

SO₂ Poisoning of Cu-CHA deNO_x Catalyst: The Most Vulnerable Cu Species Identified by X-ray Absorption Spectroscopy

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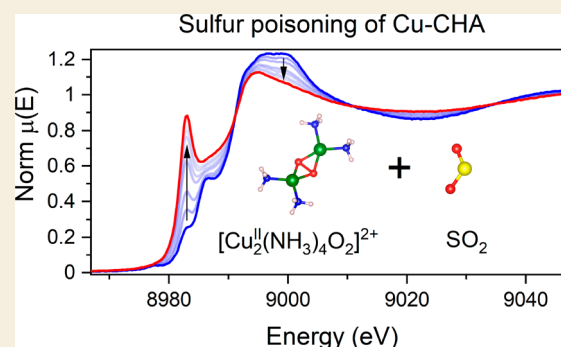
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Supporting Information

ABSTRACT: Cu-exchanged chabazite zeolites (Cu-CHA) are effective catalysts for the NH₃-assisted selective catalytic reduction of NO (NH₃-SCR) for the abatement of NO_x emission from diesel vehicles. However, the presence of a small amount of SO₂ in diesel exhaust gases leads to a severe reduction in the low-temperature activity of these catalysts. To shed light on the nature of such deactivation, we characterized a Cu-CHA catalyst under well-defined exposures to SO₂ using *in situ* X-ray absorption spectroscopy. By varying the pretreatment procedure prior to the SO₂ exposure, we have selectively prepared Cu^I and Cu^{II} species with different ligations, which are relevant for the NH₃-SCR reaction. The highest reactivity toward SO₂ was observed for Cu^{II} species coordinated to both NH₃ and extraframework oxygen, in particular for [Cu^{II}₂(NH₃)₄O₂]²⁺ complexes. Cu species without either ammonia or extraframework oxygen ligands were much less reactive, and the associated SO₂ uptake was significantly lower. These results explain why SO₂ mostly affects the low-temperature activity of Cu-CHA catalysts, since the dimeric complex [Cu^{II}₂(NH₃)₄O₂]²⁺ is a crucial intermediate in the low-temperature NH₃-SCR catalytic cycle.

KEYWORDS: selective catalytic reduction, Cu-CHA, deNO_x catalysis, sulfur poisoning, X-ray absorption spectroscopy, X-ray adsorbate quantification, XAS, XAQ



The emission of nitrogen oxides (NO_x) from diesel vehicles is a global environmental challenge.^{1,2} State of the art exhaust gas aftertreatment systems contain catalysts for selective catalytic reduction of NO_x by ammonia (NH₃-SCR), capable of reducing well over 90% of the NO_x emitted by the engine. In the NH₃-SCR reaction, NO reacts with NH₃ in the presence of O₂ to form N₂ and H₂O. At present, Cu-exchanged chabazites (Cu-CHA) are the preferred catalysts for NH₃-SCR, due to their superior low-temperature activity (150–350 °C)^{3,4} and hydrothermal stability.^{5,6} The temperature dependence of the NH₃-SCR activity of Cu-CHA catalysts shows a minimum at around 350 °C, which indicates that the reaction mechanism at low temperatures is different from that at higher temperatures.⁷

The NH₃-SCR reaction cycle for the low-temperature activity is a redox cycle, consisting of a series of oxidation and reduction steps, in which the oxidation state of Cu changes between Cu^I and Cu^{II}. The NO and NH₃ coordinate to Cu in the zeolite, giving rise to a variety of Cu species along the NH₃-SCR cycle.^{8–11} The low-temperature activity of Cu-CHA catalysts originates from the ability to form mobile Cu^I(NH₃)₂ complexes under SCR conditions. Pairs of these species constitute the active Cu sites capable of O₂ activation via the

formation of [Cu^{II}₂(NH₃)₄O₂]²⁺ dimers around 200 °C, which is a crucial step in the NH₃-SCR reaction cycle.^{12,13}

In practice, the application of Cu-CHA catalysts for the NH₃-SCR is restricted to ultralow-sulfur diesel fuels, due to the fact that a few ppm of SO₂ present in the exhaust gas drastically reduces the activity at low temperatures.^{3,4,14} Multiple studies show that SO₂ affects the Cu mobility, the amount of Cu active sites,¹⁴ and the redox behavior of the Cu in the NH₃-SCR cycle.^{9,15} Most studies have focused on the overall effect of SO₂ on the performance of the catalysts,^{14–21} while the chemistry behind SO₂ poisoning at the molecular level remains poorly understood. To determine a mechanism for SO₂ poisoning, one must identify the species in the Cu-CHA catalysts that interact with SO₂. To this end, we have selectively prepared well-defined Cu^I and Cu^{II} species with

