

Supporting information

The Chemical nature of SO₂ poisoning of Cu-CHA based SCR Catalysts for NO_x removal in diesel exhausts

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1. Experimental setup and protocols

1.1 Temperature programmed reaction with NO

NO-TPR experiments were performed in a flow reactor setup, equipped with a quartz U-tube with a 100 mg sample of the Cu-CHA catalyst (150-300 µm sieve fraction) held in place by quartz wool plugs. Prior to NO exposure, the catalyst was pre-treated by heating in air to 550 °C, followed by cooling down to 200 °C and reduction in 500 ppm NO and 600 ppm NH₃ at 200 °C. The

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$[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^+$ species are then formed by exposure of the reduced catalyst to 10 % O_2 at 200 °C [1-5]. The pre-treatment for the protocol without exposure to SO_2 was concluded at this stage, whereas the second protocol included also exposure of the $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^+$ species to 400 ppm of SO_2 for 3 hours at 200 °C. After the pre-treatment, for both protocols, the reactor was cooled down to 50 °C, and a flow of 500 ppm NO was introduced to the system. Then the Cu-CHA catalyst was heated up to 550 °C with a ramp rate of 1 °C/min, keeping the NO flow. The concentration of the gases was monitored by a Gasetm CX4000 FTIR analyzer, connected to the reactor outlet. The feed gas concentrations were measured bypassing the reactor. A graphical scheme of the protocol is presented in Section 1.2.

1.2 XAS + DRIFTS + MS experimental details

We conducted two experiments, “not exposed to SO_2 ” and “exposed SO_2 ”, employing a combined XAS+DRIFTS approach to investigate the reaction between $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ and NO . The procedure, denoted as “not exposed SO_2 ”, involved exposing $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ to NO for 1.5 hours at 200 °C. In the “exposed to SO_2 ” protocol, first, we exposed the $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ species to a mixture of 360 ppm SO_2 and 10% O_2 in He. Second, the sulfated Cu-CHA was exposed to NO at 200 °C for 1.5 hours, followed by heating to 300 °C in NO with a ramp rate of 5 °C/min. For the SO_2 exposure, we used a mixture of SO_2 and O_2 , because the reaction mechanism is the same as without O_2 but it leads to a higher SO_2 uptake due to reoxidation of Cu^{I} species back to the $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ species able to react with SO_2 and form sulfated species [5].

The XAS experiment was performed at BM23 beamline of the ESRF [6]. The storage ring was operating in 16-bunch top-up mode at 75 mA maximum current. Measurements were performed in transmission mode at Cu K-edge, using a double-crystal Si(111) monochromator moving in a continuous mode. Acquisition time for one XAS spectrum was 3 min, energy range of 8800-10000 eV, energy binning of 0.3 eV. A pair of flat Si mirrors at 2.8 mrad angle was used for harmonic rejection. Ionization chambers were used to detect incident and transmitted photons. I_0 chamber was filled with 1.57 bar N_2 , I_1 and I_2 with 0.33 bar Ar, all three of them topped-up with He to the total pressure of 2 bar. The spectra of the Cu reference foil were measured simultaneously with the sample using the I_2 ion chamber and then used for energy calibration and alignment. The samples were measured in a reactor cell compatible with XAS and DRIFTS measurements [7]. The samples mass was around 50 mg of powder. For both experiments we used the same sample

loading, first performing the “not exposed to SO₂” protocol and then reactivating the sample at 350 °C in 10% O₂ and performing the “exposed to SO₂” protocol. The XAS data were analyzed using Athena program from Demeter package [8] and Larch-based [9] python code. FT-EXAFS spectra were extracted in 3-11 Å⁻¹ k-range using Hanning window.

DRIFT spectra were measured with a Varian 680 FTIR instrument with 2 cm⁻¹ energy resolution. Spectra were recorded using a Mercury-Cadmium-Telluride (MCT) detector. Every spectrum resulted from the average of 128 scans. Background was measured prior the experiment by filling the reactor with KBr under He atmosphere. Background spectrum resulted from the average of 256 scans.

MS measurements were done with a Pfeiffer OmniStar GSD 350 gas analyser. The acquisition was done in a scan mode from 0 to 100 with 5 points per amu. Both protocols were performed sequentially without changing the sample, which ensures the optimal comparability of the obtained MS data.

