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Importance of the Cu oxidation state for the SO₂-poisoning of a Cu-SAPO-34 catalyst in the NH₃-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_x with NH₃ in diesel aftertreatment systems. However, these catalysts deactivate in the presence of SO₂, 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 SO₂ concentrations and durations, but with the same total SO₂ exposure, calculated as the product of partial pressure of SO₂ and exposure time, lead to the same degree of deactivation. Exposure of the Cu-SAPO-34 catalyst to SO₂ in the presence and absence of NO and NH₃ 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 NH₃, while it decreased with increasing temperature in the presence of NO and NH₃. This is explained by the ability of NO and NH₃ to reduce Cu(II) to Cu(I). DFT calculations show that SO₂ 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 NH₃. In all cases, the S/Cu ratio is lower than 1. This is not compatible with extensive deposition of ammonium sulfate when co-feeding SO₂, H₂O and NH₃. A more likely explanation for the deactivation is that SO₂ is mainly related to the Cu sites. This is further corroborated by DFT calculations showing that SO₂ and SO₃, which is possibly formed by oxidation of SO₂ over Cu sites, interact similar with Cu in Cu-SAPO-34 and Cu-SSZ-13.

Keywords

NH₃-SCR, SO₂ poisoning, Deactivation, Cu-CHA, DFT

1. Introduction

Diesel engines operate with excess air in the combustion, leading to production of nitrogen oxides (NO_x). NO_x emissions from diesel engines are a source of air pollution and are therefore regulated. To meet legislation requirements for NO_x emissions, a modern aftertreatment systems for diesel engines contain one or more catalysts for the reduction of NO_x to N₂ by selective catalytic reduction with NH₃ (NH₃-SCR). The NH₃-SCR proceeds according to the reaction: $4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$. Urea injected in the exhaust gas stream is commonly used as a source for NH₃, and, if properly controlled, the NH₃-SCR reaction can reach very high degrees of NO_x removal. The currently applied catalysts for NH₃-SCR are based on V-oxide, Fe-zeolites or Cu-zeolites.

Current zeolite state-of-the-art NH₃-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_nAl_nSi_{1-n}O₂ (SSZ-13) or H_nSi_nAlP_{1-n}O₄ (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 N₂O selectivity [2,3]. A disadvantage of the Cu-CHA catalysts is their susceptibility towards poisoning by SO₂ [4,5]. SO₂ 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 SO₂ 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 SO₂ 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 SO₂, including but not limited to O₂, H₂O, NO and NH₃. These compounds may affect the interaction of SO₂ with the Cu-CHA catalyst. Several SO₂-poisoning studies have been carried out in gas compositions where NO and NH₃ are omitted [4–11]. Such experiments have shown that the deactivation is due to SO₂ interactions with Cu, which is dependent on the temperature of SO₂ exposure. Adsorption of SO₂

mainly takes place at temperatures around 200 °C [5], while chemical reactions between SO₂ and Cu become more dominating at temperatures around 400 °C [5]. SO₂ 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 CuSO₄ [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 SO₂ is oxidized over the catalyst, and the rate of oxidation increases with temperature [10]. The effect of the gas composition on the deactivation by SO₂ is not fully understood, and therefore, it is important to improve the understanding in order to be able to transfer results to the SO₂-poisoning occurring in real exhausts.

It has been argued that the effect of NO and NH₃ on SO₂-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 NH₃, or release of NH₃ from ammonium sulfate, has a suggested beneficial effect on the regeneration of SO₂-poisoned catalysts, due to the reducing properties of the SCR gas mixture and NH₃ [8,16].

In this article the SO₂ 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 SO₂ exposure time, SO₂ concentration, and the presence of NO and NH₃ on the deactivation by SO₂. DFT calculations were used to evaluate the interactions between Cu, SO₂ and SO₃ in order to obtain a better understanding of the temperature dependence, and effect of NO and NH₃, on the deactivation.

