areas under the three TPR curves. The decrease in the population of Cu^{2+} species reduced at ~250°C was compensated by the increase of the ones reduced at ~350°C. The two Cu species could be quantified through peak deconvolution as shown in Fig. 6(b): in 550°C 4h degreened sample, Cu species that can be reduced at 250°C account for 87% of the total reducible Cu^{2+} , which decreased to 75% and 55% upon aging to 650°C and 750°C, respectively. If correlated with DRIFTS spectra shown in Fig. 5(b), it is clear that Cu species reduced at 250°C induced IR band at 950 cm^{-1} , while and Cu species reduced at 350°C induced band at 900 cm^{-1} . It is important to mention that the height of IR bands cannot be used to quantify the amounts of the respective species, due to potential differences in their IR absorption coefficients. In particular, even though Cu species causing perturbed T-O-T band at 950 cm^{-1} is dominant in this catalyst based on TPR, this band is considerably weaker as compared to the IR band at 900 cm^{-1} . Note that CuO and/or CuAl_2O_4 formation can be safely ruled out upon such a mild hydrothermal

aging. Based on our recent NH_3 oxidation reaction testing study on Cu/SSZ-13, it was discovered that the presence of CuO and/or CuAl_2O_4 was sensitively reflected by the increased selectivity to NO_x for this probe reaction, which only occurred on catalysts hydrothermally aged under severe conditions, such as above 750 °C [12].

Figure 6. H_2 -TPR profiles of Cu/SSZ-13 samples upon aging at different temperatures (peak deconvolution on the right figure)

3.3.3 Assignment of the DRIFTS and TPR features based on model samples

Two model samples were used to further elucidate the nature of the different active sites, identified by DRIFTS and H_2 -TPR. As described in the Experimental section, one sample, noted as Model_6, was prepared using a SSZ-13 zeolite with a low Si/Al ratio of 6 in order to maximize the Z2Cu configuration, the thermodynamically most favorable position for Cu^{2+} in SSZ-13 [21]. The other sample, noted as Model_35, was prepared by using SSZ with high a Si/Al ratio of 35, thus minimizing the Z2Cu configuration. The catalyst was subsequently ion-exchange to a rather high Cu/Al ration of 0.62 in order to maximize the population of ZCuOH.

The results of DRIFTS and H_2 -TPR characterization of these two samples are shown in Fig. 7. Clearly, the employed preparation methods succeeded in producing samples with one dominant Cu species, as evidenced by the TPR results reported in Fig. 7(a). In particular, TPR spectrum for the Model_6 sample in which Z2Cu was expected to be the prevalent Cu species, was dominated by a high-temperature reduction peak centered around 380°C. In contrast, for the Model_35 sample prepared in attempt to generate predominantly ZCuOH species, the spectrum was dominated by a low-temperature peak centered around 250°C. Differential DRIFTS spectra before and after NH_3 adsorption for these two samples, reported in Fig. 7(b), are consistent with these findings. Once again, these indicated much lower absorption coefficient for the 950 cm^{-1} band. It should be mentioned that such a difference in IR sensitivity (absorption coefficient) of the two Cu species deserves separate investigations.

The above analyses of the model samples further confirm the presence of two isolated Cu(II) ions in Cu/SSZ-13: a strongly bound Z2Cu species reduced at ~350°C, and a more weakly bound

ZCuOH species that is reduced at $\sim 250^{\circ}\text{C}$. The former species caused perturbed T-O-T vibration at 900cm^{-1} , while the latter at 950cm^{-1} .

