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The presence of SO₂ in diesel exhaust gases causes severe deactivation of the Cu-CHA catalysts for the reduction of NO_x by selective catalytic reduction with ammonia (NH₃-SCR). The deactivation of Cu-CHA catalysts after exposure to SO₂ at 550 °C for 0.5, 4, 8, 16 and 32 h, and subsequent regeneration in SO₂-free gas at 550 °C was related to the site-dependent interactions of SO₂ with Cu ions associated with one or two framework Al centers (Z-CuOH or Z₂-Cu), as determined by electron paramagnetic resonance (EPR). SO₂ primarily interacts with the EPR-silent Z-CuOH sites, but a new, EPR-active Z₂-Cu phase develops with SO₂ exposure time as well. A part of the original Z₂-Cu species remain unaffected by SO₂, which is associated with a maximum deactivation level of about 90%. Regeneration at 550 °C leads to the release of most of the SO₂ from the Z-CuOH sites and some relocation of sulfur to Z₂-Cu sites occurs. The activation energy for NH₃-SCR on the SO₂ exposed catalysts decreases with S content from about 65 kJ/mol to 30 kJ/mol. For the regenerated catalysts, the activation energy is restored to about 65 kJ/mol, showing the importance of the Z-CuOH sites for the NH₃-SCR reaction.

Introduction

The selective catalytic reduction of NO_x (NO and NO₂) with NH₃ (NH₃-SCR) is the predominant method for removal of NO_x from exhaust gas of heavy-duty diesel vehicles. The catalysts used for this reaction are based on V₂O₅, Fe-zeolites or Cu-zeolites. Future legislation will require tighter NO_x emission limits, and therefore, a more efficient removal of NO_x in the low-temperature region becomes crucial. In this respect, the Cu-zeolites with the CHA structure are attractive,^{1,2} because of the significantly higher activity of the Cu-CHA catalysts at low temperatures down to 180 °C, which is unmatched by Fe-zeolites and V₂O₅-based catalysts.^{1,3,4}

According to the current understanding, the low-temperature activity of Cu-CHA catalysts is related to the ability to form mobile [Cu(NH₃)₂]⁺ complexes. These complexes facilitate the formation Cu pairs,^{5,6} on which the dissociation of oxygen can take place.^{5–12}

A drawback of Cu-CHA catalysts, and Cu-zeolite based catalysts in general, is their sensitivity to SO₂ in the exhaust gas that originates from the sulfur present in the fuel. Ultra-low sulfur diesel contains less than 10 wt ppm (Europe) or 15 wt ppm (US) sulfur, and the SO₂ concentration in the exhaust gas typically

reaches a few ppmv, which is nevertheless sufficient to reduce the low-temperature activity of the Cu-CHA catalysts significantly.^{13–24} To be able to preserve the good low-temperature activity, it is important to understand the impact of SO₂ on the NH₃-SCR activity of Cu-CHA based catalysts.

We have recently shown that deactivation of Cu-CHA catalysts depends on the total SO₂ exposure, which is the product of the SO₂ concentration and the exposure time.¹⁴ Deactivation by SO₂ is almost immediate: at about 1% of the total lifetime exposure to SO₂, the activity is reduced to about 30% of the original activity, and it stabilizes at about 10% of the original activity after 5–10% of the lifetime SO₂ exposure.¹⁷ The sulfur uptake in the Cu-CHA catalyst follows a similar pattern as the activity and, dependent on the temperature, a maximum S/Cu molar ratio of 0.5–1 is reached. The observation that the S/Cu ratio usually does not exceed 1 points to the formation of Cu₂S species.^{13,14,17} Thermal regeneration at 550 °C, which is feasible in a typical EURO VI exhaust system, can restore most of the activity if carried out in SO₂-free gas.^{13,14,17} During the regeneration, SO₂ is released from the catalyst, but a certain fraction of the sulfur is retained in a stable form that resemble Cu sulfate.^{13,14,17–19,22} The observations that heating to 550 °C results both in a partial regeneration of Cu-CHA catalysts and in the formation of a certain amount Cu sulfate, indicates that there are distinct Cu sites with a different reactivity towards SO₂.^{13,15,17,22}