2. Experimental

2.1. Catalyst material and reactor testing conditions

A commercial Cu-SAPO-34 catalyst was used for this study. The catalyst has 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 NH₃-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 NH₃, 10 % O₂ and 5 % H₂O, in N₂ at a total flow of 225 NmL min⁻¹. The inlet and outlet gas composition was determined using a Gasmet CX4000 FTIR analyser. Prior to the NH₃-SCR activity measurements, the catalyst was heated for 1 h in the SCR-feed gas at 550 °C. The effect of SO₂ on the NH₃-SCR activity was determined from a comparison of the NO_x conversion before and after exposure of the catalyst to an SO₂-containing feed gas in the same reactor setup.

The catalyst was exposed to SO₂ in a flow with either SCR-feed gas, or with 10 % O₂ and 5 % H₂O, balanced by N₂ to a total flow rate of 225 NmL min⁻¹. The inlet concentrations of SO₂ were 1.5 or 15 ppmv. The temperature and duration of SO₂ exposure were varied and are stated specifically with the results.

The evaluation of the NH₃-SCR activity is based on the rate constant for the NH₃-SCR reaction. The rate constants (k) are derived from measured steady state NO_x conversions, as shown in Eq. (1), assuming plug flow of the gas and that the NH₃-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_x conversion.

The deactivation of the catalyst is calculated from a comparison of rate constants after SO₂ 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 O₂, SO₂ and SO₃ 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 $h = 0.2$ 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: $a, b = 13.886 \text{ \AA}$, $c = 15.116 \text{ \AA}$, $\alpha = 120^\circ$, $\beta, \gamma = 90^\circ$ and SAPO-34 cell parameters: $a, b = 14.602 \text{ \AA}$, $c = 15.287 \text{ \AA}$, $\alpha = 120^\circ$, $\beta, \gamma = 90^\circ$).

3. Results

3.1. Deactivation by SO₂ exposure and scalability

Figure 1A shows the measured steady state NO_x conversions for the fresh catalyst, after exposure to SO₂, and after regeneration at 550 °C. For the SO₂ exposure, 1.5 ppmv of SO₂ was added to the SCR-feed, which is in the SO₂ 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 SO₂. Exposure to SO₂ leads to significantly lower steady state NO_x conversions in the temperature range 150-300 °C. Regeneration at 550 °C restores most of the original NO_x 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 SO₂ exposure and regeneration at 550 °C is the reversible deactivation.

For practical reasons when investigating SO₂ deactivation, it is often useful to accelerate the SO₂-poisoning by increasing the SO₂ concentration and proportionally shortening the exposure time. The results are then interpreted in terms of the total SO₂ exposure, calculated as the product of the SO₂ partial pressure and the exposure time, rather than the SO₂ concentration. This interpretation requires that a direct proportionality exists between the exposure time and SO₂ concentration, such that these two parameters can be scaled with respect to SO₂-poisoning. This scalability was investigated by comparing the results of the non-accelerated SO₂ exposure, i.e. exposure to 1.5 ppmv SO₂, to the results from a catalyst exposed to an accelerated SO₂

exposure. For the accelerated SO_2 exposure, the SO_2 concentration was increased by a factor 10 and the exposure time was correspondingly decreased, thus exposing to 15 ppmv SO_2 in SCR-feed gas for 48 min at 300 °C. The steady state NO_x conversions before and after the accelerated SO_2 exposure, and after 1 h regeneration at 550 °C in SCR-feed gas, are plotted in Figure 1B.

The appearance of the NO_x conversion curve for the accelerated SO_2 exposed catalyst in Figure 1B, is very similar to that shown in Figure 1A. The NO_x conversions of the fresh catalyst shown in Figure 1B are slightly lower than those of the fresh catalyst in Figure 1A, which is due to small differences in the catalyst loads. Therefore, in order to further confirm the similarity of the impact of the accelerated and non-accelerated SO_2 exposure conditions on the SCR performance of the catalyst, the deactivation (evaluated at 180 °C) after SO_2 exposure and regeneration are plotted in Figure 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_2 exposure, and indicates that the SO_2 concentration and exposure time are scalable.

