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In Situ Spectroscopic Studies on the Redox Cycle of NH₃–SCR over Cu-CHA Zeolites

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Abstract

The selective catalytic reduction of NO with ammonia (NH₃-SCR) catalyzed by Cu-CHA zeolites is thoroughly investigated using *in situ* spectroscopic experiments combined with on-line mass spectroscopy (MS) under steady-state NH₃-SCR conditions and transient conditions for Cu(II)/Cu(I) redox cycles. Quantitative analysis of the *in situ* XANES spectra of Cu-CHA under steady-state conditions of NH₃-SCR show that NH₃-coordinated Cu(II) species is the dominant Cu species at low temperatures (100–150 °C). At higher temperatures, Cu(II) species and [Cu(NH₃)₂]⁺ complex coexist, possibly because the rate of the Cu(II) → Cu(I) reduction step is comparable to that of the Cu(I) → Cu(II) oxidation step. *In situ* XANES, IR/MS, and UV-vis/MS experiments on the reduction half cycle demonstrate that the reduction of Cu(II) species occurs via the reaction of NH₃-liganded Cu(II) with NO to yield N₂ and H₂O. For the oxidation half cycle, *in situ* XANES experiments of Cu(I) oxidation in 10% O₂ at 200 °C indicate that an increased density in CHA zeolite exhibits a higher oxidation rate. *In situ* UV-vis experiments of Cu(I) reoxidation using different mixtures of oxidant feed gas demonstrate the key role of O₂ in the oxidation cycle. It is suggested that the reoxidation of Cu(I) to Cu(II) species occurs with only O₂ as the oxidant, and a high Cu density in CHA zeolite promotes SCR activity by enhancing the oxidative activation of Cu(I) to Cu(II) during the catalytic cycle.

Introduction

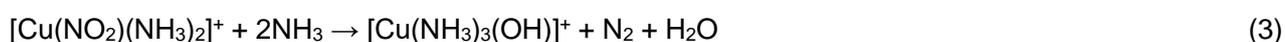
Selective catalytic reduction using ammonia (NH₃-SCR) to convert nitrogen oxides (NO_x) plays a significant role in diesel engine emissions control.^[1-3] The most commonly used catalysts for this process are V oxides and Cu- or Fe-exchanged zeolites.^[4-7] Attention has recently focused on small-pore Cu-exchanged chabazite-type SSZ-13 zeolite (Cu-CHA) due to its sufficiently high activity and hydrothermal durability for practical viability during diesel NO_x emission control.^[8-15] SSZ-13 zeolite with CHA topology shows a small-pore framework (maximum ring size 8 T-sites with an effective diameter of around 3.8 Å at room temperature), which consists of double-6-ring (d6r) and chabazite cages with the d6r cages in an AABCC packing sequence.^[16,17] This unique microporous structure has been described to account for the high catalytic performance and hydrothermal durability of Cu-CHA catalysts.^[8] Although Cu-CHA catalysts have been successfully commercialized for vehicle applications, their activities and stabilities still need to be improved to meet current and future strict regulations.^[18] Rational catalyst design based on the reaction mechanism with molecular level insights are necessary for this purpose.

There is a consensus that the standard NH₃-SCR reaction over Cu-zeolite catalysts proceeds via the reduction of Cu(II) to Cu(I) and the subsequent reoxidation of Cu(I) to Cu(II).^[19-25] It was proposed that isolated Cu species solvated with NH₃ play an important role in the NH₃-SCR reaction, according to the investigation of Cu-SSZ-13 catalysts.^[20,26] The reduction half-cycle accompanied by the reduction of Cu(II) to Cu(I) is relatively well established based on experimental and theoretical evidence. For a Cu-CHA catalyst with a high Si/Al ratio and moderate to high Cu/Al ratio, in which [Cu(NH₃)₃(OH)]⁺ is exchanged to one [AlO₂]⁻ site of the zeolite framework, the reduction half cycle is described in Eqn. (1).



It should be noted that although this mechanism is widely accepted, only a few studies have reported *in situ* direct observation of Cu(II) → Cu(I) reduction.^[20,27]

On the contrary, for the oxidation half cycle accompanied by the activation of Cu(I) to Cu(II), the detailed mechanism is still in debate. A proposed oxidation mechanism is the NO_x-assisted activation as follows:



The sum of these steps gives the stoichiometry of the standard SCR:



