



# Importance of the Cu oxidation state for the SO<sub>2</sub>-poisoning of a Cu-SAPO-34 catalyst in the NH<sub>3</sub>-SCR reaction

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## ABSTRACT

Cu-exchanged zeolites of the CHA structure are state-of-the-art catalysts for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> in diesel aftertreatment systems. However, these catalysts deactivate in the presence of SO<sub>2</sub>, which is a constituent of diesel exhaust gas. In this article, the deactivation behavior and mechanisms of a Cu-SAPO-34 catalyst were studied with reactor tests and DFT calculations. Exposure of the catalyst to two different SO<sub>2</sub> concentrations and durations, but with the same total SO<sub>2</sub> exposure, calculated as the product of partial pressure of SO<sub>2</sub> and exposure time, lead to the same degree of deactivation. Exposure of the Cu-SAPO-34 catalyst to SO<sub>2</sub> in the presence and absence of NO and NH<sub>3</sub> at different temperatures between 200–600 °C showed different trends for the deactivation. Below 400 °C, the S/Cu ratio on the catalyst increased with temperature in absence of NO and NH<sub>3</sub>, while it decreased with increasing temperature in the presence of NO and NH<sub>3</sub>. This is explained by the ability of NO and NH<sub>3</sub> to reduce Cu(II) to Cu(I). DFT calculations show that SO<sub>2</sub> adsorbs more strongly on Cu(I) than on Cu (II). Above 400 °C, the S/Cu ratio decreased with temperature irrespective of the presence of NO and NH<sub>3</sub>. In all cases, the S/Cu ratio is lower than 1. This is not compatible with extensive deposition of ammonium sulfate when co-feeding SO<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub>. A more likely explanation for the deactivation is that SO<sub>2</sub> is mainly related to the Cu sites. This is further corroborated by DFT calculations showing that SO<sub>2</sub> and SO<sub>3</sub>, which is possibly formed by oxidation of SO<sub>2</sub> over Cu sites, interact similar with Cu in Cu-SAPO-34 and Cu-SSZ-13.

## 1. Introduction

Diesel engines operate with excess air in the combustion, leading to production of nitrogen oxides (NO<sub>x</sub>). NO<sub>x</sub> emissions from diesel engines are a source of air pollution and are therefore regulated. To meet legislation requirements for NO<sub>x</sub> emissions, a modern aftertreatment systems for diesel engines contain one or more catalysts for the reduction of NO<sub>x</sub> to N<sub>2</sub> by selective catalytic reduction with NH<sub>3</sub> (NH<sub>3</sub>-SCR). The NH<sub>3</sub>-SCR proceeds according to the reaction: 4NH<sub>3</sub> + 4NO + O<sub>2</sub> → 4N<sub>2</sub> + 6H<sub>2</sub>O. Urea injected in the exhaust gas stream is commonly used as a source for NH<sub>3</sub>, and, if properly controlled, the NH<sub>3</sub>-SCR reaction can reach very high degrees of NO<sub>x</sub> removal. The currently applied catalysts for NH<sub>3</sub>-SCR are based on V-oxide, Fe-zeolites or Cu-zeolites.

Current zeolite state-of-the-art NH<sub>3</sub>-SCR catalysts are based on the CHA structure due to its better hydrothermal stability than other commercial zeolite structures [1]. The CHA structure exists with an

overall chemical composition of H<sub>n</sub>Al<sub>n</sub>Si<sub>1-n</sub>O<sub>2</sub> (SSZ-13) or H<sub>n</sub>Si<sub>n</sub>AlP<sub>1-n</sub>O<sub>4</sub> (SAPO-34), under the assumption that only P is substituted by Si. Cu ions are introduced into the ion-exchange positions in these materials, and these Cu sites are the source of the catalytic activity of Cu-CHA catalysts. Compared to Fe-zeolites and vanadia-based SCR catalysts, the main advantages of the Cu-CHA catalysts are superior low-temperature SCR activity and lower N<sub>2</sub>O selectivity [2,3]. A disadvantage of the Cu-CHA catalysts is their susceptibility towards poisoning by SO<sub>2</sub> [4,5]. SO<sub>2</sub> is an inevitable compound in diesel exhausts, and even at concentration levels below 15 ppm, as in ultra-low sulfur diesel [4,6], the resulting SO<sub>2</sub> in the exhaust gas, typically about 1–2 ppmv, has a significant impact on the performance of Cu-CHA catalysts. It is therefore important to understand how SO<sub>2</sub> affects the Cu-CHA catalysts.

The gas stream that the SCR catalyst is exposed to in a diesel exhaust system consists of several other compounds than SO<sub>2</sub>, including but not limited to O<sub>2</sub>, H<sub>2</sub>O, NO and NH<sub>3</sub>. These compounds may affect the

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interaction of SO<sub>2</sub> with the Cu-CHA catalyst. Several SO<sub>2</sub>-poisoning studies have been carried out in gas compositions where NO and NH<sub>3</sub> are omitted [4–11]. Such experiments have shown that the deactivation is due to SO<sub>2</sub> interactions with Cu, which is dependent on the temperature of SO<sub>2</sub> exposure. Adsorption of SO<sub>2</sub> mainly takes place at temperatures around 200 °C [5], while chemical reactions between SO<sub>2</sub> and Cu become more dominating at temperatures around 400 °C [5]. SO<sub>2</sub> reacts at the Cu sites in the CHA, resulting in (Cu,S) species with S in oxidation state +6, which are assigned to isolated Cu-sulfates [4,12]. This assignment is corroborated by their decomposition temperature of around 650 °C, which is consistent with the decomposition of bulk CuSO<sub>4</sub> [4,11,13], and by an observed 1:1 correlation between the S/Cu ratio of these species and the deactivation [11]. The formation of sulfates implies that SO<sub>2</sub> is oxidized over the catalyst, and the rate of oxidation increases with temperature [10]. The effect of the gas composition on the deactivation by SO<sub>2</sub> is not fully understood, and therefore, it is important to improve the understanding in order to be able to transfer results to the SO<sub>2</sub>-poisoning occurring in real exhausts.

