The H₂O Effect on Cu Speciation in Cu-CHA-Catalysts for NH₃-SCR Probed by NH₃ Titration

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Abstract: The present work is focused on the effect of water on NH₃ adsorption over Cu-CHA SCR catalysts. For this purpose, samples characterized by different SAR (SiO₂/Al₂O₃) ratios and Cu loadings were studied under both dry and wet conditions. H₂O adversely affects NH₃ adsorption on Lewis acid sites (Cu ions) over all the tested catalysts, as indicated by the decreased NH₃ desorption at low temperature during TPD. Interestingly, the NH₃/Cu ratio, herein regarded as an index for the speciation of Cu cations, fell in the range of 3–4 (in the presence of gaseous NH₃) or 1–2 (no gaseous NH₃) in dry conditions, in line with the formation of different NH₃-solvated Cu species (e.g., [CuⅡ(NH₃)₂]²⁺ and [CuⅡ(OH)(NH₃)₃]⁺) with gaseous NH₃, [Z₂CuⅢ(NH₃)₃]²⁺ and [ZCuⅢ(OH)(NH₃)₃]⁺ without gaseous NH₃. When H₂O was fed to the system, on the contrary, the NH₃/Cu ratio was always close to 3 (or 1), while the Brønsted acidity was slightly increased. These results are consistent both with competition between H₂O and NH₃ for adsorption on Lewis sites and with the hydrolysis of a fraction of Z₂CuⅢ species into ZCuⅢOH.

Keywords: Cu-CHA; NH₃-SCR; Si/Al ratio; Cu loading; H₂O effect; Cu speciation

1. Introduction

NH₃/urea SCR is recognized worldwide as an effective technology in controlling automotive emissions to meet increasingly stricter NOx emission regulations [1,2]. Amongst state-of-the-art metal-promoted zeolite catalysts used in this process, Cu-exchanged chabazite (Cu-CHA) shows excellent activity and extraordinary hydrothermal stability over a broad temperature range under SCR conditions, triggering intensive research on the relationship between its unique structure and its DeNOx performance [3–11]. In this regard, the SiO₂/Al₂O₃ ratio (SAR) and the Cu loading content are important structure indexes, which could affect the nature of Cu cations existing in the catalyst framework and, based on their nature, location and redox properties, further impact the SCR activity [3–9]. Two Cu species are recognized to be present in the Cu-CHA catalyst: Z₂CuⅢ (doubly coordinated to the framework) and ZCuⅢOH (balanced by one framework negative charge), whose relative ratio can be predicted based on Si/Al and Cu/Al ratios [5,6,11]. The proportion of such Cu species could also be affected by several factors, for example, hydrothermal aging [4,6,12] or hydrated/dehydrated conditions [5,6]. It was also proposed, based on DFT calculations, DRIFTS, XAS and NH₃-TPD tests [4,5,8,13], that these two species are able to coordinate a different number of NH₃ molecules, thus influencing, in turn, the NH₃ storage capacity, a relevant parameter for the SCR process. In line with Paolucci et al. [5], our recent paper concluded that upon full catalyst saturation, the Z₂CuⅢ species could coordinate up to four NH₃ molecules, while the hydroxylated CuⅢ site could bind only three molecules [8]. The
NH₃ adsorption chemistry on the Lewis acid sites can be summarized by the following reactions [13]:

\[
Z_{2}Cu^{\text{II}}(s) + 4NH_{3}(g) \rightarrow Z_{2}Cu^{\text{II}}(NH_{3})_{4}(s) \tag{1}
\]

\[
ZCu^{\text{II}}OH(s) + 3NH_{3}(g) \rightarrow ZCu^{\text{II}}OH(NH_{3})_{3}(s) \tag{2}
\]

When Cu-CHA catalysts were not fully saturated and Cu ions were not able to detach from the zeolite framework, however, we observed a stoichiometry different from reaction (1) and (2) for the two copper species: \(Z_{2}Cu^{\text{II}}\) ions adsorb two NH₃ molecules while only one NH₃ is bound to \(ZCu^{\text{II}}OH\), in agreement with Luo et al. [4].

