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Reversible and irreversible deactivation of Cu-CHA NH₃-SCR catalysts by SO₂ and SO₃

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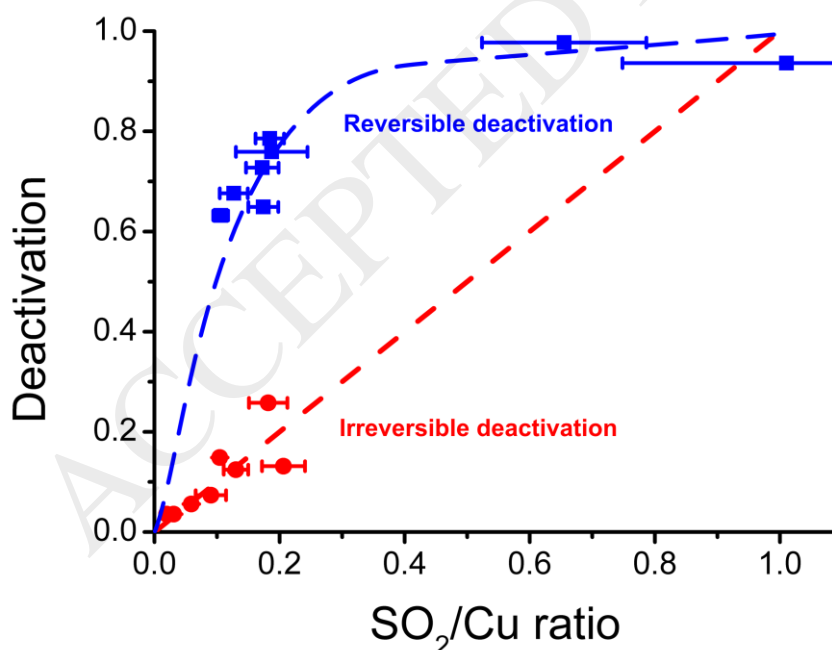
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Graphical abstract



Highlights

- SO_x -poisoned Cu-CHA is partially regenerated by heating to 550 °C.
- The irreversible part of deactivation scales with S/Cu ratio; reversible deactivation is higher than expected from S/Cu ratios.
- Presence of SO_3 affects deactivation at 200 °C, but not at 550 °C.
- Presence of H_2O and SO_x exposure at low temperature lead to higher irreversible deactivation

Abstract

Sulfur oxides are a common source for the deactivation of Cu-exchanged CHA zeolite based catalysts used for NO_x reduction in diesel exhausts by selective catalytic reduction with NH_3 (NH_3 -SCR). Since water and possible formation of SO_3 affect the deactivation of Cu-CHA catalysts, the deactivation in the presence of SO_2 or a mixture of SO_2 and SO_3 was studied by measuring the SCR activity in wet and dry gas at 200 and 550 °C. The estimated S-content in the catalysts before and after 4 h regeneration at 550 °C in NO , NH_3 , O_2 and H_2O was related to the deactivation. The deactivation can be divided into two parts: a reversible deactivation that is restored by the regeneration treatment, and an irreversible part. The irreversible deactivation does not affect the activation energy for NH_3 -SCR and display a 1:1 correlation with the S-content, consistent with deactivation by Cu-sulfate formation. The reversible deactivation results in a lower activation energy and a deactivation that is larger than expected from the S-content. The presence of SO_3 at 200 °C leads to higher reversible and irreversible deactivation, but has no significant impact at 550 °C. Furthermore, the irreversible deactivation is always higher when exposed at 200 °C than at 550 °C, and in wet conditions, compared to a dry feed. The deactivation is predominantly reversible, making regeneration at 550 °C a realistic approach to handle S-poisoning in exhaust systems.

Keywords NH_3 -SCR, Cu-CHA, deactivation, sulfur oxides, regeneration

1. Introduction

Combustion of diesel fuel in automotive engines produces NO_x (NO and NO_2). Due to the environmentally negative impact of NO_x , emissions of these compounds are subject to strict regulations, which requires NO_x reduction from the exhaust gas. The current technology for the removal of NO_x is selective catalytic reduction (SCR) of NO_x with NH_3 . Apart from an NH_3 -SCR catalyst, a complete diesel exhaust after-treatment system also contains a diesel oxidation catalyst to oxidize CO and unburnt fuel, a particle filter to remove soot, and an ammonia slip catalyst to remove the ammonia not used in the upstream NH_3 -SCR reaction.

The best known NH_3 -SCR catalysts are based on V_2O_5 , or Cu- or Fe-zeolites. Compared to V_2O_5 -based catalyst systems, Cu-zeolites generally work well in a broader temperature region (~ 150 - 500 °C) [1]. In particular, the better low temperature activity for Cu-zeolites is of interest for cold-start conditions. Combined with the good hydrothermal stability of small-pore zeolites, these traits have led to commercialization of Cu-zeolites in diesel engine exhaust systems, and Cu-CHA is the current state-of-the-art Cu-zeolite catalyst for diesel emission control.

Another important requirement for NH_3 -SCR catalysts is low susceptibility to SO_2 -poisoning. Diesel fuels contain a small amount of sulfur, and even ultra-low sulfur fuel will result in SO_2 in the exhaust gas. The performance of NH_3 -SCR catalysts, however, can be very sensitive to the presence of SO_2 , even at low concentrations, as in ultra-low sulfur diesel [2]. It is therefore important to know the effect of SO_2 on the performance of an NH_3 -SCR catalysts.

Unfortunately, Cu-zeolite catalysts deactivate more in the presence of SO_2 in the exhaust gas, while Fe-zeolites are less affected by SO_2 and V_2O_5 is not affected [1,3,4]. Consequently, to be able to exploit the potentially better performance of Cu-zeolite catalysts in an exhaust after-treatment system, it is important to understand how the presence of SO_2 influences the performance of these catalysts.

Furthermore, it is also important to know to what degree the deactivation of Cu-zeolites induced by SO_2 is reversible versus irreversible.

