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# Direct measurement of enthalpy and entropy changes in NH<sub>3</sub> promoted O<sub>2</sub> activation over Cu–CHA at low temperature

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Oxygen activation is a key step in the selective catalytic reduction of nitrogen oxides with ammonia (NH<sub>3</sub>-SCR) over Cu-chabazite. We present direct measurements of oxygen adsorption at low temperatures over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes and framework-bound Cu<sup>+</sup> species in Cu-chabazite with Si/Al = 14 using isothermal microcalorimetry combined with mass spectrometry. The enthalpy change for O<sub>2</sub> adsorption over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes at 200 °C is determined to be

–79 kJ/mol. By fitting a Langmuir isotherm, the corresponding entropy change is determined to be –142 J/(mol\*K) at 10% O<sub>2</sub>. The results show that O<sub>2</sub> adsorption at low temperatures over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes is more facile than on framework-bound Cu<sup>+</sup> species. The experimental results are in agreement with density functional theory calculations showing a lower barrier for O<sub>2</sub> activation over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes as compared to the framework-bound Cu<sup>+</sup> species.

## Introduction

Copper-functionalised zeolites with the chabazite framework structure (Cu–CHA) are efficient catalysts for selective catalytic reduction of nitrogen oxides (NO<sub>x</sub>) by ammonia (NH<sub>3</sub>-SCR). This reaction is the basis for the current technology to control NO<sub>x</sub> emissions from diesel and bio-diesel exhausts.<sup>[1,2]</sup> The NH<sub>3</sub>-SCR reaction over Cu–CHA has been intensively studied and reaction mechanisms have been proposed with some variations in elementary steps and structural configurations.<sup>[3–6]</sup> In general, the reaction is based on a redox cycle, where Cu(I) is oxidised by O<sub>2</sub> and reduced by NH<sub>3</sub> and NO.<sup>[3,6,7]</sup> Furthermore, the reaction mechanism at temperatures below 250 °C has been shown to be different from that at higher temperatures.<sup>[8,9]</sup> The change in

reaction mechanism often leads to a decrease in the NO<sub>x</sub> conversion with increasing temperature in the range 250–350 °C. According to the current views of the NH<sub>3</sub>-SCR reaction, the change in reaction mechanism is related to a change in the character of the active Cu(I) species. At low temperature, the Cu(I) species are solvated by NH<sub>3</sub>-ligands forming mobile [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes, whereas Cu(I) species become bound to the framework at higher temperatures.<sup>[5,7,9–12]</sup> At low temperatures, it has been suggested that O<sub>2</sub> is activated over a pair of [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes.<sup>[4,5,12,13]</sup> This suggestion is based experimentally on the observation that, at low Cu loadings, the NH<sub>3</sub>-SCR reaction shows a second order dependence on the Cu loading and that the oxidation of Cu(I) with O<sub>2</sub> has a second order behaviour.<sup>[4,9]</sup> Moreover, density functional theory (DFT) calculations have revealed that O<sub>2</sub> activation over single framework-bound Cu<sup>+</sup> species is strongly endothermic, whereas O<sub>2</sub> activation becomes feasible if O<sub>2</sub> reacts with a pair of Cu(I)-ions.<sup>[12,14,15]</sup>

According to the present understanding, the oxidation of Cu(I) with O<sub>2</sub> should be more efficient over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complex, as compared to framework-bound Cu<sup>+</sup>. In this work, we present a microcalorimetry study of O<sub>2</sub> adsorption on [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes and framework-bound Cu<sup>+</sup> species in Cu–CHA, and compare the experimental results with DFT calculations. The measurements allow for direct determination of the enthalpy change upon O<sub>2</sub> adsorption over pairs of [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes. By fitting a Langmuir isotherm, the corresponding entropy change can also be determined. By simultaneously monitoring the heat release and the amount of oxygen adsorbed using mass spectrometry, we show that O<sub>2</sub> adsorbs on both types of Cu(I) species at 200 °C. The process is, however, considerably more facile over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes. The apparent activation energy of O<sub>2</sub> adsorption over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes is determined to be lower than over the framework-bound Cu<sup>+</sup> species. The experimental results are in agreement with the DFT calculations showing a lower