It has been argued that the effect of NO and NH<sub>3</sub> on SO<sub>2</sub>-poisoning is the formation of ammonium sulfate, which may infer mass transfer limitations by pore-blocking [14–16]. However, ammonium sulfate decomposes at about 350 °C, and can therefore feasibly be removed [16]. Moreover, the presence of NO and NH<sub>3</sub>, or release of NH<sub>3</sub> from ammonium sulfate, has a suggested beneficial effect on the regeneration of SO<sub>2</sub>-poisoned catalysts, due to the reducing properties of the SCR gas mixture and NH<sub>3</sub> [8,16].

In this article the SO<sub>2</sub> deactivation behavior of a Cu-SAPO-34 catalyst was investigated. The Cu-SAPO-34 was chosen because of its high hydrothermal stability so that high-temperature regeneration did not result in deterioration of the zeolite structure; something that cannot always be avoided with SSZ-13. We investigated the effect of SO<sub>2</sub> exposure time, SO<sub>2</sub> concentration, and the presence of NO and NH<sub>3</sub> on the deactivation by SO<sub>2</sub>. DFT calculations were used to evaluate the interactions between Cu, SO<sub>2</sub> and SO<sub>3</sub> in order to obtain a better understanding of the temperature dependence, and effect of NO and NH<sub>3</sub>, on the deactivation.

## 2. Experimental

### 2.1. Catalyst material and reactor testing conditions

In this study, we used a Cu-SAPO-34 catalyst with a (P+Al)/Si of 6.5 and a Cu-loading of 1.9 wt%, as determined by ICP-OES. The steady-state conversions of NO in the NH<sub>3</sub>-SCR reaction were measured in a fixed-bed quartz reactor with an inner diameter of 2 mm, using 5 mg catalyst on dry matter basis, and a sieve fraction of 150–300 μm. The SCR-feed gas for the activity measurements consisted of 500 ppmv NO, 530 ppmv NH<sub>3</sub>, 10% O<sub>2</sub> and 5% H<sub>2</sub>O, in N<sub>2</sub> at a total flow of 225 N mL/min. The inlet and outlet gas composition was determined using a Gasmet CX4000 FTIR analyser. Prior to the NH<sub>3</sub>-SCR activity measurements, the catalyst was heated for 1 h in the SCR-feed gas at 550 °C. The effect of SO<sub>2</sub> on the NH<sub>3</sub>-SCR activity was determined from a comparison of the NO<sub>x</sub> conversion before and after exposure of the catalyst to an SO<sub>2</sub>-containing feed gas in the same reactor setup.

The catalyst was exposed to SO<sub>2</sub> in a flow with either SCR-feed gas, or with 10% O<sub>2</sub> and 5% H<sub>2</sub>O, balanced by N<sub>2</sub> to a total flow rate of 225 N mL/min. The inlet concentrations of SO<sub>2</sub> were 1.5 or 15 ppmv. The temperature and duration of SO<sub>2</sub> exposure were varied and are stated specifically with the results.

The evaluation of the NH<sub>3</sub>-SCR activity is based on the rate constant for the NH<sub>3</sub>-SCR reaction. The rate constants (*k*) are derived from measured steady state NO<sub>x</sub> conversions, as shown in Eq. (1), assuming plug flow of the gas and that the NH<sub>3</sub>-SCR reaction is first order in NO.

$$k = -\frac{F}{W} \ln(1-X) \quad (1)$$

*F* is the total molar flow rate, *W* is the total mass of catalyst on a dry matter basis, and *X* is the NO<sub>x</sub> conversion.

The deactivation of the catalyst is calculated from a comparison of rate constants after SO<sub>2</sub> exposure or regeneration with the corresponding rate constant of the fresh catalyst. In this article, we define the deactivation as:

$$\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} \quad (2)$$

### 2.2. Computational

Spin polarized Density Functional Theory (DFT) calculations were used to obtain adsorption energies of O<sub>2</sub>, SO<sub>2</sub> and SO<sub>3</sub> on Cu species in SAPO-34 and SSZ-13. The calculations were performed with the GPAW package [17,18] using a real space grid-based projector augmented wave method. A grid spacing of *h* = 0.2 Å and a Fermi smearing of 0.1 K were found sufficient to obtain a satisfactory convergence of the relative energies. To account for Van der Waals interactions the BEEF-vdW functional was used [19]. This functional has shown to produce reliable results for the interaction of molecules with zeolites [20,21]. Both SSZ-13 and SAPO-34 were represented by periodic cells with hexagonal symmetry containing 36 T-atoms (SSZ-13 cell parameters: *a*, *b* = 13.886 Å, *c* = 15.116 Å, α = 120°, β, γ = 90° and SAPO-34 cell parameters: *a*, *b* = 14.602 Å, *c* = 15.287 Å, α = 120°, β, γ = 90°).