NH₃ can also be adsorbed on the Brønsted acid sites typical of the zeolite framework, according to the adsorption chemistry reported below [12]:

\[
NH_{3}(g) + ZH(s) \rightarrow ZNH_{4}(s) \tag{3}
\]

Herein, we carried out NH₃ adsorption + TPD tests under both dry and wet conditions over several Cu-CHA samples with different SARs and Cu loadings, which therefore contain distinct fractions of the two Cu species populations and different Brønsted sites [5,8]. The aim of the present investigation is to verify if H₂O affects the Lewis and Brønsted acidity in chabazite-based materials and the possibility to use NH₃-TPD as a probe technique for Cu speciation. In the literature, this method was implemented to characterize Cu-CHA catalysts in dry environments only in [8] or in the presence of water only in [4,12]. On the contrary, to assess the role of H₂O in NH₃ adsorption, we compared the performance of different samples under both wet and dry conditions.

2. Results and Discussion

An example of an NH₃ adsorption/desorption run is provided in Figure 1A, depicting the three stages of the test, namely isothermal adsorption, isothermal desorption, and TPD. The run was performed after having pre-oxidized the sample at 550 °C. The aim was not only to evaluate the NH₃ storage capacity, but more specifically to identify the different sites present in the catalyst [8].

\[\begin{array}{c}
\text{NH}_3 \text{ in} \\
\text{Time, s} \\
12,000, 14,000, 16,000, 18,000, 20,000, 22,000, 24,000, 26,000, 28,000, 30,000, 32,000 \\
\text{Concentration, ppm} \\
\end{array}\]

\[\begin{array}{c}
\text{NH}_3 \\
\text{Temperature, °C} \\
150, 200, 250, 300, 350, 400, 450, 500, 550, 600 \\
\end{array}\]

Figure 1. (A) NH₃ adsorption + TPD test over 1.7Cu-CHA 25 catalyst. GHSV = 266,250 cm³/(gcat* h) (STP). Pre-oxidized catalysts. NH₃ = 500 ppm, TPD heating rate = 15 °C/min, He. (B) TPD plot.

For this purpose, we analyze the TPD phase. As shown in Figure 1A, the temperature ramp featured a release of NH₃ together with a small N₂ peak (about 25 ppm). The integral of the N₂ released (i.e., \(\approx 0.68 \mu \text{mol}\)) is in line with the full reduction in Cu²⁺ ions (i.e., 4.3 µmol of Cu loaded) by adsorbed NH₃ according to the following stoichiometries [13,14]:

\[
6Cu^{\text{II}}(s) + 2NH_{3}(g) \rightarrow N_{2}(g) + 6H_{2}(g) + 6Cu^{\text{I}}(s) \tag{4}
\]

\[
6Cu^{\text{II}}OH(s) + 2NH_{3}(g) \rightarrow N_{2}(g) + 6H_{2}O(g) + 6Cu^{\text{I}}(s) \tag{5}
\]
Figure 1B displays the NH₃ and N₂ traces during the TPD, whereas the corresponding integral balances are reported in Table 1. The N balance error improves significantly if the production of nitrogen is taken into account. In line with this result, Borfecchia et al. showed by means of XAS spectroscopy and UV-vis-NIR experiments that at the end of the TPD, after NH₃ adsorption, the Cu sites in their Cu-CHA catalysts were almost completely reduced [13].

Table 1. Integral balances for the NH₃ adsorption + TPD test over 1.7Cu-CHA25 shown in Figure 1.

|                          | 1.7Cu-CHA25 |
|--------------------------|-------------|
| Cu₄Tot (ICP) (µmol)      | 4.3         |
| NH₃ adsorbed (µmol)      | 23.4        |
| NH₃ physisorbed (µmol)   | 8.0         |
| NH₃ chemisorbed (µmol)   | 14.1        |
| N₂ produced (µmol)       | 0.7         |
| N balance error w/o N₂ (%)| 5.6        |
| N balance error with N₂ (%)| 0.1        |