The current understanding of Cu-zeolite catalyst deactivation by SO_2 , and Cu-CHA in particular, is that it originates from SO_2 interaction with the Cu-sites. This can simply be adsorption of SO_2 or could involve a chemical reaction between the SO_2 and Cu-sites [2,5–13]. X-ray photoemission and X-ray absorption spectroscopy indicate that the Cu in the ion-exchange positions reacts to form a CuSO_4 -like species [2]. The formation of sulfates suggests that some oxidation of SO_2 to SO_3 takes place. In an after-treatment system, oxidation of SO_2 to SO_3 can occur on the diesel oxidation catalyst [2,11], and on the NH_3 -SCR catalyst [5]. A higher sulfur uptake and stronger deactivation has been observed in the presence of SO_3 in the feed gas [2,11]. Therefore, a better understanding of the effect of SO_3 on the performance of NH_3 -SCR catalysts is needed.

Another mechanism for deactivation of NH_3 -SCR catalysts is the formation of ammonium sulfate on the catalyst, which restricts access to the active sites. The presence of SO_2 or SO_3 in a standard, NH_3 -containing SCR-gas causes formation of ammonium sulfate, which is a solid below 300 °C, and therefore, deactivation by ammonium sulfate only occurs in the low-temperature range. Ammonium sulfate can be removed by heating the catalyst to above 350 °C, which means that regeneration from this type of deactivation is possible in an exhaust system [5,9,10].

An NH_3 -SCR catalyst in a diesel exhaust treatment system is typically operated between 200-550 °C, and in the presence of 5-10% water vapor. The effect of temperature on catalyst deactivation by SO_x depends on the presence of SO_3 [2,11]. With SO_2 only, the deactivation is more severe at 200 °C than at 400 °C, while the opposite trend is observed in the presence of SO_3 [2,11].

Water also interacts with the Cu ions, changing the environment of and around the active sites in a Cu-CHA catalyst. Water vapor is known to partially hydrolyze the Cu-sites at temperatures below 250 °C

[14], affecting the performance for NH_3 -SCR. In a similar way, reactions between different Cu-sites with sulfur oxides can be affected by water as well [8,15]. From a mechanistic point of view, the impact of water vapor on the deactivation by SO_2 and SO_3 should be understood, with the additional consideration that SO_3 and H_2O combine and form sulfuric acid below $400\text{ }^\circ\text{C}$ [11].

In practice, there are essentially two ways to deal with the presence of SO_x in an exhaust gas. The first one is to design the Cu-CHA SCR catalysts in such a way that the amounts of SO_2 and SO_3 passing through the system during its lifetime can be accommodated in the system. Alternatively, periodic regeneration strategies must be designed that restore at least a part of the catalytic activity. It is therefore important to know how the presence of SO_2 and SO_3 in the exhaust gas stream affects the performance of Cu-CHA catalyst and if regeneration of a Cu-CHA catalyst is possible. In this article, we focus on the effect of the temperature and H_2O and SO_3 on the SO_x -induced deactivation of a monolithic Cu-CHA catalyst for NH_3 -SCR. The stability of species formed was studied by comparing the activities of a deactivated catalyst with that after heating to $550\text{ }^\circ\text{C}$, which is a temperature that can be reached in an exhaust system.

2. Experimental

2.1. Preparation of the catalysts

In this study we used both a Cu-CHA powder catalyst and a monolithic Cu-CHA catalyst. For the powdered catalyst, Cu was introduced into the H-CHA zeolite by ion-exchange for 24 h with an aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (5 mmol/kg) at $20\text{ }^\circ\text{C}$, using 20 g H-CHA zeolite powder in 5 kg solution. After ion-exchange the Cu-CHA was filtered and washed with approx. 20 L MilliQ water, which resulted in a colorless filtrate. The Cu-CHA powder was then dried overnight at $95\text{ }^\circ\text{C}$, and calcined at $550\text{ }^\circ\text{C}$ for 3 h. The Si/Al ratio was 14.7 and the Cu/Al ratio was 0.5, corresponding to a Cu-loading of 2.8 wt%, as determined by ICP-OES.

The monolithic Cu-CHA catalyst was prepared by washcoating a cordierite monolith with a slurry of H₂O, xanthan gum, colloidal silica and Cu-CHA powder. The Cu-CHA powder was prepared by impregnating 1 kg of H-CHA powder (Si/Al = 16.6) with Cu in 1 kg of an aqueous solution of 0.39 mmol/g Cu(NO₃)₂·3H₂O in a rotary evaporator for 4 h at 95 °C. The Cu-loading of the powder was 2.5 wt%, based on the amount of Cu added for the impregnation. After impregnation, the powder was calcined at 550 °C for 3 h. A cordierite monolith (D×L = 25.4×10.2 cm, 300 cpsi, 0.005 mm wall thickness) was washcoated with the Cu-CHA slurry to a washcoat-loading of 151 g/L. The Cu-CHA/cordierite monolith was dried at 100 °C, and calcined at 550 °C for 3 h.

2.2. Catalytic test on powder

The NH₃-SCR activity measurements on the Cu-CHA powder were carried out in a fixed-bed quartz reactor with a 2 mm inner diameter, using 5.0 mg catalyst (150-300 μm sieve fraction) on a dry matter basis. The SCR feed gas composition was 500 ppmv NO, 530 ppmv NH₃, 10 % O₂, 5 % H₂O balanced by N₂, which we hereafter refer to as “SCR-gas”. The total flow rate used in the measurements was 0.225 NL/min (10 mmol/min, standard conditions: T = 0 °C, P = 1 atm). The outlet gas was analyzed by a Gasmeter CX4000 FTIR analyzer.

The Cu-CHA powder exposure to SO₂ was either done in situ in the reactor at 550 °C for 1 h with 40 ppmv SO₂, 10 % O₂, 5 % H₂O balanced by N₂ with a total flow rate of 0.2 NL/min (9 mmol/min), or ex situ in a tube furnace at 550 °C for 16 h with 100 ppmv SO₂, 16 % O₂ balanced by N₂ with a total flow rate of 0.2 NL/min. Regeneration was always carried out in situ in the reactor at 550 °C with an SCR-gas flow of 0.225 NL/min. 550 °C was chosen, as this is a typical temperature for regeneration of diesel after-treatment systems operating with passive filter regeneration.