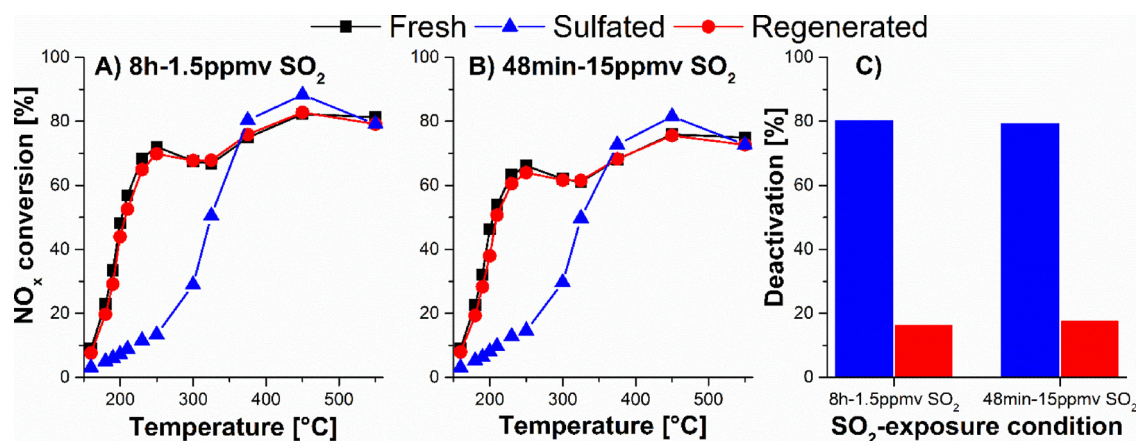
## 3. Results

### 3.1. Deactivation by SO<sub>2</sub> exposure and scalability

Fig. 1A shows the measured steady state NO<sub>x</sub> conversions for the fresh catalyst, after exposure to SO<sub>2</sub>, and after regeneration at 550 °C. For the SO<sub>2</sub> exposure, 1.5 ppmv of SO<sub>2</sub> was added to the SCR-feed, which is in the SO<sub>2</sub> concentration range expected in automotive diesel exhaust, and the catalyst was held at 300 °C for 8 h. The regeneration of the catalyst was performed at 550 °C for 1 h in SCR-feed gas without SO<sub>2</sub>. Exposure to SO<sub>2</sub> leads to significantly lower steady state NO<sub>x</sub> conversions in the temperature range 150–300 °C. Regeneration at 550 °C restores most of the original NO<sub>x</sub> conversion in this temperature range. This behavior has also been observed for an aluminosilicate Cu-CHA catalyst, and can be understood in terms of irreversible and reversible deactivation [11]. According to the definitions in [11], the deactivation measured after regeneration at 550 °C is the irreversible deactivation, and the difference in deactivation after SO<sub>2</sub> exposure and regeneration at 550 °C is the reversible deactivation.

For practical reasons when investigating SO<sub>2</sub> deactivation, it is often useful to accelerate the SO<sub>2</sub>-poisoning by increasing the SO<sub>2</sub> concentration and proportionally shortening the exposure time. The results are then interpreted in terms of the total SO<sub>2</sub> exposure, calculated as the product of the SO<sub>2</sub> partial pressure and the exposure time, rather than the SO<sub>2</sub> concentration. This interpretation requires that a direct proportionality exists between the exposure time and SO<sub>2</sub> concentration, such that these two parameters can be scaled with respect to SO<sub>2</sub>-poisoning. This scalability was investigated by comparing the results of the non-accelerated SO<sub>2</sub> exposure, i.e. exposure to 1.5 ppmv SO<sub>2</sub>, to the results from a catalyst exposed to an accelerated SO<sub>2</sub> exposure. For the accelerated SO<sub>2</sub> exposure, the SO<sub>2</sub> concentration was increased by a factor 10 and the exposure time was correspondingly decreased, thus exposing to 15 ppmv SO<sub>2</sub> in SCR-feed gas for 48 min at 300 °C. The steady state NO<sub>x</sub> conversions before and after the accelerated SO<sub>2</sub> exposure, and after 1 h regeneration at 550 °C in SCR-feed gas, are plotted in Fig. 1B.

The appearance of the NO<sub>x</sub> conversion curve for the accelerated SO<sub>2</sub> exposed catalyst in Fig. 1B, is very similar to that shown in Fig. 1A. The NO<sub>x</sub> conversions of the fresh catalyst shown in Fig. 1B are slightly lower than those of the fresh catalyst in Fig. 1A, which is due to small

