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Interpretation of NH$_3$-TPD Profiles from Cu-CHA Using First-Principles Calculations

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Abstract

Temperature-programmed desorption (TPD) with ammonia is widely used for zeolite characterization revealing information on acidity and adsorption sites. The interpretation of TPD measurements is, however, often challenging. One example is the NH$_3$-TPD profile from Cu-chabazite (Cu-CHA) which generally is deconvoluted in three peaks with contributions from NH$_3$ on Lewis acid sites, copper sites and Brønsted acid sites. Here, we use density functional theory calculations combined with kinetic simulations to analyze this case. We find a large number of possible species, giving rise to overlapping features in the NH$_3$-TPD. The experimental low-temperature peak (below 200 °C) is assigned to NH$_3$ desorption from Lewis acid sites together with NH$_3$ desorption from a [Cu(II)(OH)(NH$_3$)$_3$]$^+$ complex. The intermediate-temperature peak (250–350 °C) is attributed to decomposition of a linear [Cu(I)(NH$_3$)$_2$]$^+$ complex and a residual from [Cu(II)(OH)(NH$_3$)$_3$]$^+$. The high-temperature peak is predicted to have contributions from Brønsted acid sites (NH$_4^+$), [Cu(I)NH$_3$]$^+$ and [Cu(II)(NH$_3$)$_4$]$_2$$^{2+}$. The present work shows that NH$_3$-TPD from Cu-CHA can be reconciled with copper complexes as NH$_3$ storage sites.

Keywords NH$_3$-TPD · Zeolites · Cu-CHA · Acidity

1 Introduction

Temperature-programmed desorption (TPD) is widely used for characterization of heterogeneous catalysts. The method is straightforward and based on the measurement of the desorption profile of a pre-adsorbed probe molecule during controlled heating. For zeolites and oxide surfaces, NH$_3$-TPD is generally used to measure the amount of acid sites together with the acid strength [1, 2]. Despite its simplicity, the interpretation of TPD profiles is often hampered by limited knowledge on the active sites, sample heterogeneity and coverage dependent adsorbate–adsorbate interactions. Due to these complications, TPD measurements are commonly used merely as a catalyst signature of acidity rather than a means to obtain site-specific information. One example is NH$_3$-TPD profiles from zeolites functionalized with copper ions.

Zeolites exchanged with copper ions are efficient catalysts for selective catalytic reduction of NO$_x$ with ammonia (NH$_3$-SCR), which is the basis of the current technology for the abatement of NO$_x$ emission from diesel engines [3, 4]. In particular, copper-exchanged zeolites and zeotypes with the small-pore chabazite framework structure (Cu-CHA) is the state-of-the-art catalyst for NH$_3$-SCR which combines a good performance in the temperature range 200–550 °C with a high hydrothermal stability [5–7]. The NH$_3$-TPD profile of Cu-CHA is characterized by three desorption peaks [8–17]; a low-temperature peak below 200 °C, an intermediate-temperature peak at 250–350 °C and a high-temperature peak at 400–500 °C.

The low-temperature peak is generally assigned to NH$_3$ adsorbed to Lewis acid sites [8–13, 17] whereas the peak at 400–500 °C has been attributed to NH$_3$ adsorbed on Brønsted acid sites. NH$_3$ adsorbed at Cu-sites has been suggested to give rise to the intermediate-temperature peak at 250–350 °C [8–12]. An attempt to assign the peaks to specific Cu sites was made in Ref. [8] where the intermediate- and high temperature peaks were attributed to Cu
coordinated to the zeolite framework in 6- and 8-membered rings, respectively.

The understanding of the active sites in Cu-CHA during operating conditions has advanced during the recent years. Experimental as well as computational studies have shown that Cu\(^+\) is preferably solvated by two \textit{NH}_3 ligands forming a linear [Cu(I)(\textit{NH}_3)]\(^+\) complex under low-temperature \textit{NH}_3-SCR conditions [18–24]. The [Cu(I)(\textit{NH}_3)]\(^+\) complex is mobile with low barriers for inter-cage diffusion and suggested to be important also for the solid-state ion-exchange reaction [25]. In addition to Cu\(^+\) species, Cu-CHA also contain solvated Cu\(^{2+}\) species in the form of [Cu(II)(\textit{NH}_3)]\(^2+\) or [Cu(II)(OH)(\textit{NH}_3)]\(^+\) [15, 18, 20].