2.3. Catalytic test on monoliths

With the purpose of studying the impact of temperature and H₂O and SO₃ gas components on Cu-CHA/cordierite monolith catalyst deactivation by SO₂, steady-state NO_x conversions were measured before and after SO_x exposure, and after regeneration at 550 °C in a laboratory flow reactor system with a horizontal quartz reactor with an inner diameter of 25.4 mm. Upstream and downstream tubing inside surfaces were coated with SilcoNert to minimize adsorption of SO_x (and NH₃). Monolith samples of approx. 20×27 mm were cut out from the larger prepared sample (sample masses were between 4.5-5 g). The reactor temperature was measured at the inlet, inside, and at the outlet of the monolith samples by thermocouples placed in the radial center of the reactor/sample. The steady-state NO_x conversions were measured at various temperatures (130-250 °C), at a flow of 8.0 NL/min (357 mmol/min). The SCR feed gas composition was 500 ppmv NO, 530 ppmv NH₃, 10 % O₂, 5 % H₂O balanced by N₂. The outlet gas was analyzed using a MKS MultiGas 2030 FTIR. SO_x exposure was always 3 h in 10 % O₂ with 100 ppmv SO_x balanced by N₂ with a total flow rate of 8.0 NL/min. The variations in the SO_x exposure conditions and the assigned sample names, are listed in Table 1. The SO₃ for the SO_x exposures, was produced in an upstream reactor by oxidizing SO₂ over a Pt/Al₂O₃ monolith catalyst. The temperature of the upstream reactor was adjusted to reach a steady-state conversion of SO₂ of 30 %, which was added to the main feed prior to the inlet of the quartz reactor containing the Cu-CHA/cordierite catalyst. Regeneration was carried out in the SCR feed gas at 550 °C, heating at 10 °C/min, for 4 h. In order to check if there were S-species remaining on the samples after regeneration, temperature-programmed desorption (TPD) to 900 °C was carried out after the final NO_x conversion measurement that followed the regeneration. The SO₂-TPD was carried out in N₂ at a flow rate of 8.0 NL/min, and with a temperature ramp at 10 °C/min. The concentrations of H₂O, NO, NO₂, NH₃, SO₂, SO₃ and H₂SO₄ were monitored during regenerations and TPD measurements.

2.4. Evaluation of activity and deactivation

The activities of the catalysts are evaluated by the rate constants, which are derived from the steady-state NO_x conversion measurements. If we assume that the NH_3 -SCR reaction is first order in NO , the rate constant is given by:

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

where F is the total molar flow rate, W is the mass of the Cu-CHA powder in both tested catalysts, and X is the conversion of NO . The deactivation is expressed as the relative rate constant of a sulfated or regenerated catalyst with respect to the rate constant for the fresh catalyst:

$$\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} = 1 - \frac{A \exp\left(-\frac{E_a}{RT}\right)}{A_{\text{fresh}} \exp\left(-\frac{E_{a,\text{fresh}}}{RT}\right)} \quad (2)$$

Multiplication by 100 then yields the deactivation expressed as a percentage.

3. Results

3.1. Powder experiments

The general behavior of a Cu-CHA catalyst upon exposure to SO_2 and regeneration at 550 °C is illustrated in Figure 1 for the powder catalyst, which shows the measured NO_x conversions for a fresh catalyst, after exposure to 100 ppm SO_2 at 550 °C (sulfated), and after regeneration at 550 °C in SCR-gas (regenerated).

The most significant effect of exposure to SO_2 is seen in the lower temperature range, up to 300 °C, where NO_x conversion was significantly inhibited compared to the fresh sample. Above 300 °C, the NO_x conversion increases rapidly with temperature to slightly above the conversion measured for the fresh catalyst. After regeneration by heating to 550 °C, the conversion above 300 °C was slightly higher, but close to that of the fresh catalyst. Below 300 °C, the conversion remained slightly below

that of the fresh catalyst. This shows that exposure to SO₂ results mainly in deactivation of the low-temperature ($T < 350$ °C) activity of the catalyst, which is consistent with previously reported observations [5,9,11], and regeneration at 550 °C does not fully restore the activity below 300 °C entirely.

To investigate if the incomplete regeneration at 550 °C is due to a too short regeneration time, the regeneration process was monitored by heating the samples at 550 °C for a total of 12 h in intervals, where after each interval the activity at 200 °C was re-evaluated. Figure 2A shows the measured activity at 200 °C obtained in this way, which indicates that a stable activity level is reached at about 75-80% of the original activity after approximately 4 h of regeneration. This means that a complete regeneration by heating at 550 °C seems not possible.

Figure 1 shows that the NO_x conversion over a catalyst after exposure to SO₂ increases slightly with temperature up to 300 °C, followed by a steep increase. To determine whether the slight increase below 300 °C is due to a normal temperature dependency of a possible residual activity, or to a slow regeneration in this temperature range, we checked the influence of the temperature on activity of a Cu-CHA catalyst at 200 °C. To do this measurement, a single catalyst sample deactivated by SO₂ was sequentially exposed to heating for 2 h in 5% H₂O/10% O₂/N₂ at a chosen temperature between 200 and 450 °C in increasing order, and then cooled down to 200 °C where the NO_x conversion was then re-measured. Figure 2B shows the rate constant at 200 °C, determined according to Eq. (1) as a function of the heating temperature. The rate constant at 200 °C does not increase by heating to a temperature of 300 °C or lower, which clearly indicates that the regeneration of a catalyst exposed to SO₂ does not start below 300 °C, and the slight increase in conversion in Figure 1 is therefore due to the temperature dependence of a residual activity. This also means that measured SCR activities after exposure to SO₂ are not affected by regeneration if the measurements are done at 300 °C or lower.

The observation that the activity after SO₂ exposure cannot be completely restored by heating to 550 °C indicates that there are different forms of deactivation. Based on these data, we define these different forms of deactivation as follows: the part of the deactivation that can be restored by 4 h heating at 550 °C will be referred to as the *reversible deactivation*, and the remaining part as the *irreversible deactivation*. The *total deactivation* is the sum of these two contributions. An activity measured after exposure to SO_x before regeneration, represents the total deactivation, the irreversible deactivation is found from the activity after regeneration. The reversible deactivation can then be determined as the difference in activity of a SO_x-treated catalyst before and after regeneration. The following expression is used to determine the relative reversible deactivation with respect to the activity of the fresh catalyst:

$$1 - \frac{k_{sulfated}}{k_{fresh}} = \text{Reversible deactivation} + \left(1 - \frac{k_{irreversible}}{k_{fresh}}\right) \quad (3)$$

3.2. Monolith experiments

The effects of SO₃, water and SO_x exposure temperature on the catalyst deactivation and regeneration was studied by measurement of NO conversions over Cu-CHA/cordierite monolith samples after exposure to SO_x at the conditions listed in Table 1, and after subsequent heating at 550 °C. In all these measurements, the deactivation and regeneration followed the same general trend as observed for the Cu-CHA powder. Figure 3 shows the measured NO_x conversion in the range 150-250 °C after deactivation in wet SO₂ without SO₃ as an example. Exposure to SO₂ leads to a lower NO_x conversion, which is mostly restored by heating at 550 °C. It is noted that all activity measurements shown in Figure 3 are obtained below 300 °C, and are therefore not influenced by regeneration during the measurements.