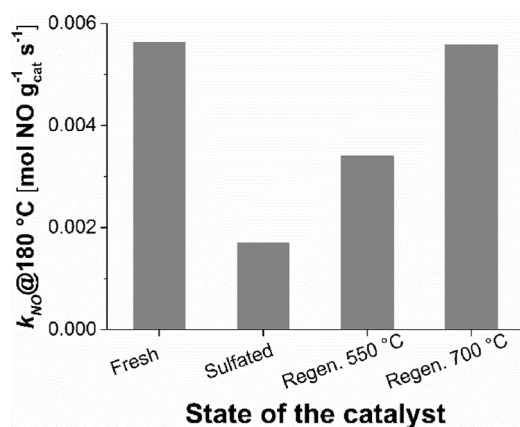


**Fig. 1.** (A) NO<sub>x</sub> conversion as function of temperature for the Cu-SAPO-34 catalyst before and after exposure to 1.5 ppmv SO<sub>2</sub> for 8 h at 300 °C, and after 1 h regeneration at 550 °C. (B) NO<sub>x</sub> conversion as function of temperature for the Cu-SAPO-34 catalyst before and after exposure to 15 ppmv SO<sub>2</sub> for 48 min at 300 °C, and after 1 h regeneration at 550 °C. Gas flow conditions for NO<sub>x</sub> measurements and regenerations were 500 ppmv NO, 530 ppmv NH<sub>3</sub>, 10% O<sub>2</sub>, and 5% H<sub>2</sub>O in N<sub>2</sub> at 225 N mL/min. The same gas flow conditions, with addition of SO<sub>2</sub>, were used for SO<sub>2</sub> exposures. (C) Deactivation of the sulfated (blue bars) and regenerated (red bars) states of the Cu-SAPO-34 catalyst evaluated at 180 °C, after exposure to 1.5 ppmv SO<sub>2</sub> for 8 h and 15 ppmv SO<sub>2</sub> for 48 min (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

differences in the catalyst loads. Therefore, in order to further confirm the similarity of the impact of the accelerated and non-accelerated SO<sub>2</sub> exposure conditions on the SCR performance of the catalyst, the deactivation (evaluated at 180 °C) after SO<sub>2</sub> exposure and regeneration are plotted in Fig. 1C. The degree of deactivation after both treatments are similar, with total deactivations of 80 and 79% and irreversible deactivations of 16 and 18%. This means that the deactivation is the same for the same total SO<sub>2</sub> exposure, and indicates that the SO<sub>2</sub> concentration and exposure time are scalable.

### 3.2. Regeneration of the irreversible deactivation

A possible explanation for the irreversible deactivation is the formation of Cu-sulfates that are stable up to ~650 °C [4,11,13]. If this is true, a full restoration of the activity of the catalyst by heating to 700 °C should be possible. This was verified by measuring the SCR activity over the Cu-SAPO-34 catalyst after SO<sub>2</sub> exposure and again after regeneration at 550 °C and 700 °C. Fig. 2 shows that at 180 °C, the SCR reaction rate constant is lowest for the sulfated state of the catalyst, and that regeneration first at 550 °C, partially restores the activity, while subsequent regeneration at 700 °C restores the activity to the original



**Fig. 2.** The NH<sub>3</sub>-SCR rate constants of the different states of the Cu-SAPO-34 catalyst, i.e. fresh, sulfated, regenerated at 550 °C, and regenerated at 700 °C. Sulfation was 24 h at 550 °C in 15 ppmv SO<sub>2</sub>, 500 ppmv NO, 530 ppmv NH<sub>3</sub>, 10% O<sub>2</sub>, and 5% H<sub>2</sub>O in N<sub>2</sub> at 225 N mL/min. The regenerations were 1 h at 550 °C and 2 h at 700 °C, and were carried out with the same flow conditions as the sulfation, but in absence of SO<sub>2</sub>.

level of the fresh catalyst. This result is consistent with Cu-sulfate species causing the irreversible deactivation, since heating to 700 °C, which is above the decomposition temperature of CuSO<sub>4</sub>, restores the activity of the catalyst completely.

### 3.3. SO<sub>2</sub> exposure in presence of NO and NH<sub>3</sub>

The SCR catalyst in a diesel exhaust system is exposed to a wide range of temperatures up to approx. 550 °C, with typical operating temperatures between 200–500 °C. Therefore, the impact of temperature on the deactivation was investigated by exposing the Cu-SAPO-34 catalyst to 1.5 ppmv SO<sub>2</sub> for 8 h in the presence of SCR-feed gas at 200, 300, 400 and 500 °C. The measured steady state NO<sub>x</sub> conversions are shown in Fig. 3A–D before and after SO<sub>2</sub> exposure, and after 1 h of regeneration at 550 °C in SCR-feed gas. The NO<sub>x</sub> conversion below 325 °C is lower than for the fresh catalyst in all measurements, for both the sulfated and regenerated states of the catalyst. Furthermore, the deactivations in Fig. 4B show that there is a clear trend of more extensive deactivation of the sulfated state of the catalyst at lower SO<sub>2</sub> exposure temperature. The S/Cu ratios of the catalyst shown in Fig. 4A, which were estimated by integration of the measured decrease in SO<sub>2</sub> concentrations in the outlet of the reactor during SO<sub>2</sub> exposure, also increase at lower SO<sub>2</sub> exposure temperature. This is consistent with an interpretation that larger S-uptakes lead to more pronounced deactivation. A different trend is observed for the deactivation of the regenerated states of the catalyst, where only the catalyst exposed to SO<sub>2</sub> at 200 °C stands out with a significantly larger deactivation than the rest.