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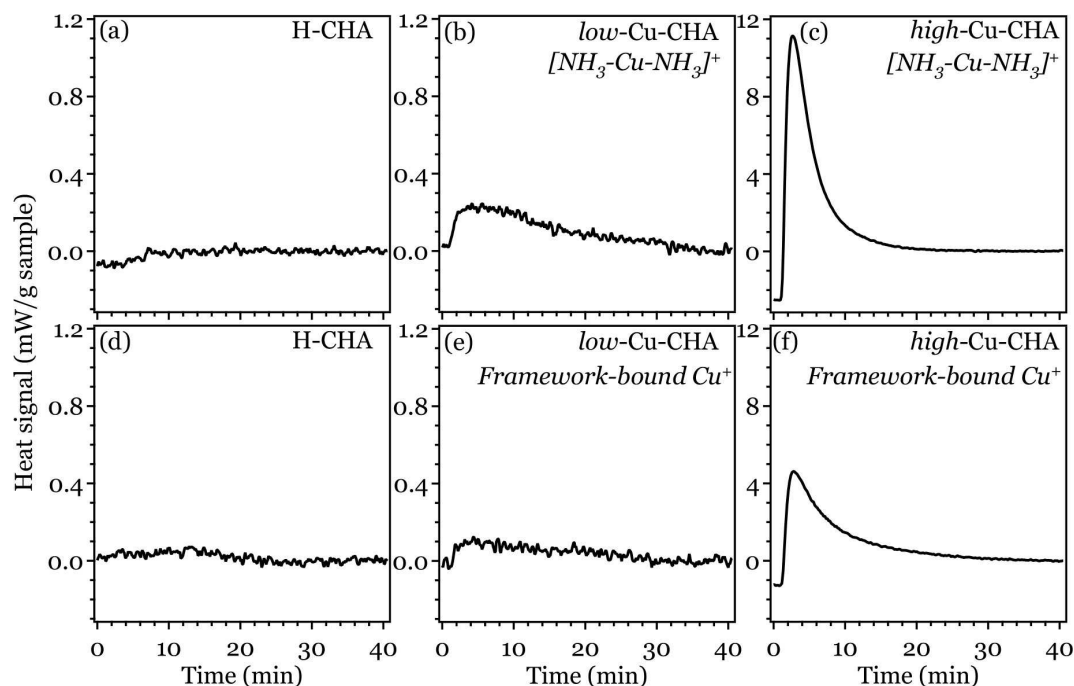
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**Figure 1.** Heat signal recorded during  $O_2$  exposure (500 ppm) at  $200^\circ\text{C}$  over the H-CHA, *low*- and *high*-Cu-CHA samples. (a-c) are pre-treated in NO and  $NH_3$  at  $200^\circ\text{C}$  (see SI, S1.2) yielding  $[NH_3-Cu-NH_3]^+$  complexes for (b) and (c). (d-f) are subsequently pre-treated in  $O_2$  at  $500^\circ\text{C}$  (see SI, S1.2) yielding framework-bound  $Cu^+$  species for (e) and (f). Note that the range of the y-axis for the *high*-Cu-CHA sample is a magnitude higher than that of the other samples.

barrier for  $O_2$  activation over the  $[NH_3-Cu-NH_3]^+$  complexes as compared to the framework-bound  $Cu^+$  species.

## Experimental

Two aqueous ion-exchanged Cu-CHA (Si/Al = 14) samples with low and high copper loading were prepared, *i.e.* *low*-Cu-CHA (0.60 wt.% Cu) and *high*-Cu-CHA (3.3 wt.% Cu) (see SI, S1.1). The parent H-CHA zeolite was used as reference. To form the  $[NH_3-Cu-NH_3]^+$  complexes, the Cu-CHA samples were reduced in NO and  $NH_3$  at  $250^\circ\text{C}$  for 30 min and subsequently at  $200^\circ\text{C}$  for 30 min.<sup>[8,16]</sup> The framework-bound  $Cu^+$  species were formed by heating the reduced sample in Ar to  $500^\circ\text{C}$  for 60 min whereby the  $[NH_3-Cu-NH_3]^+$  complexes decompose yielding predominantly framework-bound  $Cu^+$  species (see SI, S1.2).<sup>[8,17]</sup> The  $[NH_3-Cu-NH_3]^+$  complexes and the framework-bound  $Cu^+$  species have been identified using X-ray absorption spectroscopy in previous studies in Cu-CHA samples with similar Si/Al ratio and Cu loadings.<sup>[8,16,17]</sup> The heat signal during exposure of the  $[NH_3-Cu-NH_3]^+$  complexes and the framework-bound  $Cu^+$  species in a gas flow containing 500 ppm of  $O_2$  in Ar at  $200^\circ\text{C}$  was recorded for the two Cu-CHA samples and the parent H-CHA zeolite, using a flow-through sample cell for the calorimetry. The amount of adsorbed oxygen was determined from the difference of  $m/Z = 32$ , and the scaled  $m/Z = 84$  intensity of Kr as trace gas, using a mass spectrometer connected to the outlet of the sample cell.