Figure 7. H₂-TPR profiles (a) and DRIFTS spectra (b) of model Cu/SSZ-13 samples

3.3.4 Interpretation of the increased low-temperature NH₃ desorption peak with aging

Applying the above findings from DRIFTS and TPR techniques to the commercial Cu/SSZ-13 catalyst, we can conclude that in the as-prepared state it contains both types of Cu sites, and that aging leads to a progressive transformation of ZCuOH into the thermodynamically more favorable Z₂Cu species. According to literature, ZCuOH species are likely located in the CHA cage and close to the 8-member window, while Z₂Cu are anchored to the 6-member ring plane [7, 21, 28]. Such a location change at Cu ions, in response to hydrothermal aging, may lead to changes in the unit cell parameters. Figure S2 provides schematics of a hexagonal unit cell of Chabazite with the corresponding lattice parameters. Next, in-situ XRD was used to track such changes. In Fig.8, the unit cell parameters were plotted upon aging at 600°C for varying durations. Clearly, there is a trend of continuous decrease in “a” and increase in “c” lattice parameters with aging time. The only possible cause for such changes in unit cell parameters is the migration of Cu ions from CHA cages to windows of 6MR since, as shown by the characterization results displayed above, as well as by ²⁷Al NMR examinations shown in the next section, no any structural degradation is likely at this aging temperature. Meanwhile, additional IR characterization on the framework shows further evidence of the decreased Cu-OH bond vibration ($\sim 3650\text{cm}^{-1}$) upon aging (Fig. S4) [29]. To summarize, combination of DRIFTS and TPR indicates the transformation of Cu species from ZCuOH to Z₂Cu, and in-situ XRD confirms that this transformation is accompanied with Cu migration. Note that this is fully consistent with theoretical calculations which confirmed that the hydrothermally most stable locations for ZCuOH are within CHA cages while those for Z₂Cu are windows of 6MR with paired Al [21, 28].

Figure 8. Variation in SSZ-13 unit cell lattice parameters as a function of hydrothermal aging time at 600 °C. Parameters at time zero were from the sample treated at 500°C.

This finding can offer a key to interpreting the results of the NH_3 -TPD experiment reported in Figure 1. The increase in the low-temperature NH_3 desorption peak with aging can be reconciled based on the progressive transformation of ZCuOH species into Z_2Cu , as long as the latter ones are capable of adsorbing more NH_3 molecules per site. In fact, difference in NH_3 storage ability of the two types of Cu sites has been suggested from a recent combined experimental (XAS) and theoretical study [21].

Figure 9. NH_3 -TPD profiles of Cu/SSZ-13 samples aged at 550°C, 650°C and 750°C. In these experiments, NH_3 adsorption was performed at 150°C instead of 200°C to ensure a more complete saturation, and a 10min purge was performed prior to NH_3 -TPD in order to remove the physically adsorbed NH_3 .

Next, additional NH_3 -TPD results are reported in Fig. 9 for the purpose of quantifying the number of NH_3 molecules adsorbed on each ZCuOH and Z_2Cu site prior to TPD. In this case,

three aged commercial samples were used for the measurements, and the NH₃ desorption curves are shown in Fig. 9(a). Again, with increasing aging temperature, NH₃ desorption progressively shifted to lower temperatures. From the discussions above, this is attributed to transformation of ZCuOH species into Z2Cu, rather than zeolite dealumination. From the NH₃ TPD peak deconvolution as shown in Fig. 9(b), the amounts of NH₃ adsorbed at low temperatures (i.e., by both types of Cu sites) on the three samples can be derived. These values are reported in Table 1.

Table 1. Quantification of NH₃-TPD on Cu/SSZ-13 sample after different stages of aging

Temperature of aging, °C	Low-Temperature NH ₃ TPD peak, mol NH ₃ /mol Cu	Integrated total TPD yields, μmol/g		
		Low-Temperature peak	High-Temperature peak	Total TPD yield
550	1.08	531	471	1002
650	1.27	626	321	947
750	1.53	752	93	845

For every sample, the following balance should be observed

$$NH_{3_low_T} = a * [Z2Cu] + b * [ZCuOH] \quad (R1)$$

where:

$NH_{3_low_T}$ – integrated low-temperature NH₃ adsorption (from Table 1);

$[Z2Cu]$, $[ZCuOH]$ – relative amounts of each type of active sites (from H₂-TPR in Fig. 6);

a , b – numbers of NH₃ molecules adsorbed on one Z2Cu and ZCuOH site, respectively (unknown).

Data from the three aged samples yield three variants of the equation (R1) with two unknowns. Arithmetic solution of this over-defined system of equations indicates that upon NH₃ saturation at 150°C, each ZCuOH site could adsorb ~1 NH₃ molecule ($b=0.9$), while each Z2Cu site can adsorb up to ~2 NH₃ molecules ($a=2.3$). In fact, such difference in the NH₃ storage ability of the two types of sites is consistent with the recent results from combined experimental (XAS) and theoretical study [21]. We note that upon full saturation, Cu²⁺ can ligate up to 4 NH₃ molecules and Cu(OH) can ligate 3 [21]. Quantification results shown here indicate that under our **test conditions, these Cu ions do not completely detach from the zeolite, which is consistent with our temperature-dependent T-O-T vibration titrated with NH₃ adsorption FTIR (Figure S5);** therefore, they ligate with both lattice oxygen and NH₃ molecules.