In order to see if there is a significant impact of NO and NH<sub>3</sub> presence on the uptake of SO<sub>2</sub>, the S-uptakes were measured after SO<sub>2</sub> exposure in absence of NO and NH<sub>3</sub> as well. This was done in a separate experiment by measuring the SO<sub>2</sub> desorption during heating to 700 °C after 3 h exposure to 15 ppmv SO<sub>2</sub> in 10% O<sub>2</sub> and 5% H<sub>2</sub>O at 200–600 °C. This is possible because all S species desorb as SO<sub>2</sub> [4,13], and the complete restoration of the activity by heating to 700 °C indicates that no sulfur is left on the catalyst (see Fig. 2) [11]. The area of the SO<sub>2</sub> desorption peaks in Fig. 5 reveal that there is a maximum S-uptake at 400 °C, after SO<sub>2</sub> exposure in absence of NO and NH<sub>3</sub>, which is different from the SO<sub>2</sub> exposure in the presence of NO and NH<sub>3</sub>.

A comparison of the SO<sub>2</sub> uptake at different temperatures in the presence and absence of NO and NH<sub>3</sub> is shown in Fig. 6. Since the SO<sub>2</sub> exposure conditions of the two series are different, the absolute S/Cu ratios are not directly comparable, but the trends with respect to the



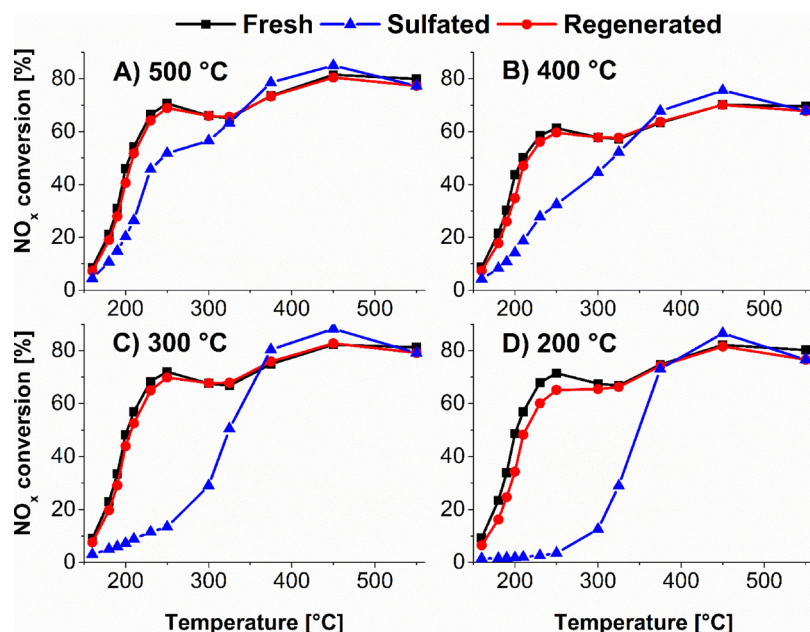


Fig. 3. NO<sub>x</sub> conversions as functions of temperature for the Cu-SAPO-34 catalyst before and after SO<sub>2</sub> exposure for 8 h at (A) 500 °C, (B) 400 °C, (C) 300 °C, and D) 200 °C, and after 1 h regeneration at 550 °C. NO<sub>x</sub> conversion measurements and regenerations were carried out in 500 ppmv NO, 530 ppmv NH<sub>3</sub>, 10% O<sub>2</sub>, and 5% H<sub>2</sub>O in N<sub>2</sub> at 225 N mL/min, and the same for the SO<sub>2</sub> exposures, but with the addition of 1.5 ppmv SO<sub>2</sub>.

exposure temperature are. In the presence of NO and NH<sub>3</sub>, the S/Cu ratio decreases monotonically at increased temperature, whereas a maximum for the S/Cu ratio is observed at 400 °C in the absence of NO and NH<sub>3</sub>. A possible explanation for the different trends below 400 °C is the deposition of ammonium sulfates in the zeolite pores at low temperatures, which decompose above 350 °C to restore catalytic activity [14–16]. Interestingly, the trends of the S/Cu ratios in the presence and absence of NO and NH<sub>3</sub> appear similar above 400 °C. These results indicate that above 400 °C, the SO<sub>2</sub> exposure conditions are similar despite the different inlet gas compositions. This may be rationalized by the faster SCR reaction rate at higher temperatures, where NO and NH<sub>3</sub> are converted to N<sub>2</sub> and H<sub>2</sub>O faster, which means that increasing parts of the catalyst bed are effectively exposed to SO<sub>2</sub> in absence of NO and NH<sub>3</sub> at higher temperatures.

### 3.4. Stability of reaction products of Cu sites with SO<sub>2</sub> and SO<sub>3</sub>

DFT calculations have been carried out to obtain information about the stability of possible SO<sub>x</sub> species that can be formed in reactions between different Cu sites in the Cu-SAPO-34 catalyst and SO<sub>2</sub>. Because we cannot exclude the formation of some SO<sub>3</sub> when exposing to SO<sub>2</sub> only, especially at higher temperatures, reactions between Cu sites and SO<sub>3</sub> have also been considered in the calculations. The Cu species that are present in the catalyst is determined by the conditions of the SO<sub>2</sub>