## Results and Discussion

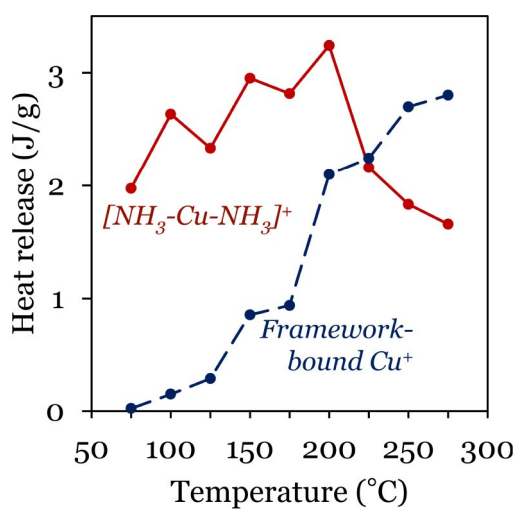
Figure 1 shows the heat release during  $O_2$  adsorption for the parent zeolite, and for the  $NH_3$  solvated and framework-bound

Cu(I) in the two Cu-CHA catalysts. The corresponding heat release, calculated heat of adsorption and O/Cu ratio are presented in Table 1. No significant heat release is observed during  $O_2$  exposure of the H-CHA zeolite at  $200^\circ\text{C}$ , while there are clear heat effects for the Cu-CHA samples. For the samples with the  $[NH_3-Cu-NH_3]^+$  complexes, we find a heat release of 0.23 J/g for the *low*-Cu-CHA sample, and a significantly higher release of 3.2 J/g for the *high*-Cu-CHA sample. The corresponding numbers for the samples with framework-bound  $Cu^+$  species are 0.09 J/g for the *low*-Cu-CHA sample and 2.1 J/g for the *high*-Cu-CHA sample. The two important observations are (1) the heat release for the catalysts with the  $[NH_3-Cu-NH_3]^+$  complexes is higher than the heat release for the framework-bound  $Cu^+$  species, and (2) the heat release for the *high*-Cu-CHA sample is considerably higher than for the *low*-Cu-CHA sample.

Figure 2 presents the heat release during  $O_2$  exposure over the  $[NH_3-Cu-NH_3]^+$  complexes and the framework-bound  $Cu^+$  species in the *high*-Cu-CHA sample between 75 to  $275^\circ\text{C}$ . For the  $[NH_3-Cu-NH_3]^+$  complexes, the heat release increases with increasing temperature up to  $200^\circ\text{C}$  after which it substantially decreases. Below  $200^\circ\text{C}$ , we speculate that the possibility to activate  $O_2$  over Cu(I)-pairs increases with increasing temperature thanks to faster diffusion of the  $[NH_3-Cu-NH_3]^+$  complexes, resulting in an increased heat release. It is known that  $[NH_3-Cu-NH_3]^+$  starts to decompose above  $200^\circ\text{C}$ , yielding framework-bound  $[Cu-NH_3]^+$  and  $Cu^+$  species.<sup>[8,18]</sup> It is anticipated that the sharp decrease in heat release for temperatures above  $200^\circ\text{C}$  is a result of decomposition of the  $[NH_3-Cu-NH_3]^+$  complexes. For the framework-bound  $Cu^+$  species, the heat release instead increases within the entire temperature range examined. No

		H-CHA	low-Cu-CHA	high-Cu-CHA <sup>[a]</sup>
[NH <sub>3</sub> -Cu-NH <sub>3</sub> ] <sup>+</sup>	J/g sample	0.00	0.23	3.2 ± 0.1
	kJ/mol Cu	n.a.	2.5	6.2 ± 0.3
	kJ/mol O <sub>2</sub>	n.a.	n.a.	79 ± 6
	O/Cu <sup>[b]</sup>	n.a.	n.a.	0.16 ± 0.01
Framework-bound Cu <sup>+</sup>	J/g sample	0.04	0.09	2.1 ± 0.3
	kJ/mol Cu	n.a.	1.0	4.0 ± 0.5
	kJ/mol O <sub>2</sub>	n.a.	n.a.	120 ± 9
	O/Cu <sup>[b]</sup>	n.a.	n.a.	0.07 ± 0.01

<sup>[a]</sup> The values are averaged from three separate measurements for each Cu species, see SI, S3.1. <sup>[b]</sup> The O/Cu ratio is calculated by dividing double the amount of adsorbed O<sub>2</sub> [mol/g catalyst], by the total amount of Cu [mol/g catalyst].



