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# Mechanism for SO<sub>2</sub> poisoning of Cu-CHA during low temperature NH<sub>3</sub>-SCR

Joachim D. Bjerregaard<sup>a,\*</sup>, Martin Votsmeier<sup>b</sup>, Henrik Grönbeck<sup>a,\*</sup>

<sup>a</sup> Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

<sup>b</sup> Umicore AG & Co. KG, Rodenbacher Chaussee 4, 63457 Hanau, Germany

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## ABSTRACT

Density Functional Theory (DFT) calculations are used to investigate low temperature SO<sub>2</sub> deactivation of Cu-CHA during ammonia assisted selective catalytic reduction of NO (NH<sub>3</sub>-SCR). SO<sub>2</sub> is found to adsorb on [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> forming a copper sulfate complex. NO and NH<sub>3</sub> react over the sulfate complex forming N<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>SO<sub>4</sub> undergoes an acid-base reaction with NH<sub>3</sub> yielding SO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub> and HSO<sub>4</sub>(NH<sub>4</sub>), where HSO<sub>4</sub>(NH<sub>4</sub>) is thermodynamically preferred during typical reaction conditions. The SO<sub>2</sub>-derived species are bulky and have considerable barriers for inter-cage diffusion. Moreover, the presence of HSO<sub>4</sub>(NH<sub>4</sub>) species reduces the probability of having two [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes in one cage, which is a requirement for O<sub>2</sub> activation. The results suggest that the key mechanism for low temperature SO<sub>2</sub> deactivation is of physical origin and that the catalyst can be regenerated by exposure to high temperatures where HSO<sub>4</sub>(NH<sub>4</sub>) decomposes. The suggested mechanism agrees with experimental observations and provides atomistic understanding of sulfur poisoning of Cu-CHA during NH<sub>3</sub>-SCR.

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## 1. Introduction

Exhaust from combustion engines contains hazardous nitrogen oxides (NO<sub>x</sub>), which should be removed by an aftertreatment system [1]. NO<sub>x</sub> in oxygen excess can efficiently be reduced to N<sub>2</sub> and H<sub>2</sub>O via ammonia assisted selective catalytic reduction (NH<sub>3</sub>-SCR) over transition metal functionalized small pore zeolites. In particular, copper exchanged chabazite (Cu-CHA) has shown good low-temperature catalytic activity and selectivity [2,3] and simultaneously a good hydrothermal stability [4,5]. The overall reaction scheme for the, so called, standard NH<sub>3</sub>-SCR reaction is



The NH<sub>3</sub> to NO ratio is one and O<sub>2</sub> is required for the hydrogen abstraction. The catalytic reaction is a redox cycle, where the oxidation state of Cu changes between Cu<sup>I</sup> and Cu<sup>II</sup>. Cu<sup>I</sup> is oxidized to Cu<sup>II</sup> upon O<sub>2</sub> adsorption and reduced to Cu<sup>I</sup> during NH<sub>3</sub>-NO coupling. The catalytic activity has been measured to have a quadratic dependence on the copper loading at low temperatures, which suggests that two copper ions are involved in the standard SCR mechanism [6–8]. Thus, the diffusion and paring of the copper ions is a critical

step for the low-temperature activity. Two experimentally reported states of the Cu-ions are Z<sub>2</sub>Cu and ZCuOH [9,10]. Z refers to the Al-environment; Z being one Al-site and Z<sub>2</sub> two Al-sites. The copper ions are solvated in the presence of ammonia, forming mobile [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes [11–14], which diffuse between the zeolite cages with small barriers [15,16]. By having two [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes in the same cage, O<sub>2</sub> can be activated forming a [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> peroxo complex, over which NO and NH<sub>3</sub> couple to H<sub>2</sub>NNO and HONO. It has been suggested that H<sub>2</sub>NNO and HONO decompose to N<sub>2</sub> and H<sub>2</sub>O over Brønsted acid sites [17,18].

Despite high activity and selectivity, one issue with the Cu-CHA catalyst is a sensitivity to SO<sub>2</sub> and SO<sub>3</sub> exposure. Even small concentrations of sulfur compounds in the exhaust have shown to accumulate in the catalyst and significantly decrease the SCR-activity [19–21], which lowers the operational lifetime of the catalyst. The mechanism behind the deactivation is not well understood and the degree of deactivation appears to depend on numerous variables such as temperature, gas composition, Cu loading, Si/Al ratio and the state of the Cu-ion (ZCuOH or Z<sub>2</sub>Cu) [19,22,23]. Moreover, SO<sub>2</sub> and SO<sub>3</sub> shows differences in the degree of induced deactivation, with SO<sub>3</sub> being more severe [24]. Presence of SO<sub>3</sub> in the exhaust stream could originate from the diesel oxidation catalyst (DOC) commonly placed upstream of the NH<sub>3</sub>-SCR catalyst.

\* Corresponding authors.

E-mail addresses: [joabje@chalmers.se](mailto:joabje@chalmers.se) (J.D. Bjerregaard), [ghj@chalmers.se](mailto:ghj@chalmers.se) (H. Grönbeck).

The  $\text{SO}_2$ -deactivation can be divided into reversible and irreversible deactivation [25,20]. The deactivation for Cu-CHA is predominately reversible and the catalyst activity can be regained by periodically heating to 500–550 °C [20,26]. The reversible deactivation has been measured to be pronounced over a wide range of S/Cu ratios and associated with a lowering of the apparent activation energy of the SCR reaction [25]. The reversible deactivation can, therefore, not be directly related to sulfur adsorption at copper sites. Recent measurements have instead indicated that  $\text{SO}_2$  affect the mobility and redox behavior of copper species [27]. The irreversible deactivation has been measured to have a close to 1:1 relationship between the deactivation and the S/Cu ratio. Furthermore, the apparent activation energy of the SCR reaction does not change dramatically during the irreversible deactivation [25]. This suggests that the irreversible deactivation is related to sulfur species that blocks the copper sites.

The interaction of  $\text{SO}_2$  with copper species and reaction intermediates during low temperature  $\text{NH}_3$ -SCR is not well understood. Using X-ray absorption spectroscopy measurements, Molokova et al., [28] studied recently the reactivity of  $\text{SO}_2$  with different reaction intermediates. It was found that  $\text{SO}_2$  is reactive towards the peroxo species  $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$  reducing the Cu-ion from  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . Although first-principles calculations have been used to investigate mechanisms for the  $\text{NH}_3$ -SCR reaction in Cu-CHA [17,18,29,30,7], the influence of sulfur on the reaction has mainly concerned the relative thermodynamic stability [31,22] of different sulfur containing species and the reaction of  $\text{SO}_x$  with framework bound copper, namely  $\text{Z}_2\text{Cu}$  and  $\text{ZCuOH}$  [23,32]. The conclusions from the thermodynamic analyses are that copper bisulfates ( $\text{CuHSO}_4$ ) and copper ammonium sulfate ( $\text{CuSO}_4(\text{NH}_4)$ ) are the preferred species during reaction conditions [31,22]. A higher stability has been predicted for  $\text{SO}_x$  species formed over  $\text{ZCuOH}$  as compared to  $\text{Z}_2\text{Cu}$ . In addition,  $\text{SO}_3$  adsorption over  $\text{ZCuOH}$  has been found to form  $\text{CuHSO}_x$  complexes with higher stability than adsorption of  $\text{SO}_2$  over  $\text{ZCuOH}$  [23,32].