The evidence of \textit{NH}_3-solvated complexes under \textit{NH}_3-SCR conditions should have consequences for the interpretation of \textit{NH}_3-TPD profile from Cu-CHA. In particular, the desorbed \textit{NH}_3 should partly originate from \textit{NH}_3-solvated Cu-complexes. In this study, density functional theory calculations in combination with kinetic simulations are used to elucidate the \textit{NH}_3-TPD profile from Cu-CHA. We find that the experimental \textit{NH}_3-TPD curves can be reconciled with \textit{NH}_3 desorbing from Lewis acid sites, solvated copper species and Brønsted acid sites. By simulating the \textit{NH}_3-TPD curves based on the stability of different species as calculated by DFT, we obtain insights on the observed features of \textit{NH}_3-TPD from Cu-CHA. Moreover, the identification of the decomposition temperature of [Cu(I)(\textit{NH}_3)]\(^+\) complexes provides information that elucidates the temperature dependent activity of the Cu-CHA catalyst, including the often observed decrease in NO conversion with increasing temperature.

2 Computational Methods

2.1 Density Functional Theory Calculations

Spin-polarised density functional theory calculations are performed with the Vienna Ab-Initio Simulation Package (VASP) [26–29].\(^1\) The Kohn–Sham orbitals are expanded with plane waves using an energy cut-off of 480 eV and the interaction between the valence electrons and the cores is described with the plane augmented wave (PAW) method [30, 31]. The number of valence electrons used in the calculations are 11 for Cu, 4 for Si, 3 for Al, 6 for O, 5 for N and 1 for H. The exchange-correlation functional is approximated with the PBE+cx van der Waals functional [32]. PBE+cx makes use of the vdW-DF [33] description, which provides an accurate description of binding energies of, for example, molecular dimers [32]. Structures are optimized with the conjugate gradient method and geometries are considered to be converged when the electronic energy difference between subsequent steps is smaller than \(1 \times 10^{-5}\) eV and the largest force is smaller than \(3 \times 10^{-2}\) eV/Å. The k-point sampling is restricted to the Γ-point. The calculated energies are zero-point corrected and the harmonic vibrational frequencies are computed using a finite-difference approach.

The chabazite structure is modeled using a rhombohedral unit cell which includes 12 Si atoms in tetrahedral (T) positions. The optimized cell parameters are \(a, b, c = 9.42\) Å and \(\alpha, \beta, \gamma = 94^\circ\). The lattice parameters are kept fixed during the geometry relaxations.\(^2\) The Si/Al ratio is 11 and 5 when considering cationic and double cationic species, respectively. Both Si/Al ratios are within the common experimental range between 20 and 5 [20, 34–36]. To study the influence of complex and adsorbate concentration, calculations were performed also in a \((2 \times 2 \times 2)\) super-cell increasing the Si/Al ratio by a factor of 8.

2.2 Evaluation of \textit{NH}_3-TPD

The \textit{NH}_3 desorption profiles have been analyzed following Refs. [37, 38] taking readsorption into account. Consequently, the simulated process is:

\[
\text{NH}_3^+ \xrightleftharpoons[\text{ads}]{k_d}{k_a} \text{NH}_3(g) + * \tag{1}
\]

where \(\ast\) denotes an adsorption site and \textit{NH}_3(g) is ammonia in the gas phase. \(k_a\) and \(k_d\) are the desorption and adsorption rate constants, respectively. In the mean-field assumption, the time derivative of the \textit{NH}_3 coverage (\(\theta\)) is given by:

\[
\frac{d\theta}{dt} = k_a \frac{P_g}{P_0} (1 - \theta) - k_d \theta \tag{2}
\]

where \(P_g\) is the pressure of ammonia and \(P_0\) is the pressure at standard conditions. Using the ideal gas law, \(P_g\) can be written as \(RTC_g\), where \(R\) is the gas constant, \(T\) is the temperature and \(C_g\) is the ammonia concentration. The concentration can be calculated assuming equilibrium between the gaseous and adsorbed ammonia:

\[
C_g = \frac{\theta}{1 - \theta} \frac{P_0}{RT} K \tag{3}
\]

where \(K\) is the equilibrium constant given by the enthalpy and entropy changes (\(\Delta H\) and \(\Delta S\)) upon desorption:

\(^1\) We used VASP version 5.4.1.