In line with the literature, the TPD curve in Figure 1B showed two distinct NH₃ release peaks, ascribed to energetically different populations of acidic sites [4,8,15] (Figure 2). The physical nature of the different sites was estimated via Gaussian deconvolution of the NH₃-TPD profile over 1.7Cu-CHA 25 catalyst in Figure 1B. As established in several works within the literature [4,8,12,16], the first peak in Figure 1B is related to the NH₃ adsorbed onto both Cu species and a small amount of Al extra-framework (quantified in [8] and reported in Table S1), while the second one is attributed to NH₃ desorption from Brønsted sites associated with the bare zeolite framework. It is notable that the nitrogen production in Figure 1A was well aligned with the low temperature peak of the NH₃-TPD curve, implying that mostly Lewis NH₃ is responsible for the reduction in CuII cations into CuI according to (4) and (5).

2.1. H₂O Effect with Changes in Cu Loading

Figure 3 shows the Cu loading effect on the NH₃-TPD data collected over each catalyst under both dry and wet conditions.
Figure 3A refers to the simplest case, i.e., the TPD profiles over the unpromoted chabazite catalyst with SAR 25. The curves obtained in the presence and absence of H₂O are almost overlapped, showing a single desorption peak centered at about 440 °C with a similar intensity in both tests. This peak corresponds to the desorption of NH₃ stored onto the Brønsted acid sites of the zeolite [11,17–19]. The small shoulder visible at 250 °C under dry conditions (black line) is linked to the extra-framework aluminum species, which confers a slight Lewis acidity to the catalyst [6,17–21]. This peak disappeared under wet conditions, in accordance with findings in the literature [6,20,21]. Interestingly, H₂O significantly affects the weakly bound NH₃, since H₂O molecules are stored preferentially on Lewis acid sites. A clear confirmation of this behavior was obtained comparing the NH₃ desorption profiles of the copper-exchanged samples under dry and wet conditions. Figure 3B–D show the TPD results for the zeolite catalysts with the same SAR (25) and loaded with 0.7, 1.7 and 2.1% w/w copper, respectively. The presence of H₂O considerably lowered the NH₃ storage capacity of all catalysts, affecting mostly the low-T peak, associated predominantly with Cu ions. The high-temperature Brønsted NH₃ peak was less affected by H₂O. The negative effect of H₂O on the NH₃ storage capacity of Lewis sites was confirmed by the faster dynamics during the catalyst saturation in the isothermal adsorption phase, when the samples were previously treated with H₂O (not shown): indeed, the dead time recorded during this phase was reduced from 530–860 s under dry conditions to 380–595 s under wet conditions. In addition, the integral of the TPD curves (NH₃ + 2N₂) was lower in the presence of H₂O even considering the negligible contribution of the extra-framework Al sites (Tables S1 and S2).

**Figure 3.** Comparison between dry and wet NH₃-TPD (NH₃ + 2N₂) after adsorption at 150 °C on Cu-CHA catalysts with SAR = 25 and different Cu loadings: (A) 0% w/w; (B) 0.7% w/w; (C) 1.7% w/w; (D) 2.1% w/w. NH₃ = 500 ppm, H₂O = 0–5% v/v; heating rate = 15 °C/min, He. GHSV = 266,250 cm³/(g_cat*h) (STP). Pre-oxidized catalysts.
2.2. Water Effect with Changes in SAR

Results were also collected over Cu-CHA catalysts with fixed Cu loading (1.7% w/w) and different SARs (10, 13, 22, 25): the corresponding TPD curves are shown in Figure 4. Under dry conditions, the differences in the relative intensities of the low and high temperature peaks indicate that on increasing the SAR, the overall stability of the adsorbed NH$_3$ molecules decreased [8]. In fact, in line with our previous studies, intensities of the low-T peaks were lower than those of the high-T peaks for high SARs (22, 25), and the opposite trend was seen at low SARs (10, 13), where the intensities of the low-T peaks were higher [8]. In all cases, the overall amount of chemisorbed NH$_3$ calculated from the integration of the TPD curves was found fairly constant upon changing the SAR, in the range of 950–1120 µmol/g.