Herein, we use DFT calculations to study the mechanism for low temperature  $\text{SO}_2$  deactivation of Cu-CHA during  $\text{NH}_3$ -SCR. Reaction landscapes, diffusion paths, and thermodynamic preferences are investigated. We find that  $\text{SO}_2$  interacts strongly with the peroxo complex  $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ , forming primarily ammonium bisulfate ( $\text{HSO}_4(\text{NH}_4)$ ) under reaction conditions. The sulfur species are found to accumulate in the CHA cage due to high diffusion barriers. The presence of sulfate species in the cage reduces the stability of paired  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes, which are required for  $\text{O}_2$  activation, thereby deactivating the catalyst. Our work provides insights and possible explanations for the considerable deactivation by small amounts of  $\text{SO}_2$  in Cu-CHA and highlights the importance of facile  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  diffusion and pairing for maintained  $\text{NH}_3$ -SCR activity.

## 2. Computational methods

### 2.1. DFT calculations

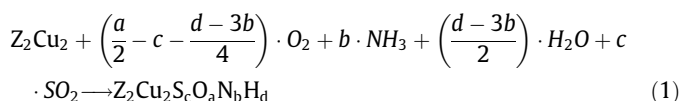
Spin polarised density functional theory (DFT) calculations are performed with the Vienna Ab initio Simulation Package (VASP) [33,34]. The Perdew-Burke-Ernzerhof (PBE) [35] version of the generalized gradient approximation is used to describe the exchange-correlation energy. The Grimme D3 approach [36] is applied to account for van der Waals interactions and a Hubbard term of 6 eV [37] is employed to reduce spurious delocalization of the Cu 3d electrons. The combination of Grimme D3 and PBE + U(6) has previously been shown to describe the Cu-CHA with reasonable accuracy when compared to experimental temperature

programmed desorption (TPD) measurements of  $\text{NH}_3$ , stability of  $\text{Cu}_2\text{O}_2$ -motif crystals and XPS/UPS spectra of copper oxides [38]. Pure GGA functionals tend to overestimate the binding energy for adsorption of NO on copper, when compared to hybrid functionals [39] and the inclusion of the Hubbard-U term is crucial to describe the changes in the oxidation states of Cu [38].

The Kohn-Sham orbitals are expanded with plane waves using a cut-off value of 480 eV and the interaction between the valence electrons and core is described by the Projector Augmented Wave (PAW) method [40,41]. The valence electrons considered for each element is Cu(11), Si(4), S(6), Al(3), O(6), N(5), and H(1). The k-point sampling is restricted to the gamma point. The self-consistent field (SCF) loop is considered to be converged, when the energy difference is less than  $10^{-5}$  eV, and the structure is considered to be a minimum if the norm of all forces acting on the atoms is lower than 0.02 eV/Å. The transition states are determined by the climbing image nudged elastic band (CI-NEB) method [42,43], and confirmed by vibrational analysis showing only one imaginary frequency. The vibrational analysis is done using the method of finite differences. All reaction landscapes are zero-point corrected. To explore the flat energy landscape for the different species in the zeolite, ab initio molecular dynamics (AIMD) simulations are performed and structures are relaxed from several point along the AIMD trajectory. The temperature is in the AIMD controlled using a Nosé-Hoover thermostat in the NVT ensemble [44,45]. The mass of hydrogen is replaced with that of tritium to facilitate integration of the equations of motion allowing a time step of 1 fs. In addition, constrained AIMD simulations are performed to explore both the inter- and intra-cage diffusion of various species. The free energy change along the trajectory is evaluated by thermodynamic integration of the free energy gradients [46]. Bader charge analyses are performed as implemented by the Henkelman group [47,48]. The CHA cage is modelled with a hexagonal unit cell consisting of 34 Si, 2 Al, and 72 O atoms, corresponding to a Si/Al ratio of 17, which is within the range of typical experimental values [22,23,20]. When two copper species are placed inside the cage, two aluminum atoms are placed opposite to each other in one six-membered ring, which previously has been reported to represent a stable configuration [49]. The choice of the Al configuration could potentially influence the energetics of the system. It has been shown that the stability of activated  $\text{O}_2$  on paired  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes can change up to 0.2 eV for relevant Al configurations [50]. However, the energy involved in  $\text{SO}_2$  adsorption, is significantly higher than 0.2 eV, suggesting that the choice of Al configuration will not affect the main conclusions in the present study.

### 2.2. Construction of phase diagrams

To evaluate the relative stability of different species as a function of temperature and  $\text{NH}_3$  pressure, we construct phase diagrams from the relative Gibbs free energies of formation.



The considered reservoirs are the gas phase species  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{NH}_3$  and the framework bound copper  $\text{Z}_2\text{Cu}_2$ . The Gibbs free energy of formation is calculated for each state according to:

$$\Delta G = E^{\text{DFT}} - c \cdot \Delta \mu_{\text{SO}_2} - \left(\frac{a}{2} - c - \frac{d-3b}{4}\right) \cdot \Delta \mu_{\text{O}_2} - \left(\frac{d-3b}{2}\right) \cdot \Delta \mu_{\text{H}_2\text{O}} - b \cdot \Delta \mu_{\text{NH}_3} - T\Delta S(T) \quad (2)$$

We neglect the pV term and approximate the enthalpy as the zero-point corrected electronic energy ( $E^{DFT}$ ).  $E^{DFT}$  is given by

$$E^{DFT} = E_{Z_2Cu_2ScO_6N_6H_4}^{DFT} - E_{Z_2Cu_2}^{DFT} - \left(\frac{a}{2} - c - \frac{d-3b}{4}\right) \cdot E_{O_2}^{DFT} - b \cdot E_{NH_3}^{DFT} - \left(\frac{d-3b}{2}\right) \cdot E_{H_2O}^{DFT} - c \cdot E_{SO_2}^{DFT} \quad (3)$$

By including the chemical potential ( $\Delta\mu_x$ ), the stability as a function of  $SO_2$ ,  $H_2O$ ,  $NH_3$  and  $O_2$  pressure is taken into account.