Density functional theory (DFT) calculations show that direct dissociation of an O₂ molecule on a single [Cu(NH₃)₂]⁺ complex does not occur, which is consistent with the NO_x-assisted oxidation model.^[28,29] However, there is limited experimental evidence to support the NO_x-assisted oxidation half cycle.^[22,27] A new concept on the oxidation half cycle was recently proposed in which O₂ activation occurs via a Cu dimer species to accomplish the reoxidation process of Cu(I).^[21,22] The [Cu(NH₃)₂]⁺ complex in Cu-CHA

interacts weakly with the zeolite framework, allowing the $[\text{Cu}(\text{NH}_3)_2]^+$ complex to move about 9 Å away from the cation exchange site of CHA.^[22] As a consequence, two mobile $[\text{Cu}(\text{NH}_3)_2]^+$ complexes, which can travel through the eight-membered rings (8-MR) of the CHA window, react with one O_2 molecule to form Cu(II) dimer species, namely $[\text{Cu}_2(\mu\text{-O})_2(\text{NH}_3)_4]$, via a transient $[\text{Cu}(\text{NH}_3)_2]^+\text{-O}_2\text{-}[\text{Cu}(\text{NH}_3)_2]^+$ intermediate (Eqn. 5).^[21] It was assumed that the release of mononuclear Cu(II) species from the $[\text{Cu}_2(\mu\text{-O})_2(\text{NH}_3)_4]$ complex proceeds via a NO-assisted mechanism as shown in Eqn. (6).



The sum of steps (1), (5), and (6) gives the stoichiometry of the standard $\text{NH}_3\text{-SCR}$ in Eqn. (4). Validation of this dimer model remains an open question as it lacks experimental and theoretical evidence for step (6), which can be divided into several elementary steps. Although considerable effort has been devoted to the $\text{NH}_3\text{-SCR}$ process, a fundamental understanding of the reaction mechanism, especially the Cu reoxidation pathways, is still lacking, despite its obvious importance in industry.

In this study, we assess the standard $\text{NH}_3\text{-SCR}$ mechanism by using various *in situ* spectroscopic techniques. We show *in situ* X-ray absorption near-edge structure (XANES), IR, and diffuse-reflectance UV-vis measurements under steady-state $\text{NH}_3\text{-SCR}$ conditions and transient Cu(II) \leftrightarrow Cu(I) redox conditions. The oxidation states of Cu species under $\text{NH}_3\text{-SCR}$ conditions are quantitatively discussed based on the steady-state spectroscopic observations. The transient kinetics of Cu(II) \rightarrow Cu(I) reduction and Cu(I) \rightarrow Cu(II) oxidation are studied in combination with the analysis of gas-phase product formation.

Results and Discussion

States of Cu under steady-state standard $\text{NH}_3\text{-SCR}$ reaction conditions

First, we discuss the structures and states of the Cu species under steady-state $\text{NH}_3\text{-SCR}$ conditions as a function of the reaction temperature. Figure 1a shows the *in situ* XANES spectra of Cu2.0-CHA under steady-state conditions of $\text{NH}_3\text{-SCR}$ (1000 ppm NH_3 , 1000 ppm NO, 10% O_2) in a temperature range of 100–500 °C. The relatively low contact time ($W/F = 4.6 \times 10^{-4}$ g s cm^{-3} , $W = 7.6$ mg, $F = 1000$ mL min^{-1}), or in other words, high space velocity (SV) conditions in this study will afford lower NO and NH_3 conversion levels than the previously reported *in situ* or *operando* XANES measurements of Cu-zeolite-catalyzed $\text{NH}_3\text{-SCR}$.^[30–32] Thus, the XANES results in this study, especially at low temperatures, correspond to the oxidation states of Cu under the conditions that NO and NH_3 are sufficiently supplied. The XANES spectrum at 100 °C has two unresolved peaks, at 8994 and 8998 eV, with a shoulder around 8987 eV (Figure 1a). These features are close to those of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ in the reference spectra (Figure 1b), indicating that the NH_3 -coordinated Cu complexes such as $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Cu}(\text{NH}_3)_m\text{X}_n]^{2+}$, where X denotes oxygen-based ligands, are the dominant Cu species at 100 °C. Above 200 °C, a peak appears at 8983 eV due to the $1s \rightarrow 4p$ transition in the linear $[\text{Cu}(\text{NH}_3)_2]^+$ complex,^[24,26,30,33] and its intensity increases with the rise in reaction temperature.