**Figure 2.** Heat release during O<sub>2</sub> exposure (500 ppm) over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes (red dots with solid line for guidance) and the framework-bound Cu<sup>+</sup> species (blue dots with dashed line for guidance) in the high-Cu-CHA sample between 75 and 275 °C.

significant heat release is in this case observed below 150 °C. From the O<sub>2</sub> exposure experiments the apparent activation energies were obtained. The activation enthalpy for O<sub>2</sub> adsorption over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes and framework-bound Cu<sup>+</sup> species is determined to be 15 and 39 kJ/mol, respectively (see SI, S3.2).

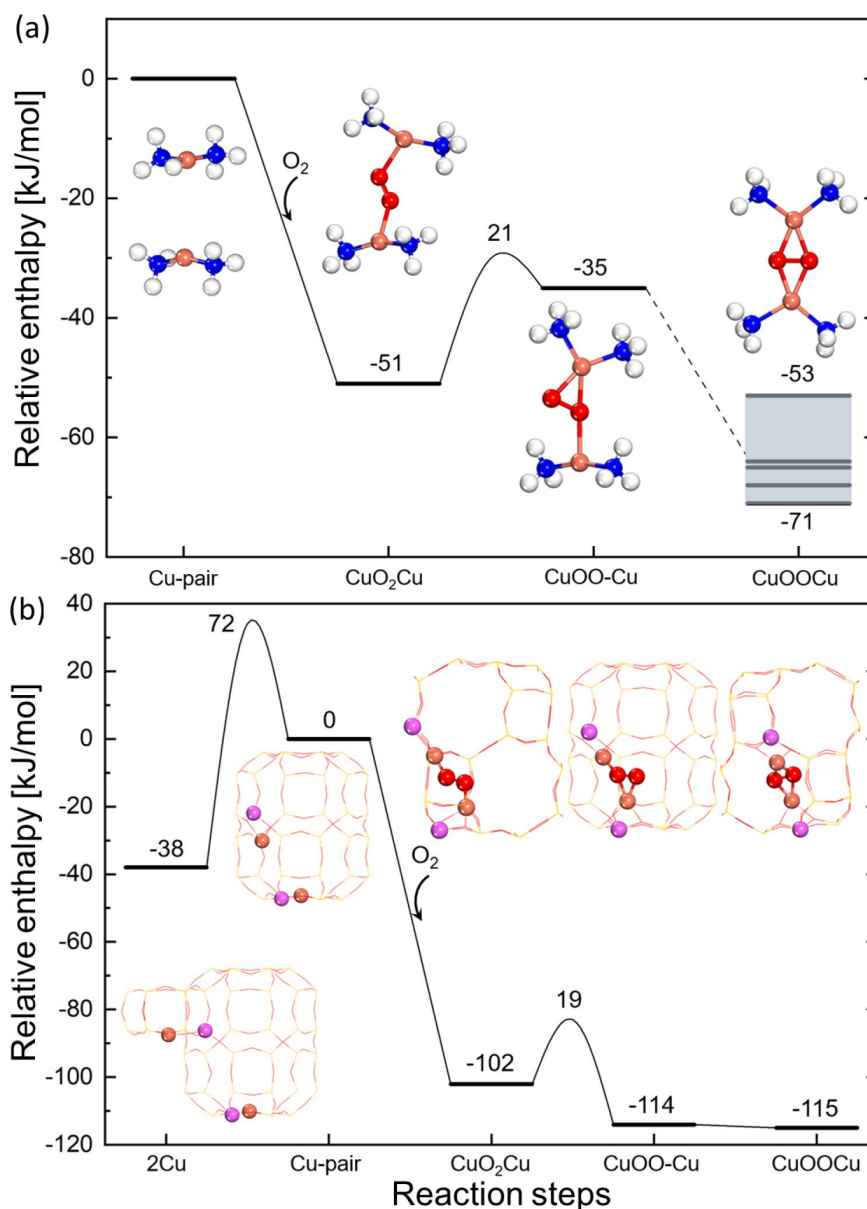
The measured heats of O<sub>2</sub> adsorption on the different Cu(I) species are compared with DFT calculations. Figure 3 shows possible reaction paths for the O<sub>2</sub> adsorption over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pairs and framework-bound Cu<sup>+</sup>-pairs. The CHA structure is modelled using a hexagonal unit cell, which includes 36 tetrahedral positions with two Al atoms per unit cell, corresponding to an Si/Al ratio of 17. Because it is unlikely to have Al-O-Si-O-Al sequences in Si-rich zeolites,<sup>[19]</sup> we use an Al-O-(Si-O)<sub>2</sub>-Al sequence with two Al atoms placed in neighbouring six-membered rings to describe the general trends. In our previous work,<sup>[14]</sup> the Al-distribution has been found to have an effect on the stability of the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pairs in Cu-CHA, which probably will affect the probability for [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pair formation. The dependence of the O<sub>2</sub> adsorption energy on the Al-distribution is studied by considering five different structural