$$\mu_x(p_x, T) = k_b \cdot T \cdot \ln\left(\frac{p_x}{p^0}\right) - T\Delta S(T)_x \quad (4)$$

The entropies of the gas phase species are taken from the JANAF table [51], and is linearly interpolated between the experimental data points. Estimation of the adsorbate entropies inside the zeolite cages are challenging as it may contain a significant amount of translational and rotational entropy, which are not captured properly in the harmonic approximation [10,17,52]. However, in this study we have considered bulky  $SO_4^{2-}$ ,  $[Cu^I(NH_3)_2]^+$  and  $NH_4^+$  species confined in the small CHA cage, which implies that the translation and rotational degrees of freedom are significantly reduced. We have, therefore, assumed that the adsorbates lose most of their

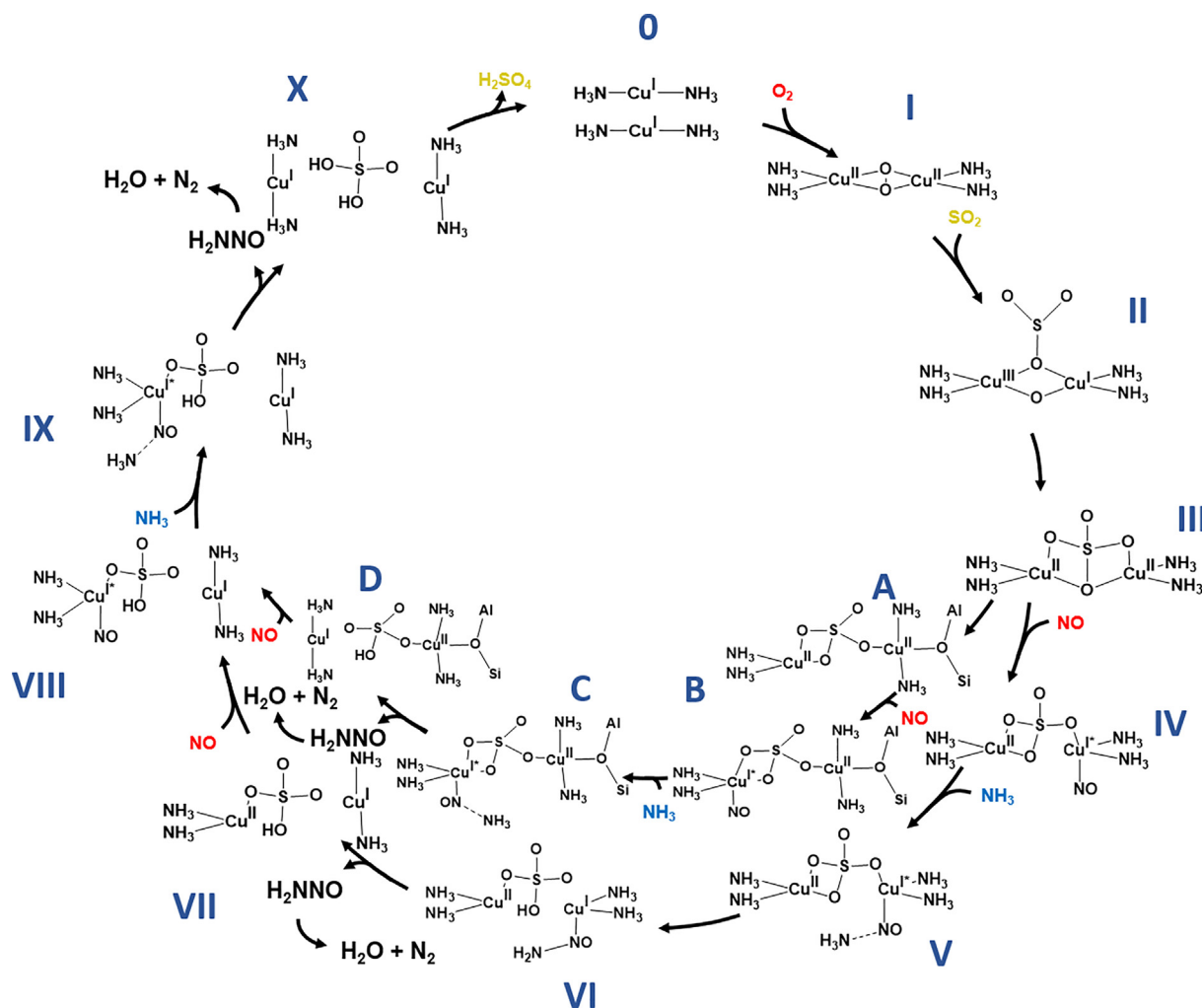
rotational and translational entropy and have evaluated these contributions as frustrated vibrations.

### 3. Results

#### 3.1. Reaction cycle with $SO_2$

Copper is solvated by two ammonia ligands forming  $[Cu^I(NH_3)_2]^+$  during typical reaction conditions [11–14]. Previously proposed reaction cycles have shown that a key step for the  $NH_3$ -SCR reaction is the adsorption of  $O_2$  on a pair of  $[Cu^I(NH_3)_2]^+$  forming a peroxo complex  $[Cu_2^{II}(NH_3)_4O_2]^{2+}$  [7,17,18,53]. NO and  $NH_3$  can couple over the peroxo complex forming  $H_2NNO$  and HONO, which can diffuse to Brønsted acid site and decompose to  $H_2O$  and  $N_2$  [17,18].

The proposed reaction cycles for  $NH_3$ -SCR [17,18] are here extended by the interaction with  $SO_2$  (Fig. 1). The reaction consists of one cycle without chemical bonds to the framework (the outer circle with structures denoted by roman numbers). However, a part of the reaction is able to follow an alternative route, forming chemical bonds to the framework (the inner circle with structures denoted by letters). The corresponding energy landscapes are



**Fig. 1.** Proposed reaction cycle for low temperature  $NH_3$ -SCR in the presence of  $SO_2$ . The oxidation state for Cu is indicated. Al-O-Si represents a Brønsted acid site, and is only shown if the  $[Cu^I(NH_3)_2]^+$  complex is chemically bound to the framework. Oxidation state of I\* indicate an intermediate oxidation state between I and II with magnetic moment of 0.2–0.3.  $H_2SO_4$  is formed during the SCR reaction.

reported in Figs. 2 and 3. Note that the energy landscapes include more structures than the catalytic cycles.

The starting point of the considered reaction is two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes in the same CHA-cage (structure **0**). One suggestion for the origin of this configuration could be the reduction of a  $\text{Z}_2\text{Cu}$  site, initially forming  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  and a Brønsted acid site, that in presence of  $\text{NH}_3$ , would be  $\text{NH}_4^+$ . As  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  and  $\text{NH}_4^+$  are mobile, the  $\text{NH}_4^+$  ion could diffuse to a neighboring cage, and a second  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complex could counter diffuse into the cage to retain the charge neutrality. This type of exchange is also the basis of the solid-state ion exchange [15].