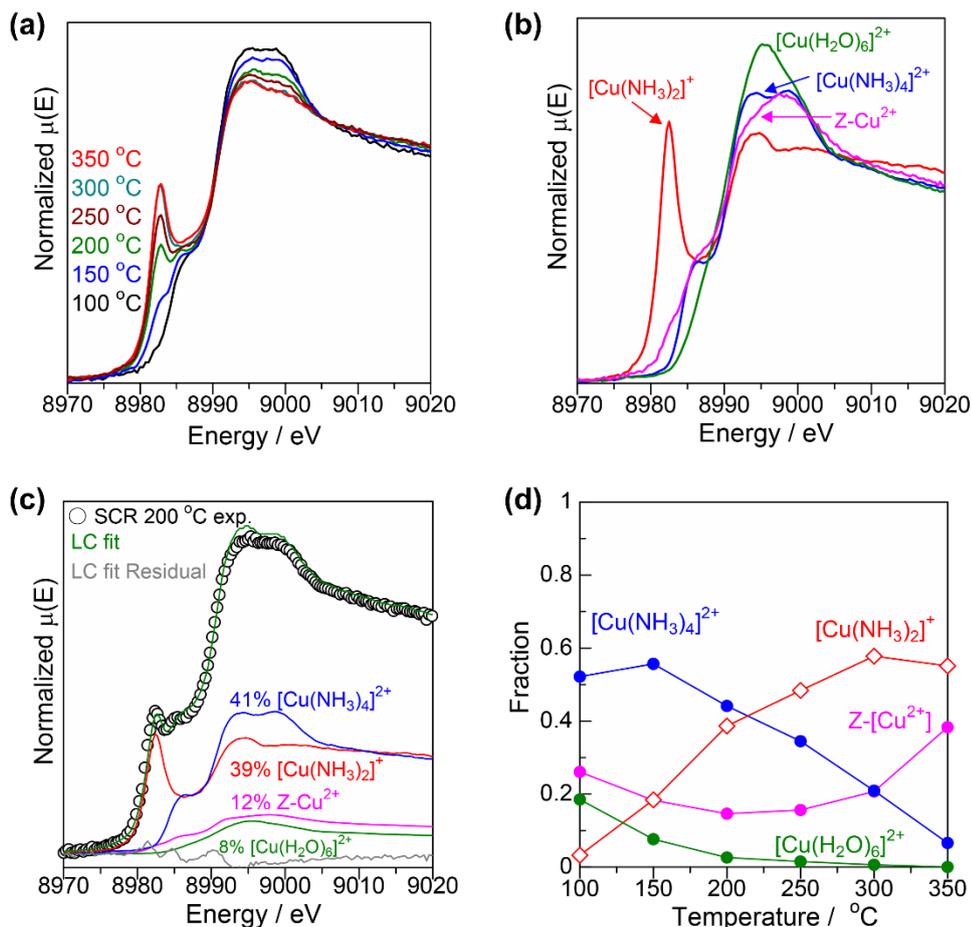


Figure 1. *In situ* Cu K-edge XANES spectra of (a) Cu_{2.0}-CHA under NH₃-SCR reaction conditions at various temperatures, (b) standard compounds, and (c) LCF analysis at 200 °C; (d) proportion of each Cu species at different reaction temperatures. NH₃-SCR reaction conditions: 1000 ppm NH₃, 1000 ppm NO, 10% O₂, He balance (1000 mL min⁻¹); catalyst weight = 7.6 mg. The spectra of the standard compounds were collected at room temperature except that the framework-interacting Z-Cu(II) species was obtained at 200 °C.

Based on the fact that the XANES spectra depend negligibly on the collection temperature,^[30] we carried out linear combination fitting (LCF) analysis of the XANES spectra. According to the method by Lomachenko et al.,^[30] we used the XANES spectra of four reference compounds for the LCF analysis in the energy range of 8970–9020 eV (Figure 1b). The spectra of [Cu(H₂O)₆]²⁺, [Cu(NH₃)₄]²⁺, and [Cu(NH₃)₂]²⁺ in aqueous solution were collected at room temperature. According to the literature,^[30] both [Cu(NH₃)₄]²⁺ and [Cu(NH₃)₃(OH)]⁺ complexes co-exist in the oxidized Cu-CHA catalysts. For the XANES analysis, [Cu(NH₃)₄]²⁺ complex was used as reference because of the absence of reference compounds for [Cu(NH₃)₃(OH)]⁺ structure, which may have XANES features similar to [Cu(NH₃)₄]²⁺ complex. The spectrum for the framework-interacting Z-Cu(II) species was obtained *in situ* at 200 °C under a flow of 10% O₂/He. Figure 1c shows a typical example of LCF analysis, where the experimental XANES spectrum under working conditions at 200 °C is compared with a best fit curve estimated by a linear combination of

the four XANES curves of the reference compounds. The LCF weight for each reference compound corresponds to the fraction of each Cu species (Table S1), which is plotted as a function of the reaction temperature (Figure 1d). The following conclusions are derived from the LCF analysis. In a low temperature range (100–150 °C), an NH₃-coordinated Cu(II) species, most likely the [Cu(NH₃)₄]²⁺ complex in the zeolite cage, is the dominant Cu species. The fraction of a Cu(I) species, corresponding to the linear [Cu(NH₃)₂]⁺ complex, increases with the reaction temperature up to 300 °C. At 350 °C, Cu(II) coordinated to the anionic framework oxygen of CHA, Z-Cu(II), appears. Considering the Cu(II)↔Cu(I) redox-driven NH₃-SCR mechanism, the results suggest that the reduction half cycle is relatively slow at low temperatures (100–150 °C). At higher temperatures, the Cu(II) species and [Cu(NH₃)₂]⁺ complex coexist, possibly because the rate of the Cu(II) → Cu(I) reduction step is comparable to that of the Cu(I) → Cu(II) oxidation step. At the high temperature region where the conversion of NH₃ is high, the amount of [Cu(NH₃)₂]⁺ levels off because the concentrations of the reducing agents (NO and NH₃) are too low.

