Site selective adsorption and relocation of SO\textsubscript{x} in deactivation of Cu-CHA catalysts for NH\textsubscript{3}-SCR

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Introduction

The selective catalytic reduction of NOx (NO and NO2) with NH3 (NH3-SCR) is the predominant method for removal of NOx 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 NOx emission limits, and therefore, a more efficient removal of NOx 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)4]** 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.15 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 Cu-S 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 resembles 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 CuII sites: Z-CuOH and Z-Cu, and these sites have different chemical properties.10,25-30 The relative amounts of these Cu sites depend...

Site selective adsorption and relocation of SOx in deactivation of Cu-CHA catalysts for NH3-SCR

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The presence of SO2 in diesel exhaust gases causes severe deactivation of the Cu-CHA catalysts for the reduction of NOx 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 Z-Cu), as determined by electron paramagnetic resonance (EPR). SO2 primarily interacts with the EPR-silent Z-CuOH sites, but a new, EPR-active Z-Cu phase develops with SO2 exposure time as well. A part of the original Z-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 Z-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.

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on synthesis conditions, the Si/Al ratio of the zeolite, and the Cu loading. 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, which has been used in other EPR studies as well. 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-greased for 1 h at 550 °C in technical air. After the exposure to SO2, each catalyst portion was divided into 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 Gasmet 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:

\[
k = \frac{F}{W \left( \frac{\Delta P}{2} \right)} \ln(1 - X)
\]  

(1)

Here, F is the total molar flow rate, W is the dry weight of the catalyst powder, \(\Delta P\) 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:

\[
\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}}
\]  

(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·H2O diluted in K2SO4) measured the same day at exactly the same instrument settings. 2. The EPR intensity for the dehydrated samples, Iw, is determined by...
relating the EPR intensity, \( I(T) \), to the intensity of the starting (fully hydrated) EPR spectrum, \( I(T_{\text{start}}) \), and corrected according to the Boltzmann distribution for the temperature differences according to \(^{30,32}\):

\[
I_{\text{rel}} = \frac{I(T)}{I(T_{\text{start}})} \frac{T}{T_{\text{start}}}
\]

EPR spectra were fitted as a sum of contributions from each Cu species. Each species is modeled using an axial spin Hamiltonian \(^{28}\) with 4 parameters, \( g_1 \), \( g_2 \), \( A_1 \), and \( A_2 \) as well as linewidth parameters. The fittings and simulations are performed using the EasySpin Toolbox in Matlab.\(^ {33}\)

**Results**

**NH\(_3\)-SCR activity and impact of SO\(_2\) exposure**

The effect of increasing SO\(_2\) exposure time over Cu-CHA on the NH\(_3\)-SCR NO conversion is illustrated in Figure 1. Low-temperature activity (<350 °C) of the Cu-CHA catalyst is strongly reduced upon exposure to SO\(_2\) (Figure 1A). The impact of SO\(_2\) at temperatures above 350 °C is clearly less, indicating that deactivation by SO\(_2\) is mainly relevant for the low-temperature performance, in agreement with earlier observations.\(^ {13–24}\) The low-temperature activity after SO\(_2\) exposure is partially restored by heating the Cu-CHA catalysts to 550 °C in SO\(_2\)-free gas (Figure 1B).\(^ {13,14,17}\)

The changes in the deactivation of NH\(_3\)-SCR activity with time of SO\(_2\) 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 SO\(_2\) exposure, and after 16 h of SO\(_2\) exposure, the loss of activity stabilizes at 90%. This means that the deactivation of the SO\(_2\) exposed catalysts does not reach 100%, but a certain NH\(_3\)-SCR activity, although low, is maintained even after prolonged exposure to SO\(_2\).\(^ {17}\) The deactivation of the regenerated catalysts increases with SO\(_2\) 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 SO\(_2\) exposed catalysts after exposure to 100 ppmv SO\(_2\) and 16 % O\(_2\) in N\(_2\) at 550 °C for different durations, and B) the regenerated catalysts after regeneration in 10 % O\(_2\) and 3 % H\(_2\)O in N\(_2\) at 550 °C for 5 h.

To determine the relation of the deactivation with the uptake of sulfur, the sulfur contents of the SO\(_2\) exposed and regenerated catalysts were measured with ICP-OES. The measured S/Cu ratios are also included in Figure 2A. For the SO\(_2\) 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 SO\(_2\) 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 SO\(_2\) exposed and regenerated catalysts: All of the SO\(_2\) 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 SO\(_2\) 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 Cu,S 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

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.

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

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.

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.

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.

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Cu density. This indicates that the decrease in activity of the SO$_2$ 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 Å$^3$. The change to higher activation energies for the samples with low effective Cu densities, after regeneration, suggests that chemical changes have 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.

In both A) and B), the SO$_2$ exposure and regeneration.