Due to variations in temperature in the different measurements, a common base for comparison of the measured NO_x conversions is needed. To this end, Arrhenius plots were constructed; Figure 4 shows

the Arrhenius plot based on the data in Figure 3, and represents the general observation for all samples (see supporting information). For all conditions, the slopes of the fresh and regenerated states of the catalyst are nearly the same, while the slope of the sulfated state of the catalyst is always smaller. Our interpretation is that the activation energies for the fresh and regenerated catalysts are the same, and the activation energy was determined from the combined data points of the fresh and regenerated states. Consequently, the differences in activity for fresh and regenerated catalysts are translated to differences in the pre-exponential factor. The relative irreversible deactivation then becomes independent of the temperature for the conditions used here. The assignment of irreversible deactivation to changes in the pre-exponential factor implies a mechanism in which deactivation is caused by loss of active sites, without major changes in the chemistry of the reaction.

The situation is different for the sulfated catalysts, which consistently have lower activation energy than the fresh and regenerated catalysts. Table 2 lists the activation energies for the fresh and sulfated samples, and the ratio of the two values. The lower activation energies of the sulfated catalysts also mean that the measured reversible deactivation depends on the temperature of the SCR activity measurement. A change in activation energy cannot be due to a loss of active sites only. Phenomena that could change the activation energy are a change in the chemistry of the NH_3 -SCR reaction and diffusion limitations of the NH_3 -SCR reaction rate in the zeolite crystals after exposure to SO_x . In the limit of strong pore diffusion limitations, the observed activation energy will be half the value of the intrinsic value. In principle, this is an option for the samples treated with SO_2 alone. For the samples treated with SO_3 , the activation energy ratios are lower than 0.5, which cannot be explained by internal diffusion limitations alone, suggesting that chemical effects are more pronounced in this case.

3.3. Desorption of SO_2

To determine the amount of sulfur deposited on the catalysts, SO_2 concentrations were measured during the regeneration up to and at $550\text{ }^\circ\text{C}$ in SCR-gas, and during heating to $900\text{ }^\circ\text{C}$ in N_2 after all activity measurements. The measured SO_2 desorption during the regeneration to $550\text{ }^\circ\text{C}$, shown in Figure 5A, is related to the reversible deactivation. No SO_3 or H_2SO_4 desorption was observed during the regeneration. Clearly, the two samples exposed to SO_3 at $200\text{ }^\circ\text{C}$ stand out with a substantially higher SO_2 desorption around $400\text{ }^\circ\text{C}$. Since the two catalysts exposed to SO_2 at $200\text{ }^\circ\text{C}$ did not show a similar high SO_2 desorption around $400\text{ }^\circ\text{C}$, the higher desorption of SO_2 from the two catalysts exposed to SO_3 at $200\text{ }^\circ\text{C}$ must be due to decomposition of SO_3 or sulfates [2,11,12]. The desorption temperature of $400\text{ }^\circ\text{C}$ is about $200\text{-}250\text{ }^\circ\text{C}$ lower than the decomposition temperature of bulk Cu sulfate [12]. This indicates that only little Cu sulfate is formed from SO_3 at $200\text{ }^\circ\text{C}$, or that the Cu-sulfate species formed this way in the Cu-CHA catalysts are less stable than bulk Cu-sulfate.

All other samples, exposed to SO_2 at $200\text{ }^\circ\text{C}$ or $\text{SO}_2 + \text{SO}_3$ at $550\text{ }^\circ\text{C}$, show similar SO_2 desorption peaks at approx. $300\text{ }^\circ\text{C}$ and $475\text{ }^\circ\text{C}$. This means that exposure to SO_3 at $550\text{ }^\circ\text{C}$ essentially results in similar sulfur species as exposure to SO_2 at 200 or $550\text{ }^\circ\text{C}$, and the influence of water is limited. The observed desorption temperatures are consistent with decomposition of ammonium sulfate [5] and sulfuric acid [12,15]. Ammonium sulfates can possibly have been formed by the exposure of the sulfated samples to NH_3 during the SCR activity measurement directly after the SO_x exposure [10], which would imply a reaction of the adsorbed sulfur species and ammonia.

Figure 5B shows the desorption of SO_2 during heating in N_2 to $900\text{ }^\circ\text{C}$ after SO_x exposure and regeneration, which represents the sulfur species associated with irreversible deactivation. The catalysts exposed to SO_3 at $200\text{ }^\circ\text{C}$ show again the largest amount of SO_2 . The desorption peak is centered around $675\text{ }^\circ\text{C}$ for all samples, indicating that the same species is formed in all catalysts, but in different amounts, dependent on the conditions for SO_2 exposure. The temperature of $675\text{ }^\circ\text{C}$ is consistent with the irreversible deactivation being related to formation of Cu-sulfate [12].

From integration of the curves in Figure 5, the amounts of sulfur in the sulfated and regenerated catalysts can be estimated, and we highlight the differences in sulfur content between the samples exposed to SO_3 at 200 °C and the other samples. The quality of the measured SO_2 concentrations during regeneration is poor, but the differences between the samples exposed to SO_3 at 200 °C and the other ones are quite clear. We also note that no SO_3 was detected during the temperature programmed desorption, and no sulfur was found in an ICP-OES analysis of the catalysts after heating to 900 °C. This means that the amounts of sulfur detected in the desorption measurements accounts for all sulfur present in the catalysts.

Table 3 lists the SO_2/Cu ratios related to the reversible and irreversible deactivation as derived from integration of the SO_2 desorption curves and the Cu content in the zeolite. The SO_2/Cu ratios of all samples are below 1, which indicates that not all Cu has reacted with SO_x , which would be required for complete formation of Cu-sulfate. The SO_2/Cu ratio after exposure to SO_3 at 200 °C in dry gas is 0.58, and 0.90 in the presence of water, and 70-80% of this amount is released during regeneration at 550 °C. In all other cases, the SO_2/Cu ratio is 0.1-0.2.