We then carried out *in situ* XANES experiments at 200 °C during the NH₃-SCR reaction under varying O₂ partial pressures (0.5–10%) for Cu-CHA catalysts with different Cu densities (Cu/Al = 0.03 and 0.29). LCF analysis of the *in situ* XANES spectra of Cu-CHA provides the fractions of Cu(I) and Cu(II) species (Tables S2 and S3), which are plotted versus the O₂ pressures in Figure 2. The comparison of the two samples indicates that a lower Cu loading affords larger fractions of Cu(I) species under the steady-state NH₃-SCR conditions. Based on the assumption of a homogeneous Cu distribution in CHA, we calculated the Cu density (Cu/1000 Å³) and the mean Cu-Cu distance (Table 1).^[22] Clearly, a lower Cu loading leads to a lower Cu density and therefore a larger mean Cu-Cu distance, which suggests that more isolated Cu distributions promote higher fractions of Cu(I) in the CHA zeolite particles. The results are consistent with the XANES experiments by Paolucci et al.^[22] In accordance with their proposal, our results indicate that the reoxidation half cycle is relatively slow when the Cu(I) species are strongly separated from each other inside the zeolite particles. Independent of the Cu density, the fraction of Cu(II) does not depend strongly on the O₂ pressure, affording low slopes (n = 0.14) in the logarithmic plots for both samples. This suggests that the reoxidation half cycle is not the rate-limiting step of NH₃-SCR at 200 °C.

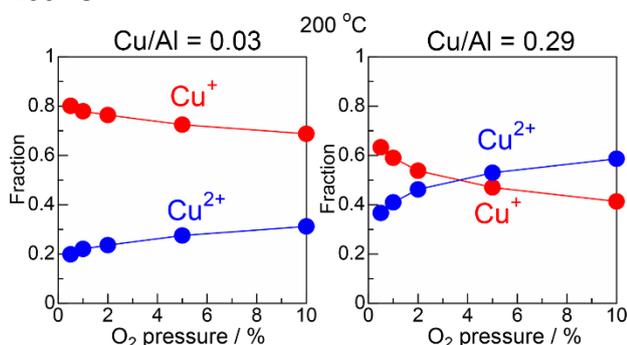


Figure 2. Effect of O₂ pressure on the fraction of Cu(I) and Cu(II) species during NH₃-SCR at 200 °C in Cu-CHA catalysts with different Cu/Al ratios. The fraction was determined by LCF analysis of *in situ* Cu K-edge XANES spectra. NH₃-SCR reaction conditions: 1000 ppm NH₃, 1000 ppm NO, O₂, He balance (1000 mL min⁻¹); catalyst weight = 7.6 mg for Cu2.0-CHA and 89.9 mg for Cu0.2-CHA.

Table 1. Composition of the Cu_x-CHA catalysts (x denotes Cu loading in wt%).^a

Sample	Si/Al	Cu (wt%)	Cu/Al	Cu density (Cu/1000 Å ³)	Mean Cu–Cu distance (Å)
Cu2.0-CHA	14	2.0	0.29	0.29	18.7
Cu0.2-CHA	14	0.2	0.03	0.03	40.6

^a The Cu loading (wt%) and Cu/Al ratio were determined based on the results of EDX analysis. The Cu density and mean Cu–Cu distance were estimated assuming a homogeneous Cu distribution in CHA zeolite (for details, see Supporting Information).

Diffuse reflectance UV-vis spectroscopy was further used for *in situ* characterization of the Cu(II) species in Cu-CHA under the NH₃–SCR conditions. Cu(II) cations in octahedral coordination exhibit a d–d transition peak centered at approximately 730–790 nm.^[34,35] Figure 3a shows *in situ* UV-vis spectra of Cu2.0-CHA at 200 °C during NH₃–SCR under different O₂ partial pressures (0.1–10%). UV-vis spectra show a broad d–d transition peak centered at 760 nm due to the presence of Cu(II) species. The height of the d–d band at 760 nm is plotted versus the O₂ pressures in Figure 3b. To carry out *in situ* UV-vis measurement combined with the analysis of evolved N₂ (m/e = 28) in the outlet gas, online MS was employed. Note that the MS intensity under the flow reactor corresponds to the relative rate of the NH₃–SCR reaction. The rate of NH₃–SCR and the relative amount of Cu(II) species increases steeply with O₂ pressure up to 1% O₂, but the slopes became smaller at higher O₂ pressure (>1%). The *in situ* UV-vis results show that the oxidation of Cu(I) to Cu(II) species is relatively slow under low O₂ pressure conditions (<1%), but the reoxidation step does not limit the NH₃–SCR under typical lean conditions (5–10 % O₂) at 200 °C.

