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 \textit{in situ}/\textit{operando} spectroscopic experiments

\textit{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 \textit{in situ} cell in a 10% O\textsubscript{2} flow diluted with He (1000 mL min\textsuperscript{-1}) under atmospheric pressure. Normalization and linear combination fitting (LCF) analysis of XANES were carried out by using Athena software \textsuperscript{1}. XAS spectra for the reference compounds were collected using equivalent data collection procedures with specific acquisition parameters optimized for each sample, either measured after \textit{in situ} treatment of Cu-AFX (Z-[Cu\textsuperscript{2+}]; Z = zeolite framework) or prepared as solution-phase complexes according to the literatures \textsuperscript{2-3}. The Cu-AFX (Si/Al = 5.3) with 4.1 wt\% of Cu loading exposed to 10% O\textsubscript{2} flow (20 min) at 200 °C was used as a reference for Z-[Cu\textsuperscript{2+}]. The [Cu(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} solution was prepared by pouring 0.15 mL of 10% NH\textsubscript{3} 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(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} solution was prepared by adding 0.03 mL of hydrazine to 50 mL of the [Cu(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} solution described above. It should be noted here that the spectrum was recorded just after the preparation, without exposure to air.

\textit{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 \textit{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. BaSO\textsubscript{4} was used to collect a background spectrum. Various gas mixtures were fed to Cu2.1-AFX (10 mg) at a flow rate of 100 ml min\textsuperscript{-1}. The relative concentration of N\textsubscript{2} 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.
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 were derived from Si/Al ratio ($r_{\text{Si/Al}}$) and Cu/Al ratio ($r_{\text{Cu/Al}}$):

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

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

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

The volume of AFX unit cell ($V_{\text{AFX}}$) 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 Å³.

The Cu density described by the number of Cu per 1000 Å³ (Cu/1000Å³) was estimated as

\[ \text{Cu/1000Å}^3 = n(\text{Cu per cell}) \times 1000 / V_{\text{AFX}} \]

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

\[
\text{Volume per Cu} = \frac{V_{\text{AFX}}}{n(\text{Cu per cell})}
\]

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 NH\textsubscript{3}-SCR by Cu4.1-AFX with a laboratory reactor at the same reaction conditions as for \textit{in situ} XANES (Fig. 2). Conditions: catalyst weight = 3.8 mg; 1000 ppm NH\textsubscript{3}, 1000 ppm NO, 10% O\textsubscript{2}, He balance (1000 mL min\textsuperscript{-1}).
Fig. S2 Effect of temperature on the fraction of Cu(I) species in the Cu-AFX samples during the steady-state NH₃–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 Cu3.2-AFX at 150 °C under 10% O₂ for 10 min (black), followed by flowing 500 ppm NO for 10 min (red). The Cu3.2-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 $[\text{Cu}_2(\mu-O)_2]^{2+}$ 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 $[\text{Cu}_2(\mu-O)_2]^{2+}(\text{H}_2\text{O})$ is first generated and then hydrolyzed via the reaction pathway as described in Fig. 10.

References