3.3.5 Interpretation of the decline in high-temperature NH₃ TPD peak

As discussed above, the high-temperature NH₃ peak at ~380 °C in these catalysts can be unambiguously attributed to desorption from Brønsted acid sites. Thus, the decline in the high-temperature TPD peak with aging observed in Fig. 1, 3, and 9 implies loss of Brønsted acid sites during hydrothermal aging, consistent with our earlier publication [12]. This loss, in turn, could be caused by either dealumination of the zeolite, or consumption of Brønsted sites in the process of formation of Z2Cu from ZCuOH. In particular, the latter transformation requires that one

Brønsted site is consumed per each transition, as ZCuOH is singly bound to the zeolite while Z2Cu doubly-bound. The following equation (R2) can be used to describe this chemistry.

Thus, the key distinguishing factor between these two processes, dealumination vs. transformation of Cu sites, is the presence or absence of the change in the total NH₃ storage capacity. For H/SSZ-13, where Brønsted protons represent the sole type of NH₃ adsorption sites, dealumination offers the only viable explanation for the decline in the high-temperature TPD peak and in the total NH₃ storage (Fig. 3 and 4).

In contrast, for Cu/SSZ-13 aged at 600°C, the transformation of the TPD profile occurred with virtually no change to the total amount of stored NH₃ (Fig. 4). This implies that virtually no dealumination was taking place in this catalyst under these aging conditions, and that changes to the TPD profile (Figure 1a) can be quantitatively reconciled based on the ZCuOH→Z2Cu transition. This absence of dealumination is also confirmed by ²⁷Al NMR analysis, as shown in Fig. 10, on a model sample (Si/Al = 12, Cu/Al = 0.27) with similar composition as the commercial catalyst. Using the tetrahedral Al site intensity (framework Al^{IV}, appeared at ~57.5 ppm) for the freshly prepared sample as unity, the amounts of Al^{IV} in aged samples were normalized in terms of sample weight and scanning duration, and the results are displayed adjacent to each spectrum. The results indicate that after hydrothermal aging at 600 °C for 16 h, sample dealumination is still very minimal. On the other hand, the fresh sample appears to have Al sites slightly more distorted considering its broader signal width since signal width reflects the degree of distortion of the tetrahedral Al. Mild aging appears to allow the zeolite body to relax and decrease this type of distortion. This is not related to dealumination since dealumination (i.e., structure degradation) will always cause signal to broaden instead of narrow down. This notion is further corroborated by the corresponding ²⁹Si NMR spectra displayed in Fig. 10(b). The fresh catalyst contains two framework tetrahedral Si (Q4) features: one at -105 ppm assigned to tetrahedral Si with three Si and one Al neighbors (i.e., Si(OSi)₃(OAl)) and one at -111 ppm assigned to tetrahedral Si with four Si neighbors (i.e., Si(OSi)₄) [30]. In this case, dealumination will cause intensity of the -105 ppm signal to decrease. Clearly, intensity for this signal only decreases upon hydrothermal aging at 750 °C. Note that this sample has Si/Al and Cu/Al ratios close to the state-of-the-art catalysts; these two materials should have similar hydrothermal stabilities. Note also that the commercial catalyst was not chosen for NMR analysis to avoid potential complexities caused by the cordierite support and other unknown additives. This further implies that Cu-exchanged catalyst is more robust against hydrothermal aging as compared with H-SSZ-13, a fact well supported by other studies [31]. It is worth pointing out that upon more severe aging, for example at 750 °C, apparent dealumination has occurred, as suggested by the decline in the total NH₃ storage values reported in the last column of Table 1, as well as the NMR results shown in Fig. 10.

Figure 10. (a) ^{27}Al solid-state NMR spectra for fresh and hydrothermally aged Cu/SSZ-13 model catalysts (Si/Al = 12, Cu/Al = 0.27). Hydrothermal aging temperatures are marked adjacent to the corresponding spectrum. Al^{IV} signal areas were normalized against that of the fresh sample based on sample weight and scanning times. The values are also displayed adjacent to the corresponding spectrum. (b) the corresponding ^{29}Si NMR spectra for fresh and aged catalysts.