configurations. The five configurations are selected from our previous work,<sup>[14]</sup> and corresponds to an Al-Al distance of 6.28, 7.24, 8.60, 11.46 and 13.77 Å, respectively. Further details of the calculations are given in SI, S2.

To directly compare the experimentally measured heats of O<sub>2</sub> adsorption with the calculated values, the reference (zero level) for the O<sub>2</sub> adsorption over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pair is considered to be the precursor state of the molecularly adsorbed O<sub>2</sub> (see the structure Cu-pair in Figure 3(a)). In similarity, the reference for the O<sub>2</sub> adsorption over the framework-bound Cu<sup>+</sup>-pairs is taken when the two Cu ions are close enough for O<sub>2</sub> to adsorb (see the structure Cu-pair in Figure 3(b)). The final structure for the adsorption of O<sub>2</sub> in a peroxo-state has been studied in detail in Refs. [6, 16, 20].

Previously, the linear [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complex has been shown to be mobile at reaction temperatures<sup>[7]</sup> and the diffusion barrier between cages is calculated to be low (~0.3 eV).<sup>[21]</sup> Thus, the diffusion step has not been considered in this reaction mechanism (Figure 3(a)). The adsorption of O<sub>2</sub> over the complex-pair proceeds via molecular O<sub>2</sub> adsorption (CuO<sub>2</sub>Cu) to the peroxo-state (CuOO-Cu) with a low barrier of 21 kJ/mol. The final CuOOCu configuration is a singlet with two antiferromagnetically coupled magnetic moments (0.6 μ<sub>B</sub> per copper ion), implying that the formal oxidation state of copper in this configuration is +2.<sup>[20]</sup> The five different Al-distribution configurations give a span of the adsorption enthalpy of O<sub>2</sub>, which ranges from 53 to 71 kJ/mol. The difference between the configurations originates mainly from the different Coulomb interactions among the five configurations.

The adsorption of O<sub>2</sub> over the framework-bound Cu<sup>+</sup> also requires a pair of Cu<sup>+</sup> ions, which has been discussed in Ref. [15]. A possible reaction path for O<sub>2</sub> activation over the framework-bound Cu<sup>+</sup>-pair is shown in Figure 3(b). Here, the locations of the two Al atoms are similar with that used in Ref. [15]. Each Cu<sup>+</sup> species is preferably located in the six-membered ring bridging two framework oxygen atoms (2Cu).<sup>[21-23]</sup> To make it feasible to adsorb O<sub>2</sub>, the two Cu<sup>+</sup> ions need to be sufficiently close. The barrier for Cu<sup>+</sup> ion diffusion forming the Cu-pair structure is calculated to be 72 kJ/mol and the pair formation is endothermic by 38 kJ/mol. The activation of O<sub>2</sub> over the framework-bound Cu ions from this configuration (Cu-pair) has a low barrier of 19 kJ/mol. The final



**Figure 3.** The potential enthalpy landscape at 200 °C of: (a) O<sub>2</sub> adsorption over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pairs in Cu-CHA; (b) O<sub>2</sub> adsorption over framework-bound Cu<sup>+</sup>-pairs. Five selected different Al-distribution configurations for the mobile Cu-complex pair case have been chosen to study the dependence of adsorption energies on the Al-distribution, which results in a span of adsorption enthalpy. The structure for each step is shown. For clarity, the CHA framework is removed in (a) and kept as lines in (b). All energies are zero-point corrected. Atom colour codes: copper (light brown), aluminium (purple), nitrogen (blue), oxygen (red) and hydrogen (white).