The most obvious possibility for distinct Cu sites in Cu-CHA catalysts is that the Cu can be associated with either one or two Al centers in the zeolite framework. This leads to two main Cu^{II} sites: Z-CuOH and Z₂-Cu, and these sites have different chemical properties.^{10,25–30} The relative amounts of these Cu sites depend

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on synthesis conditions, the Si/Al ratio of the zeolite, and the Cu loading.¹⁰ Therefore, it is important to understand which role the Z-CuOH sites and Z₂-Cu sites play in the deactivation by SO₂. Electron paramagnetic resonance (EPR) spectroscopy is a powerful method for selective monitoring of the Z₂-Cu sites in Cu-CHA catalysts, and the presence of sulfur-species on these sites can be detected. In this article, EPR is used in combination with elemental analysis to localize sulfur in SO₂ exposed and regenerated Cu-CHA catalysts after total SO₂ exposures up to 3200 ppm·h at 550 °C. This is compared to the deactivation of the catalysts in the NH₃-SCR reaction, which reveals how Z-CuOH sites and Z₂-Cu sites behave in the deactivation of Cu-CHA catalysts by SO₂.

Experimental

Catalyst preparation

The parent CHA zeolite powder used in this study was prepared according to a previously published procedure,²⁸ which has been used in other EPR studies as well.^{29–31} Cu was introduced by ion-exchange of the parent H-SSZ-13 (Si/Al = 15) with an aqueous solution of Cu(CH₃COO)₂ for 24 h at 20 °C. The suspensions consisted of 1 g per 250 mL Cu(CH₃COO)₂ solution. To obtain the different Cu loadings in the Cu-CHA, the concentration of the Cu(CH₃COO)₂ solution was varied. The concentrations used for the catalysts in this study were 0.5, 1.0, 1.5, 2.0, and 5.0 mM, which resulted in Cu loadings of 0.72, 1.23, 1.63, 1.93, and 2.81 wt%, as determined by ICP-OES analysis.

SO₂ exposure and regeneration

To study the deactivation of Cu-CHA catalysts by SO₂ exposure, 0.5 g portions of the Cu-CHA with 2.81 wt% Cu were exposed to SO₂ for 0.5, 4, 8, 16, and 32 h at 550 °C in a quartz tube furnace. These catalyst samples are referred to as “SO₂ exposed”. The gas mixture used in these treatments consisted of 100 ppmv SO₂ and 16 % O₂ in N₂. Prior to the SO₂ exposure, the catalyst samples were de-greened for 1 h at 550 °C in technical air. After the exposure to SO₂, each catalyst portion was divided in two equal parts, and one half of each sample was regenerated in the same tube furnace at 550 °C for 5 h in a flow of 10 % O₂ and 3 % H₂O in N₂ at a flow rate of 200 NmL/min. These catalyst samples are referred to as “regenerated”.

NH₃-SCR activity measurements

The NH₃-SCR activities of the fresh, SO₂ exposed, and regenerated catalysts were determined from measurement of steady state NO conversions. For these measurements, a 5 mg sample (on a dry matter basis, sieve fraction 150–300 μm) was loaded in a fixed bed quartz reactor with an inner diameter of 2 mm. The reaction feed consisted of 500 ppmv NO, 530 ppmv NH₃, 10 % O₂ and 5 % H₂O in N₂ at a flow rate of 225 NmL/min. The concentrations of NO, NO₂, N₂O, NH₃ and H₂O were determined online, using a Gaset CX4000 FTIR analyzer connected to the reactor outlet. For the activity measurements, the reactor temperature was stepwise increased from 160 to 550 °C and allowed to stabilize for 40 min at each temperature.

The activity of the catalysts was derived from the NO conversion as the first order rate constant, *k*, of the SCR reaction:

$$k = -\frac{F}{W\left(1 + \frac{\Delta P}{2}\right)} \ln(1 - X) \quad (1)$$

Here, *F* is the total molar flow rate, *W* is the dry weight of the catalyst powder, ΔP is the pressure drop over the catalyst bed, and *X* is the fractional NO conversion. The deactivation of the catalysts is calculated as the relative loss of activity as follows:

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

EPR: Measurement of the total Cu content

The EPR spectra were collected on a CW X-band Bruker EMX EPR spectrometer with an ER 4102ST cavity and a gunn diode microwave source. To measure the total amount of Cu in the zeolite, the total EPR intensity of a 25 mg of the Cu-CHA sample, placed in a quartz tube, was compared to the measured intensities for a series of samples where CuSO₄ is diluted in K₂SO₄ to obtain a known Cu concentration in the range 0.2–5 wt%. In the fresh untreated Cu-CHA samples, the Cu is present as an EPR active hydrated form, allowing for an accurate measurement of the total Cu content.