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Table 1. Pretreatment Procedures and Resulting Cu Species

procedure	conditions	dominant Cu state	designation in the text and figures	ref
1	1% H ₂ at 400 °C; cooling to 200 °C in He	fw-Cu ^I	fw-Cu ^I	24
2	500 ppm of NO + 600 ppm of NH ₃ at 200 °C	mobile [Cu ^I (NH ₃) ₂] ⁺	[Cu ^I (NH ₃) ₂] ⁺	24
3	500 ppm of NO + 600 ppm of NH ₃ at 200 °C; heating to 550 °C in He; cooling back to 200 °C in He	fw-Cu ^I (after thermal treatment of [Cu ^I (NH ₃) ₂] ⁺)	[Cu ^I (NH ₃) ₂] ⁺ + T	24
4	10% O ₂ at 200 °C	fw-Cu ^{II}	fw-Cu ^{II}	25
5	500 ppm of NO + 600 ppm of NH ₃ at 200 °C; He purge; 10% O ₂ at 200 °C	mobile [Cu ^{II} ₂ (NH ₃) ₄ O ₂] ²⁺ dimer	[Cu ^{II} ₂ (NH ₃) ₄ O ₂] ²⁺	13
6	600 ppm of NH ₃ at 200 °C	mixed ^a	Cu ^{II} + NH ₃	this work

^aProcedure 6 results in a mixture of two NH₃-coordinated Cu species, as discussed further in the text.

different ligands inside the pores of the Cu-CHA catalyst and exposed them to SO₂ under well-defined conditions. We monitored the changes in the Cu K-edge X-ray absorption spectra (XAS) during the absorption of SO₂. This allowed us to determine the chemical state of the Cu that interacts with SO₂. The results were corroborated by X-ray emission spectroscopy (XES) and measurements of the SO₂ uptake using temperature-programmed desorption (TPD) of SO₂.

The Cu-CHA catalyst used in this study had a Si/Al ratio of 6.7 and a Cu loading of 3.2 wt % (Cu/Al = 0.24). The Cu K-edge XAS and Cu Kβ valence-to-core XES measurements were carried out at the BM23²² and ID26²³ beamlines of the European Synchrotron Radiation Facility (ESRF), respectively. Sample treatment protocols consisted of three distinct steps. First, all samples were heated to 550 °C in a 10% O₂/He flow, removing water and forming Cu^{II} species bound to the framework of the zeolite (fw-Cu^{II}). Then, the specific state of Cu was prepared, using one of the six different pretreatment procedures summarized in Table 1. Finally, the catalyst was exposed to 400 ppm SO₂/He flow at 200 °C for 3 h until no visible changes in the spectra occurred. Further experimental details are given in the Supporting Information.

The Cu species formed with the pretreatments differ in three aspects: (1) the oxidation state of Cu (Cu^I or Cu^{II}), (2) the coordination of the Cu (NH₃ or/and O), and (3) the interaction of the Cu with the framework (fw-coordinated or mobile species).

Figure 1 shows the evolution of Cu K-edge XANES and EXAFS spectra during the exposure of the pretreated Cu-CHA catalyst to 400 ppm SO₂/He flow at 200 °C. For all Cu^I species and fw-Cu^{II} species (procedures 1–4 in Table 1), only minor changes are observed upon SO₂ exposure, indicating that these species are not very reactive toward SO₂. In contrast, for Cu^{II} species in the presence of NH₃ (procedures 5 and 6) significant changes are observed in the spectra. In these cases, the exposure to SO₂ results in a pronounced increase of the XANES peak at 8983 eV, characteristic for linear Cu^I complexes,^{9,26,27} and a decrease in the intensity of the first shell in the EXAFS FT. This means that some of the Cu^{II} species are reduced to Cu^I upon interaction with SO₂. The decrease in the first-shell intensity indicates a reduction of the coordination number for the Cu ions, which is also in line with the formation of a linear Cu^I species.