3.4. Influence of SO_2/SO_3 , water and temperature on deactivation

Having established the general trends in performance and sulfur content after sulfation, and regeneration of the Cu-CHA catalyst, we now turn our attention to the effects of temperature of SO_x exposure, and the presence of water or SO_3 . Figure 6A and B show the reversible and irreversible deactivation for the samples exposed to SO_2 only and SO_2+SO_3 . The reversible deactivation was derived from interpolation of the activity data to 180 °C, using the Arrhenius plots given in Figure 2 and supporting information. The deactivation is given as a percentage according to Eq. (2).

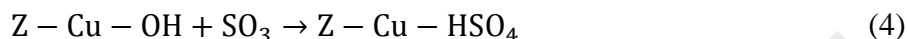
The effect of SO_3 on deactivation is most noticeable with SO_x exposure at 200 °C, leading to significantly stronger deactivation, compared to exposure to SO_2 alone both in dry and wet feed gases. At 550 °C, there is no apparent influence of SO_3 in the feed gas. This shows that the specific deactivation by SO_3 is most important in the lower temperature range, and that the effect of SO_3 on deactivation is related to the pronounced decomposition of SO_3 or sulfate at 400 °C, as shown in Figure 5A.

The presence of H_2O during SO_x exposure always leads to higher irreversible deactivation than the corresponding dry SO_x exposure condition, but appears to have no consistent influence on reversible deactivation. With respect to the impact of temperature, irreversible deactivation is always greater in the samples exposed at 200 °C than the corresponding sample exposed at 550 °C, whereas no consistent impact of temperature is observed on reversible deactivation. The general picture that emerges is that the presence of SO_3 and water at 200 °C has a stronger effect on the deactivation than at 550 °C, in particular on irreversible deactivation.

4. Discussion

The similar activation energies in the SCR reaction for the fresh and regenerated states of the catalysts indicates that irreversible deactivation is the result of having fewer active sites available, and the desorption temperature for SO_2 from the regenerated catalysts points to the formation of Cu-sulfate. If Cu-sulfate formation is the cause of deactivation, a 1:1 correlation should exist between the irreversible deactivation and the sulfur content. Figure 7 shows the measured irreversible deactivation as a function of the SO_2/Cu ratio, derived from the corresponding SO_2 desorption measurements in Figure 5B, together with the line for the 1:1 correlation. The measured irreversible deactivation actually follows the 1:1 correlation with the sulfur content fairly well, corroborating the idea that Cu-sulfate formation is responsible for the irreversible deactivation [2,5–13].

A way to envision the irreversible deactivation by formation of a Cu-sulfate species is a reaction of SO_3 with a Cu-ion balanced by a single Al and a hydroxide ligand (Z-Cu-OH), as in reaction scheme (4).



In this case, the hydroxide ligand provides the oxygen required for formation of sulfate. A Cu^{2+} ion balanced by two Al-sites ($\text{Z}_2\text{-Cu}$) does not have the hydroxide ligand, but this does not necessarily mean that these Cu-species are incapable of sulfate formation. In the presence of water, a $\text{Z}_2\text{-Cu}$ can react to a Z-Cu-OH and a Brønsted acid site [14], and the Z-Cu-OH can then react further with SO_3 according to reaction scheme (4). The overall reaction then becomes:



A similar scenario is a reaction with sulfuric acid (H_2SO_4) and a $\text{Z}_2\text{-Cu}$ site, where the sulfuric acid is formed by reaction of SO_3 and water. Either way, the presence of water would facilitate formation of Cu-sulfate as this leads to a higher amount of Z-Cu-OH-sites compared to dry conditions. The suggested reaction schemes then offer an explanation for the increase in irreversible deactivation in the presence of water. This means that a model that describes the irreversible deactivation by formation of Cu-sulfate is also consistent with the observed effects of the presence of water.

A comparison of measured deactivation and the sulfur content for the sulfated catalysts reveals a different behavior for reversible deactivation. Figure 8 shows the total deactivation of the sulfated catalysts as a function of their total SO_2/Cu ratios. Clearly, there is no consistent 1:1 dependence of the total deactivation on SO_2/Cu ratio, with only small SO_2/Cu ratios, between 10-20%, leading to degrees of deactivation as high as 60-80%. This indicates that the loss of activity in this case is not caused by a direct interaction of a single sulfur atom with a single Cu ion, as the measured deactivation is 5-10 times higher than expected from a 1:1 correlation.

The lower activation energies of the sulfated catalysts might be due to formation of internal diffusion limitations induced by SO_x deactivation, which can play a role in the deactivation process. In case of increased diffusion limitations, the effectiveness factor should become lower in addition to the loss of sites, resulting in an overall deactivation that is higher than the fraction of Cu sites in contact with sulfur. This agrees, at least qualitatively, with the results shown in Figure 8. To evaluate a possible effect of diffusion limitations, the effectiveness factor, η , was calculated for the fresh catalyst, assuming spherical zeolite crystals and first order reaction kinetics in NO. For the calculations, the crystal radius was set to 0.5 μm , which is a reasonable value given that the crystal size of the zeolite is on the order of 1 μm . A further description of the calculation of the effectiveness factor is given in supporting information. Figure 9 shows the effectiveness factor as a function of the effective diffusion coefficient, D_{eff} , at 180 °C. By extrapolation of experimentally determined values for effective diffusion coefficients for NH_3 in a Cu-CHA catalyst, using the corresponding activation energy [16], we find a diffusion coefficient of $1.2 \cdot 10^{-9} \text{ m}^2/\text{s}$. Using this diffusion coefficient, Figure 9 shows that the effectiveness factor for the fresh catalyst is close to 1. This implies that no internal diffusion limitation is expected in the crystals of the fresh catalyst. Because the activation energy of the regenerated catalysts is the same as for the fresh, diffusion effects can be excluded for the irreversible deactivation as well.

If the reduction of the effective activation energy to half the intrinsic value would be due to diffusion limitations, the effectiveness factor should decrease to be lower than 0.8, where there is a linear relationship between $\log(\eta)$ and $\log(D_{eff})$ resulting in a straight line in Figure 9. According to Figure 9, to obtain an effectiveness factor of 0.8, a decrease of the diffusion coefficient by about a factor of 100 would be required. This would mean that the small amount of sulfur, corresponding to less than 20% coverage of the Cu-sites, reduces the diffusion coefficient by a factor of 100. This seems unlikely, also

taking into account that a similar sulfur content in the regenerated catalysts does not affect the activation energy and diffusion.