EPR results

To address the location of sulfur and possible changes in the Cu phase, catalyst samples were investigated with EPR after SO$_2$ 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. The amounts of EPR active Cu in the hydrated fresh, SO$_2$ 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 SO$_2$ 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 SO$_2$ 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 SO$_2$ exposure and regeneration.

Table 1 - Cu contents of fresh, SO$_2$ exposed and regenerated catalysts, as determined with EPR and ICP.

<table>
<thead>
<tr>
<th>SO$_2$ exposure time (h)</th>
<th>Cu wt% in SO$_2$ exposed catalysts</th>
<th>Cu wt% in regenerated catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>EPR 2.43</td>
<td>ICP 2.38</td>
</tr>
<tr>
<td>0.5 h</td>
<td>EPR 2.55</td>
<td>ICP 2.52</td>
</tr>
<tr>
<td>4 h</td>
<td>EPR 2.47</td>
<td>ICP 2.44</td>
</tr>
<tr>
<td>8 h</td>
<td>EPR 2.57</td>
<td>ICP 2.37</td>
</tr>
<tr>
<td>16 h</td>
<td>EPR 2.70</td>
<td>ICP 2.37</td>
</tr>
<tr>
<td>32 h</td>
<td>EPR 2.74</td>
<td>ICP 2.38</td>
</tr>
</tbody>
</table>

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, Z$_2$-Cu. The EPR spectra of the dehydrated catalysts contain information about the identity and amount of Z$_2$-Cu sites: After in situ dehydration only the Z$_2$-Cu sites are EPR active, whereas any Z-CuOH sites formed are EPR silent due to 3-fold coordination around Cu$^{II}$. Minority species such as Cu dimers and Cu$_2$O$_2$ oligomers are also EPR silent due to magnetic coupling between Cu centers. The EPR spectra of the fresh, SO$_2$ 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 Easyspin and listed in Table 2. The observed species have been identified earlier as follows. The A1 and A2 species are assigned to Z$_2$-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. 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 SO$_2$ for longer time. Concurrently, the

Figure 4 – A) SCR rate constants at 220 °C for the fresh, SO$_2$ 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 SO$_2$ exposed catalysts. B) Apparent activation energies for the fresh, SO$_2$ 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.
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.

The fitted intensity of each Cu$^\text{n}$ 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$^\text{n}$ species relative to the total Cu content in each SO$_2$ exposed and regenerated catalyst were estimated and are listed 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$^\text{n}$ species) increases with SO$_2$ 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 SO$_2$. This is an indirect indication that SO$_2$ 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 SO$_2$ 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 Z$_2$ positions (A1 and A2 combined) decreases with SO$_2$ exposure time, and stabilize around 8 h of SO$_2$ 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.

Table 3 – Intensities of EPR active Cu after dehydration in the fresh, SO$_2$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPR intensity after dehydration (%)</th>
<th>Distribution of EPR active Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO$_2$ exposed</td>
<td>Regenerated</td>
</tr>
<tr>
<td>Fresh</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>0.5 h</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>4 h</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>8 h</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>16 h</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>32 h</td>
<td>58</td>
<td>55</td>
</tr>
</tbody>
</table>

*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.
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 Cu,S 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.

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 Cu,S 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 Cu,S 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 A1. 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 Cu,S 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 Cu,S that are stable at 550 °C. Such stable Cu,S 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 Cu,S species, and leads to formation of the “irreversible” Cu,S 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. The subsequent 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 CO2 dissociation on Cu pairs that are formed by mobile [Cu(NH3)4]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 to the same level as that of the fresh catalyst.
energies of the SO\textsubscript{2} exposed catalysts and the quadratic dependence of the SCR activity of the SO\textsubscript{2} 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 O\textsubscript{2} 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 SO\textsubscript{2} exposed catalysts with the same exposure to SO\textsubscript{2}. 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 SO\textsubscript{2} exposed and regenerated catalysts, on the overall NH\textsubscript{3}-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 SO\textsubscript{2} on the catalytic performance of a Cu-CHA catalyst in the NH\textsubscript{3}-SCR reaction was studied. Exposure of a Cu-CHA catalyst to 100 ppmv SO\textsubscript{2} 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 Z\textsubscript{2}-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 SO\textsubscript{2}-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 SO\textsubscript{2} exposed catalysts, compared to the regenerated catalysts. The rate constants and apparent activation energies of the SO\textsubscript{2} exposed catalysts in the NH\textsubscript{3}-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 SO\textsubscript{2} 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 Cu\textsubscript{S} species is likely part of the formation of more stable Cu\textsubscript{S} species via a kinetically limited oxidation of SO\textsubscript{2}.

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 Z\textsubscript{2}-Cu sites.

Conflicts of interest

There are no conflicts to declare.

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Notes and references