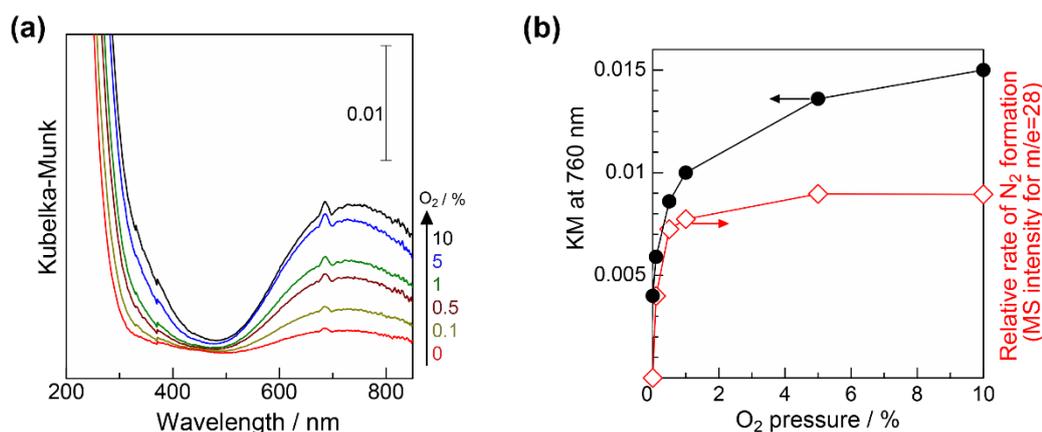


Figure 3. (a) *In situ* UV-vis spectra of Cu2.0-CHA during NH₃–SCR at 200 °C under different O₂ pressures; (b) band intensity due to the d–d transition of Cu(II) during NH₃–SCR and MS intensity of N₂ versus O₂ pressure. Reaction conditions: 500 ppm NH₃, 500 ppm NO, O₂, Ar balance (100 mL min⁻¹); sample weight = 10 mg.

Reduction half cycle

Next, we present comprehensive experimental studies on the reduction half cycle. The reduction of Cu(II) to Cu(I) by a NO/NH₃ mixture was monitored by *in situ* Cu K-edge XANES experiments at 200 °C for the Cu_{2.0}-CHA catalyst (Figure S1). Note that this experiment was carried out using larger amount of the sample (102.6 mg) in order to obtain superior quality spectra. The XANES spectrum after initial oxidation in 10% O₂ exhibits a shoulder around 8987 eV and a broad peak centered around 8998 eV, both of which are characteristic features of isolated Cu(II) coordinated to the cation exchange site of zeolites.^[30] After exposure of the sample to NH₃ + NO, the XANES spectrum appeared with an intense peak at 8983 eV. This is due to the 1s → 4p transitions and characteristics of the linear [Cu(NH₃)₂]⁺ complex, showing data consistent with the reported results.^[20,26] Considering the consistency of the model with the literature, our XANES results also indicate that the Cu(II) cations are reduced by NH₃/NO to give the [Cu(NH₃)₂]⁺ complex. LCF analysis of the XANES spectrum of Cu_{2.0}-CHA under NO/NH₃ at 200 °C (Figure S1) shows Cu(I)/Cu(II) ratio of 75/25. This indicates that part of Cu(II) ions remains unreduced possibly due to the presence of less reducible or less accessible Cu(II) sites in CHA.

Based on DFT and XANES evidence, Paolucci et al. proposed a detailed mechanism of the Cu(II) → Cu(I) half cycle.^[20] The attack of NO on NH₃ coordinated to the Cu(II) site results in NO-assisted NH₃ dissociation to give H₂NNO and H⁺, and H₂NNO decomposes to N₂ and H₂O. To verify this proposal, we further carried out *in situ* IR experiments on the reaction of the adsorbed NH₃ species with NO at 200 °C. The IR disc of Cu-CHA in the IR cell was first exposed to 1000 ppm NH₃/He. After the He purge, the IR spectrum shows a peak at 1620 cm⁻¹ due to NH₃ coordinated to Cu(II) [NH₃-Cu(II)] together with a strong band due to NH₄⁺ (NH₃ on Brønsted acid sites) at 1450 cm⁻¹ (Figure 4).^[36–38] After the catalyst was exposed to a flow of 500 ppm NO/He, the intensity of the NH₃-Cu(II) band (1620 cm⁻¹) decreases, while that of the NH₄⁺ band (1450 cm⁻¹) remains unchanged. Simultaneously with the *in situ* IR measurements, N₂ evolution in the outlet gas was monitored by online MS. The N₂ formation coincides with the consumption of NH₃ coordinated to Cu(II) (1620 cm⁻¹). This indicates that NH₃ adsorbed on Cu(II) reacts with NO to yield N₂.