CuOOCu species is a triplet with magnetic moments on the copper ions for which we assign the formal oxidation state of copper to be +2. The total adsorption energy for the activated O<sub>2</sub> over the framework-bound Cu<sup>+</sup>-pair is 115 kJ/mol.

The DFT results are in good agreement with the microcalorimetry data, showing a lower barrier over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes as compared to framework-bound Cu<sup>+</sup> species. The barrier for O<sub>2</sub> adsorption is calculated to be 21 kJ/mol over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> pair, which is close to our experimental value of 15 kJ/mol determined from the Eyring plot (SI S3.2). The corresponding barriers are not as close for the framework-bound case (72 vs 39 kJ/mol), which can be attributed to the

choice of Al-distribution. The DFT calculations show that the origin of the apparent activation energy is different for the two cases. The barrier for O<sub>2</sub> activation over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> pair originates from the formation of the CuOO-Cu species, whereas the barrier over framework-bound Cu<sup>+</sup> is connected with diffusion of Cu<sup>+</sup> ions, forming a Cu<sup>+</sup>-pair.

From the DFT calculations, the adsorption enthalpy of activated O<sub>2</sub> over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pairs is within a range (from 53 to 71 kJ/mol), which is slightly lower than the measured heat (79 kJ/mol). Possible reasons for the discrepancy in the absolute energies can be related to the Al-distribution as well as the difficulty to accurately describe the Cu-O bond by

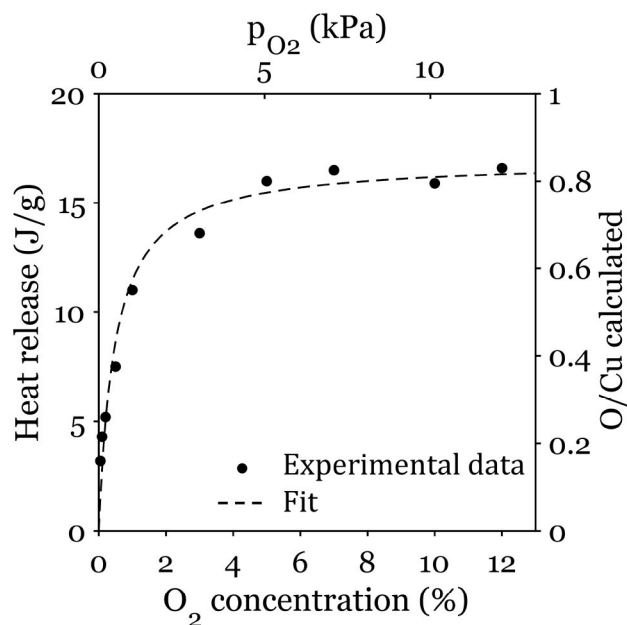
the current exchange correlational functional.<sup>[20]</sup> However, our DFT results predict the trend in a good agreement with the measured heat of adsorption, which shows a lower heat of adsorption for the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes (79 kJ/mol) compared to that of the framework-bound  $\text{Cu}^+$  species (120 kJ/mol) for the *high*-Cu-CHA sample.

The calorimetric measurements at 200 °C show that the heat release is higher for the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes than for the framework-bound  $\text{Cu}^+$  species regardless of Cu loading. The difference in heat release is related to a higher amount of oxygen adsorbed on the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes compared to the framework-bound  $\text{Cu}^+$  species (see SI, S3.1). As the direct  $\text{O}_2$  activation requires Cu(I)-pairs for both framework bound and  $\text{NH}_3$ -solvated copper species, this implies that the propensity for pair formation is higher for  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes than for framework-bound  $\text{Cu}^+$  species. This supports the idea that pair formation is facilitated by the higher mobility of the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes.<sup>[7,21,24]</sup> For framework-bound  $\text{Cu}^+$  species, pair-formation is associated with a barrier of 72 kJ/mol originating from  $\text{Cu}^+$  diffusion between adjacent cages (Figure 3(b)), rendering  $\text{Cu}^+$ -pair formation less probable. Therefore, the higher heat release for the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes is related to the higher mobility, providing more sites for  $\text{O}_2$  activation.