Since Z2Cu located at 6MR is thermodynamically more favorable than ZCuOH located at 8MR, it is generally assumed that ZCuOH sites only develop upon saturation of the Z2Cu sites. For example, theoretical study by Paolucci et al [21] demonstrated that the free energy associated with Cu near 2Al is substantially lower than that with Cu near 1Al at 298 K (-142 kJ/mol). However, the present study demonstrates clearly that for our state-of-the-art catalyst in the fresh form, ZCuOH sites populate prior to the saturation of Z2Cu. We believe a reasonable explanation is that at relatively high Cu loading conditions, whether or not Cu ions first saturate 6MR and then occupy 8MR is not determined by thermodynamics alone. Kinetics must be considered. For example, kinetic stabilization of CuOH ions in 8MR will prevent some Cu^{2+} ions from finding energetically most favorable sites. However, a kinetically stabilized, metastable catalyst will convert to a thermodynamically stable state if sufficient relaxation time is given. This is fully consistent with our experimental finding that during hydrothermal aging, ZCuOH gradually migrates and converts to Z2Cu. Importantly, the notion that Z2Cu must saturate does not apply to freshly prepared Cu/SSZ-13 catalysts with relatively high Cu loadings. This explains why Cu/SSZ-13 catalysts with 100% ion exchange level still contain sufficient amounts of Brønsted acid sites [15].

4. Conclusion

At least three NH_3 adsorption sites were identified in Cu/SSZ-13, including two types of exchanged Cu sites and a population of Brønsted acid sites. The two Cu sites appear to adsorb

NH₃ with similar energy, resulting in a TPD desorption peak around 300°C, while the Brønsted sites show higher energy, resulting in a TPD peak around 400°C.

The attribution of Cu vs. Brønsted sites was easily confirmed by comparing Cu- and H-form samples of the otherwise similar composition and preparation. However, resolving the two types of Cu sites proved more complex. It required preparing model samples with the dominance of singly- or double-bonded Cu-species (ZCuOH and Z₂Cu, respectively) and characterizing them via H₂-TPR and DRIFTS.

Aging was found to alter the relative populations of these sites, leading to a unique NH₃ release feature, namely an increase in a low-temperature TPD peak accompanied by a decrease in a high-temperature TPD peak. Remarkably, with mild hydrothermal aging, this transformation occurred with virtually no change to the total NH₃ storage. ZCuOH → Z₂Cu transition, accompanied by the proportional consumption of Brønsted protons, appears to account for this phenomenon. Each ZCuOH site appears capable of accommodating one and each Z₂Cu site – two NH₃ molecules under the studied conditions. Upon more severe hydrothermal aging, some loss of Brønsted acid sites can also be observed due to dealumination, resulting in the decline of the total NH₃ storage.

One important implication of the above observations is that, contrary to the conventional wisdom, a loss of Brønsted acidity with aging does not necessarily imply dealumination, but rather may be induced by re-distribution of Cu sites. In the Part II of this publication, we will further explore practical application of these changes and of the bi-modal NH₃ desorption profile, unique to Cu/SSZ-13 among other types of Cu-zeolite SCR catalysts.

Acknowledgements

Authors would like to thank Randall Jines for his help with collecting the reactor data, Nancy W. Washton for measuring the NMR data and Tamas Varga for in-situ XRD measurements. FG and CHFP gratefully acknowledge supports from the United States Department of Energy (DOE), Energy Efficiency and Renewable Energy, Vehicle Technologies Office. Part of the research described in this paper was performed at the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for the US DOE by Battelle.

References

- [1] A.M. Beale, F. Gao, I. Lezcano-Gonzales, C.H.F. Peden, J. Szanyi, Chem. Soc. Rev. 44(2015)7371-7405.
- [2] J.H. Kwak, R.G. Tonkyn, D.H. Kim, J. Szanyi, C.H.F. Peden, J. Catal. 275(2010)187-190.
- [3] J.H. Kwak, D. Tran, S.D. Burton, J. Szanyi, J.H. Lee, C.H.F. Peden, J. Catal. 287(2012)203-209.