The species obtained in procedure 5 are the oxygen-bridged diamine dicopper complexes [Cu^{II}₂(NH₃)₄O₂]²⁺, which are formed by the reaction of O₂ with a pair of [Cu^I(NH₃)₂]⁺ complexes.¹³ In the reaction cycle for the low-temperature NH₃-SCR reaction,^{11,13,28} the [Cu^{II}₂(NH₃)₄O₂]²⁺ complexes react with NO, which eventually leads to the production of N₂

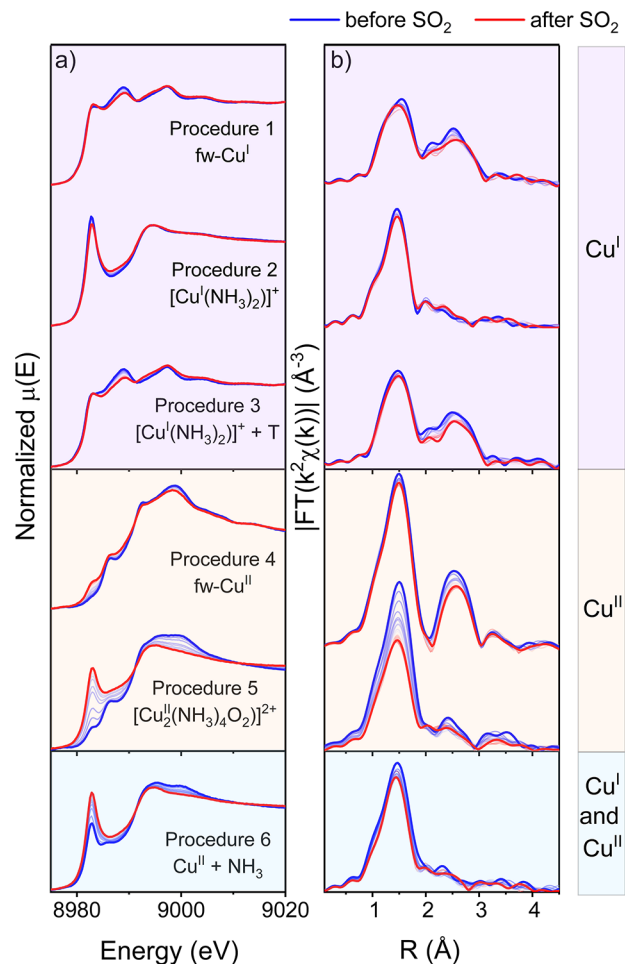


Figure 1. Cu K-edge XANES (a) and FT-EXAFS spectra (b) collected *in situ* during the exposure of Cu species obtained in procedures 1–6 to SO₂ at 200 °C.

and H₂O. The observation that the [Cu^{II}₂(NH₃)₄O₂]²⁺ complexes are reactive toward SO₂ is therefore a good explanation for the SO₂-induced deactivation of Cu-CHA catalysts for NH₃-SCR: the reaction with SO₂ interrupts the NH₃-SCR cycle, thereby decreasing the activity of the catalyst.

The other case where Cu reacts with SO₂ is obtained in procedure 6 by exposure of the fw-Cu^{II} species to NH₃. Previously, a similar pretreatment resulted in a mixture of linear [Cu^I(NH₃)₂]⁺ and either square-planar [Cu^{II}(NH₃)₄]²⁺ complexes or mixed-ligand [Cu^{II}O_x(NH₃)_y]²⁺ moieties.^{9,24} For the sample reported in this work, the mixed-ligand configuration is more likely. Indeed, linear combination fits

of the XANES data on the basis of references for the linear $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ complex and pure $\text{Cu}^{\text{II}}(\text{NH}_3)_4$ groups (aqueous $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]^{2+}$ or solid-state $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$) resulted in visible discrepancies with the data (Figure S7 in the Supporting Information). A better agreement is obtained when the spectrum of oxygen-bridged diamine dicopper complex $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ is used as a Cu^{II} reference in combination with $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$, with approximately equal weights for each component (Figure 2). The necessary stock of available oxygen

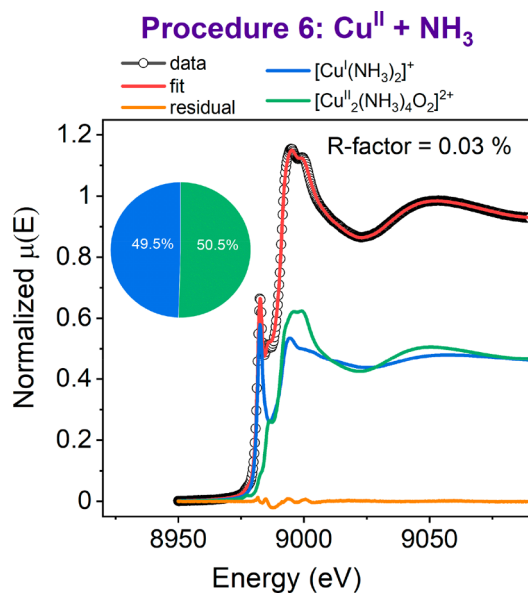


Figure 2. Linear combination fit of Cu K-edge XANES spectra obtained in Cu-CHA after exposing fw- Cu^{II} species to NH_3 at 200 °C ($\text{Cu}^{\text{II}} + \text{NH}_3$ pretreatment).

needed for the formation of the mixed-ligand species is expected to be present in the sample, as a wavelet analysis of the EXAFS collected after heating to 550 °C and cooling to 200 °C in 10% O_2/He flow reveals the presence of Cu–Cu scattering usually attributed to the oxygen-containing dimers^{29,30} (Figure S8 in the Supporting Information), which may be susceptible to form mixed-ligand species upon exposure to NH_3 .