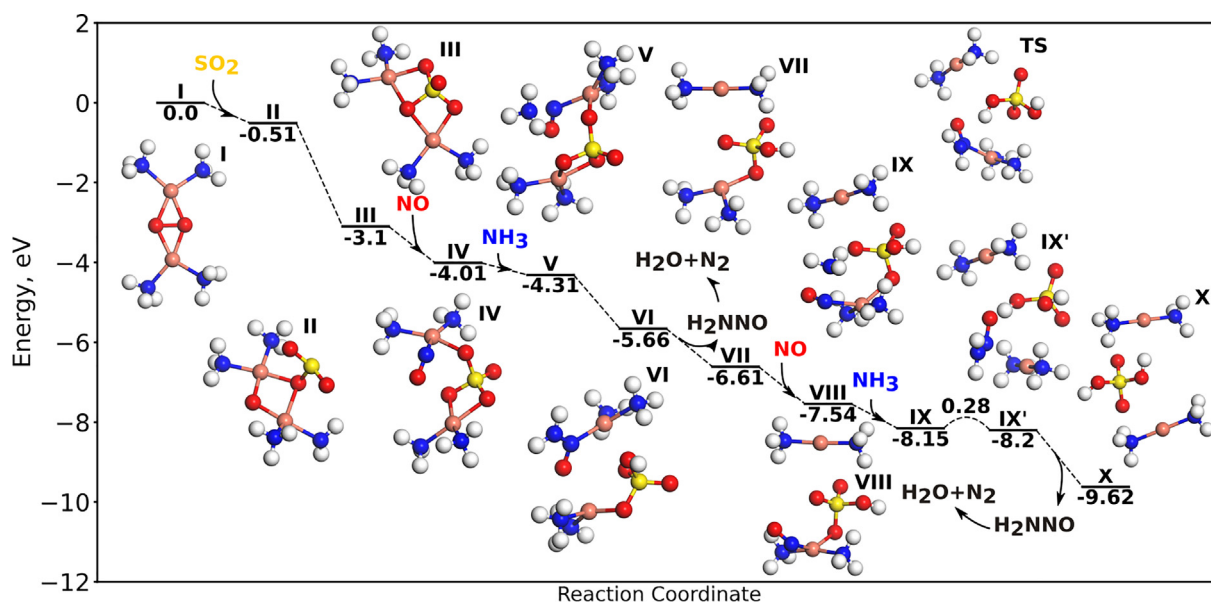
We find that  $\text{SO}_2$  interacts weakly with  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  (structure **0**) without any chemical bonds.  $\text{SO}_2$  is merely coordinated to the  $\text{Cu}^+$  ion with a long (O–Cu) distance of 3.0 Å.  $\text{SO}_2$  interacts instead strongly with the peroxo complex (**I**  $\Rightarrow$  **II**). In this case,  $\text{SO}_2$  adsorbs on one oxygen atom with an adsorption energy of  $-0.51$  eV, forming  $\text{SO}_3$  with an S–O bond length of 1.6 Å. One of the copper ions is oxidized to  $\text{Cu}^{\text{III}}$  upon formation of  $\text{SO}_3$ . From a Bader analysis, we find that sulfur in  $\text{SO}_3$  is close to a +4 oxidation state, similar to the case of  $\text{SO}_2$ . The  $\text{SO}_3$  species reacts without barrier with the second oxygen forming a very stable sulfate species (**III**). The sulfate species is preferred by 2.59 eV with respect to structure **II**. The oxidation state of sulfur is +6 in structure **III**. The formation of sulfur in a +6 oxidation state upon  $\text{SO}_2$  exposure of Cu-CHA has previously been observed using XAS and XPS [22,54,55]. The two copper ions in **III** are in +2 oxidation states ( $\text{Cu}^{\text{II}}$ ), thus providing the two electrons needed to form a sulfate ( $\text{SO}_4^{2-}$ ).  $\text{NH}_3$  and NO can react over **III** in a similar fashion as in the previously proposed low temperature  $\text{NH}_3$ -SCR cycles [17,18]. NO adsorbs at the Cu-site with a bond length of 2.04 Å and an adsorption energy of  $-0.91$  eV giving structure **IV**. NO adsorption results in the breaking of one of the Cu–O bonds. An electron is transferred during the adsorption forming  $\text{NO}^+$  and a partially reduced Cu. Attempts to adsorb NO at an oxygen anion did not result in any chemical bond. As NO is positively charged,  $\text{NH}_3$  can coordinate to NO, with an N–N length of 2.03 Å and an adsorption energy of  $-0.30$  eV (Structure **V**). One of the

hydrogen atoms in  $\text{H}_2\text{NNO}$ -Cu is only 2.10 Å from the nearest oxygen and transfers without barrier to the oxygen forming  $\text{H}_2\text{NNO}$  and a copper bisulfate (**V**  $\Rightarrow$  **VI**).

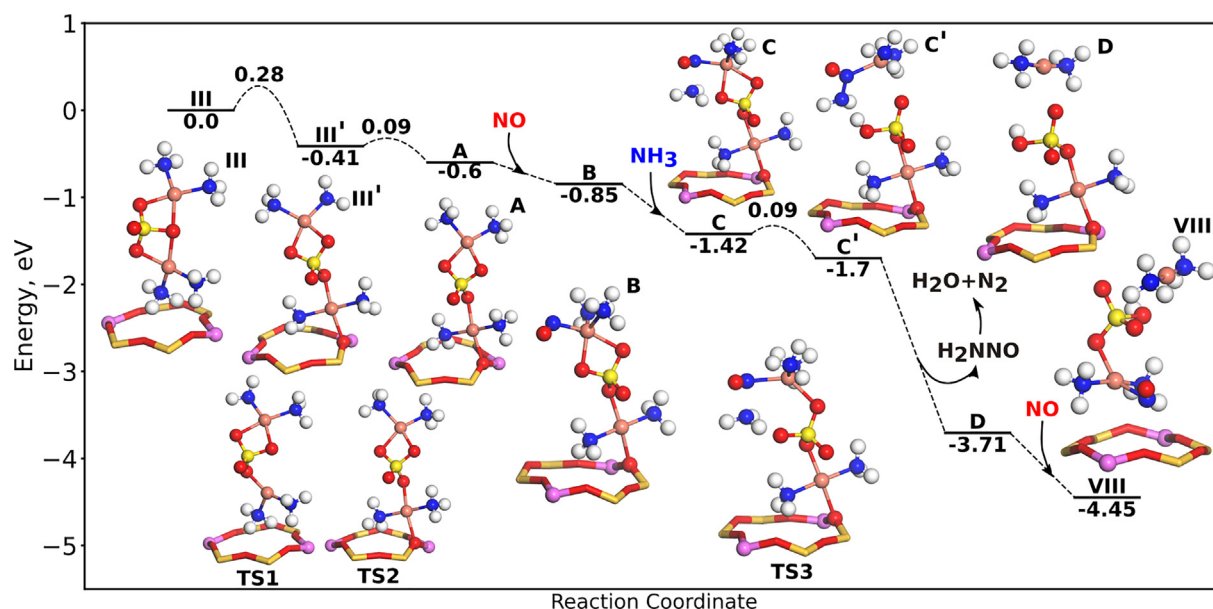
As the bisulfate species ( $\text{HSO}_4^-$ ) only is singly charged, one of the Cu ions is reduced ( $\text{Cu}^{\text{II}} \Rightarrow \text{Cu}^{\text{I}}$ ), which is accompanied by the breaking of one of the Cu–O bonds. The  $\text{H}_2\text{NNO}$  group can desorb, diffuse and decompose over a Brønsted acid site (**VI**  $\Rightarrow$  **VII**) forming  $\text{N}_2$  and  $\text{H}_2\text{O}$  [17]. The adsorption of NO and  $\text{NH}_3$ , can be repeated on structure **VII** where NO is adsorbed on the  $\text{Cu}^{\text{II}}$  site bound to the bisulfate. This proceeds with an adsorption energy of  $-0.93$  eV and  $-0.61$  eV for NO (structure **VIII**) and  $\text{NH}_3$  (structure **IX**), respectively. The hydrogen transfer has a low barrier of 0.28 eV, which breaks the O–Cu bond and results in two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  species and one sulfuric acid molecule.