The measurements were done within the field interval 220–400 mT, with a microwave power of 6.3 mW, a microwave frequency of 9.4–9.6 GHz, a modulation frequency of 100 kHz, and a modulation amplitude of 8 G. The spectra were collected with 2000 points and averaged over 3 scans. The Q-value was noted and carefully observed to be the same for the different samples. The EPR intensity was calculated as the double integral of the measured spectra, after background correction.

In-situ dehydration with EPR

For selective measurement of the Z₂-Cu species present in the Cu-CHA catalysts, the catalysts must be dehydrated. The dehydration was done in a flow of 50 mL/min of 20 % O₂ in He while heating to 250 °C at a rate of 7 °C/min, using a heater attached to the EPR cavity. The EPR spectra were continuously collected, using the parameters as given above, with a time constant of 20.48 msec and conversion time of 15 msec, which results in approximately 41–42 seconds between the start of each spectrum. A final spectrum was collected in pure He atmosphere. All spectra are background corrected by subtracting the spectrum of an empty tube and, if necessary, also by performing a linear baseline correction. The intensity of each EPR spectrum is found by double integration of the background corrected spectrum.

Quantification of EPR active copper was performed in two steps: 1. All hydrated catalysts were measured ex-situ and the intensity of the EPR spectra was compared to a standard curve based on EPR intensity of 5 reference samples (different concentrations of CuSO₄·5H₂O diluted in K₂SO₄) measured the same day at exactly the same instrument settings. 2. The EPR intensity for the dehydrated samples, *I_{rel}*, is determined by

relating the EPR intensity, $I(T)$, to the intensity of the starting (fully hydrated) EPR spectrum, $I(T_{start})$, and corrected according to the Boltzmann distribution for the temperature differences according to ^{30,32}:

$$I_{rel} = \frac{I(T)}{I(T_{start})} \cdot \frac{T}{T_{start}} \quad (2)$$

EPR spectra were fitted as a sum of contributions from each Cu species. Each species is modeled using an axial spin Hamiltonian ²⁹ with 4 parameters, $g_{||}$, $g_{\perp}$, $A_{||}$, and $A_{\perp}$ as well as linewidth parameters. The fittings and simulations are performed using the EasySpin Toolbox in Matlab.³³

Results

NH₃-SCR activity and impact of SO₂ exposure

The effect of increasing SO₂ exposure time over Cu-CHA on the NH₃-SCR NO conversion is illustrated in Figure 1. Low-temperature activity (<350 °C) of the Cu-CHA catalyst is strongly reduced upon exposure to SO₂ (Figure 1A). The impact of SO₂ at temperatures above 350 °C is clearly less, indicating that deactivation by SO₂ is mainly relevant for the low-temperature performance, in agreement with earlier observations.^{13–24} The low-temperature activity after SO₂ exposure is partially restored by heating the Cu-CHA catalysts to 550 °C in SO₂-free gas (Figure 1B).^{13,14,17}

The changes in the deactivation of NH₃-SCR activity with time of SO₂ exposure are illustrated in Figure 2A, which shows the deactivation, according to Eq. 2, based on the measured NO conversion at 220 °C. About 80% of the activity is lost during the first 8 h of SO₂ exposure, and after 16 h of SO₂ exposure, the loss of activity stabilizes at 90%. This means that the deactivation of the SO₂ exposed catalysts does not reach 100%, but a certain NH₃-SCR activity, although low, is maintained even after prolonged exposure to SO₂.¹⁷ The deactivation of the regenerated catalysts increases with SO₂ exposure in a similar manner, reaching a maximum of 50% deactivation.

Figure 1 – Steady state NO conversion of the fresh catalyst in comparison with those of A) the SO₂ exposed catalysts after exposure to 100 ppmv SO₂ and 16 % O₂ in N₂ at 550 °C for different durations, and B) the regenerated catalysts after regeneration in 10 % O₂ and 3 % H₂O in N₂ at 550 °C for 5 h.