- [4] H.Y. Chen, Z. Wei, M. Kollar, F. Gao, Y. Wang, J. Szanyi, C.H.F. Peden, *J. Catal.* 329(2015)490-498.
- [5] F. Gao, E.D. Walter, E.M. Karp, J.Y. Luo, R.G. Tonkyn, J.H. Kwak, J. Szanyi, C.H.F. Peden, *J. Catal.* 300(2013)20-29.
- [6] J. Wang, H. Zhao, G. Haller, Y. Li, *Appl. Catal. B* 202 (2017) 346-354.
- [7] J.H. Kwak, H. Zhu, J.H. Lee, C.H.F. Peden, J. Szanyi, *Chem. Commun.* 48(2012)4758-4760.
- [8] J.H. Kwak, T. Varga, C.H.F. Peden, F. Gao, J.C. Hanson, J. Szanyi, *J. Catal.* 314(2014)83-93.
- [9] C. Paolucci, A.A. Verma, S.A. Bates, V.F. Kispersky, J.T. Miller, R. Gounder, W.N. Deglass, F.H. Fabio, W.F. Schneider, *Angew. Chem. Int. Ed.* 53(2014)1-7.
- [10] J.Y. Luo, A. Yezerets, C. Henry, H. Hess, H. An, K. Kamasamudram, H.Y. Chen, W.S. Epling, *SAE* 2011-01-1096.
- [11] J.Y. Luo, D. Wang, A. Kumar, J.H. Li, K. Kamasamudram, N. Currier, A. Yezerets, *Catal. Today* 267 (2016) 3-9.
- [12] J.Y. Luo, H. An, K. Kamasamudram, N. Currier, A. Yezerets, *SAE* 2015-01-1022.
- [13] K. Kamasamudram, A. Kumar, J.Y. Luo, N. Currier, A. Yezerets, T. Watkins, L. Allard, *SAE* 2014-01-1542.
- [14] F. Gao, N.M. Washton, Y. Wang, M. Kollar, J. Szanyi, C.H.F. Peden, *J. Catal.* 331 (2015) 25-38.
- [15] I. Lezcano-Gonzalez, U. Deka, B. Arstad, A. Van Yperen-De Deyne, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, B.M. Weckhuysen, A.M. Beale, *Phys. Chem. Chem. Phys.* 16 (2014) 1639-1650.
- [16] F. Gao, Y. Wang, N.M. Washton, M. Kollar, J. Szanyi, C.H.F. Peden, *ACS Catal.* 5 (2015) 6780-6791.
- [17] S.A. Bates, W.N. Deglass, F.H. Ribeiro, J.T. Miller, R. Gounder, *J. Catal.* 312(2014)26-36.
- [18] G. Bagnasco, *J. Catal.* 159 (1996) 249-252.
- [19] J.R.D. Iorio, S.A. Bates, A.A. Verma, W.N. Deglass, F.H. Ribeiro, J.T. Miller, R. Gounder, *Top. Catal.* 58 (2015) 424-434.
- [20] L. Olsson, K. Wijayanti, K. Leistner, A. Kumar, S.Y. Joshi, K. Kamasamudram, N.W. Currier, A. Yezerets, *Appl. Catal.* 174-175 (2015) 212-224.
- [21] C. Paolucci, A.A. Parekh, I. Khurana, J.R. Iorio, H. Li, J.D.A. Caballero, A.J. Shih, T. Anggara, W.N. Deglass, J.T. Miller, F.H. Ribeiro, R. Gounder, W.F. Schneider, *J. Am. Chem. Soc.* 138 (2016) 6028-6048.
- [22] N. Wilken, K. Wijayanti, K. Kamasamudram, N.W. Currier, R. Vedaiyan, A. Yezerets, L. Olsson, *Appl. Catal. B* 111-112 (2012) 58-66.
- [23] A. Sultana, T. Nanba, M. Sasaki, M. Haneda, K. Suzuki, H. Hamada, *164* (2011) 495-499.
- [24] H. Zhu, J.H. Kwak, C.H.F. Peden, J. Szanyi, *Catal. Today* 205 (2013) 16-23.
- [25] L. Wang, J.R. Gaudet, W. Li, D. Weng, *J. Catal.* 306 (2013) 68-77.
- [26] S. Shwan, M. Skoglundh, L.F. Lundegaard, R.R. Tiruvalam, T.V.W. Janssens, A. Carlsson, P.N.R. Vennestrom, *ACS Catal.* 5 (2015) 16-19.
- [27] D. Wang, Y. Jangjou, Y. Liu, M.K. Sharma, J. Luo, K. Kamasamudram, W.S. Epling, *Appl. Catal. B* 165 (2015) 438-445.
- [28] R. Zhang, J.S. McEwen, M. Kollar, F. Gao, Y. Wang, J. Szanyi, C.H.F. Peden, *ACS Catal.* 4 (2014) 4093-4105.
- [29] E. Borfecchi, K.A. Lomachenko, F. Fiordano, H. Falsig, P. Beato, A.V. Soldatov, S. Bordiga, C. Lamberti, *Chem. Sci.* 6 (2015) 548-563.

- [30] D. Engelhardt, D. Michel, High Resolution Solid-State NMR of Silicates and Zeolites; Wiley: New York, 1987
- [31] D.W. Fickel, R.F. Lobo, J. Phys. Chem. 114 (2010) 1633-1640.

Graphical Abstract

NH₃-TPD of Cu/SSZ-13 upon hydrothermal aging