An alternative reaction path where copper binds to the framework is described in the inner circle of Fig. 1, with the reaction landscape reported in Fig. 3. Structure **III** can be turned into a framework bound species (structure **A**) via barriers of 0.28 eV and 0.09 eV. In structure **A** of Fig. 3, Cu binds to a Brønsted acid site forming a square planar-like species. Structure **III'** is separated by a barrier of only 0.09 eV to structure **A**, which is energetically preferred by  $-0.6$  eV with respect to the mobile complex. NO and  $\text{NH}_3$  can react over structure **A** in a similar fashion as discussed for the mobile complexes. The adsorption energies of NO and  $\text{NH}_3$  are  $-0.25$  eV (structure **B**) and  $-0.57$  eV (structure **C**), respectively. The hydrogen transfer has a barrier of 0.09 eV forming bisulfate (structure **C'**). As already discussed, the  $\text{H}_2\text{NNO}$  group can desorb and decompose into  $\text{H}_2\text{O}$  and  $\text{N}_2$ . The adsorption of the second NO in the reaction cycle, which is done on the framework bound Cu, results in a partial reduction of the Cu ion. The reduction leads to the breaking of the Al–O–Cu bond, forming structure **VIII**. From here on, the reaction proceeds along the outer circle in Fig. 1.

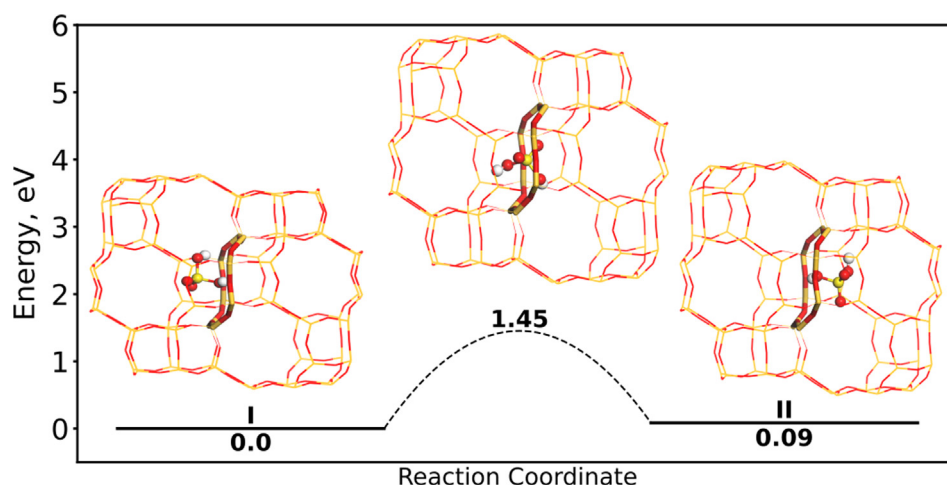
Closing the catalytic cycle requires that  $\text{H}_2\text{SO}_4$  leaves the cage. Our calculations show that the barrier for  $\text{H}_2\text{SO}_4$  diffusion to a neighboring cage is 1.45 eV, see Fig. 4, which indicates that  $\text{H}_2\text{SO}_4$  at low temperatures will accumulate in the CHA-cage.



**Fig. 2.** Energy landscape for the proposed reaction cycle for low temperature  $\text{NH}_3$ -SCR in the presence of  $\text{SO}_2$  without any framework bound  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ . (Outer circle in Fig. 1.) The zeolite cage is not shown for clarity. Atomic color codes: H(white), N(blue), O(red), S(yellow), and Cu(Bronze). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



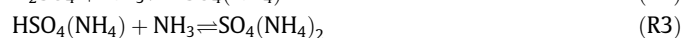
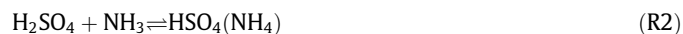
**Fig. 3.** Energy landscape for the proposed reaction cycle for low temperature  $\text{NH}_3$ -SCR with framework bound  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ . (Inner circle in Fig. 1.) Only the six-membered ring of CHA is shown. Atomic color codes as in Fig. 2 with Si (dark yellow sticks) and Al (pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Energy landscape for diffusion of  $\text{H}_2\text{SO}_4$  through an eight-membered ring in CHA. Atomic color codes as in Fig. 3.