Figure 1 – A) NO_x conversion as function of temperature for the Cu-SAPO-34 catalyst before and after exposure to 1.5 ppmv SO_2 for 8 h at 300 °C, and after 1 h regeneration at 550 °C. B) NO_x conversion as function of temperature for the Cu-SAPO-34 catalyst before and after exposure to 15 ppmv SO_2 for 48 min at 300 °C, and after 1 h regeneration at 550 °C. Gas flow conditions for NO_x measurements and regenerations were 500 ppmv NO, 530 ppmv NH_3 , 10 % O_2 , and 5 % H_2O in N_2 at 225 NmL/min. The same gas flow

conditions, with addition of SO_2 , were used for SO_2 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_2 for 8 h and 15 ppmv SO_2 for 48 min.

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_2 exposure and again after regeneration at 550 °C and 700 °C. Figure 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 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_4 , restores the activity of the catalyst completely.

Figure 2 – The NH_3 -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_2 , 500 ppmv NO, 530 ppmv NH_3 , 10 % O_2 , and 5 % H_2O in N_2 at 225 NmL/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_2 .

3.3. SO₂ exposure in presence of NO and NH₃

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 SO₂ for 8 h in the presence of SCR-feed gas at 200, 300, 400 and 500 °C. The measured steady state NO_x conversions are shown in Figure 3A-D before and after SO₂ exposure, and after 1 h of regeneration at 550 °C in SCR-feed gas. The NO_x 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 Figure 4B show that there is a clear trend of more extensive deactivation of the sulfated state of the catalyst at lower SO₂ exposure temperature. The S/Cu ratios of the catalyst shown in Figure 4A, which were estimated by integration of the measured decrease in SO₂ concentrations in the outlet of the reactor during SO₂ exposure, also increase at lower SO₂ 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 SO₂ at 200 °C stands out with a significantly larger deactivation than the rest.

Figure 3 – NO_x conversions as functions of temperature for the Cu-SAPO-34 catalyst before and after SO_2 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_x conversion measurements and regenerations were carried out in 500 ppmv NO, 530 ppmv NH_3 , 10 % O_2 , and 5 % H_2O in N_2 at 225 NmL/min, and the same for the SO_2 exposures, but with the addition of 1.5 ppmv SO_2 .

Figure 4 – A) S/Cu ratios for each SO_2 exposure temperature of the Cu-SAPO-34 catalyst after exposure to 1.5 ppmv SO_2 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_2 exposure temperature with 1.5 ppmv SO_2 in SCR-feed gas for 8h.

In order to see if there is a significant impact of NO and NH_3 presence on the uptake of SO_2 , the S-uptakes were measured after SO_2 exposure in absence of NO and NH_3 as well. This was done in a separate experiment by measuring the SO_2 desorption during heating to 700 °C after 3 h exposure to 15 ppmv SO_2 in 10 % O_2 and 5 % H_2O at 200-600 °C. This is possible because all S species desorb as SO_2 [4,13], and the complete restoration of the activity by heating to 700 °C indicates that no sulfur is left on the catalyst (see Figure 2) [11]. The area of the SO_2 desorption peaks in Figure 5 reveal that there is a maximum S-uptake at 400 °C, after SO_2 exposure in absence of NO and NH_3 , which is different from the SO_2 exposure in the presence of NO and NH_3 .

A comparison of the SO_2 uptake at different temperatures in the presence and absence of NO and NH_3 is shown in Figure 6. Since the SO_2 exposure conditions of the two series are different, the absolute S/Cu ratios are not directly comparable, but the trends with respect to the exposure temperature are. In the presence of NO and NH_3 , 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_3 . 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_3 appear similar above 400 °C. These results indicate that above 400 °C, the SO_2 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_3 are converted to N_2 and H_2O faster,

which means that increasing parts of the catalyst bed are effectively exposed to SO_2 in absence of NO and NH_3 at higher temperatures.

Figure 5 – Outlet SO_2 concentrations during heating to 700 °C after exposing the Cu-SAPO-34 catalyst for 3 h to 15 ppmv SO_2 , 10 % O_2 , and 5 % H_2O in N_2 at 225 NmL/min and at 200-600 °C. The dashed line is the zero-desorption line.