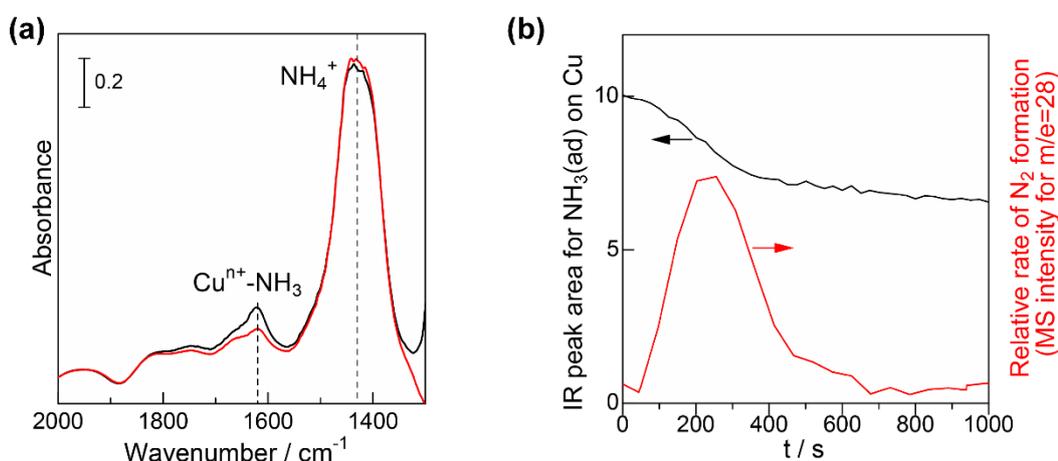


Figure 4. (a) *In situ* IR spectra of adsorbed species in Cu_{2.0}-CHA at 200 °C. The catalyst was first exposed to a flow of 0.1% NH₃/He (100 mL min⁻¹) for 0.5 h and purged with He for 10 min (black line), followed by exposure to 500 ppm NO/He flow (100 mL min⁻¹) (red line); (b) time dependence of the IR peak area due to NH₃ on the Cu(II) site and MS intensity of N₂. Sample weight = 40 mg.

In situ UV-vis experiments were also performed for the reduction half cycle at 200 °C (Figure 5a). The UV-vis spectrum of Cu-CHA under 10% O₂ shows a broad d–d transition peak centered at 760 nm assignable to Cu(II) at the zeolite framework oxygen.^[34,35] The band shows three features at 500, 610, and 760 nm. Similar splitting of the d–d band was previously reported by Giordanino et al. who observed a d–d quadruplet in the UV-vis spectrum of O₂-activated Cu-CHA with a Cu/Al ratio of 0.444 (Si/Al = 13.1).^[39] Recently, Li et al. observed the quadruplet feature (20,077, 16,379, 13,593, and 11,059 cm⁻¹) in the UV-vis spectrum of O₂-activated Cu-CHA samples with Cu/Al ratios of 0.15 and 0.24 (Si/Al = 15), whereas the quadruplet feature did not appear for the Al-rich Cu-CHA (Si/Al = 5; Cu/Al = 0.2).^[40] Combined with the fact that the former Cu(II) species was more reducible than the latter one, the quadruplet feature was assigned to mononuclear [CuOH]⁺ species mixed with dimeric/multimeric Cu(II)-oxo species.^[40] The positions of the splitting peaks for the O₂-treated Cu_{2.0}-CHA (Cu/Al = 0.3; Si/Al = 14) in Figure 5a (20,000, 16,393, and 13,158 cm⁻¹) are close to those reported by Li et al. (20,077, 16,379, and 13,593 cm⁻¹) for a similar Cu-CHA sample (Cu/Al = 0.15–0.2; Si/Al = 15). Combined with the IR results, we conclude that the mononuclear [CuOH]⁺ species coordinated to one zeolite framework oxygen (1Al site) is the dominant Cu(II) species in the O₂-activated Cu_{2.0}-CHA. Hereafter, we discuss the SCR mechanism assuming the [CuOH]⁺ species coordinated to one negatively charged oxygen site of the zeolite framework (1Al site) as an initial state of the reduction half cycle.

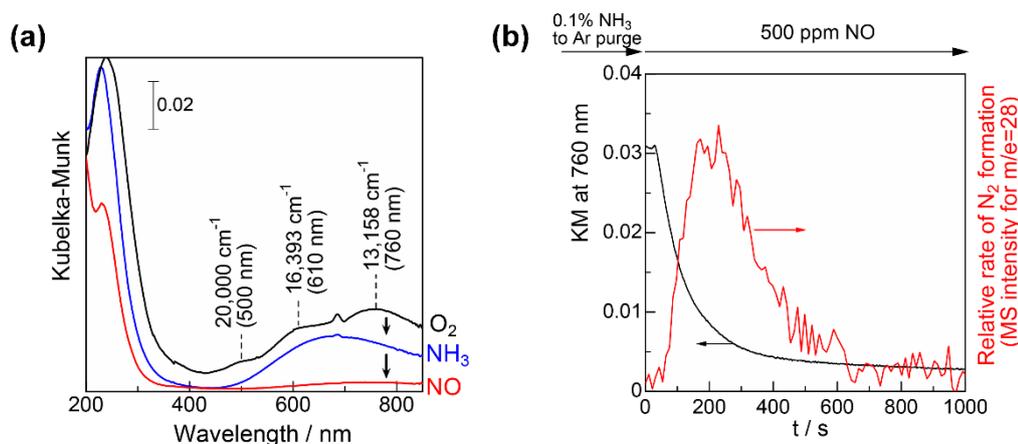


Figure 5. (a) *In situ* UV-vis spectra of Cu_{2.0}-CHA at 200 °C. The catalyst was first oxidized under 10% O₂/Ar (100 mL min⁻¹), followed by exposure to 0.1% NH₃/Ar flow (100 mL min⁻¹) for 0.5 h, and to 500 ppm NO/Ar flow (100 mL min⁻¹); (b) time dependence of the band intensity due to Cu(II) and MS intensity of N₂. Sample weight = 10 mg.