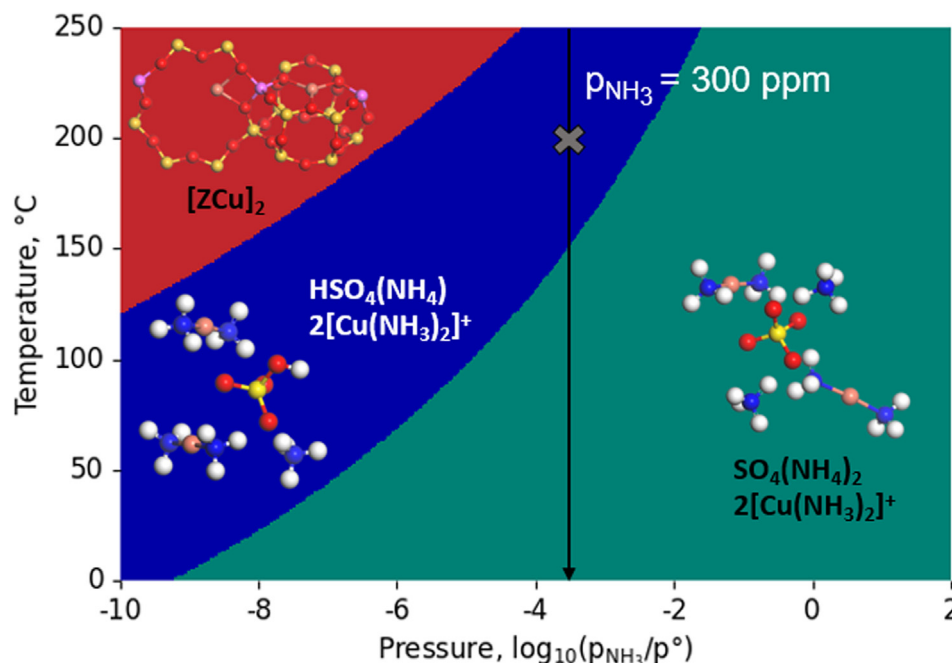
### 3.2. Formation of ammonium (bi) sulfate

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is one of the products in the reaction cycle described in Fig. 1. However, sulfuric acid can in the presence of  $\text{NH}_3$  undergo an acid-base reaction forming ammonium bisulfate ( $\text{HSO}_4(\text{NH}_4)$ ) and ammonium sulfate ( $\text{SO}_4(\text{NH}_4)_2$ ), (R2 and R3).



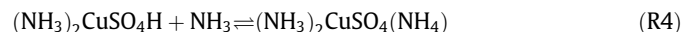
AIMD simulations at 473 K reveal that the protons bonded to  $\text{SO}_4$  are exchanged spontaneously forming either  $\text{HSO}_4(\text{NH}_4)$  or  $\text{SO}_4(\text{NH}_4)_2$ , if an  $\text{NH}_3$  molecule is added to the CHA-cage. Thus, the simulations suggest that the activation barriers to form  $\text{HSO}_4(\text{NH}_4)$  and  $\text{SO}_4(\text{NH}_4)_2$  are negligible. To investigate the dominant species at  $\text{NH}_3$ -SCR conditions, a phase diagram assessing the thermodynamic stability as a function of temperature and ammonia pressure is presented in Fig. 5. The structures considered

in the phase diagram are two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes together with  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4(\text{NH}_4)$ , and  $\text{SO}_4(\text{NH}_4)_2$ . This represents the state of the catalyst after  $\text{H}_2\text{SO}_4$  is formed corresponding to structure **X** in Fig. 1. The gas-phase concentrations used to construct the phase diagram are 10 %  $\text{O}_2$ , 5 %  $\text{H}_2\text{O}$  and 20 ppm  $\text{SO}_2$ . The arrow represents a typical ammonia concentration under SCR conditions ( $p_{\text{NH}_3} = 300$  ppm). At reaction conditions ( $T = 200$  °C), it is clear that the dominant species is  $\text{HSO}_4(\text{NH}_4)$ , whereas  $\text{SO}_4(\text{NH}_4)_2$  requires higher pressures of  $\text{NH}_3$  or lower temperatures.  $\text{H}_2\text{SO}_4$  is not stable enough to be present in the phase diagram. Thus, as soon as  $\text{H}_2\text{SO}_4$  is formed in presence of  $\text{NH}_3$  it will react to  $\text{HSO}_4(\text{NH}_4)$ . Note that  $\text{HSO}_4(\text{NH}_4)$  and the mobile  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes are predicted to decompose simultaneously, which is a consequence of their mutual stabilization. We stress that the phase diagram only represents the equilibrium situation without possible kinetic limitations and the assumption that the concentration of ammonia is the same in the gas phase as inside the CHA cage.



**Fig. 5.** Phase diagram showing the state of Cu and sulfur-containing species. Structures considered in the phase diagram are framework  $[ZCu]_2$ ,  $H_2SO_4$ ,  $HSO_4(NH_4)$  and  $SO_4(NH_4)_2$ . The pressures for the gas phase species are set to 10 % for  $O_2$ , 5 % for  $H_2O$ , and 20 ppm for  $SO_2$ . The black arrow represents an  $NH_3$  pressure of 300 ppm. The grey cross indicates typical reaction conditions of 300 ppm  $NH_3$  and 200 °C. Atomic color codes as in Fig. 3.

The phase diagram is constructed with acid-base reactions with structure **X** in Fig. 1. Exchange of protons between  $NH_3$  and sulfur-species could also take place early in the reaction cycle. One possibility is  $NH_3$  reacting with copper bisulfate, structure **VII** in Fig. 1. Structure **VII**, will form copper ammonium bisulfate in presence of  $NH_3$  (**R4**).

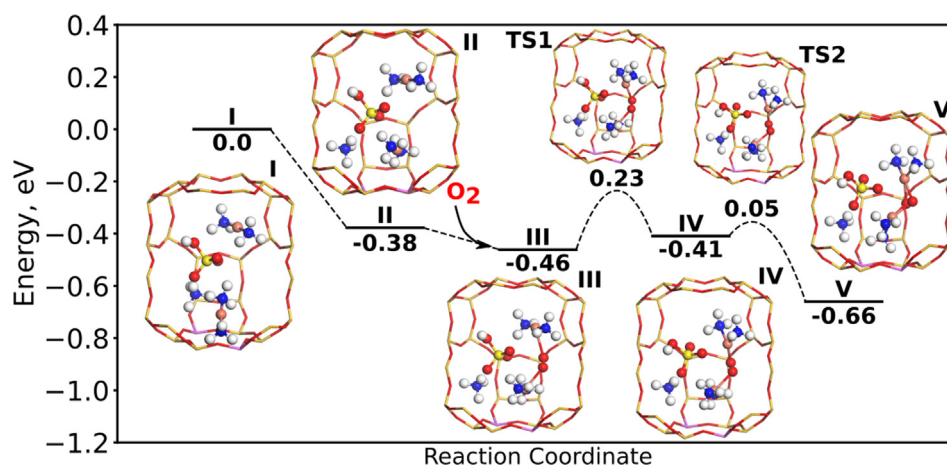


This reaction is barrierless and exothermic, see Supplementary Material (SM).