Figure 4. Comparison between dry and wet NH$_3$-TPD (NH$_3$ + 2N$_2$) after adsorption at 150 °C on Cu-CHA catalysts with Cu loading = 1.7% w/w and different SAR: (A) 10; (B) 13; (C) 22; (D) 25. NH$_3$ = 500 ppm, H$_2$O = 0–5% v/v; heating rate = 15 °C/min, He. GHSV = 266,250 cm$^3$/(g$_{\text{cat}}$*h) (STP). Pre-oxidized catalysts.

A similar effect was observed in presence of H$_2$O (light-blue lines). Comparing the TPD under wet and dry conditions, it is apparent that H$_2$O reduced ammonia storage (Figure 4). Similarly to the data presented in the previous section, the low-temperature desorption feature diminished as a result of H$_2$O addition. Furthermore, the overall chemisorbed NH$_3$ decreased to 830–880 µmol/g for all the catalysts. Accordingly, the deadtime recorded during the adsorption phase was affected by the presence of water (not shown), decreasing from about 800 to 650 s.

2.3. H$_2$O Effect on Cu Speciation

At this point, we used Gaussian deconvolution of the bimodal TPD profiles to compare the amount of NH$_3$ to Cu atoms and to Brønsted acid sites in wet and dry atmosphere. Notice that the NH$_3$ ligated to the Al extra-framework was completely lost in the presence
of water, as apparent in Figure 3A for H-CHA (SAR 25) and in Figure S1 for H-CHA (SAR 13).

The results in Figure 5 and in Table S1 indicate that by cofeeding water: (i) the quantity of NH₃ stored on Brønsted sites slightly increased, while (ii) the Lewis NH₃ decreased. This trend could be related to the hydrolysis of Z₂Cu^{II} species, reaction (6) [6,22]:

$$Z₂Cu^{II} (s) + H₂O (g) → ZCu^{II}OH (s) + ZH (s)$$ (6)

In fact, according to this reaction, the transformation of Z₂Cu^{II} into ZCu^{II}OH implies a loss in Cu-NH₃ ligands. Indeed, the Z₂Cu^{II} species can bind up to four NH₃ molecules, while the hydroxylated Cu ions can coordinate only three molecules [5,8,23].

According to our deconvolution results, however, the increment in Brønsted NH₃ in wet conditions was less than the decrease in Lewis NH₃ for some samples. This behavior could be explained by a further loss of Lewis NH₃ due to the competitive adsorption of water on the Cu sites [20], as indicated by the decrease in the overall NH₃ storage capacity (i.e., the sum of Brønsted and Lewis NH₃ in Figure 5).

The fraction of Z₂Cu^{II} transformed into ZCu^{II}OH was estimated by the following equation:

$$\frac{\text{Amount of } Z₂Cu^{II} \text{ hydrolysed}}{\text{initial amount of } Z₂Cu^{II} \text{(Table 2)}} = \frac{NH₃ \text{ Brønsted wet} - NH₃ \text{ Brønsted dry}}{\text{initial amount of } Z₂Cu^{II} \text{(Table 2)}} \%$$ (7)

![Figure 5](https://example.com/figure5.png)

Figure 5. Deconvolution of the TPD profiles: evaluation of NH₃ stored on Lewis and Brønsted sites. Comparison between dry and wet conditions over different Cu-CHA samples: (A) 0.7% w/w Cu, SAR = 25; (B) 1.7% w/w Cu, SAR = 25; (C) 2.1% w/w Cu, SAR = 25; (D) 1.7% w/w Cu, SAR = 10; (E) 1.7% w/w Cu, SAR = 13; (F) 1.7% w/w Cu, SAR = 22. NH₃ = 500 ppm, H₂O = 0–5% v/v, He. GHSV = 266,250 cm³/(gcat*h) (STP). Pre-oxidized catalysts. Red symbols = Error bar.
From the results in Table 2 it can be noticed that only a fraction of \( \text{Z}_2\text{Cu}^{\text{II}} \) (40–70%) was hydrolyzed after the wet \( \text{NH}_3 \) adsorption. Furthermore, even if \( 1.7\text{Cu-SAR25} \) and \( 1.7\text{Cu-SAR22} \) are characterized by similar speciation and \( \text{Cu}/\text{Al} \) ratio, they display different behaviors in a wet atmosphere, more specifically the \( 1.7\text{Cu-SAR22} \) shows a more enhanced hydrolysis of the \( \text{Z}_2\text{Cu}^{\text{II}} \) sites. One possible parameter affecting this reaction could be the distribution of the \( \text{Al} \) atoms in the zeolite framework. In addition, two different types of the \( \text{Z}_2\text{Cu}^{\text{II}} \) sites are viable, with para and metal configuration, respectively, which show distinct features in EPR spectra and distinct reactivity under Standard SCR conditions [24]. In principle, these species could be associated with a different response to the hydrolysis reaction. A dedicated investigation of the hydrolysis reaction is ongoing.