\(^2\) We also performed tests with the \((1 \times 1 \times 1)\) unit cell relaxing the cell parameters. The volume of the relaxed cell is decreased by 1–4% depending on the considered complex. The adsorption energies are \(-0.1\) eV lower than for the case with a fixed cell. However, as the Cu loading in our calculations is much higher than in the experiments, the effect of relaxation is most likely overestimated.
\[ K = \frac{k_d}{k_a} = \exp \left( -\frac{\Delta H}{RT} \right) \exp \left( \frac{\Delta S}{R} \right) \]  
(4)

The mass balance in the flowing gas is:

\[ FC_g = -A_0 W \frac{d\theta}{dt} = -\beta A_0 W \frac{d\theta}{dT} \]  
(5)

where \( F \) is the flow rate of the carrier gas, \( A_0 \) is the concentration of the adsorption sites, \( W \) is the zeolite weight and \( \beta \) is the heating rate (\( \Delta T = \beta \delta t \)). The concentration can in this way be written:

\[ C_g = -\frac{\beta A_0 W}{F} \frac{d\theta}{dT} = \frac{\theta - \theta^0}{1 - \theta} \exp \left( -\frac{\Delta H}{RT} \right) \exp \left( \frac{\Delta S}{R} \right) \]  
(6)

The calculated \( NH_3 \)-TPD profiles are compared to experimental data for a Cu-CHA catalyst with Si/Al = 15 and a Cu loading of 2.9 wt% Cu. The \( NH_3 \)-TPD was measured with a microreactor system, using a 50 mg sample of the catalyst in a quartz U-tube (4 mm inner diameter). The flow rate was 190 Nml/min during the entire procedure. The catalyst was initially reduced in a mixture of 800 ppm NO and 900 ppm NH\(_3\) at 200 °C; under these conditions the [Cu(I)(NH\(_3\))\(_2\)]\(^+\) complex is formed \(^{[39]}\). NO was thereafter removed from the gas phase, and the catalyst was saturated in 900 ppm NH\(_3\) at 200 °C, followed by 2 h purge in \( N_2 \) at the same temperature. To measure the NH\(_3\)-TPD, the sample was cooled down to 150 °C, and thereafter heated to 550 °C at a rate of 3 °C/min, while the concentration of NH\(_3\) in the reactor exit gas was recorded using a FTIR spectrometer (Gasmet CX4000) connected to the reactor outlet.

### 3 Results and Discussion

The desorption peaks in the TPD-profile are sensitive to the change in free energy (\( \Delta G = \Delta H - T\Delta S \)). The change in entropy (\( \Delta S \)) has been measured to be close to constant (ca 150 J/K/mol) over a wide range of zeolites and experimental conditions \(^{[38]}\), therefore we use this value. The change in enthalpy (\( \Delta H \)) is here calculated using DFT. To verify the ability of the current approach to describe the interactions between Cu ions and NH\(_3\), we calculated the sequential NH\(_3\) binding energies of [Cu(I)(NH\(_3\))\(_x\)]\(^+\) (\( x = 1-4 \)) in gas phase. This is a system which has been experimentally investigated by collision-induced dissociation \(^{[40]}\). Our calculated (zero-point corrected) sequential binding energies of [Cu(I)(NH\(_3\))\(_x\)]\(^+\) (\( x = 1-4 \)) are 2.41, 2.58, 0.51 and 0.41 eV, respectively. This is in good agreement with the experimental values of 2.49, 2.60, 0.52 and 0.42 eV \(^{[40]}\), indicating that the Cu–NH\(_3\) bond strength is accurately described by PBE+cx.

For NH\(_3\) adsorption in Cu-CHA, we have considered the species shown in Fig. 1. Figure 1a shows NH\(_3\) adsorbed at a Brønsted acid site forming NH\(_4^+\) and Fig. 1b–f show the different Cu complexes. The sequential desorption energies are reported in Table 1.

Considering the case with adsorbates in each rhombohedral unit cell (\( E_{des}^{[x\times1\times1]} \)), the energy required for decomposition of NH\(_4^+\) is calculated to be 1.46 eV, which is within the range (1.34–1.67 eV) measured for the NH\(_3\) adsorption on Brønsted acid sites in H-ZSM-5 \(^{[41]}\). The desorption energies for [Cu(I)(NH\(_3\))\(_2\)]\(^+\) are 1.29 and 1.54 eV, respectively. The clear separation between the two energies should result in different peaks in the TPD profile. Cu\(^{2+}\) is considered with one to four NH\(_3\) ligands. The highest desorption energy is obtained when going from four to three ligands. The sequential desorption energies for the remaining ligands are all lower. Thus, once the decomposition of the [Cu(II)(NH\(_3\))\(_2\)]\(^+\) complex starts, all ligands should desorb. The situation is slightly more complex for [Cu(II)(OH)(NH\(_3\))\(_1\)]\(^+\) which shows a non-monotonous behaviour with the highest energy calculated for decompositions of the second NH\(_3\). Thus, also this species should give rise to multiple peaks in the TPD profile.