Alternatively, pore-blocking by possible formation of ammonium sulfates may be considered as a cause for the reversible deactivation behavior. We note that the sulfated catalysts are exposed to SO_2 without ammonia present, and therefore, the resulting sulfur species is most likely bound to the Cu-ions [13]. If ammonium sulfate is formed by subsequent exposure to ammonia, this implies that the ammonium sulfate species is also located close to the Cu-ions. The SO_2/Cu ratios in the sulfated catalysts is about 0.15 (except in those exposed to SO_3 at 200 °C), which is similar to the SO_2/Cu ratio in some of the regenerated catalysts, where it was argued that there is no diffusion limitation. Therefore, it seems unlikely that the presence of these fairly small amounts of ammonium sulfate effectively block access to most of the zeolite. At present, the question of how the limited amount of sulfur can have such a strong impact on the reversible deactivation remains unanswered.

Having ruled out diffusion as a cause for reversible deactivation, the lower activation energy must then be related to changes in the chemistry. An interesting concept is Cu being able to form a mobile diamine species at SCR conditions. These mobile Cu-diamine species are important for the low-temperature activity of Cu-CHA catalysts [17–20]. Possibly, the reversible deactivation by sulfur oxide species inhibits the formation of these mobile Cu diamine complexes, thereby lowering the mobility of Cu and the NH_3 -SCR activity, which might lead to the observed high degree of reversible deactivation with low amounts of sulfur.

Finally, our data clearly show that exposure to SO_x at lower temperatures result in the largest deactivation. However, most of the catalytic activity can be regained by heating to 550 °C, even after exposure to SO_3 at 200 °C. This is an interesting result from an application point of view, since it

indicates that regeneration strategies based on heating to easily obtainable temperatures in exhaust systems are a feasible solution to handle deactivation of Cu-zeolites by SO_2 and SO_3 [10,13].

5. Conclusion

To evaluate different aspects of sulfur poisoning of NH_3 -SCR activity, Cu-CHA catalysts were exposed to SO_2 or a 70:30 mixture of SO_2 and SO_3 , in dry or moist conditions and at low and high temperature, and were evaluated before and after regeneration at 550 °C. After SO_x exposure, a high degree of deactivation is observed at temperatures below 300 °C. A major part of this deactivation is reversible by heating to 550 °C for 4 h, while a smaller, but appreciable, level of irreversible deactivation remains.

The mechanisms behind the reversible and irreversible deactivation differs. Irreversible deactivation is proportional to the sulfur content in the catalyst and consistent with the formation of a Cu-sulfate species. Reversible deactivation is not proportional to the sulfur content, and shows a strong deactivation already at low SO_2/Cu ratios.

The presence of water always increases irreversible deactivation, but has no apparent effect on reversible deactivation. Exposure to SO_x at 200 °C, always leads to a higher level of irreversible deactivation compared to exposure at 550 °C. The presence of SO_3 at 200 °C leads to significantly stronger deactivation; at 550 °C, deactivation by SO_3 is not significantly different from that by SO_2 . Regeneration of Cu-CHA exposed to SO_3 at 200 °C is accompanied by a decomposition of SO_3 and release of SO_2 around 400 °C.

In all experiments, the reversible deactivation accounts for most of the total deactivation, which makes regeneration by heating to 550 °C, an easily obtainable temperature in exhaust systems, a realistic approach to deal with deactivation by SO_x .

6. Acknowledgements

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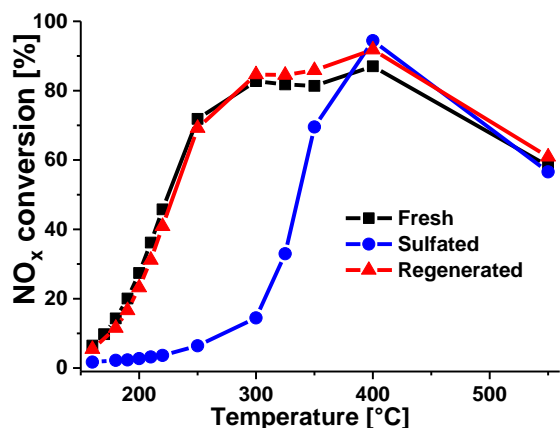


Figure 1 – NO_x conversion as function of temperature of a Cu-CHA catalyst (Si/Al = 14.7, Cu/Al = 0.5, and 2.8 wt% Cu) in fresh, sulfated and regenerated state. SCR conditions: 500 ppmv NO, 530 ppmv NH₃, 10 % O₂, 5 % H₂O, N₂ balance to 0.225 NL/min on 5.0 mg catalyst in reactor with an inner diameter of 2 mm. SO_x exposure conditions: 100 ppmv SO₂, 16 % O₂, N₂ balance to 0.2 NL/min for 16 h at 550 °C. Regeneration conditions: 4.6 h at 550 °C in SCR-gas.

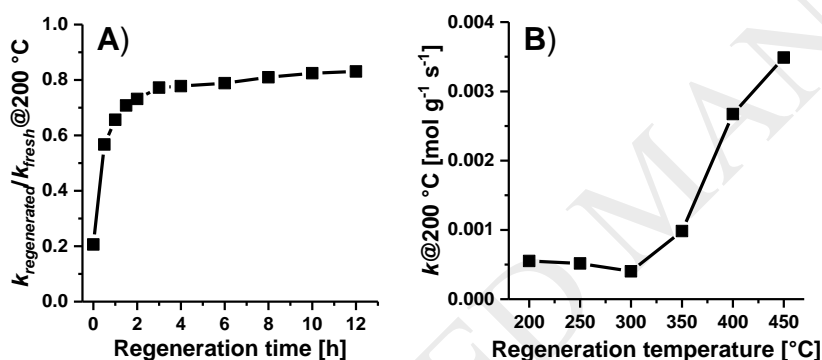


Figure 2 – Cu-CHA catalyst (Si/Al = 14.7, Cu/Al = 0.5, and 2.8 wt% Cu) A) Relative NH₃-SCR activity plotted as function of regeneration time. NO_x conversions measured on 5.0 mg catalyst at 200 °C on fresh catalyst, after SO₂ exposure, and after every regeneration step at 550 °C in SCR-gas. SO_x exposure conditions: 40 ppmv SO₂, 10 % O₂, 5 % H₂O, N₂ balance to 0.225 NL/min for 1 h at 550 °C. B) NH₃-SCR activity at 200 °C plotted as function of regeneration temperature (2 h at each regeneration temperature). NO_x conversions measured on 5.0 mg catalyst at 200 °C on fresh catalyst, after SO₂ exposure, and after every regeneration step at increasing temperature in SCR-gas. SO₂ exposure conditions: 100 ppmv SO₂, 16 % O₂, N₂ balance to 0.2 NL/min for 16 h at 550 °C.