To determine the relation of the deactivation with the uptake of sulfur, the sulfur contents of the SO₂ exposed and regenerated catalysts were measured with ICP-OES. The measured S/Cu ratios are also included in Figure 2A. For the SO₂ exposed catalysts, a maximum S/Cu ratio of 0.8 is reached. The fact that the S/Cu ratio does not exceed 1 is consistent with the deactivation being related to interactions between sulfur and Cu.^{13,14,17} After regeneration at 550 °C the S/Cu ratios remain unchanged in the catalysts exposed to SO₂ for up to 4 h, while the S/Cu ratios drops for the catalysts subjected to longer exposures as part of the sulfur is released from the catalyst during regeneration.^{13,14} The highest S/Cu ratio for the regenerated catalysts is 0.5. The similar trends in the S/Cu ratio and deactivation curves in Figure 2A suggest a correlation. Figure 2B shows the deactivation as a function of the S/Cu ratios. The grey dashed line represents a 1:1 relation between the deactivation and S/Cu ratio. There is a distinct difference between the SO₂ exposed and regenerated catalysts: All of the SO₂ exposed catalysts have deactivation levels that are above the 1:1 proportionality line, whereas all of the regenerated catalysts are below the line, except for a single catalyst sample. This shows that sulfur causes a stronger deactivation before regeneration than after. This is particularly pronounced when comparing the SO₂ exposed and regenerated catalysts after 0.5

and 4 h of SO₂ exposure. In these catalysts, the deactivation levels are significantly different, but the S/Cu ratios are very similar. This shows that the regeneration is not just a consequence of the release of sulfur from the catalyst. During regeneration, the Cu₂S species also changes to a form which affects the NH₃-SCR activity of the catalyst less. This change could be related to the sulfation of different Cu sites.^{14,15,22}

Figure 2 – A) shows the deactivation (full lines) and S/Cu ratios (dashed lines) of the SO₂ exposed (red) and regenerated (blue) catalysts as functions of the exposure time to SO₂. B) shows the deactivation as function of the S/Cu ratio for the SO₂ exposed (red squares) and regenerated (blue circles) catalysts. The grey dashed line indicates the 1:1 correlation between the deactivation and S/Cu. The deactivation in both graphs are at 220 °C.

The sulfur also affects the activation energy for NH₃-SCR in a different way before and after regeneration. Figure 3 shows the apparent activation energies (190–250 °C) for the SO₂ exposed and regenerated catalysts as a function of the SO₂ exposure time. The activation energies for the SO₂ exposed catalysts decrease with increasing exposure time, while those of the regenerated catalysts remain stable and close to the activation energy of the fresh catalyst. This is consistent with a difference in how the sulfur interacts with the copper before and after regeneration.

Figure 3 – Activation energies (190–250 °C) for the fresh (black), SO₂ exposed (red), and regenerated (blue) catalysts in the NH₃-SCR reaction, as function of the SO₂ exposure time.

Recently, it was proposed that the NH₃-SCR activity depends on the ability of the catalyst to form Cu pairs from mobile [Cu(NH₃)₂]⁺ species.^{5,6} It was also shown that at low Cu loading, the relation between activity and Cu loading becomes quadratic because it depends on two copper sites to form the active Cu pair site, and that the activation energy increases with increasing Cu loading. In this situation, if single Cu sites were blocked, the deactivation would be disproportionately larger than the amount of affected Cu sites, as observed for the SO₂ exposed catalysts in Figure 2B. A part of the explanation for the observed disproportional effect of sulfur on the activity of the SO₂ exposed catalysts, seems likely to be related to this behavior, as well as the influence on the activation energy.

To understand the consequences of a Cu-site blocking by sulfur better, we compare in Figure 4 the activities and the apparent activation energies of the deactivated catalysts (both SO₂ exposed and regenerated) to those of fresh Cu-CHA catalysts with various Cu loadings as a function of the sulfur-free Cu density. The sulfur-free Cu density was calculated as the difference between the total molar Cu content of the fresh catalyst and the total molar S content of the deactivated catalysts. The general trends of the rate constants of both the SO₂ exposed and regenerated catalysts are similar to that of the fresh catalysts, but there are some differences as well. In the higher Cu density range, the rate constants of the SO₂ exposed catalysts are slightly lower compared to the fresh catalysts. Furthermore, the rate constants for the SO₂ exposed catalysts show a quadratic dependence on the sulfur-free Cu density up to 0.44 Cu/1000 Å³. In contrast, the rate constants for the fresh catalysts only appear to follow a quadratic dependence up to about 0.33 Cu/1000 Å³. The regenerated catalysts generally show a higher rate constant per sulfur-free Cu atom compared to the corresponding fresh catalysts, and they do not exhibit a quadratic dependence on the sulfur-free Cu density at all.