### 3.3. Possible deactivation routes

The catalytic cycle (Fig. 1) and the phase diagram (Fig. 5) indicate that sulfate species will accumulate in CHA cages during

reaction conditions, however the results do not reveal why and how the accumulation leads to deactivation. An important step in low temperature  $NH_3$ -SCR is the activation of  $O_2$  by a pair of  $[Cu^I(NH_3)_2]^+$  complexes, forming a peroxo complex ( $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ ). Here we investigate how the formation of the peroxo complex is affected by the presence of a bisulfate species. The potential energy diagram for  $O_2$  activation in presence of ammonium bisulfate is shown in Fig. 6. Structure **I**, represents the catalytic site after the reaction cycle in Fig. 1, thus  $H_2SO_4$  and two  $[Cu^I(NH_3)_2]^+$  complexes. The first step, (**I**  $\Rightarrow$  **II**), is intra cage diffusion of the two  $[Cu^I(NH_3)_2]^+$  complexes to be close enough for  $O_2$  adsorption. The diffusion is barrierless according to constrained AIMD simulations (see SM). The adsorption energy for oxygen is 0.08 eV (structure **III**). The adsorption energy is 0.2 eV



**Fig. 6.** Energy landscape for the formation of  $[Cu^{II}(NH_3)_4O_2]^{2+}$  in the presence of  $HSO_4(NH_4)$  in the zeolite cage. Atomic color codes as in Fig. 3.

in the absence of ammonium bisulfate,[17] thus the presence of ammonium bisulfate lowers the adsorption energy. We note that the  $O_2$  adsorption energy is likely underestimated using the applied computational approach,[18] and that the reduction of the adsorption energy in the presence of ammonium bisulfate has a higher significance than the absolute energy. Although a reduced  $O_2$  adsorption energy slows down the reaction, the reaction may still proceed and the mere presence of ammonium bisulfate is likely not the cause of deactivation.

The subsequent barriers to form the peroxo complex (structure **V**) are 0.23 eV and 0.05 eV, respectively. The formed peroxo complex has a bent configuration and similar structures are obtained also in the presence of  $H_2SO_4$  and  $SO_4(NH_4)_2$  (see SM). NO can adsorb on the bent peroxo species forming  $NO^+$ , which is required for the coupling of NO and  $NH_3$  and the formation of  $H_2NNO$ [18]. Thus, the  $NH_3$ -SCR appears to proceed also in the presence of one  $HSO_4(NH_4)$ . Similar results are calculated for  $O_2$  adsorption in the presence of  $H_2SO_4$  and  $SO_4(NH_4)_2$ , see SM.  $O_2$  is found to adsorb on a  $[Cu^I(NH_3)_2]^+$  pair also in the presence of two  $HSO_4(NH_4)$  in the cage forming a third  $HSO_4(NH_4)$  with a reaction landscapes similar to that in Fig. 6.

To evaluate the thermodynamic stability of multiple  $SO_4(NH_4)_2$  species, a phase diagram is constructed. The phase diagram contains zero, one, two and three  $HSO_4(NH_4)$  species together with the two  $[Cu^I(NH_3)_2]^+$  complexes. The stable structure at reaction conditions is calculated to be the case with three  $HSO_4(NH_4)$ , see SM. Using constrained AIMD we find that two  $[Cu^I(NH_3)_2]^+$  complexes can not get close enough to allow for  $O_2$  adsorption in the presence of three  $HSO_4(NH_4)$  species in the cage, see S7. Thus, from kinetic and thermodynamic considerations up to three  $HSO_4(NH_4)$  could, in principle, form per  $[Cu^I(NH_3)_2]^+$  pair. However, it has been measured that the S/Cu ratio rarely exceeds one [20,25], which indicates alternative origins of deactivation.

The analysis in Fig. 6 is based on the assumption of having two  $[Cu^I(NH_3)_2]^+$  complexes in the same cage. Thus, the stability of paired  $[Cu^I(NH_3)_2]^+$  complexes in the presence of bulky  $HSO_4(NH_4)$  is critical. To investigate the stability, we have performed constrained AIMD simulations for three scenarios with different numbers of  $HSO_4(NH_4)$ . The simulations are shown in Fig. 7 (more

information can be found in SM). The simulations are performed with two  $[Cu^I(NH_3)_2]^+$  complexes, studying the diffusion of one of the complexes through an eight-membered ring to a neighboring cage. The energies are reported with respect to the situation with the complexes in two different cages. For the case without any  $HSO_4(NH_4)$  (only complexes), a barrier of 0.3 eV is calculated, which is in agreement with a previous report using CI-NEB [15]. The situation with two complexes in the same cage is slightly preferred. The presence of one  $HSO_4(NH_4)$  inside the cage, further stabilizes the pairing of  $[Cu^I(NH_3)_2]^+$ . The situation is qualitatively changed in the presence of two  $HSO_4(NH_4)$ . The free energy in presence of two  $HSO_4(NH_4)$  is lower for the case with complexes in separate cages. Moreover, the barrier for diffusion is lowered to 0.1 eV. The simulations suggest that sulfur deactivation originates from a low probability of having paired  $[Cu^I(NH_3)_2]^+$  complexes as the presence of multiple  $HSO_4(NH_4)$  favours the separation of the  $[Cu^I(NH_3)_2]^+$  complexes.

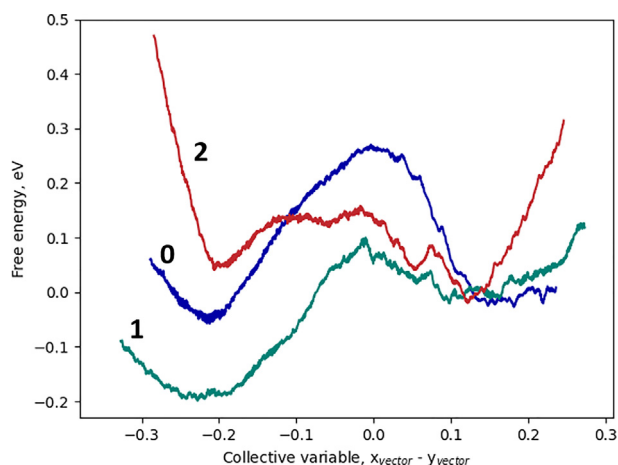
#### 4. Discussion

The main results of the presented calculations are that i)  $HSO_4(NH_4)$  is the preferred species from the reaction of  $SO_2$  with the  $[Cu_2^II(NH_3)_4O_2]^{2+}$  peroxo complex and that ii) the presence of multiple  $HSO_4(NH_4)$  species hinder  $O_2$  adsorption by effectively separating the two  $[Cu^I(NH_3)_2]^+$  complexes. The calculations suggest that the low temperature deactivation of the  $NH_3$ -SCR reaction by  $SO_2$  is of physical origin and reversible as  $HSO_4(NH_4)$  decompose at elevated temperatures. Here we discuss our results in relation to experimental observations.