To study the influence of complex and adsorbate concentration, calculations were performed also in a \( (2 \times 2 \times 2) \) super-cell. In this case, the Si/Al ratio was reduced by a factor of 8 and adsorption was considered only in one of the eight unit cells. The differences in adsorption energies are small, all being within 0.1 eV. In comparison with the high coverage results, cases with Cu-species not directly bonded to the framework, have slightly lower NH\(_3\) adsorption energies, whereas NH\(_3\) bonded to framework-coordinated Cu ions have slightly higher adsorption energies.

Turning to the TPD profiles, we have simulated desorption curves for some representative cases using the \( E_{des}^{[x\times1\times1]} \) energies. Figure 2a shows the desorption profiles for the linear complex. The peak at ca. 350 °C originates from decomposition of [Cu(I)(NH\(_3\))\(_2\)]\(^+\), whereas the higher desorption energy for the remaining NH\(_3\) ligand yields a peak at about 460 °C. Figure 2b shows the desorption peaks from NH\(_4^+\) (Brønsted acid site) and [Cu(II)(NH\(_3\))\(_2\)]\(^2+\) at 430 °C and 475 °C, respectively. As the desorption energies of the remaining NH\(_3\) adsorbed on Cu\(^{2+}\) are lower than the first, only one peak should appear for this complex.

We compare the simulated TPD profiles with experiments performed for Cu-CHA (Fig. 2c). The experiment was performed with NH\(_3\) adsorbed at 200 °C. The temperature was lowered to 150 °C before starting the TPD measurement. The results show the two features at 290 and
430 °C, respectively. Based on the calculations, we attribute the lower temperature feature to the decomposition of [Cu(I)(NH₃)₂]⁺. The feature at higher temperature could be assigned to [Cu(I)NH₃]⁺, Brønsted acid sites (NH₄⁺), and decomposition of [Cu(II)(NH₃)₄]²⁺.

Previously it has been shown that the stability of the [Cu(I)(NH₃)₂]⁺ pairs depends on the local Al-distribution [24]. Similar effects could be anticipated for complexes considered here, which will lead to a broadening of the TPD features. In addition to the Al-distribution, the concentration of species in the zeolite can give rise to a broadening. The difference between the adsorption energies calculated in the (1 × 1 × 1) and the (2 × 2 × 2) cells gives an estimate of such effects.

In the literature, three peaks are generally present in the desorption profile of ammonia from Cu-CHA [8–11]. A low-temperature peak below 200 °C, an intermediate-temperature peak at 250–350 °C and a high-temperature peak at 400–500 °C. The intermediate and high-temperature peaks are present in Fig. 2c. It has been suggested that the low-temperature peak should be assigned to NH₃ desorption from Lewis acid sites, the intermediate-temperature
could elucidate the known drop in NH$_3$-SCR activity with increasing temperature at 300–350 °C. The low-temperature activity is governed by the linear complexes which are known to activate oxygen while forming transient pairs [21–24]. Our calculations show that [Cu(I)(NH$_3$)$_2$]$^{2+}$ decomposes at temperatures when the loss of activity is observed. The residual [Cu(I)NH$_3$]$^+$ species is coordinated to a framework oxygen which hinders activation of O$_2$. Meanwhile, the [Cu(II)(NH$_3$)$_4$]$^{4+}$ complex is still intact and not available for taking part in the catalytic cycle. As the temperature is raised above 350 °C, bare framework coordinated Cu-species are present reactive to oxygen [42]. Thus, NH$_3$ inhibits the SCR reaction in the intermediate temperature regime.

4 Conclusions

We have used DFT calculations in combination with kinetic simulations to elucidate NH$_3$-TPD from Cu-CHA. Experimentally, three peaks are generally observed in the desorption profile. A low-temperature peak below 200 °C, an intermediate-temperature peak at 250–350 °C and a high-temperature peak at 400–500 °C. Based on our calculations, the low-temperature peak is assigned to NH$_3$ desorption from Lewis acid sites together with NH$_3$ desorption from a [Cu(II)(OH)(NH$_3$)$_4$]$^{4+}$ complex. The intermediate-temperature peak is attributed to decomposition of the linear [Cu(I)(OH)(NH$_3$)$_2$]$^+$ complex and a residual from [Cu(II)(OH)(NH$_3$)$_3$]$^+$. The high temperature peak is predicted to have contributions from NH$_4^+$, [Cu(I)NH$_3$]$^+$ and [Cu(II)(NH$_3$)$_4$]$^{2+}$. A suggestion for the observed NH$_3$ inhibition of the SCR reaction during intermediate temperatures was discussed based on the calculated NH$_3$ adsorption energies.

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