The observed trend in the activation energy for the SO₂ exposed catalysts is similar to that of the sulfur-free catalysts. At Cu densities above 0.3 Cu/1000 Å³, the activation energy is constant around 65 kJ/mol. Below 0.3 Cu/1000 Å³, the activation energy gradually decreases to about 30 kJ/mol with

Cu density. This indicates that the decrease in activity of the SO₂ exposed catalysts can be explained as a loss of the active Cu that is necessary for Cu pair formation. The apparent activation energies of the regenerated catalysts do not show a decrease, but remain at a constant level of about 65 kJ/mol down to 0.22 Cu/1000 Å³. The change to higher activation energies for the samples with low effective Cu densities, after regeneration, suggests that chemical changes has occurred in the Cu phase, or that certain sites are more affected than others. Although the single site-blocking mechanism does not describe the deactivation to a full extent, it provides a useful framework to assess the deactivation behavior.

Figure 4 – A) SCR rate constants at 220 °C for the fresh, SO₂ exposed and regenerated catalysts as function of the sulfur-free Cu density, assuming that a single S occupies a single Cu. The black line is a parabolic fit to the 4 fresh catalysts with lowest Cu densities, and the red line is a parabolic fit to all SO₂ exposed catalysts. B) Apparent activation energies for the fresh, SO₂ exposed and regenerated catalysts as function of the sulfur-free Cu density. In both A) and B), the sulfur-free Cu density is calculated from the difference between the total molar Cu content of the fresh catalyst and the molar S content of the deactivated catalysts.

EPR results

To address the location of sulfur and possible changes in the Cu phase, catalyst samples were investigated with EPR after SO₂ exposure and regeneration. It has previously been shown that the amount of EPR active Cu in a hydrated and fresh Cu-CHA catalyst sample correlates to the total Cu amount measured by ICP.^{28,34,35} The amounts of EPR active Cu in the hydrated fresh, SO₂ exposed and regenerated catalysts were obtained by

double integration of the hydrated EPR spectra. Based on the EPR analysis of the hydrated fresh catalyst, the total Cu content was measured to be 2.43 wt%. The quantitative EPR analysis of the hydrated states of the SO₂ exposed catalysts resulted in values of 2.5 – 2.7 wt% Cu, and 2.2 – 2.4 wt% Cu for the regenerated catalysts. These values are close to the Cu content measured with ICP, as shown in Table 1. There is no consistent trend of increasing or decreasing amounts of active Cu for the SO₂ exposed or regenerated catalysts, and the deviations are possibly within the uncertainty of the quantitative EPR analysis with our experimental procedure. Therefore, we assume that the total amount of EPR active Cu^{II} in the hydrated catalysts is unaffected by SO₂ exposure and regeneration.

Table 1 – Cu contents of fresh, SO₂ exposed and regenerated catalysts, as determined with EPR and ICP.

SO ₂ exposure time	Cu wt% in SO ₂ exposed catalysts		Cu wt% in regenerated catalysts	
	EPR	ICP	EPR	ICP
Fresh	2.43	-	2.38	-
0.5 h	2.55	2.20	2.52	2.39
4 h	2.47	2.40	2.44	2.35
8 h	2.57	2.32	2.37	2.36
16 h	2.70	2.35	2.37	2.37
32 h	2.74	2.35	2.38	2.35