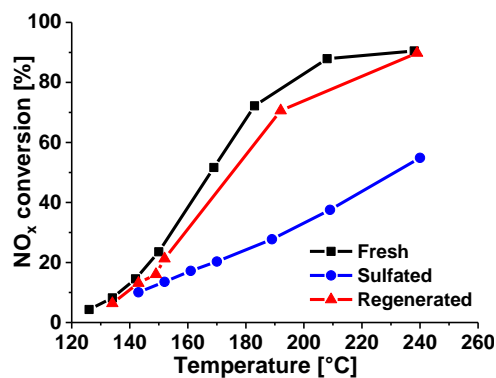


Figure 3 - NO_x conversion as function of temperature of a Cu-CHA/cordierite catalyst (Cu-CHA: Si/Al = 16.6, 2.5 wt% Cu) in fresh, sulfated and regenerated state. SCR conditions: 500 ppmv NO, 530 ppmv NH₃, 10 % O₂, 5 % H₂O, N₂ balance to 8.0 NL/min on 20×27 mm cylindrical monolith catalyst in reactor with an inner diameter of 25.4 mm. SO_x exposure conditions: 100 ppmv SO₂, 10 % O₂, 5 % H₂O, N₂ balance to 8.0 NL/min for 3 h at 200 °C. Regeneration conditions: 4 h at 550 °C in SCR-gas.

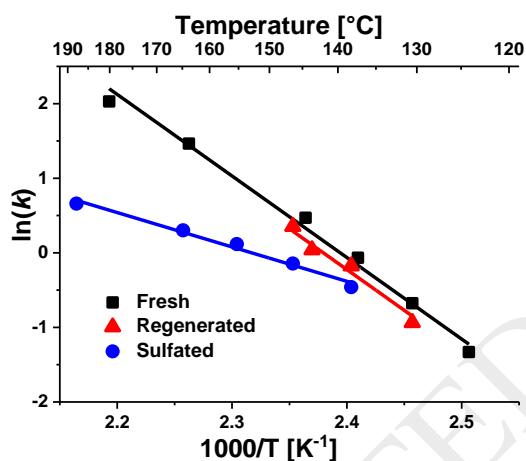


Figure 4 – Arrhenius plot of a Cu-CHA/cordierite catalyst (Cu-CHA: Si/Al = 16.6, 2.5 wt% Cu) in fresh, sulfated and regenerated state. SO_x exposure conditions: 100 ppmv SO₂, 10 % O₂, 5 % H₂O, N₂ balance to 8.0 NL/min for 3 h at 200 °C. Regeneration conditions: 4 h at 550 °C in SCR-gas.

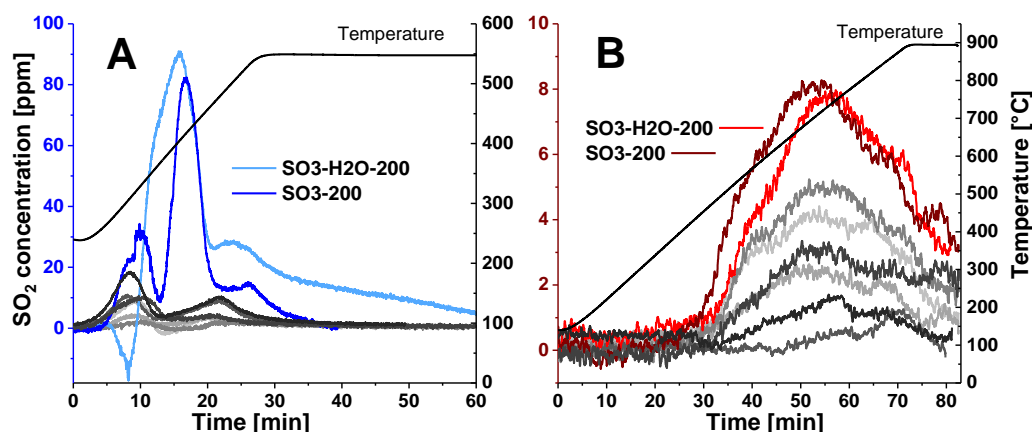


Figure 5 – SO_2 desorption spectra for sulfated Cu-CHA/cordierite catalysts, **A**) during heating to 550 °C at 10 °C/min in SCR-gas with a total flowrate of 8.0 NL/min, after sulfation, **B**) during heating to 900 °C at 10 °C/min in 8.0 NL/min N_2 , after sulfation and regeneration for 4 h at 550 °C. Curve-smoothing has been applied on the curves in **B**, using an adjacent-averaging method. In both **A** and **B**, legends are only provided for the catalysts exposed to SO_3 at 200 °C. Plots containing legends for all catalysts can be found in supporting information.