**Table 2.** Estimates of the fraction of \( \text{Z}_2\text{Cu}^{\text{II}} \) hydrolyzed according to reaction (3).

| Sample                  | Cu Loaded, \( \mu \text{mol} \) | \( \text{Z}_2\text{Cu}^{\text{II}} \) from \( \text{NO}_2 \) Adsorption, \( \mu \text{mol} \) [8] | \( \text{NH}_3 \) Bronsted dry, \( \mu \text{mol} \) | \( \text{NH}_3 \) Bronsted wet, \( \mu \text{mol} \) | \( \text{Z}_2\text{Cu}^{\text{II}} \) Hydrolysed/Initial \( \text{Z}_2\text{Cu}^{\text{II}} \), % | \( \text{Z}_2\text{Cu}^{\text{II}} \) Hydrolysed/Cu tot, % |
|-------------------------|----------------------------------|------------------------------------------------|---------------------------------|---------------------------------|--------------------------------------|--------------------------------------|
| 0.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 1.8                              | 0.8                                            | 8.02                            | 8.38                            | 45                                   | 20                                   |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 4.3                              | 1.8                                            | 7.9                             | 8.67                            | 43                                   | 19                                   |
| 2.1% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 5.2                              | 1.7                                            | 7.07                            | 8.07                            | 59                                   | 19                                   |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 10} \) | 4.3                              | 2.4                                            | 6.20                            | 7.54                            | 56                                   | 31                                   |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 13} \) | 4.3                              | 3.1                                            | 8.30                            | 9.50                            | 39                                   | 28                                   |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 22} \) | 4.3                              | 1.8                                            | 8.00                            | 9.28                            | 71                                   | 30                                   |

At this point we calculated the \( \text{NH}_3/\text{Cu} \) ratio, taking into account the area under the low-T TPD peak, proportional to the \( \text{NH}_3 \) stored only on \( \text{Cu} \) cations, and the number of copper atoms known from the weight fraction of \( \text{Cu} \) in each sample (Table 3). Figure 6 illustrates how this ratio varies with the \( \text{Cu}/\text{Al} \) ratio.

**Table 3.** Characterization of the tested catalyst samples [8].

| Sample                  | Cu Loaded, \( \mu \text{mol} \) | Cu/Al Ratio, - | \( \text{NO}_2 \) Adsorption Experiment, \( \mu \text{mol} \) | \( \text{ZCu}^{\text{II}}\text{OH}, \% \) | \( \text{Z}_2\text{Cu}^{\text{II}}, \% \) | NOx Conversion at 225 °C, % |
|-------------------------|----------------------------------|----------------|------------------------------------------------|---------------------------------|--------------------------------------|-----------------------------|
| 0.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 1.8                              | 0.11           | 1.0                                            | 55                              | 45                                   | 16                          |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 4.3                              | 0.24           | 2.5                                            | 58                              | 42                                   | 91                          |
| 2.1% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 25} \) | 5.2                              | 0.29           | 3.5                                            | 67                              | 33                                   | 96                          |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 10} \) | 4.3                              | 0.12           | 1.9                                            | 44                              | 56                                   | 58                          |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 13} \) | 4.3                              | 0.17           | 1.2                                            | 28                              | 72                                   | 67                          |
| 1.7% \( \text{w/w} \) \( \text{Cu}, \text{SAR = 22} \) | 4.3                              | 0.22           | 2.5                                            | 58                              | 41                                   | 83                          |