1.2 Experimental protocols

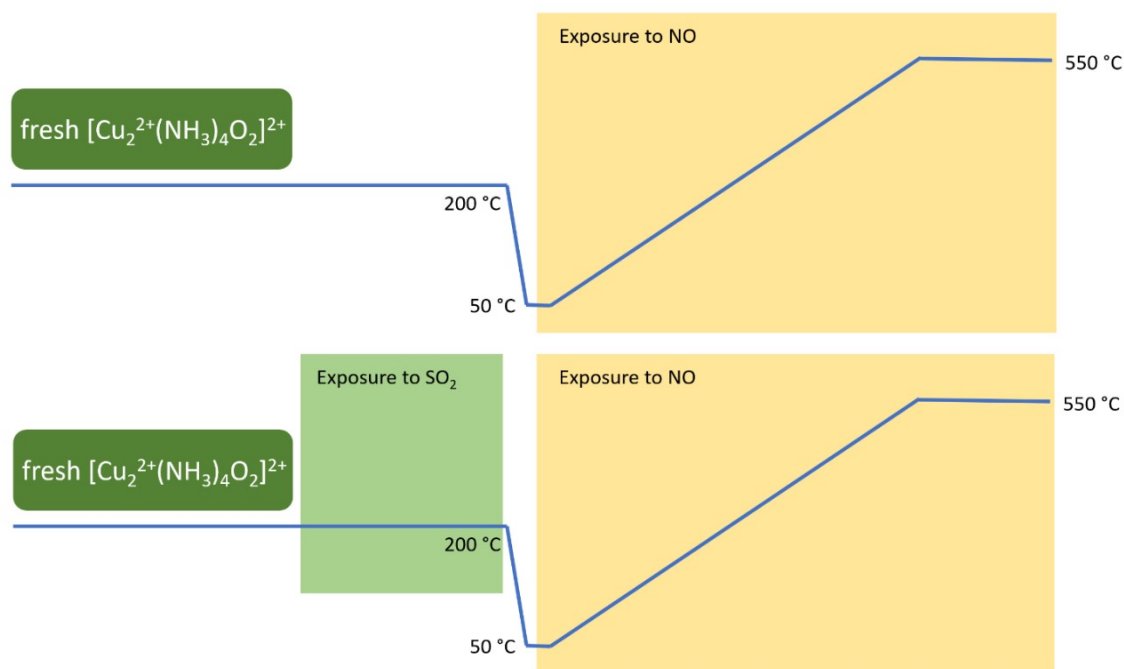


Figure S1 Scheme of the followed experimental protocol to monitor the interaction of $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ with NO by temperature programmed reaction not exposed and exposed to SO₂.

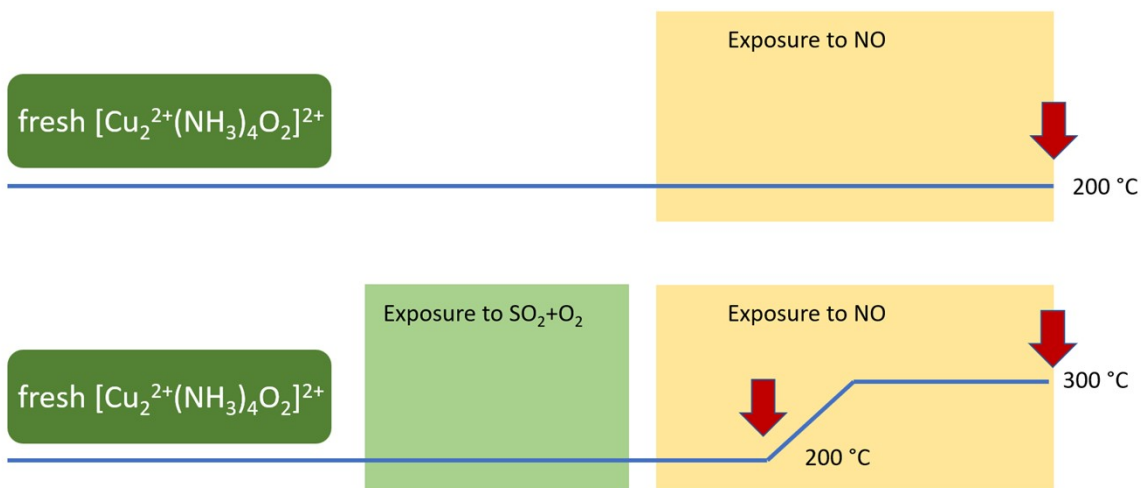


Figure S2 Scheme of the followed experimental protocol to monitor the interaction of $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ with NO by XAS and DRIFTS not exposed and exposed to SO_2 . The red arrows indicate the important points to compare the spectra.