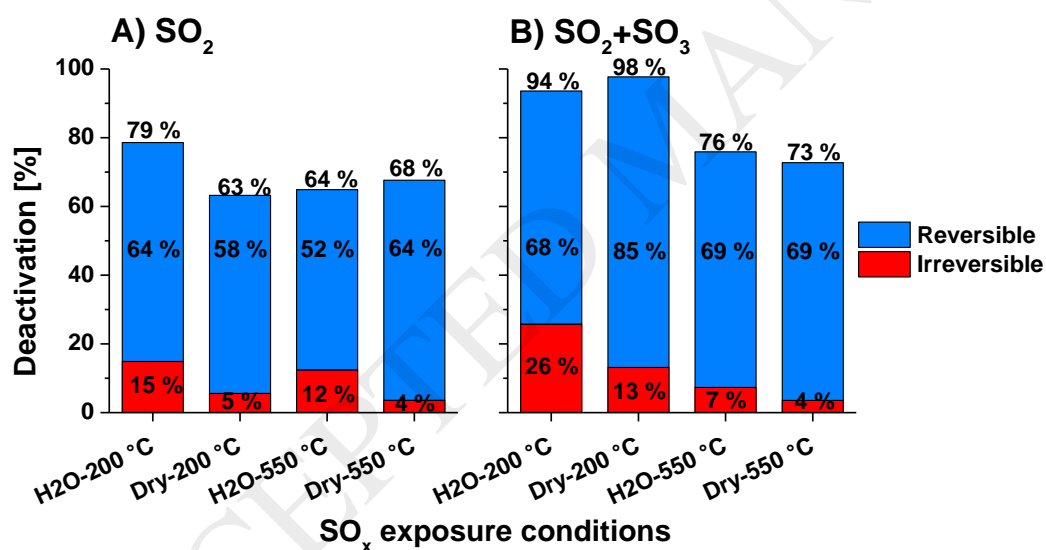


Figure 6 – The reversible deactivation (green bars), irreversible deactivation (red bars) and total deactivation (sum of red and green bars) plotted for each SO_x exposure condition of the Cu-CHA/cordierite catalysts. **A**) samples exposed to 100 ppmv SO_2 , **B**) samples exposed to 70 ppmv SO_2 and 30 ppmv SO_3 .

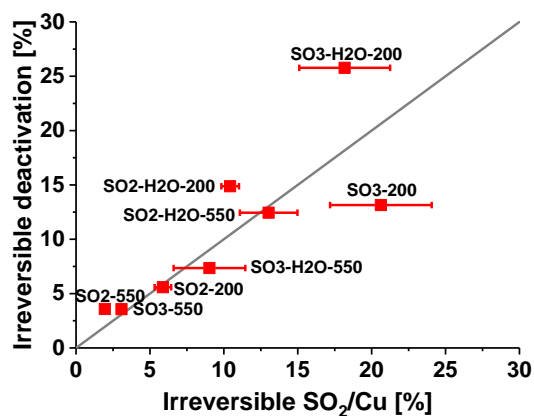


Figure 7 – The irreversible deactivation for the Cu-CHA/cordierite catalysts, determined after SO_x exposure and regeneration for 4 h at 550 °C, plotted as function of the SO₂/Cu ratio of the irreversible S-species.

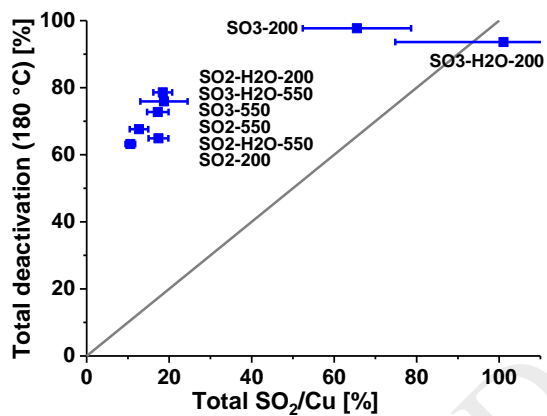


Figure 8 - The total deactivation for the Cu-CHA/cordierite catalysts, determined after SO_x exposure, plotted as function of the SO₂/Cu ratio of the total S-species.

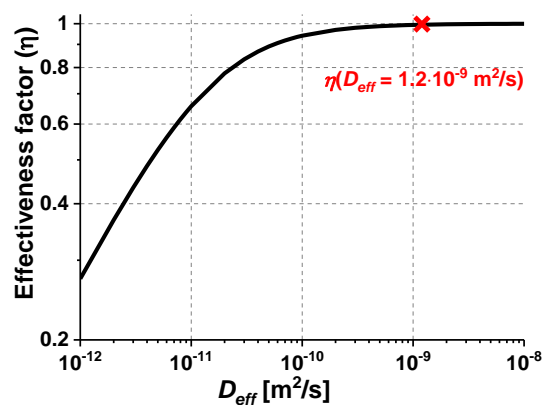


Figure 9 – Double logarithmic plot of the internal effectiveness factor in the zeolite crystals, η , at 180 °C, as a function of the effective diffusion coefficient, D_{eff} . η based on experimental values for D_{eff} of NH_3 in a Cu-CHA catalyst in the range 0-100 °C, is marked, which indicates that the reaction in the fresh catalyst is not limited by diffusion of reactants.

Table 1 – Assigned sample names according to variations in SO_x exposure conditions.

SO _x exposure conditions	100 ppm SO ₂	70 ppm SO ₂ + 30 ppm SO ₃
5 % H ₂ O T = 200 °C	SO2-H2O-200	SO3-H2O-200
Dry T = 200 °C	SO2-200	SO3-200
5 % H ₂ O T = 550 °C	SO2-H2O-550	SO3-H2O-550
Dry T = 550 °C	SO2-550	SO3-550

Table 2 – Activation energies of fresh ($E_{a,fresh}$) and sulfated ($E_{a,sulfated}$) states of the tested Cu-CHA/cordierite catalysts, and the ratios of $E_{a,sulfated}/E_{a,fresh}$.

Sample	$E_{a,fresh}$ [kJ mol ⁻¹]	$E_{a,sulfated}$ [kJ mol ⁻¹]	$E_{a,sulfated}/E_{a,fresh}$ (min-max)
SO2-H2O-200	91 ± 8	38 ± 5	0.33-0.53
SO2-200	99 ± 3	53 ± 2	0.50-0.58
SO2-H2O-550	90 ± 7	53 ± 1	0.54-0.65
SO2-550	59 ± 3	30 ± 5	0.41-0.63
SO3-H2O-200	80 ± 26	15 ± 2	0.12-0.32
SO3-200	115 ± 16	39 ± 4	0.27-0.45
SO3-H2O-550	97 ± 4	39 ± 1	0.38-0.43
SO3-550	76 ± 5	31 ± 1	0.36-0.45

Table 3 – The reversible, irreversible and total SO₂/Cu ratios of all Cu-CHA/cordierite catalyst samples.

Sample	Reversible SO ₂ /Cu	Irreversible SO ₂ /Cu	Total SO ₂ /Cu
SO2-H2O-200	0.07	0.09	0.16
SO2-200	0.04	0.05	0.09
SO2-H2O-550	0.04	0.12	0.16
SO2-550	0.10	0.02	0.12
SO3-H2O-200	0.74	0.16	0.90
SO3-200	0.40	0.18	0.58
SO3-H2O-550	0.09	0.08	0.17
SO3-550	0.13	0.03	0.16