In the dehydrated and oxidized state, Cu-CHA contains two principal Cu^{II} sites: one that is charge-balanced by a single framework Al and a hydroxide ion, Z-CuOH, and one that is charge balanced by two framework Al, Z₂-Cu. The EPR spectra of the dehydrated catalysts contain information about the identity and amount of Z₂-Cu sites: After in situ dehydration only the Z₂-Cu sites are EPR active, whereas any Z-CuOH sites formed are EPR silent due to 3-fold coordination around Cu.^{29,31} Minority species such as Cu dimers and Cu_xO_y oligomers are also EPR silent due to magnetic coupling between Cu centers.^{29,31} The EPR spectra of the fresh, SO₂ exposed, and regenerated catalysts were recorded after dehydration, and are presented in Figure 5. The total integrated intensity is collected in the two left columns of Table 3. Two sets of quartet hyperfine structure (due to interaction with the $I = 3/2$ Cu nuclei) are easily recognized in the parallel region of the Cu EPR spectrum and reveal the coexistence of at least 2 different Cu species. The hyperfine structure are indicated in Figure 5. All features of the EPR spectra can be simulated assuming two well-resolved Cu^{II} species, A1 and A2, a minority species B and an un-resolved broad species, C. The spin Hamiltonian parameters of each species are determined by simulation in Easyspin³³ and listed in Table 2. The observed species have been identified earlier as follows.²⁹ The A1 and A2 species are assigned to Z₂-Cu species in which the Cu is located near the 6 membered rings (6mr) of the CHA structure forming 4 bonds to oxygen. The B species are assigned to Cu species forming 5- or 6- bonds. Finally, the C species are assigned to a distribution of non-crystalline Cu^{II} species.^{29,31}

From Figure 5 it is seen that the signal from species C (a broad underlying feature) becomes more prominent for samples that have been exposed to SO₂ for longer time. Concurrently, the

intensity of the peak related to the A1 species decrease, while the A2 species appears unchanged.

A more detailed analysis using modeling of the EPR spectra is carried out in order to follow the individual species more quantitatively. Therefore, each spectrum was fitted as a linear combination of the 4 species A1, A2, B and C.

Table 2 - Fitted spin Hamiltonian parameters of different Cu species from the EPR spectra in Figure 5.

Species	Spin Hamiltonian Parameters				
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (MHz)	$A_{\perp}$ (MHz)	Line width (FWHM in MHz)
A1	2.32	2.07	505	45	2.2
A2	2.36	2.07	465	20	1.7-2.8
B	2.26	2.09	490	34	1-2
C	$g = 2.16$		$A = 50$		30-42

*These were not well resolved and are based on estimations

The fitted intensity of each Cu^{II} species were related to the corresponding total EPR intensity of the hydrated catalysts that reflect the total Cu content. Thus, the fractions of the four different Cu^{II} species relative to the total Cu content in each SO₂ exposed and regenerated catalyst were estimated and are listed

Table 3 – Intensities of EPR active Cu after dehydration in the fresh, SO₂ exposed and regenerated catalysts. The distributions of EPR active Cu species (A1, A2, B and C) from fittings to the raw EPR spectra after dehydration are also listed.

Sample	EPR intensity after dehydration (%)		Distribution of EPR active Cu* (%)							
	SO ₂ exposed	Regenerated	SO ₂ exposed				Regenerated			
			A1	A2	B	C	A1	A2	B	C
Fresh		38	13.2	13.8	5.5	5.5				
0.5 h	41	41	14.1	14.7	5.9	5.9	12.0	13.5	4.8	10.7
4 h	42	43	12.6	14.8	5.9	8.9	8.4	14.0	4.2	16.8
8 h	44	44	7.9	13.2	4.0	18.5	7.6	13.6	3.0	19.6
16 h	45	50	4.9	12.4	1.2	26.0	6.2	16.6	2.1	24.9
32 h	58	55	6.7	15.0	1.7	34.9	7.2	16.7	2.4	28.7

*calculated as the amount of Cu in that particular species out of the total Cu content using the amount of EPR active Cu before dehydration.

Figure 5 - EPR spectra recorded at 25 °C in a flow of He after in-situ dehydration of SO₂ exposed and regenerated Cu-CHA samples. The parallel region of the EPR spectra are expanded in the inset where the quartet hyperfine pattern of the two most well-defined Cu species, A1 and A2 are indicated.

in Table 3 and graphically displayed in Figure 6.