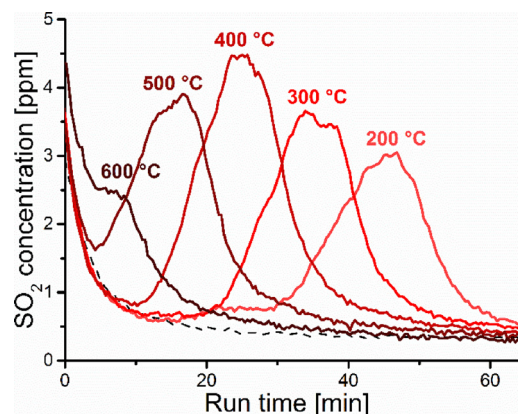


Fig. 5. Outlet SO<sub>2</sub> concentrations during heating to 700 °C after exposing the Cu-SAPO-34 catalyst for 3 h to 15 ppmv SO<sub>2</sub>, 10% O<sub>2</sub>, and 5% H<sub>2</sub>O in N<sub>2</sub> at 225 N mL/min and at 200–600 °C. The dashed line is the zero-desorption line.

exposure. In presence of NO and NH<sub>3</sub>, Cu(II) can reduce to Cu(I) [22–26], which is modelled as a naked Cu(I) atom charge-balancing a single exchange site, Z-Cu(I). In presence of O<sub>2</sub> and H<sub>2</sub>O, only Cu(II) is expected to be present, which can be in two different forms. Either as a single Cu(II) atom charge-balancing two exchange sites, Z<sub>2</sub>-Cu(II), or as

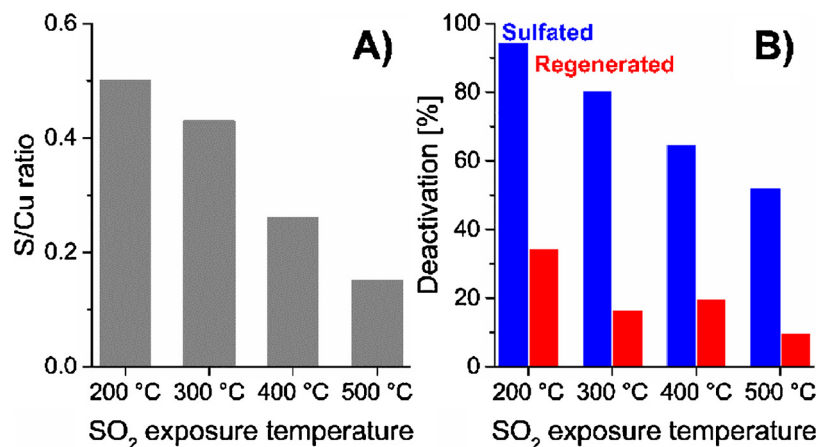


Fig. 4. (A) S/Cu ratios for each SO<sub>2</sub> exposure temperature of the Cu-SAPO-34 catalyst after exposure to 1.5 ppmv SO<sub>2</sub> in SCR-feed gas for 8 h. (B) Deactivation evaluated at 180 °C of the sulfated (blue bars) and regenerated (red bars) states of the Cu-SAPO-34 catalyst for each SO<sub>2</sub> exposure temperature with 1.5 ppmv SO<sub>2</sub> in SCR-feed gas for 8 h (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

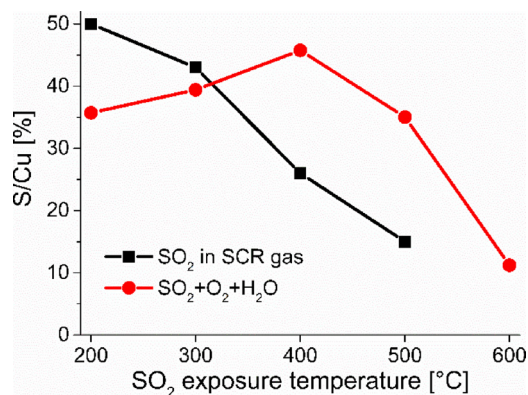


Fig. 6. The S/Cu ratios as functions of the SO<sub>2</sub> exposure temperature for the SO<sub>2</sub> exposures of the Cu-SAPO-34 catalyst in presence and absence of NO and NH<sub>3</sub>.

a Cu(II) atom with a hydroxide ion charge-balancing a single exchange site, Z-Cu(II)OH. The most stable reaction products from reactions between the three different Cu sites with SO<sub>2</sub> or SO<sub>3</sub>, as determined from DFT calculations, are listed in Table 1.

The DFT calculations show that both SO<sub>2</sub> and SO<sub>3</sub> are able to form stable species with Z-Cu(II)OH and with Z-Cu(I), in agreement with previous DFT calculations [12]. The calculated change in energy for adsorption of SO<sub>2</sub>, SO<sub>3</sub> and O<sub>2</sub> on Z<sub>2</sub>-Cu(II) is positive, indicating that neither of these species adsorb on the Z<sub>2</sub>-Cu(II) sites. Interestingly, the most stable reaction product of the Z-Cu(I) site is in reaction with SO<sub>2</sub>, while the Z-Cu(II)OH site forms the most stable species in reaction with SO<sub>3</sub>. Fig. 7 shows the calculated structures of the resulting Cu species. DFT calculations also indicate that neither SO<sub>2</sub> nor SO<sub>3</sub> bind to the mobile [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> species, which provides the active centers for NH<sub>3</sub>-SCR at low temperatures [27,28].