Under 1000 ppm NH₃/Ar, the peak is blue-shifted to 640 nm. Considering the IR evidence on the coordination of NH₃ to Cu(II) and the fact that the N-ligand causes larger d–d band splitting than the O-ligand, the blue shift of the d–d band indicates the change in the ligands of Cu(II) from zeolite oxygens by NH₃ molecules.^[41] The splitting d–d features due to the Z-[CuOH] species disappear under NH₃, indicating a change in the ligand field around the Cu(II) species due to the coordination of NH₃ to Cu(II). After purging with Ar, the subsequent reaction of the Cu(II)–NH₃ complexes with NO decreases the intensity of the d–d

band. The height of the d–d absorption band decreases with the NO flowing time, and the simultaneous evolution of N₂ (m/e = 28) was confirmed by online mass spectroscopy (Figure 5b). The results of XANES, IR/MS and UV-vis/MS indicate that the reaction of Cu(II)–NH₃ with NO results in the reduction of Cu(II) to Cu(I) accompanied by the formation of N₂ (Eqn. 1), which is consistent with the mechanism of the Cu(II) → Cu(I) half cycle reported in the literature.^[20]

The *in situ* XANES spectra in Figure 1 suggest that the reduction half cycle is relatively slow at low temperatures (100–150 °C). Using a conventional flow reactor equipped with an online GC-TCD, we measured the N₂ formation rate under steady-state NH₃–SCR conditions where the conversions were below 10% (dashed line in Figure 6). With the same reactor, we measured the N₂ formation rates for the reduction half cycle at 150 °C as follows (open circles in Figure 6). The Cu_{2.0}-CHA catalyst was first exposed to 1000 ppm NH₃/He for 0.5 h, followed by purging with He for 10 min. Then, 500 ppm NO/He was fed to the catalyst, and the outlet gas was monitored by online GC-TCD. As shown in Figure 6, the initial rate of N₂ formation for the reduction half cycle (1.7 mmol g⁻¹ h⁻¹) is in the same order of magnitude as the N₂ formation rate under steady-state NH₃–SCR (1.1 mmol g⁻¹ h⁻¹). The total number of N₂ evolved during the reduction half cycle for 2000 s (0.25 mmol g⁻¹) is close to the number of Cu atoms in the sample (0.31 mmol g⁻¹). These results would be quantitative kinetic evidence to demonstrate that the reduction half cycle is the main N₂ formation step of NH₃–SCR.

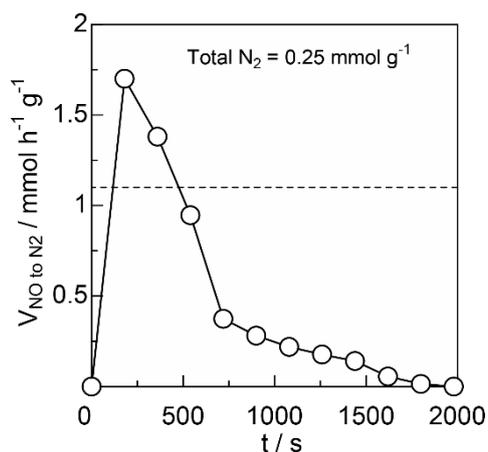


Figure 6. Comparison of steady-state (dashed line) and transient (solid line) rates of NO reduction to N₂ over Cu_{2.0}-CHA at 150 °C. The steady-state rate was measured under the standard NH₃–SCR conditions. The transient reaction for the reduction half cycle was carried out by flowing 500 ppm NO/He (100 mL min⁻¹) over Cu_{2.0}-CHA pre-exposed to 0.1% NH₃/He flow (0.5 h). Sample weight = 10 mg.