Under dry conditions, the experimental data were in accordance with the literature [8,23]: the ratio was in the range 1–2 when only the \( \text{Cu-NH}_3 \) desorbed during the TPD was considered, and in the 3–4 range when the physisorbed \( \text{NH}_3 \) was also considered (area highlighted in orange, Figure 1A). In particular, the increase in \( \text{Cu}/\text{Al} \) lead to a decrease in the \( \text{NH}_3/\text{Cu} \) ratio, from a value close to 4 (or 2 considering only the TPD phase) for the catalysts with the lowest SAR and \( \text{Cu} \) loading, to a value closer to 3 (or 1 considering only the TPD phase) for the other tested samples (Figure 6). When water was added to the system, we observed a shift of all the \( \text{NH}_3/\text{Cu} \) ratios evaluated from the TPD to values...
closer to 3 (or 1 considering only the TPD phase). These results are consistent both with competition between H$_2$O and NH$_3$ adsorption onto Lewis sites and with the hydrolysis of a fraction of Z$_2$Cu$^{II}$ species into ZCu$^{III}$OH according to reaction (6), as discussed above.

![Figure 6](image_url)

**Figure 6.** NH$_3$/Cu ratio evaluated considering only NH$_3$ stored on Cu ions (low-T peak of TPD) and NH$_3$ stored on Cu ions plus NH$_3$ physisorbed: comparison between dry and wet conditions.

At this stage of the discussion, our opinion is that analysis of the NH$_3$-TPD data is not the best method to probe the Cu speciation. First, quantification of the Lewis and Brønsted acid sites requires deconvolution of the NH$_3$-TPD curves. Second, during the temperature ramp the Cu atoms are reduced, producing N$_2$; hence, it would be important to include its trace in the TPD plot to accurately analyze the experimental data. Finally, under wet conditions the Cu species are modified by the hydrolysis reaction. The occurrence of these phenomena complicates the interpretation of experimental TPD traces, thus it is suggested not to solely use this method to quantify the fraction of Z$_2$Cu$^{II}$ and ZCu$^{III}$OH species in the catalysts. The Cu speciation could be quantified by means of simpler techniques such as, for example, NO$_x$ adsorption + TPD and H$_2$ TPR, as discussed in [8,11,25]. However, NH$_3$-TPD runs under wet conditions provide useful experimental evidence of the hydrolysis reaction over Cu-CHA materials.

3. Material and Methods

For this study, we investigated two sets of Cu-exchanged chabazite (Cu-CHA), research catalysts supplied in the form of powders by Johnson Matthey. One set was purposely characterized by different SiO$_2$/Al$_2$O$_3$ (SAR) ratios (10, 13, 22, 25), with fixed Cu loading = 1.7% w/w. The other had different Cu loadings (0, 0.7, 1.7, 2.1% w/w, with fixed SAR = 25). The textural properties of some samples, comprising the BET surface area and the micropore volume, are reported in Table S3 and are typical of commercial CHA based materials [26,27]. The samples were conditioned by heating them up to 600 °C at 5 °C/min and holding the maximum temperature for 5 h, while 10% O$_2$ and 10% H$_2$O were fed in to remove all the impurities and the species that may be formed on the sample due to contact with atmosphere.

Sixteen milligrams of catalyst powder, sieved to obtain an average particle size of 90 micron and diluted up to 130 mg with cordierite, was loaded into a quartz flow reactor (6 mm ID) inserted in a vertical electric furnace. The temperature was controlled by a K-type thermocouple directly immersed in the catalyst bed.