The same calculations of reaction products of Cu sites with SO<sub>2</sub> and SO<sub>3</sub> have also been carried out for an aluminosilicate CHA framework, and the results are similar to those for the silicoaluminophosphate Cu-SAPO-34 structure, but with a tendency to slightly less stable reaction products. This indicates that the deactivation of Cu-CHA catalysts by SO<sub>2</sub> and SO<sub>3</sub> is mainly related to the Cu-SO<sub>x</sub> chemistry, and that the framework chemistry, therefore, is of lesser importance.

#### 4. Discussion

It appears that the deactivation level by SO<sub>2</sub> correlates to the total amount of SO<sub>2</sub> that the catalyst is exposed to, as shown in Fig. 1, where the catalyst has been exposed to different SO<sub>2</sub> concentrations and durations at 300 °C. However, this result could also be due to a saturation effect. If a SO<sub>x</sub> saturation level is reached, it means that the S-uptake cannot get larger. In Fig. 6 all the S/Cu ratios are plotted as functions of the SO<sub>2</sub> exposure temperature, and the S-uptakes at 200 °C in presence of NO and NH<sub>3</sub>, and at 400 °C in only O<sub>2</sub> and H<sub>2</sub>O, are both larger than that at 300 °C in presence of NO and NH<sub>3</sub>. This shows that larger S-uptakes can be reached at higher and lower temperatures, and,

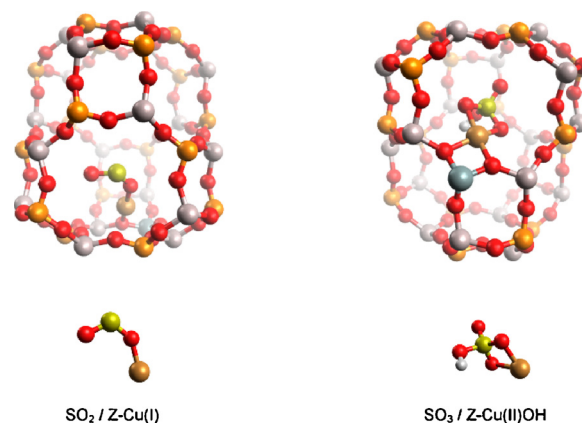


Fig. 7. Calculated structures of SO<sub>2</sub> adsorbed on Z-Cu(I) and SO<sub>3</sub> on Z-Cu(II)OH on Cu-SAPO-34. The atoms are indicated as follows: O (red), P (orange), Al (light purple), Si (grey), Cu (brown), S (yellow), H (white) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

therefore, the catalyst exposed to SO<sub>2</sub> at 300 °C in presence of NO and NH<sub>3</sub> is not saturated, which validates the interpretation that the deactivation by SO<sub>2</sub> is determined by the total exposure to SO<sub>2</sub>.

The data in Fig. 6 show that exposure to SO<sub>2</sub> at 200–600 °C results in different amounts of S-uptake by the Cu-SAPO-34 catalyst, dependent on the presence of NO and NH<sub>3</sub>. These differences can be related to the different amounts of Cu(I) and Cu(II) and the formation of SO<sub>3</sub>. The DFT calculations presented in Table 1 show, that SO<sub>2</sub> adsorbs more strongly than SO<sub>3</sub> on Z-Cu(I) sites. Since a mixture of NO and NH<sub>3</sub> has reducing properties [22–26], the presence of NO and NH<sub>3</sub> leads to a larger fraction of Z-Cu(I) species. This leads to an enhanced driving force for SO<sub>2</sub> adsorption on Cu in the presence of NO and NH<sub>3</sub>. The fraction of Z-Cu(I) species decreases with increasing temperature, as a faster SCR reaction leads to lower partial pressures of NO and NH<sub>3</sub> and faster re-oxidation of the Cu, and therefore the SO<sub>2</sub> uptake decreases with increasing temperature in the presence of NO and NH<sub>3</sub>, as shown in Fig. 6.

In the absence of NO and NH<sub>3</sub>, more Cu is present as Cu(II) species, and therefore, the adsorption of SO<sub>2</sub> on Cu(I) becomes less important. The DFT calculations show that the Z-Cu(II)OH site forms the most stable CuSO<sub>x</sub> species in reaction with SO<sub>3</sub>, while neither SO<sub>2</sub> nor SO<sub>3</sub> adsorb on the Z<sub>2</sub>-Cu(II) sites. Due to the larger amount of Cu(II), the SO<sub>2</sub> uptake is now determined by the formation of SO<sub>3</sub>, which then reacts with the Z-Cu(II)OH sites. The increasing SO<sub>2</sub> uptake with temperature in the range 200–400 °C is then a consequence of the increased rate of SO<sub>2</sub> oxidation [10]. Above 400 °C, decomposition and desorption of the CuSO<sub>x</sub> species takes place [11], resulting in the lower SO<sub>2</sub> uptake with increasing temperature.

It is noted that both in the presence and in the absence of NO and NH<sub>3</sub>, the adsorption of SO<sub>2</sub> or SO<sub>3</sub> always occurs on Cu sites. Therefore, the total SO<sub>2</sub> uptake is limited by the Cu content, in agreement with the observation that the S/Cu ratio does not exceed 1, despite excessive exposure to SO<sub>2</sub> (total exposure of SO<sub>2</sub>/Cu is at least 4.8). It has been

Table 1

The stabilities (ΔE) of most stable reaction products from reactions of three different Cu sites in Cu-SAPO-34 or Cu-SSZ-13 with either SO<sub>2</sub> or SO<sub>3</sub>. \*O<sub>2</sub> does not adsorb on Z<sub>2</sub>-Cu(II) in neither Cu-SAPO-34 nor in Cu-SSZ-13. Adsorption energies and standard deviations have been obtained from DFT using BEEF-vdW.