2. NO consumption and NH_3 desorption

Table S1 Integrated amount of NO consumed and NH_3 desorbed by the Cu-CHA catalyst exposed and not exposed to SO_2 . NO consumption is calculated in the 150-350 °C temperature range.

	Cu content, $\mu\text{mol/g}$	NO, $\mu\text{mol/g}$	NH_3 , $\mu\text{mol/g}$
Not exposed to SO_2	503	358	686
Exposed to SO_2		221	596

3. XANES and EXAFS results

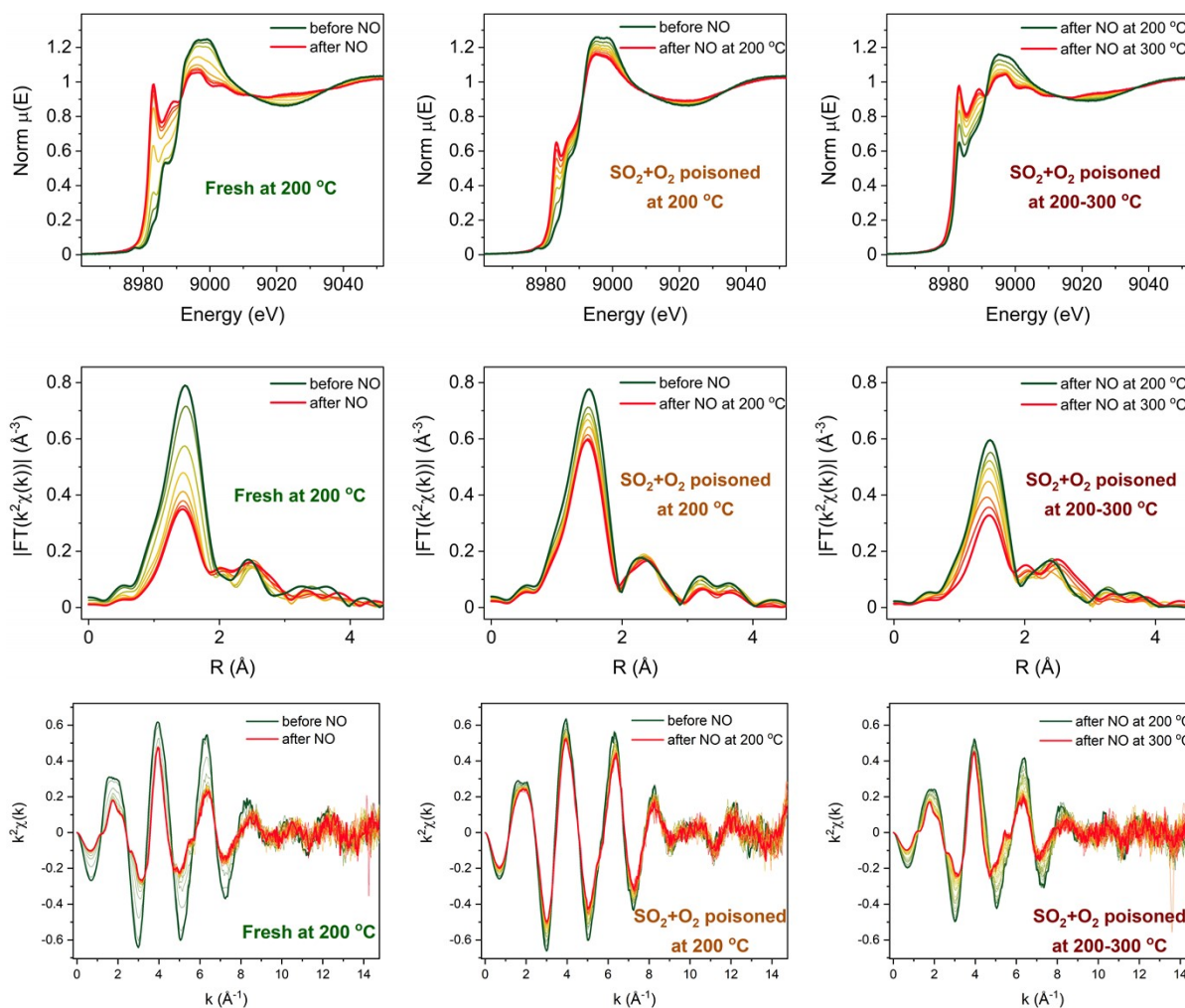


Figure S3 Time evolution of the Cu K-edge XANES (top panel), phase-uncorrected FT-EXAFS magnitude spectra (middle panel) – 5 spectra averaged, and EXAFS $\chi(k)k^2$ spectra (bottom panel) – not averaged, collected in situ during the exposure of fresh $[\text{Cu}_2^{2+}(\text{NH}_3)_4\text{O}_2]^{2+}$ species to NO at 200 °C (left), SO₂+O₂ exposed $[\text{Cu}_2^{2+}(\text{NH}_3)_4\text{O}_2]^{2+}$ species to NO at 200 °C (middle), and SO₂+O₂ exposed $[\text{Cu}_2^{2+}(\text{NH}_3)_4\text{O}_2]^{2+}$ species to NO at 200-300 °C (right).

4. MCR-ALS and LCF for XANES: details and choice of references