Figure 6 – The S/Cu ratios as functions of the SO_2 exposure temperature for the SO_2 exposures of the Cu-SAPO-34 catalyst in presence and absence of NO and NH_3 .

3.4. Stability of reaction products of Cu sites with SO_2 and SO_3

DFT calculations have been carried out to obtain information about the stability of possible SO_x species that can be formed in reactions between different Cu sites in the Cu-SAPO-34 catalyst and SO_2 . Because we cannot exclude the formation of some SO_3 when exposing to SO_2 only, especially at higher temperatures, reactions

between Cu sites and SO_3 have also been considered in the calculations. The Cu species that are present in the catalyst is determined by the conditions of the SO_2 exposure. In presence of NO and NH_3 , 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_2 and H_2O , 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, $\text{Z}_2\text{-Cu(II)}$, or as 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_2 or SO_3 , as determined from DFT calculations, are listed in Table 1.

The DFT calculations show that both SO_2 and SO_3 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_2 , SO_3 and O_2 on $\text{Z}_2\text{-Cu(II)}$ is positive, indicating that neither of these species adsorb on the $\text{Z}_2\text{-Cu(II)}$ sites. Interestingly, the most stable reaction product of the Z-Cu(I) site is in reaction with SO_2 , while the Z-Cu(II)OH site forms the most stable species in reaction with SO_3 . Figure 7 shows the calculated structures of the resulting Cu species. DFT calculations also indicate that neither SO_2 nor SO_3 bind to the mobile $[\text{Cu}(\text{NH}_3)_2]^+$ species, which provides the active centers for $\text{NH}_3\text{-SCR}$ at low temperatures [27,28].

The same calculations of reaction products of Cu sites with SO_2 and SO_3 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_2 and SO_3 is mainly related to the Cu- SO_x chemistry, and that the framework chemistry, therefore, is of lesser importance.

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_2 or SO_3 . * O_2 does not adsorb on $\text{Z}_2\text{-Cu(II)}$ 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	+ $\text{SO}_2 \rightarrow$	ΔE [eV]	ΔE [eV]	+ $\text{SO}_3 \rightarrow$	ΔE [eV]	ΔE [eV]
		Cu-SAPO-34	Cu-SSZ-13		Cu-SAPO-34	Cu-SSZ-13
Z-Cu(I)	Z-Cu(I)- SO_2 (ads)	-1.07 (+/-0.44)	-1.12 (+/- 0.48)	Z-Cu(I)- SO_3 (ads)	-0.80 (+/-0.55)	-0.89 (+/- 0.55)
Z-Cu(II)OH	Z-Cu(II)HSO ₃	-0.84 (+/-0.36)	-0.73 (+/- 0.29)	Z-Cu(II)HSO ₄	-1.80 (+/- 0.36)	-1.81 (+/-0.32)
Z₂-Cu(II)*	O_2 , SO_2 , and SO_3 do not adsorb on this site in neither Cu-SAPO-34 nor Cu-SSZ-13

Figure 7 – Calculated structures of SO_2 adsorbed on Z-Cu(I) and SO_3 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).

4. Discussion

It appears that the deactivation level by SO_2 correlates to the total amount of SO_2 that the catalyst is exposed to, as shown in Figure 1, where the catalyst has been exposed to different SO_2 concentrations and durations at 300 °C. However, this result could also be due to a saturation effect. If a SO_x saturation level is reached, it means that the S-uptake cannot get larger. In Figure 6 all the S/Cu ratios are plotted as functions of the SO_2

exposure temperature, and the S-uptakes at 200 °C in presence of NO and NH₃, and at 400 °C in only O₂ and H₂O, are both larger than that at 300 °C in presence of NO and NH₃. This shows that larger S-uptakes can be reached at higher and lower temperatures, and, therefore, the catalyst exposed to SO₂ at 300 °C in presence of NO and NH₃ is not saturated, which validates the interpretation that the deactivation by SO₂ is determined by the total exposure to SO₂.