The evolution of XANES spectra upon interaction with SO_2 shows that the most susceptible species are Cu^{II} with mixed $(\text{NH}_3)_x\text{O}_y$ ligation, whereas Cu^{I} species or Cu^{II} in the absence of NH_3 are much less affected. These findings are supported by X-ray adsorbate quantification (XAQ) data,³¹ collected simultaneously with the XAS measurements during the exposure to SO_2 , and a TPD analysis of a parallel set of catalyst samples, exposed to the same pretreatments used in XANES experiments (Figure 3a). We find the highest sulfur content (S/Cu ratio) for the $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ and $\text{Cu}^{\text{II}} + \text{NH}_3$ procedures. The sulfur uptake of the $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ and fw- Cu^{II} moieties was ca. 3 times lower, and for the bare fw- Cu^{I} species, it was ca. 6 times lower. These results show that the reaction between the $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ species and SO_2 contributes the most to the accumulation of SO_2 in the Cu-CHA catalyst.

Interestingly, the sulfur content in the $\text{Cu}^{\text{II}} + \text{NH}_3$ sample lies between those for samples with pure $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ and $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ species, which in combination with the linear combination fit shown in Figure 2 suggests that the

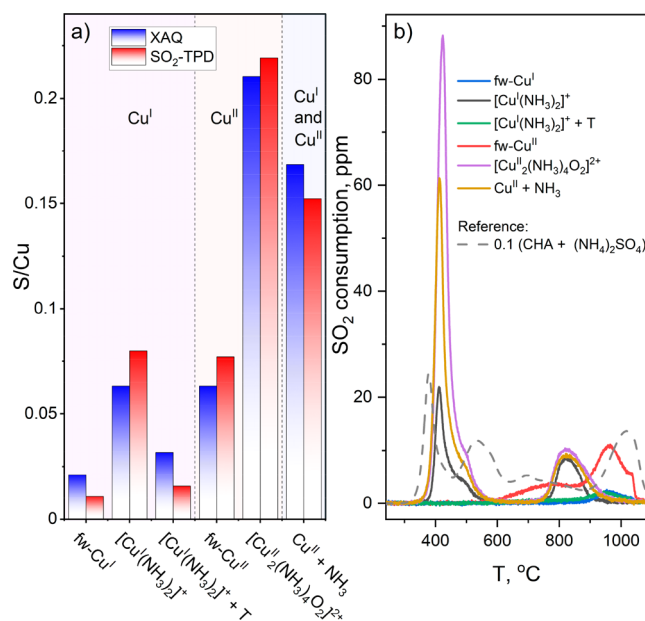


Figure 3. (a) S/Cu ratios in the samples after exposure to SO_2 obtained from SO_2 -TPD and XAQ. (b) SO_2 -TPD profiles collected after exposure of the species obtained in procedures 1–6 to SO_2 in comparison to a reference SO_2 -TPD curve of a CHA zeolite without Cu impregnated with 20 wt % $(\text{NH}_4)_2\text{SO}_4$, downscaled $\times 10$.

reactivity of the $\text{Cu}^{\text{II}}(\text{NH}_3)_x\text{O}_y$ species obtained after $\text{Cu}^{\text{II}} + \text{NH}_3$ treatment toward SO_2 is similar to that of $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$.