To resolve the Cu species forming during the experimental protocols we applied a combination of MCR-ALS and LCF described in our recent work [5]. We run an MCR-ALS on the dataset and extract the components. Some of the spectra correspond to the known ones, some are new. We choose a set of suitable references among the experimentally known ones and newly generated by

MCR and apply a linear combination fit to obtain a time evolution of coordination profiles of the chosen references.

In this work, in the MCR-ALS procedure for the “not exposed to SO₂” and “exposed to SO₂”, we resolved these two datasets together. In the end we obtained a set of 5 spectra. Then we performed a linear combination fitting using experimental spectra of fw-Cu^{II}, [Cu^I(NH₃)₂]⁺ and [Cu₂^{II}(NH₃)₄O₂]²⁺ and MCR-generated spectra of fw-Cu^I and sulfated species, since they were not appearing in the pure form in any of the stages of the experimental protocol.

5. DRIFTS

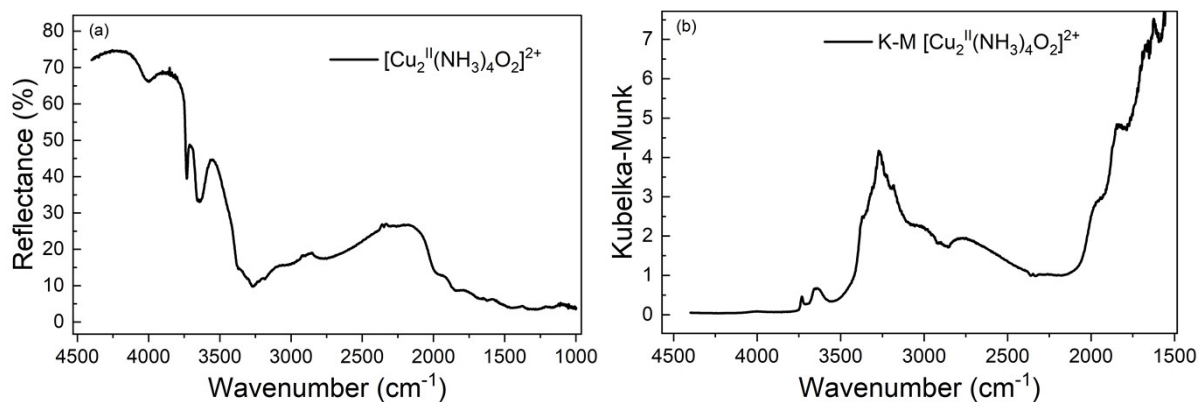


Figure S4 (a) in situ DRIFTS spectrum of [Cu₂^{II}(NH₃)₄O₂]²⁺ species formed in Cu-CHA; (b) Kubelka-Munk transform of the in situ DRIFTS spectrum of [Cu₂^{II}(NH₃)₄O₂]²⁺ species formed in Cu-CHA. This spectrum was subtracted from all the spectra presented in Figure 5a of the main text after Kubelka-Munk transform.