The data in Figure 6 show that exposure to SO₂ at 200-600 °C results in different amounts of S-uptake by the Cu-SAPO-34 catalyst, dependent on the presence of NO and NH₃. These differences can be related to the different amounts of Cu(I) and Cu(II) and the formation of SO₃. The DFT calculations presented in Table 1 show, that SO₂ adsorbs more strongly than SO₃ on Z-Cu(I) sites. Since a mixture of NO and NH₃ has reducing properties [22–26], the presence of NO and NH₃ leads to a larger fraction of Z-Cu(I) species. This leads to an enhanced driving force for SO₂ adsorption on Cu in the presence of NO and NH₃. The fraction of Z-Cu(I) species decreases with increasing temperature, as a faster SCR reaction leads to lower partial pressures of NO and NH₃ and faster re-oxidation of the Cu, and therefore the SO₂ uptake decreases with increasing temperature in the presence of NO and NH₃, as shown in Figure 6.

In the absence of NO and NH₃, more Cu is present as Cu(II) species, and therefore, the adsorption of SO₂ on Cu(I) becomes less important. The DFT calculations show that the Z-Cu(II)OH site forms the most stable CuSO_x species in reaction with SO₃, while neither SO₂ nor SO₃ adsorb on the Z₂-Cu(II) sites. Due to the larger amount of Cu(II), the SO₂ uptake is now determined by the formation of SO₃, which then reacts with the Z-Cu(II)OH sites. The increasing SO₂ uptake with temperature in the range 200-400 °C is then a consequence of the increased rate of SO₂ oxidation [10]. Above 400 °C, decomposition and desorption of the CuSO_x species takes place [11], resulting in the lower SO₂ uptake with increasing temperature.

It is noted that both in the presence and in the absence of NO and NH₃, the adsorption of SO₂ or SO₃ always occurs on Cu sites. Therefore, the total SO₂ 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 SO₂ (total exposure of SO₂/Cu is at least 4.8). It has been 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 NH₃ 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 SO₂ uptake and deactivation in the low temperature range in the presence of NO and NH₃.

Finally, the chemical nature of the CHA framework (silicoaluminophosphate or aluminosilicate) seems not to have a significant influence on the deactivation by SO₂. As argued in the previous section, the deactivation of the silicoaluminophosphate Cu-SAPO-34 catalyst by SO₂ is related to the chemistry of Cu, SO₂ and SO₃, and therefore, SO₂-poisoning of the two versions of the Cu-CHA catalysts should be comparable. The response of the Cu-SAPO-34 catalyst to SO₂ exposure and regeneration at 550 °C in Figure 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 CuSO_x species formed from SO₂ and SO₃, and the interaction energies of SO₂ and SO₃ 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 SO₂-poisoning, and means that SO₂-poisoning is similar on Cu-exchanged aluminosilicate and silicoaluminophosphate CHA materials.

5. Conclusions

The deactivation behavior of a Cu-SAPO-34 catalyst in the NH₃-SCR reaction has been evaluated at simulated operating conditions by comparing the SCR activity before and after exposing to 1.5 ppmv SO₂ in a typical SCR-feed gas feed at 300 °C. The low-temperature activity is significantly lowered by the SO₂ 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 SO₂ 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 NH₃, and decreases with increasing temperature in the presence of NO and NH₃. This can be explained by the ability of NO and NH₃ to

reduce Cu(II) to Cu(I). DFT calculations show that SO₂ binds preferably to Cu(I), while SO₃ binds stronger to Cu(II). This then leads to the higher uptake of SO₂ below 400 °C in the presence of NO and NH₃, 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 NH₃.

The S/Cu ratios are always lower than 1, which indicates that the uptake of sulfur is related to adsorption of SO₂ on Cu and that ammonium sulfate does not precipitate in the catalyst when co-feeding SO₂, H₂O and NH₃. Furthermore, DFT calculations also show that SO₂ and SO₃ interactions with Cu is similar for Cu-SAPO-34 and Cu-SSZ-13, indicating that the deactivation by SO_x is mainly associated to the chemistry of the Cu sites. Consequently, the SO₂-poisoning mechanisms for Cu-SAPO-34 and Cu-SSZ-13 are comparable.

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7. References

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