As seen in Figure 6, the total amount of EPR active Cu in the dehydrated spectra (the sum of the four different Cu^{II} species) increases with SO₂ exposure time, from initially 38% of the total Cu content to about 57%. The amounts of A1 and B species slightly decrease, and the amount of A2 species remains constant. The decrease of A1 and B species occurs in parallel to the increase of the C species. However, the total decrease in A1 and B species, i.e. from approx. 19% to 9%, is less than the increase of C species. Therefore, the increase of C, at least partially, has to arise from EPR silent Cu species becoming EPR active after the exposure to SO₂. This is an indirect indication that SO₂ interacts with the EPR silent Z-CuOH species. This is corroborated by comparing the S/Cu ratios in Figure 2, with the EPR results of the catalysts exposed to SO₂ for 16 and 32 h. The S/Cu ratios are 0.8 while the sulfur-free A1 and A2 Cu species constitute about 20% of the total Cu content, again implying that sulfur is associated with the EPR silent Z-CuOH sites leading to the C species.

The amount of Cu in the Z₂ positions (A1 and A2 combined) decreases with SO₂ exposure time, and stabilize around 8 h of SO₂ exposure. From Figure 2A it can be seen that the S/Cu ratio follows the inverse trend. After regeneration of the catalyst, the S/Cu ratio drops from 0.8 to 0.5, while there are no major changes to the EPR active Cu. This indicates that primarily sulfur associated with the Z-CuOH sites is released during regeneration.

The A2 species in both the SO₂ exposed and regenerated catalysts remain at a constant level of about 15% for all exposure times, indicating that this Cu species is not affected by the SO₂ exposure. This is also consistent with the S/Cu ratio not exceeding 0.8, as seen in Figure 2, and is a possible explanation why a complete deactivation is never observed, even after prolonged SO₂ exposures.¹⁷

There is an interesting development of the A1 and C species when comparing the SO₂ exposed and regenerated catalysts exposed to SO₂ for 0.5 h and 4 h. The EPR measurements show that the amount of the A1 species are constant up to 4 h of SO₂ exposure, but after regeneration the amount of A1 species has dropped, which occurs in parallel to an increase of the C species. The corresponding S/Cu ratios measured with ICP (Figure 2) are similar for the SO₂ exposed and regenerated catalysts, implying that sulfur is not removed during regeneration. This indicates that a relocation of sulfur, or Cu₂S species, is taking place during regeneration. Such a relocation may also occur during SO₂ exposure, as indicated by the similar amounts of A1 species that are present after 4 h of SO₂ exposure + 5 h of regeneration (effectively 9 h at 550 °C) and after 8 h of SO₂ exposure at 550 °C.

Figure 6 – Fractions of Cu species A1, A2, B and C relative to the total Cu content of the catalysts, plotted as function of the SO₂ exposure time. The values are determined by analysis of the EPR spectra in Figure 5 in the SO₂ exposed (solid lines with full symbols) and regenerated (dashed lines with open symbols) catalysts.

Discussion

In accordance with previous reports,^{13,14,17} the molar S/Cu ratios presented in Figure 2 do not exceed 1. This supports the conclusion that the SO₂ interacts with the Cu sites to form Cu₂S species. Density Functional Theory calculations show a clear difference in reactivity of the Z₂-Cu in the 6-membered ring and the Z-CuOH species towards SO₂ and SO₃. According to these calculations, SO₂ and SO₃ form stable Cu₂S species on Z-CuOH sites, but do not adsorb on Z₂-Cu in the 6-membered ring.¹⁴ This agrees with our EPR results for the A2 species, which are not influenced by SO₂. The A1 species is also assigned as a Z₂-Cu site, but with another local distribution of Al. The evidence points to the fact that sulfur interacts to some extent with this species. Also, A1 was previously shown to be more reactive than the A2 species,³⁰ and this is further demonstrated here. There is the possibility that water plays a role in the interaction of SO₂ with Z₂-Cu and this is enough to activate the A1 species but not the A2 species. Presence of trace water during the SO₂ exposure is likely, and the regeneration was carried out in the presence of water, while the presence of water was not accounted for in the DFT calculations. In line with the DFT calculations, the EPR data also indicate that SO₂ preferably interacts with the Z-CuOH species.

As argued in the results section, a relocation of sulfur or Cu₂S species occurs at extended exposure to 550 °C. This relocation appears to be part of a kinetically limited reaction, which leads to more C species, which are argued to be Cu₂S that are stable at 550 °C. Such stable Cu₂S species in Cu-CHA catalysts are described as certain Cu sulfates.^{13,14,17,18} Thus, it is plausible that the kinetically limited reaction is an oxidation reaction of SO₂ to SO₃, consistent with TGA measurements,¹⁷ that involves a relocation of sulfur or Cu₂S species, and leads to formation of the “irreversible” Cu₂S species.