Based on  $SO_2$ -TPD,  $HSO_4(NH_4)$  and  $SO_4(NH_4)_2$  species are suggested to decompose at 420 °C [19,21,23,28], which imply that catalysts deactivated by formation of  $HSO_4(NH_4)$  can be regenerated by thermal treatment. The lowering of the apparent activation energy measured for reversible deactivation [25] could, thus, be explained by diffusion limitations of the  $[Cu^I(NH_3)_2]^+$  complexes. The irreversible deactivation is instead linked to sulfur adsorption on Cu sites, which leads to chemical poisoning. The detailed mechanisms for the irreversible deactivation and the interplay between reversible and irreversible deactivation are open questions for future studies.

Molokova et al. [28] recently investigated  $SO_2$  adsorption on different Cu-species using X-ray absorption spectroscopy. It was concluded that the reaction between  $SO_2$  and  $[Cu_2^II(NH_3)_4O_2]^{2+}$  contributes significantly to the accumulation of sulfur in Cu-CHA. In addition, it was suggested that sulfur in  $SO_2$  is bonded to copper via an oxygen atom and not directly to the copper atom. The experimental observations concerning the interaction of  $SO_2$  with  $[Cu^I(NH_3)_2]^+$  and  $[Cu_2^II(NH_3)_4O_2]^{2+}$  are in line with our DFT calculations.

Temperature programmed desorption (TPD) experiments are commonly used to distinguish between different sulfur species formed during  $SO_2$  exposure to Cu-CHA. Three peaks measuring the release of  $SO_2$  is observed at 420, 540 and 720 °C. Release of  $SO_2$  at 420 °C is typically assigned to  $SO_2$  stored as  $HSO_4(NH_4)$  or  $SO_4(NH_4)_2$ [19,21,23,28]. The TPD trace from copper-free H-CHA impregnated with  $SO_4(NH_4)_2$  has a low-temperature peak at about 380 °C,[28] thus, 40 °C lower than in Cu-CHA. The stabilization of ammonium(bi) sulfate species by Cu is consistent with our AIMD simulations. In the AIMD simulations, we find that the oxygen ions in  $HSO_4(NH_4)$  are coordinating to the copper ions, which suggests an attractive electrostatic interaction. Another sign of the



**Fig. 7.** AIMD simulation of the free energy profiles for diffusion of a  $[Cu^I(NH_3)_2]^+$  complex through an eight-membered ring in the presence of a second  $[Cu^I(NH_3)_2]^+$  and different numbers of  $HSO_4(NH_4)$  species. The simulations are done with zero (blue), one (green) or two (red)  $HSO_4(NH_4)$  located in one of cages. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stabilization is that if only one  $\text{HSO}_4(\text{NH}_4)$  is present in the CHA cage, we find that the pairing of the  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes is stabilized by 0.15 eV as compared to the case without  $\text{HSO}_4(\text{NH}_4)$ , see Fig. 7.

The peaks at 540 and 720 °C are commonly attributed to sulfur-containing species bonded directly to either copper or aluminum [19,21]. These TPD peaks are at temperatures where copper is not solvated by ammonia but, instead, bonded directly to the framework, and could possibly be related to the irreversible deactivation. One speculation [19,26] is that sulfur species originating from ammonia bisulfate decomposition could bind directly to Cu or Al, forming  $\text{CuSO}_x$  or  $\text{AlSO}_x$  species. Such mechanisms would lead to chemical poisoning and require further exploration.

One important finding is that the presence of  $\text{HSO}_4(\text{NH}_4)$  hinders  $\text{O}_2$  adsorption in Cu-CHA. The structure of the zeolite has been measured to affect the  $\text{SO}_2$ -induced deactivation [56,24]. Recently, the poisoning with  $\text{SO}_2$  and  $\text{SO}_3$  of Cu-CHA was compared to poisoning of Cu-BEA [24]. It was observed that the deactivation of Cu-CHA was more severe than that of Cu-BEA even if Cu-CHA accumulated only 10 % of the sulfur accumulated in Cu-BEA. The difference was suggested to be related to the differences in cage sizes. The observation is consistent with our results. In Fig. 7, the AIMD simulations show that the pairing is hindered in the presence of more than one  $\text{HSO}_4(\text{NH}_4)$ . Larger cages and ring sizes could be expected to reduce the repulsion between species. Moreover, the larger ring size in Cu-BEA, could decrease the diffusion barriers of  $\text{HSO}_4(\text{NH}_4)$ , resulting in more evenly distributed  $\text{HSO}_4(\text{NH}_4)$  species.

Our results suggest that the reversible  $\text{SO}_2$  deactivation of Cu-CHA originates from a low probability of having paired  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes, which is required for  $\text{O}_2$  adsorption. The mobility and structural flexibility of the active site is important for the catalytic activity of Cu-CHA. The diffusion of key intermediates have been studied here and elsewhere [16] with ab initio molecular dynamics, which is computationally heavy and restricted to short simulation times and relatively small model systems. More complete exploration of how diffusion and pairing of  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes is affected by  $\text{HSO}_4(\text{NH}_4)$  would require development of efficient force fields, which is a direction for future studies.

## 5. Conclusion

We have used density functional theory (DFT) calculation to investigate low temperature  $\text{SO}_2$  poisoning of Cu-CHA during  $\text{NH}_3$ -SCR.  $\text{SO}_2$  is found to react with the  $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$  peroxo complex, which is a critical intermediate. The reaction is exothermic with low barriers, forming  $\text{N}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{SO}_4$  undergoes an acid-base reaction in the presence of  $\text{NH}_3$  forming  $\text{SO}_4(\text{NH}_4)_2$  and  $\text{HSO}_4(\text{NH}_4)$ .  $\text{HSO}_4(\text{NH}_4)$  is found to be the thermodynamically stable species during typical reaction conditions. The inter-cage diffusion barriers for  $\text{HSO}_4(\text{NH}_4)$  are calculated to be appreciable, which could result in accumulation of  $\text{HSO}_4(\text{NH}_4)$  in the zeolite cages.

The pairing of two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes is required for  $\text{O}_2$  activation in the low temperature  $\text{NH}_3$ -SCR reaction cycle.  $\text{O}_2$  adsorption is a key step for the subsequent adsorption of NO and formation of  $\text{NO}^+$ , which can couple to  $\text{NH}_3$ . Here we find that the presence of  $\text{HSO}_4(\text{NH}_4)$  species has a large effect on the probability for having two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  in the same cage. Presence of one

$\text{HSO}_4(\text{NH}_4)$  species, yields a stabilization of the paired  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes, whereas the presence of two  $\text{HSO}_4(\text{NH}_4)$  species destabilize the situation with two  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complexes in the same cage.

Our results suggest that the  $\text{SO}_2$  poisoning at low temperature is of physical origin where the sulfate species hinders the diffusion of the  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  complex and possibly the reactants. The studied poisoning is reversible as  $\text{HSO}_4(\text{NH}_4)$  decomposes at elevated temperatures. Our findings provide a link between experiments of  $\text{SO}_2$  poisoning and atomic scale mechanisms.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2022.12.023>.

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