Cu site	+ SO <sub>2</sub> →	ΔE [eV] Cu-SAPO-34	ΔE [eV] Cu-SSZ-13	+ SO <sub>3</sub> →	ΔE [eV] Cu-SAPO-34	ΔE [eV] Cu-SSZ-13
Z-Cu(I)	Z-Cu(I)-SO <sub>2</sub> (ads)	−1.07 (+/-0.44)	−1.12 (+/- 0.48)	Z-Cu(I)-SO <sub>3</sub> (ads)	−0.80 (+/-0.55)	−0.89 (+/- 0.55)
Z-Cu(II)OH	Z-Cu(II)HSO <sub>3</sub>	−0.84 (+/-0.36)	−0.73 (+/- 0.29)	Z-Cu(II)HSO <sub>4</sub>	−1.80 (+/- 0.36)	−1.81 (+/-0.32)
Z <sub>2</sub> -Cu(II)*	O <sub>2</sub> , SO <sub>2</sub> , and SO <sub>3</sub> do not adsorb on this site in neither Cu-SAPO-34 nor Cu-SSZ-13					



argued that deposition of ammonium sulfate in the zeolite pores is the cause of deactivation of Cu-CHA catalysts [14–16]. This explanation would be consistent with a larger S-uptake in presence of NO and NH<sub>3</sub> below 400 °C, since ammonium sulfate decomposes at around 350 °C [16]. However, if ammonium sulfate is formed, it is also expected that the amount of sulfur deposited in the catalyst is not limited by the Cu content. Since the S-uptake is limited by the Cu content, formation of ammonium sulfate does not seem to be the cause of the larger SO<sub>2</sub> uptake and deactivation in the low temperature range in the presence of NO and NH<sub>3</sub>.

Finally, the chemical nature of the CHA framework (silicoaluminophosphate or aluminosilicate) seems not to have a significant influence on the deactivation by SO<sub>2</sub>. As argued in the previous section, the deactivation of the silicoaluminophosphate Cu-SAPO-34 catalyst by SO<sub>2</sub> is related to the chemistry of Cu, SO<sub>2</sub> and SO<sub>3</sub>, and therefore, SO<sub>2</sub>-poisoning of the two versions of the Cu-CHA catalysts should be comparable. The response of the Cu-SAPO-34 catalyst to SO<sub>2</sub> exposure and regeneration at 550 °C in Fig. 1, is very similar to that observed on a similar aluminosilicate Cu-CHA catalyst [11]. Furthermore, the results from the DFT calculations in Table 1, show that the Cu-SO<sub>x</sub> species formed from SO<sub>2</sub> and SO<sub>3</sub>, and the interaction energies of SO<sub>2</sub> and SO<sub>3</sub> with the respective Cu(I) and Cu(II) species is similar in both CHA materials. This indicates that the framework chemistry of the two Cu-CHA catalysts does not affect the SO<sub>2</sub>-poisoning, and means that SO<sub>2</sub>-poisoning is similar on Cu-exchanged aluminosilicate and silicoaluminophosphate CHA materials.

## 5. Conclusions

The deactivation behavior of a Cu-SAPO-34 catalyst in the NH<sub>3</sub>-SCR reaction has been evaluated at simulated operating conditions by comparing the SCR activity before and after exposing to 1.5 ppmv SO<sub>2</sub> in a typical SCR-feed gas feed at 300 °C. The low-temperature activity is significantly lowered by the SO<sub>2</sub> exposure, and regeneration at 550 °C restores the activity to about 80% of the original level. Regeneration at 700 °C restores all activity, which is consistent with decomposition of Cu-sulfates. The degree of deactivation appears to depend on the total SO<sub>2</sub> exposure, calculated as the product of partial pressure and exposure time.

Below 400 °C, the S-uptake increases with temperature in absence of NO and NH<sub>3</sub>, and decreases with increasing temperature in the presence of NO and NH<sub>3</sub>. This can be explained by the ability of NO and NH<sub>3</sub> to reduce Cu(II) to Cu(I). DFT calculations show that SO<sub>2</sub> binds preferably to Cu(I), while SO<sub>3</sub> binds stronger to Cu(II). This then leads to the higher uptake of SO<sub>2</sub> below 400 °C in the presence of NO and NH<sub>3</sub>, since a larger amount of Cu(I) is present under these conditions. Above 400 °C, the S-uptake decreases with increasing temperature, independent of the presence of NO and NH<sub>3</sub>.

The S/Cu ratios are always lower than 1, which indicates that the uptake of sulfur is related to adsorption of SO<sub>2</sub> on Cu and that ammonium sulfate does not precipitate in the catalyst when co-feeding SO<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub>. Furthermore, DFT calculations also show that SO<sub>2</sub> and SO<sub>3</sub> interactions with Cu is similar for Cu-SAPO-34 and Cu-SSZ-13, indicating that the deactivation by SO<sub>x</sub> is mainly associated to the chemistry of the Cu sites. Consequently, the SO<sub>2</sub>-poisoning mechanisms for Cu-SAPO-34 and Cu-SSZ-13 are comparable.

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