The EPR results presented in Figure 6 shows that the Z₂-Cu sites are largely unaffected by SO₂ exposure and regeneration, constituting about 30% of the total Cu in the fresh catalyst and about 20% after 32 h of SO₂ exposure. Simultaneously, the ICP measurements in Figure 2 reveal that S/Cu ratios as high as 0.8 are reached after SO₂ exposure, which then drops to 0.5 after regeneration. Indirectly, this shows that predominantly the Z-CuOH sites are associated with sulfur after SO₂ exposure, and that the regeneration in SO₂-free gas mainly liberates the Z-CuOH sites from sulfur by desorption or relocation. The concurrent kinetic measurements show that after SO₂ exposure, the apparent activation energies are lowered, and that subsequent regeneration restores the apparent activation energies to the same level as that of the fresh catalyst.

We now put these observations in context with the current understanding of the low-temperature SCR mechanism over Cu-CHA catalysts. The activation energy increases with Cu loading, as shown in Figure 4B. At high Cu loadings and activation energies, the SCR reaction is limited by O₂ dissociation on Cu pairs that are formed by mobile [Cu(NH₃)₂]⁺ complexes.^{5,6,12,36} At low Cu loadings and activation energies, the reaction is limited by the formation of Cu pairs.^{5,6} Applying this understanding on the SO₂ exposed catalysts, it suggests that the blocking of Z-CuOH sites by sulfur limits the ability of the catalyst to form Cu pairs. This then leads to the lower activation

energies of the SO₂ exposed catalysts and the quadratic dependence of the SCR activity of the SO₂ exposed catalysts on the amount of sulfur-free Cu (Figure 4A). In the regenerated catalysts, where mainly the Z-CuOH sites have released the sulfur, the activation energies are back at the same level as in the fresh catalyst, where O₂ dissociation limits the SCR activity. Therefore, the ability to form Cu pairs appears to be unaffected in the regenerated catalysts, while this ability is noticeably hindered in the SO₂ exposed catalysts with the same exposure to SO₂. This implies that the ability of Cu-CHA catalysts to form Cu pairs depends on the Z-CuOH sites. The observed differences between the impacts of sulfur in the SO₂ exposed and regenerated catalysts, on the overall NH₃-SCR activity, therefore, appear to be linked to the selective deactivation of the Z-CuOH sites and the significance of these sites for Cu pair formation.

Conclusions

The impact of SO₂ on the catalytic performance of a Cu-CHA catalyst in the NH₃-SCR reaction was studied. Exposure of a Cu-CHA catalyst to 100 ppmv SO₂ at 550 °C, for up to 32 h, results in deactivation that increases with exposure time up to a limit of 90%, which is accompanied by a parallel sulfur uptake reaching a maximum S/Cu ratio of 0.8. Consistently, characterization with electron paramagnetic resonance (EPR) spectroscopy showed that certain Z₂-Cu sites, associated with 2 Al centers, were unaffected by sulfur, which added up to about 15% of the total Cu content.

Regeneration at 550 °C in SO₂-free gas lowers the maximum deactivation to 50% and the S/Cu ratio to 0.5. Generally, the impact of sulfur on the activity is higher in the SO₂ exposed catalysts, compared to the regenerated catalysts.

The rate constants and apparent activation energies of the SO₂ exposed catalysts in the NH₃-SCR reaction have a similar dependence on the sulfur-free Cu density as fresh Cu-CHA catalysts with different Cu loadings, indicative of a site-blocking deactivation mechanism.

Parallel measurements with EPR showed that SO₂ mainly interacts with Z-CuOH sites, associated with a single Al center, before regeneration. During regeneration, the Z-CuOH sites are liberated from sulfur by desorption and relocation. The relocation of sulfur or Cu₂S species is likely part of the formation of more stable Cu₂S species via a kinetically limited oxidation of SO₂.

The preference of sulfur adsorption on Z-CuOH sites before regeneration, and the associated lowering of the apparent activation energy, indicates that the Z-CuOH are more important for Cu pair formation in the Cu-CHA catalysts, compared to Z₂-Cu sites.

Conflicts of interest

There are no conflicts to declare.

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