By comparing the SO_2 -TPD curves of Cu-CHA samples with that of $(\text{NH}_4)_2\text{SO}_4$ adsorbed on Cu-free CHA (Figure 3b), we can also deduce that the elevated sulfur content in the samples with the $\text{Cu}^{\text{II}}(\text{NH}_3)_x\text{O}_y$ species is due to the reactivity toward SO_2 and not to the formation of $(\text{NH}_4)_2\text{SO}_4$ in a reaction of SO_2 with NH_3 and NH_4^+ groups stored in the zeolite framework. For the adsorbed $(\text{NH}_4)_2\text{SO}_4$, we observe SO_2 desorption at around 380, 530, and 1000 °C (gray curve in Figure 3b). The desorption at 380 °C matches the known thermal decomposition of $(\text{NH}_4)_2\text{SO}_4$,³² the other two peaks are probably due to the interaction of either $(\text{NH}_4)_2\text{SO}_4$ or products of its decomposition with the zeolite, their precise interpretation being beyond the scope of the present argument. For all three Cu-CHA samples containing NH_3 before exposure to SO_2 ($[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$, $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$, and $(\text{Cu}^{\text{II}} + \text{NH}_3)$ procedures), we observe SO_2 desorption at around 420 °C (Figure 3b). As this does not match any of the observed desorption characteristics of $(\text{NH}_4)_2\text{SO}_4$ in Cu-free Cu-CHA, the SO_2 -TPD feature at 420 °C reflects an interaction of Cu with SO_2 . Interestingly, the SO_2 -TPD curve for the sample with the dominant fw- Cu^{II} species shows a significant SO_2 desorption peak close to 1000 °C, which, together with the lack of changes in Cu K-edge XANES upon exposure to SO_2 , indicates the formation of some sulfur deposits not directly coordinated to Cu.

The presence of Cu–N and Cu–O bonds in the $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex has been independently confirmed by valence-to-core XES.^{27,33,34} XES spectra at different stages of pretreatment leading to the formation of $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ dimers are reported in Figure 4. The origin of the $K\beta'$ satellite peak is the transition from the ligand s orbitals to Cu 1s, which makes its position sensitive to the species directly coordinated to Cu and allows it to discriminate

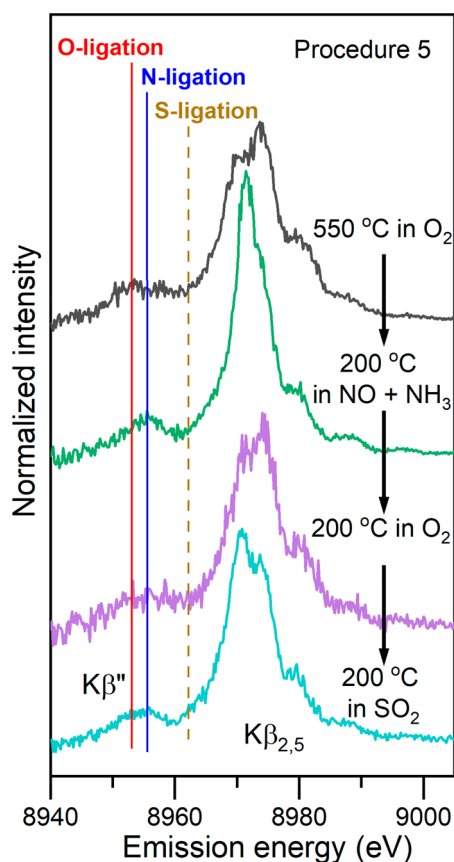


Figure 4. Background-subtracted Cu $K\beta$ valence-to-core XES spectra for different stages of procedure 5 leading to the formation of the $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex and its exposure to SO_2 .

among Cu–O, Cu–N, and Cu–S bonds.^{35–37} Figure 4 shows that after heating in O_2 Cu is predominantly coordinated by oxygens (as expected for the fw- Cu^{II} species), whereas after exposure to $\text{NO} + \text{NH}_3$ N ligands are dominating, as expected for a $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ linear complex. After subsequent exposure to O_2 and formation of $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ dimers, the peak broadens, confirming the presence of both Cu–N and Cu–O bonds. These bonds remain after exposure to SO_2 , while no significant contribution from Cu–S bonds³⁸ is observed, suggesting that the possible SO_2 binding to the Cu is carried out through an oxygen atom.

In conclusion, the *in situ* XAS and XES measurements of different Cu intermediates formed in a Cu-CHA catalyst exposed to SO_2 demonstrate that Cu^{II} species with mixed NH_3 and O ligation of Cu are particularly reactive toward SO_2 , whereas Cu^{I} species and Cu^{II} without NH_3 are much less affected by it. In particular, the $[\text{Cu}^{\text{II}}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex, which is formed upon activation of O_2 in the NH_3 -SCR cycle, shows a clear reaction with SO_2 , resulting in a partial reduction of the Cu^{II} and accumulation of sulfur in the zeolite. Therefore, we conclude that this reaction is responsible for the poisoning of Cu-CHA catalysts in NH_3 -SCR by SO_2 .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.2c00053>.

Experimental details, XANES linear combination fits before SO_2 exposure, wavelet transform analysis of the sample heated in O_2 , and EXAFS fitting results (PDF)

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Notes

The authors declare no competing financial interest.

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