

ELECTRONIC SUPPLEMENTARY INFORMATION

Selective catalytic reduction of NO over Cu-AFX zeolites: Mechanistic insights from *in situ/operando* spectroscopic and DFT studies

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Detailed descriptions of *in situ/operando* spectroscopic experiments

In situ XAS

Cu K-edge quick XAS measurements were performed in transmission mode using beamline BL14B2 at the SPring-8 synchrotron radiation facility (Harima, Japan). The storage ring was operated at 8 GeV. A Si(111) single crystal was used to obtain a monochromatic X-ray beam. A self-supported wafer form of the sample with ca. 7 mm diameter was placed in a quartz *in situ* cell in a 10% O₂ flow diluted with He (1000 mL min⁻¹) under atmospheric pressure. Normalization and linear combination fitting (LCF) analysis of XANES were carried out by using Athena software¹. XAS spectra for the reference compounds were collected using equivalent data collection procedures with specific acquisition parameters optimized for each sample, either measured after *in situ* treatment of Cu-AFX (Z-[Cu²⁺]; Z = zeolite framework) or prepared as solution-phase complexes according to the literatures^{2,3}. The Cu-AFX (Si/Al = 5.3) with 4.1 wt% of Cu loading exposed to 10% O₂ flow (20 min) at 200 °C was used as a reference for Z-[Cu²⁺]. The [Cu(NH₃)₄]²⁺ solution was prepared by pouring 0.15 mL of 10% NH₃ aqueous solution into 50 mL of aqueous solution containing tetraamminecopper(II) sulfate hydrate (50 mM). The resulting deep violet-blue solution was used for a reference. The [Cu(NH₃)₂]⁺ solution was prepared by adding 0.03 mL of hydrazine to 50 mL of the [Cu(NH₃)₄]²⁺ solution described above. It should be noted here that the spectrum was recorded just after the preparation, without exposure to air.

In situ/operando UV-vis

Diffuse reflectance UV-vis measurements were performed at 200 °C with a UV-vis spectrometer (JASCO V-670) equipped with an *in situ* flow cell with a quartz window. A diffuse reflectance sample cell is connected to a gas flow system. The light source was led to the center of an integrating sphere through optical fiber. Reflectance was converted to pseudo-absorbance using the Kubelka-Munk function. BaSO₄ was used to collect a background spectrum. Various gas mixtures were fed to Cu_{2.1}-AFX (10 mg) at a flow rate of 100 ml min⁻¹. The relative concentration of N₂ in the outlet gas mixture was monitored by the mass spectroscopy apparatus (BELMass, MicrotracBEL Corp.). To prevent changes in the operating pressure of the UV-vis cell, excess flow was removed through a vent. The

product concentration was quantified by calibrating the mass response using a calibrated mixture in Ar of each component.

Operando IR

IR spectra were recorded on a JASCO FT/IR-4600 equipped with a quartz IR cell connected to a conventional flow reaction system (100 mL min⁻¹). The sample was pressed into a 40 mg self-supporting wafer and mounted in the quartz IR cell with CaF₂ windows. Spectra were measured by accumulating 20 scans at a resolution of 4 cm⁻¹. The reference spectrum of the catalyst wafer in He taken at the measurement temperature was subtracted from each spectrum. The aforementioned mass spectroscopy apparatus was also used here.

Estimation of Cu density and mean Cu-Cu distance in Cu-AFX zeolites

AFX unit cell contains 48T atoms, and the number of Al and Cu per each unit cell was derived from Si/Al ratio ($r_{\text{Si/Al}}$) and Cu/Al ratio ($r_{\text{Cu/Al}}$):

$$n(\text{Al per cell}) = 48 / (1 + r_{\text{Si/Al}})$$

$$n(\text{Cu per cell}) = r_{\text{Cu/Al}} \times 48 / (1 + r_{\text{Si/Al}})$$

$r_{\text{Cu/Al}}$ was estimated from experimentally measured Cu loading. The parameters of AFX unit cell are $a = b = 13.70 \text{ \AA}$, $c = 19.73 \text{ \AA}$, and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

The volume of AFX unit cell (V_{AFX}) was calculated as

$$V_{\text{AFX}} = \left(\frac{\sqrt{3}}{2}\right) \times a \times b \times c$$

which gives a value of 3207.4 \AA^3 .

The Cu density described by the number of Cu per 1000 \AA^3 ($\text{Cu}/1000\text{\AA}^3$) was estimated as

$$\text{Cu}/1000\text{\AA}^3 = n(\text{Cu per cell}) \times 1000 / V_{\text{AFX}}$$

The mean Cu-Cu distance was estimated assuming that Cu atoms are homogeneously distributed. Each Cu was considered at the center of a sphere with a radius of R. Then the Cu sphere volume ($V_{\text{Cu-sphere}}$) was calculated as

$$V_{\text{Cu-sphere}} = \left(\frac{4}{3}\right) \times \pi \times R^3$$

This volume was assumed to be same as the volume per Cu calculated from Cu density, which was described as

$$\text{Volume per Cu} = V_{\text{AFX}} / n(\text{Cu per cell})$$

Therefore, the mean Cu-Cu distance can be obtained as

$$\text{Mean Cu-Cu distance} = 2R = 2 \times \sqrt[3]{\frac{\text{Volume per Cu}}{\pi} \times \frac{3}{4}}$$