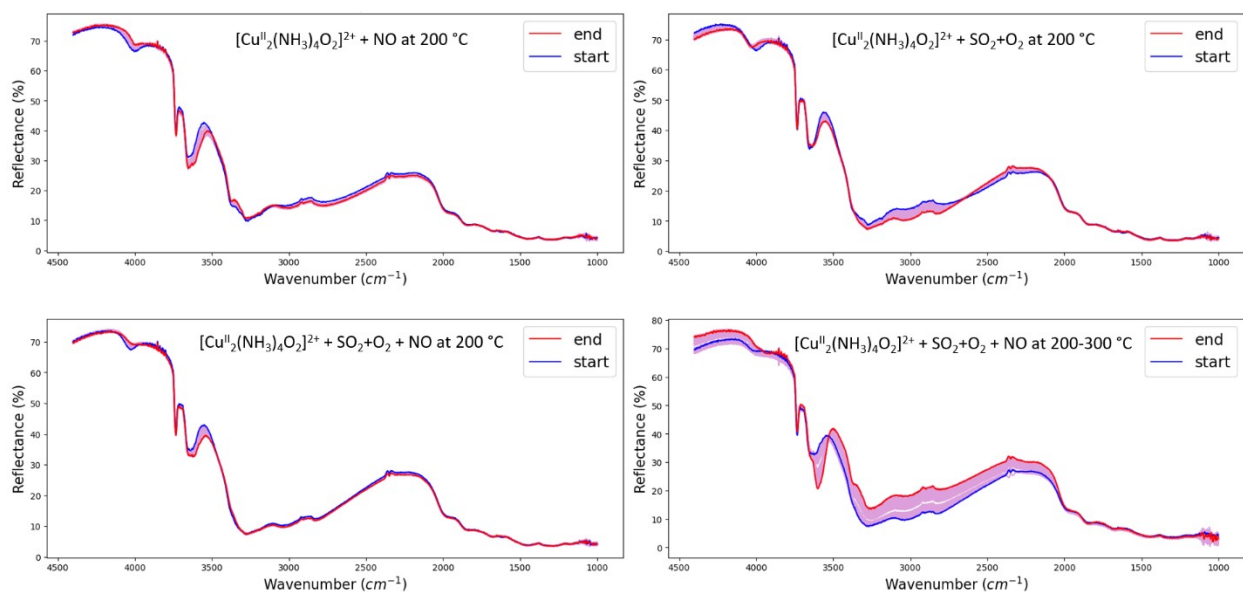


Figure S5 in situ DRIFTS spectra of the $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ exposed to NO at 200 °C; SO_2+O_2 at 200 °C; SO_2+O_2 and NO at 200 °C; SO_2+O_2 and NO at 200-300 °C.