The higher propensity of  $\text{O}_2$  adsorption on the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes is also reflected in the higher amount of oxygen adsorbed. Assuming that oxygen only adsorbs over Cu(I)-pairs, for the *high*-Cu-CHA sample with pre-treatment to form dominantly  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes, around 16% of the total Cu content is oxidised during exposure to 500 ppm  $\text{O}_2$  at 200 °C, whereas the corresponding number is about 7% for the pre-treatment forming dominantly framework-bound  $\text{Cu}^+$  species, see Table 1. Moreover, the fraction of copper participating in  $\text{O}_2$  adsorption varies for the two Cu-CHA samples, which is indicated by the heat release per Cu (shown in Table 1). The heat-release per Cu ( $[\text{NH}_3\text{-Cu-NH}_3]^+$  or framework-bound  $\text{Cu}^+$ ) is higher for the *high*-Cu-CHA sample (6.2 and 4.0 kJ/mol Cu) compared to the *low*-Cu-CHA sample (2.5 and 1.0 kJ/mol Cu). This suggests that sufficiently high Cu-density is required for Cu(I) pair formation and thereby  $\text{O}_2$  adsorption, which is in agreement with previous studies.<sup>[4,12,15]</sup>

The heat released during  $\text{O}_2$  exposure over the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes is also affected by the  $\text{O}_2$  concentration. Figure 4 presents heat release as a function of oxygen concentration from 500 ppm to 12%. Assuming the same mechanism and, therefore, heat of oxygen adsorption for all tested  $\text{O}_2$  concentrations, the O/Cu ratio can be calculated for each  $\text{O}_2$  concentration, as also presented in Figure 4. For exposure at 10%  $\text{O}_2$ , the calculated O/Cu ratio is 0.8 which is comparable to the 80–90% of Cu(II) oxidised from Cu(I) observed spectroscopically in previous studies over similar Cu-CHA samples.<sup>[4,16]</sup> The experimental data can be fitted with a Langmuir isotherm:

$$\theta = \text{O/Cu} = \frac{aK_{\text{eq}}^{\circ}(\text{T}) \frac{p_{\text{O}_2}}{p^{\circ}}}{1 + K_{\text{eq}}^{\circ}(\text{T}) \frac{p_{\text{O}_2}}{p^{\circ}}} = \frac{0.848 \times 207 \times \frac{p_{\text{O}_2}}{p^{\circ}}}{1 + 207 \times \frac{p_{\text{O}_2}}{p^{\circ}}}, R^2 = 0.979 \quad (1)$$



**Figure 4.** Heat release and O/Cu ratio during exposure of the  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complexes to  $\text{O}_2$  from 500 ppm to 12% at 200 °C. The O/Cu ratio for  $\text{O}_2$  concentrations ( $c_{\text{O}_2}$ ) higher than 500 ppm is calculated using data measured at  $c_{\text{O}_2} = 500$  ppm, assuming constant heat of adsorption under all  $c_{\text{O}_2}$ . The corresponding partial pressure of  $\text{O}_2$  ( $p_{\text{O}_2}$ ) is shown at the top axis.

where  $\theta$  is the coverage and  $K_{\text{eq}}^{\circ}(\text{T})$  is the equilibrium constant at standard pressure ( $P^{\circ}$ ). The constant  $a$  limits the coverage to the experimentally observed saturation coverage. The  $K_{\text{eq}}^{\circ}(\text{T})$  and  $a$  is fitted to be 207 and 0.848 at 200 °C, respectively.

The entropy change for reactions in zeolites has been discussed recently in the literature. For the  $\text{NH}_3$ -SCR reaction some estimates for entropy changes along the reaction path have been suggested based on simulations.<sup>[5,6,16]</sup> However, no quantitative experimental data has been reported. The information on the equilibrium constant and the heat of adsorption gives us the possibility to calculate the entropy loss for  $\text{O}_2$  adsorption over the  $[\text{NH}_3\text{-Cu-NH}_3]^+$ -pair. The equilibrium constant is given by:<sup>[25]</sup>

$$K_{\text{eq}}^{\circ}(\text{T}) \times \frac{p_{\text{O}_2}}{p^{\circ}} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \quad (2)$$

where  $\Delta H$  is the enthalpy change and  $\Delta S$  is the entropy change. Using the experimentally determined  $\Delta H$ , the entropy change  $\Delta S$  is via the equilibrium constant calculated to be  $-123 \text{ J}/(\text{mol}\cdot\text{K})$  at standard pressure. Typically, the  $\text{O}_2$  concentration during  $\text{NH}_3$ -SCR is 10%, which gives an entropy change of  $-142 \text{ J}/(\text{mol}\cdot\text{K})$ .