Helium was used as balance gas in all the micro-reactor runs. Gases were controlled using mass flow controllers (Brooks Instruments, Hatfield, PA, USA). Water vapor was fed in by means of a saturator and the water concentration was controlled by adjusting the saturator’s temperature according to Antoine’s Law. NH$_3$ was fed in using a 6-way valve,
enabling step changes in the reactant concentrations. Temporal evolution of the species at the reactor outlet was followed by a mass spectrometer (QGA Hiden Analytical, Warrington, UK) and a UV analyzer (ABB LIMAS 11 HW, Zurich, Switzerland) arranged in a parallel configuration, which allowed the simultaneous measurement of all the species involved.

The interaction between NH$_3$ molecules and the catalyst was studied by performing NH$_3$ adsorption + temperature programmed desorption (TPD) runs. The catalysts were saturated using 500 ppm of NH$_3$ and balance He (GHSV = 266,250 cm$^3$/(g$\text{cat} \cdot$ h) STP), both under dry and wet conditions (5% w/w H$_2$O), at 150 $^\circ$C. After that, the catalysts were purged with He (or He + H$_2$O) for 1 h to desorb weakly bound ammonia, and then heated in He only (or He + H$_2$O) from 150 $^\circ$C up to 550 $^\circ$C at a rate of 15 $^\circ$C/min to release the strongly adsorbed molecules. Prior to each experiment, in order to control the oxidation state of the catalysts, the samples were pre-treated at 550 $^\circ$C, feeding 8% O$_2$ in He for 1 h, then the adsorption temperature was reached by cooling down under the same gas feed, with a final purge in He for 15 min.

The catalysts were characterized in our previous work [8], the amount of Cu loaded and the Cu speciation is reported in Table 3. In particular, NO + NH$_3$ TPR and ICP-MS analysis were used to quantify the number of reducible Cu$^{II}$ sites. Meanwhile, the NO$_2$ adsorption -TPD protocol was implemented to assess the amount of ZCu$^{II}$OH species [8]. The samples show the typical deNOx activity of CHA based materials as apparent from the NO conversions in Standard SCR conditions reported in Table 3 (i.e., GHSV = 937,500 cm$^3$/h/g$\text{cat}$ (STP), $\dot{\text{g}}_{\text{cat}} = 0.016$ g, NH$_3$ = 500 ppm, NO = 500 ppm, H$_2$O = 5%, O$_2$ = 8%, T = 225 $^\circ$C).

4. Conclusions

Herein, we have studied the effect of H$_2$O on the NH$_3$ storage onto different Cu-CHA catalysts, using standard NH$_3$ adsorption/TPD experiments. According to our preliminary results, during the temperature ramp of the TPD run the adsorbed NH$_3$ fully reduces the initially oxidized Cu sites, releasing a stoichiometric amount of N$_2$. This effect is often overlooked in the literature but impacts the quantification of Cu-related and Brønsted NH$_3$ adsorption sites.

On increasing both the SAR and Cu loading, we found the adsorbed NH$_3$/Cu ratio decreased from 4 to 3 when H$_2$O was absent from the gas mixture (and from 2 to 1 in the absence of gaseous NH$_3$), which correlates nicely with the corresponding expected increase in the proportion of ZCu$^{II}$OH over Z$_2$Cu$^{II}$ species. Upon addition of water to the feed stream, all the tested catalysts showed NH$_3$/Cu ratios closer to 3 (or to 1 in the absence of gaseous NH$_3$). These results are consistent both with the hydrolysis of a fraction of Z$_2$Cu$^{II}$ species to form ZCu$^{II}$OH, even though competition between H$_2$O and NH$_3$ for adsorption onto Lewis sites cannot be ruled out.

This work is novel because it includes both the Cu reduction and the hydrolysis reaction in the analysis of the NH$_3$-TPD data. However, the occurrence of these phenomena complicates the interpretation of the experimental TPD runs, thus it is suggested not to solely use this method to probe the Cu speciation in Cu-CHA catalysts [8].

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070759/s1, Figure S1: Comparison between dry and wet NH$_3$-TPD after adsorption at 150 $^\circ$C on H-CHA catalysts with SAR = 13, Table S1: NH$_3$ adsorbed on different sites as estimated from NH$_3$-TPD deconvolution under dry conditions, Table S2: NH$_3$ adsorbed on different sites as estimated from NH$_3$-TPD deconvolution under dry conditions.

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