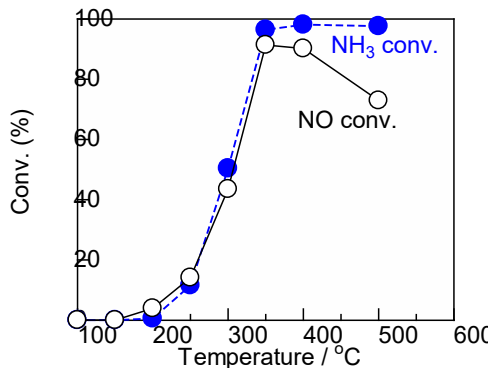


Fig. S1 Catalytic result for NH₃-SCR by Cu_{4.1}-AFX with a laboratory reactor at the same reaction conditions as for *in situ* XANES (Fig. 2). Conditions: catalyst weight = 3.8 mg; 1000 ppm NH₃, 1000 ppm NO, 10% O₂, He balance (1000 mL min⁻¹).

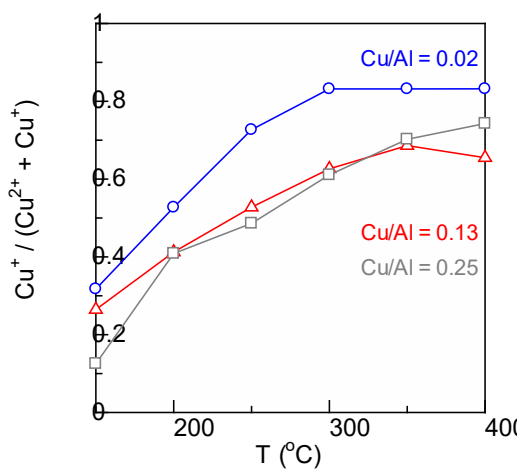


Fig. S2 Effect of temperature on the fraction of Cu(I) species in the Cu-AFX samples during the steady-state NH_3 -SCR reactions. The fractions are determined from the results of *in situ* XANES experiments shown in Fig. 2.

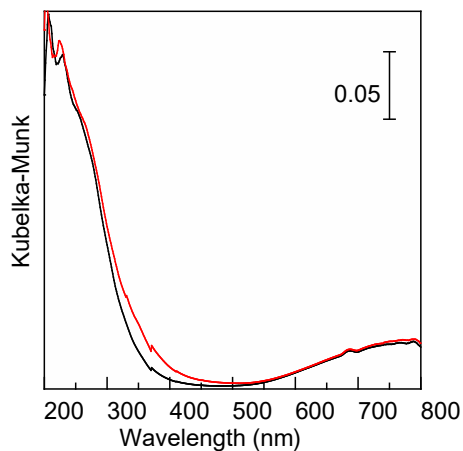


Fig. S3 *In situ* UV-vis spectra of Cu_{3.2}-AFX at 150 °C under 10% O₂ for 10 min (black), followed by flowing 500 ppm NO for 10 min (red). The Cu_{3.2}-AFX sample was prepared by the same method as described in man text (*Section 2.1*).

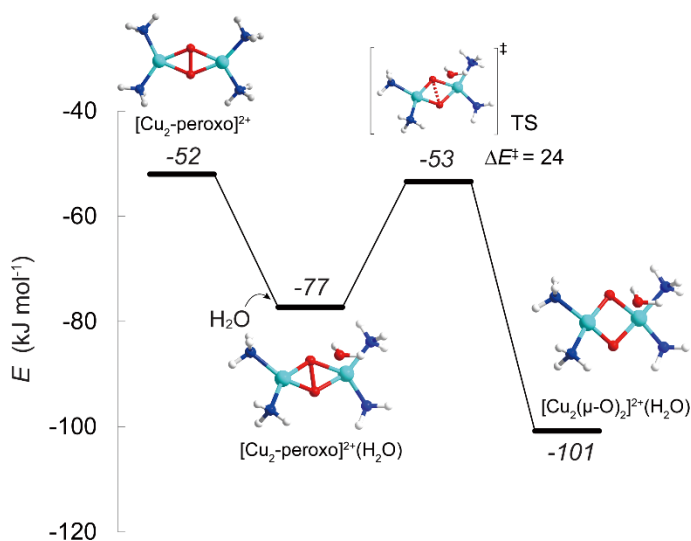


Fig. S4 Conversion of dimeric $[\text{Cu}_2\text{-peroxo}]^{2+}$ to $[\text{Cu}_2(\mu\text{-O})_2]^{2+}$ with a vicinal water as spectator in Cu-AFX. The CI-NEB calculations suggest that the hydrolysis reaction from $[\text{Cu}_2\text{-peroxo}]^{2+}(\text{H}_2\text{O})$ occurs via a stepwise mechanism in which $[\text{Cu}_2(\mu\text{-O})_2]^{2+}(\text{H}_2\text{O})$ is first generated and then hydrolyzed via the reaction pathway as described in Fig. 10.

References

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