The entropy change of  $\text{O}_2$  adsorption on a pair of complexes has three main contributions (see the schematic diagram in Figure S4 in SI). Upon entering the CHA cage from the gas phase,  $\text{O}_2$  loses entropy. Previously, we have studied the entropy loss for  $\text{N}_2$  from gas phase into CHA by performing Monte Carlo potential energy sampling,<sup>[26]</sup> which demonstrates

that N<sub>2</sub> loses approximately 50% of the gas phase entropy at 200 °C. Here, we can assume that O<sub>2</sub> also loses 50% of its gas phase entropy upon entering CHA ( $\Delta S_{O_2}^1 = -109 \text{ J}/(\text{mol}\cdot\text{K})$ ). Another part of the O<sub>2</sub> entropy ( $\Delta S_{O_2}^2$ ) is lost upon adsorption over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup>-pair. In addition, there is an entropy loss connected to the pairing of the complexes ( $\Delta S_{Cu}$ ). Here, the sum of the three contributions is fitted to be  $-123 \text{ J}/(\text{mol}\cdot\text{K})$  at standard pressure. The sum of  $\Delta S_{O_2}^2$  and  $\Delta S_{Cu}$  amounts to  $-14 \text{ J}/\text{mol}\cdot\text{K}$ , which is a minor part of the entropy loss.

## Conclusion

In summary, we have compared the heat of O<sub>2</sub> adsorption over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes and framework-bound Cu<sup>+</sup> species in CHA as measured by microcalorimetry combined with mass spectrometry and compared the results with DFT calculations. For O<sub>2</sub> adsorption over [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes at 200 °C, the heat of adsorption is 79 kJ/mol while the entropy change is analysed to be  $-142 \text{ J}/\text{mol}\cdot\text{K}$  at 10% O<sub>2</sub>. The results reveal that a higher amount of O<sub>2</sub> adsorbs over the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes than over the framework-bound Cu<sup>+</sup> species at 200 °C. The DFT calculations show that the activation of O<sub>2</sub> proceeds with low barriers over both types of Cu-pairs. However, the diffusion of framework-bound Cu<sup>+</sup> species between adjacent CHA cages is associated with considerable barriers, which makes the Cu<sup>+</sup>-pair formation less facile. The low probability of Cu<sup>+</sup>-pair formation for framework-bound Cu-CHA consequently leads to a lower O<sub>2</sub> adsorption upon O<sub>2</sub> exposure as compared to the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes. The higher amount of O<sub>2</sub> adsorbed on [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes as compared to framework-bonded Cu<sup>+</sup> species, provides further support for the suggestion that the mobility of the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes is a key factor for the activation of O<sub>2</sub> in low-temperature NH<sub>3</sub>-SCR over Cu-CHA. Furthermore, the observed differences in O<sub>2</sub> activation on the [NH<sub>3</sub>-Cu-NH<sub>3</sub>]<sup>+</sup> complexes and framework-bound Cu<sup>+</sup> species contribute to an enhanced understanding of the underlying chemistry of partial oxidation reactions, such as that of direct oxidation of methane to methanol.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** adsorption · Cu-chabazite · NH<sub>3</sub>-SCR · oxygen activation · zeolites

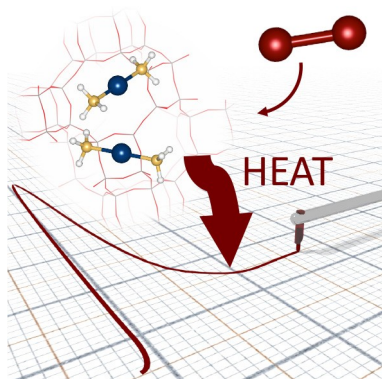
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## FULL PAPERS

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The heat release of oxygen adsorption on a pair of  $[\text{NH}_3\text{-Cu-NH}_3]^+$  complex in Cu-CHA is recorded using micro calorimetry combined with mass spectrometry. The apparent activation energy, as well as enthalpy and entropy changes of this process are determined experimentally.



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1 – 7

**Direct measurement of enthalpy and entropy changes in  $\text{NH}_3$  promoted  $\text{O}_2$  activation over Cu-CHA at low temperature**