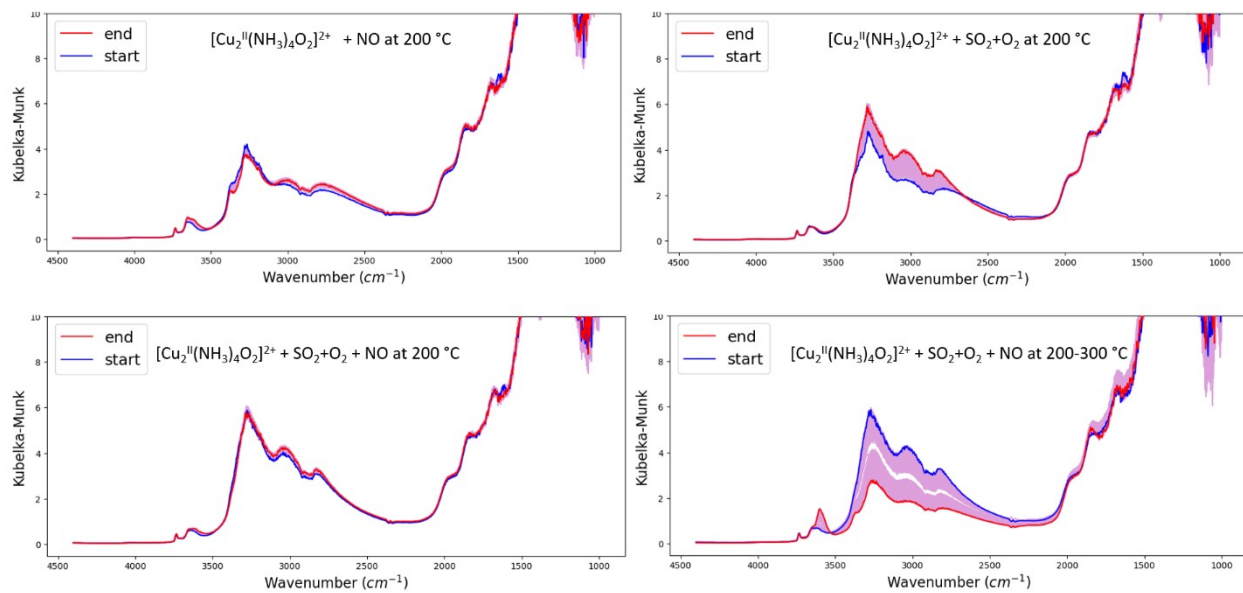


Figure S6 Kubelka-Munk transform of the in situ DRIFTS spectra of the $[\text{Cu}_2^{\text{II}}(\text{NH}_3)_4\text{O}_2]^{2+}$ exposed to NO at 200 °C; SO_2+O_2 at 200 °C; SO_2+O_2 and NO at 200 °C; SO_2+O_2 and NO at 200-300 °C.

6. Errors in the LCF fit

LCF was performed using a Linear Regression algorithm with a function from the Sklearn python library. Standard errors were calculated using Statsmodels Python library. It allows to calculate statistical parameter for the Linear Regression.

Time evolutions of the standard errors of the linear regression coefficients associated with the components used in the LCF are presented in Figure S7.

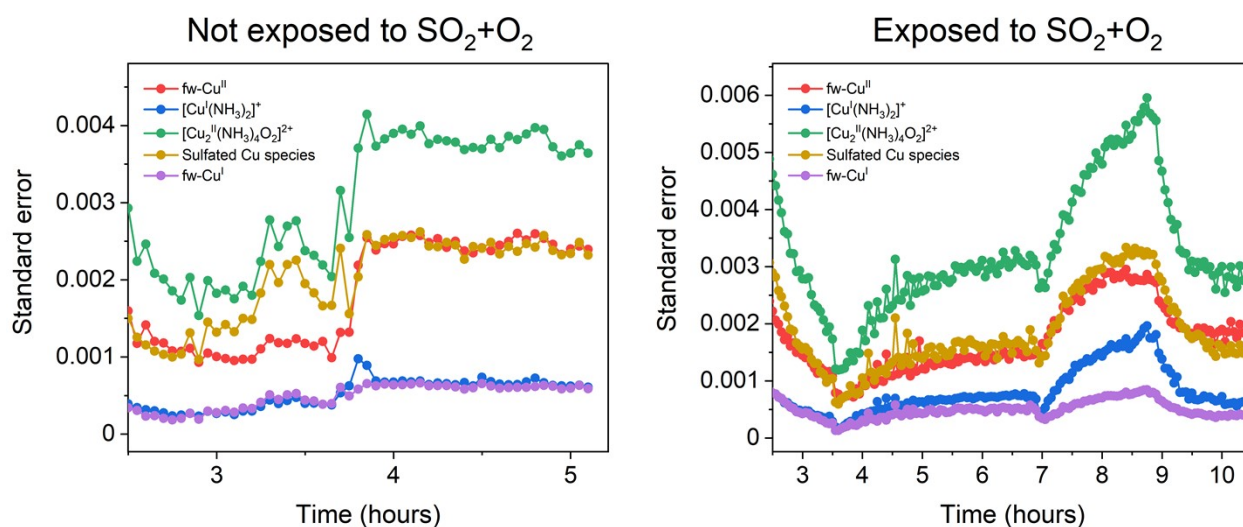


Figure S7 Time evolutions of the estimated standard errors of the linear regression coefficients associated with the components used in the LCF.

The standard errors follow the behavior of the R-factor calculated for the resulting fits and presented in the Main text. It was calculated for each spectrum in a similar to the Athena software way, using the formula:

$$R = \frac{\sum_i (f_{exp} - f_{fitted})^2}{\sum_i f_{exp}^2}$$

Where f_{exp} – is an experimental spectrum, f_{fitted} – is a fitted spectrum (the result of the LCF), the values are summed in data points (i) in the fitting region to get a resulting R-factor for each spectrum.

An average R-factor for the dataset “not exposed to SO_2 ” is $R\text{-factor} = 6 \cdot 10^{-5}$, for the dataset “exposed to SO_2 ” is $R\text{-factor} = 5 \cdot 10^{-5}$.

7. References

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