Oxidation half cycle

We then discuss a possible mechanism of the oxidation half cycle based on experimental and theoretical investigations. The oxidation kinetics of Cu(I) by 10% O₂ was monitored by *in situ* Cu K-edge XANES at 200 °C for the Cu_{2.0}-CHA and Cu_{0.2}-CHA catalysts (Figure 7). The samples were first reduced at 200 °C under a flow of NO + NH₃, followed by purging with He for 7 min. Then, we started XANES measurements as a function of the 10% O₂ flowing time. The spectrum after the pre-reduction ($t = 0$ s) has an intense $1s \rightarrow 4p$ transition peak (8983 eV) characteristic of the linear [Cu(NH₃)₂]⁺ complex.^[20,26] The intensity of the peak at 8983 eV assigned to [Cu(NH₃)₂]⁺ decreased with the O₂ flowing time. After 500 s of O₂ flowing, the XANES spectrum of Cu_{2.0}-CHA showed a broad peak centered at around 8997.7 eV with a shoulder at 8986.6 eV, which is characteristic of Cu(II) coordinated to zeolite oxygens.^[42–44] This result indicates that Cu(I) species can be oxidized with only O₂ even in the absence of NO_x. Furthermore, we performed LCF analysis of the XANES data to estimate the fractions of Cu(II) and Cu(I) species as a function of time (Tables S4 and S5). It was found that the Cu(I) species in Cu_{2.0}-CHA are oxidized faster than those in Cu_{0.2}-CHA (Figures 7c and 7d), which indicates that a higher Cu density, with a shorter distance between the Cu(I) species, results in higher efficiency in the oxidation half cycle. The high oxidation rate of the Cu species in Cu-CHA with high Cu density is consistent with the previous XAFS observations by Paolucci et al.^[22] The fractions of unoxidized Cu(I) complexes under the pseudo steady-state conditions are 5% for Cu_{2.0}-CHA (Figure 7c) and 47% for Cu_{0.2}-CHA (Figure 7d). This indicates that not all [Cu(NH₃)₂]⁺ complexes are oxidized by O₂ at 200 °C, and the fraction of unoxidized [Cu(NH₃)₂]⁺ complexes is larger for the Cu-CHA with low Cu density. This is possibly because the oxidation of Cu(I) ions becomes difficult when they are sufficiently diluted in the zeolite matrix. Based on similar XANES results and a maximum diffusion distance of 9 Å estimated by DFT calculations, Paolucci et al. proposed that a [Cu(NH₃)₂]⁺ complex located more than 9 Å away from another [Cu(NH₃)₂]⁺ complex cannot be oxidized only by O₂ feed.^[22]

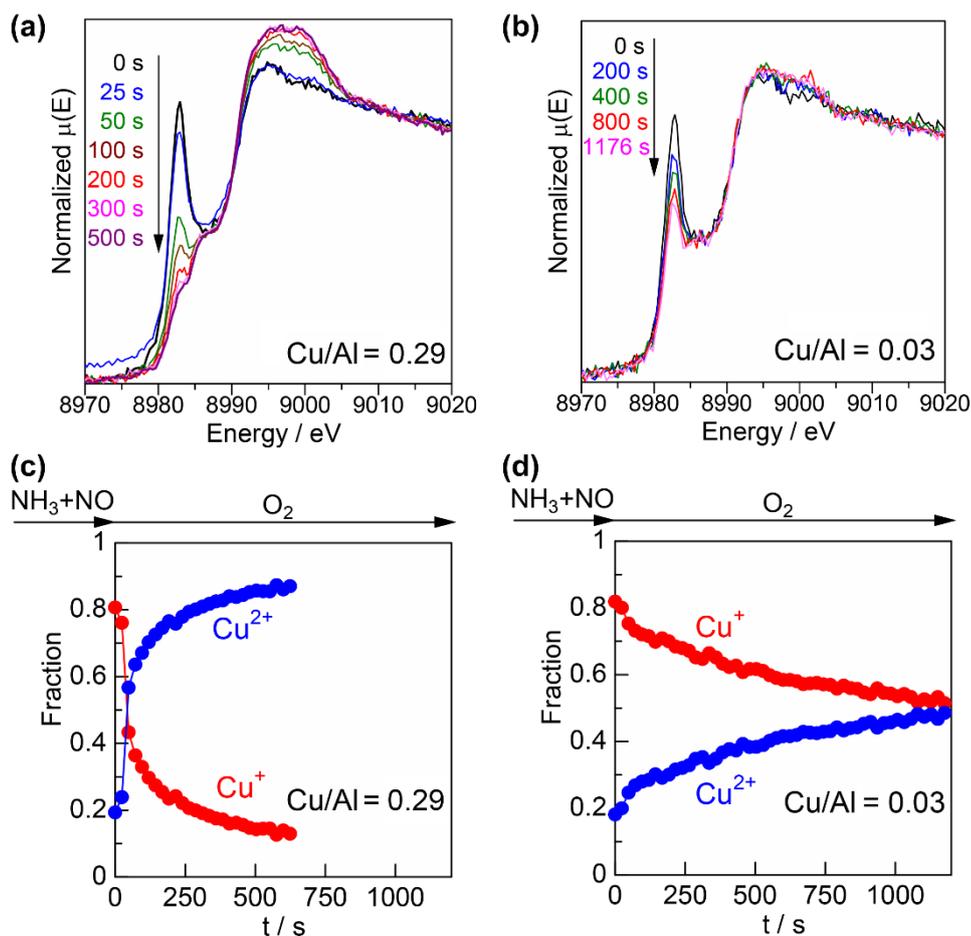


Figure 7. Time-dependence of *in situ* XANES spectra of (a) Cu_{2.0}-CHA and (b) Cu_{0.2}-CHA, pre-reduced by 0.1%NH₃/0.1%NO/He, during the reoxidation half cycle (under 10% O₂) at 200 °C. Fractions of Cu(II) and Cu(I) in (c) Cu_{2.0}-CHA, and (d) Cu_{0.2}-CHA as a function of the reoxidation time. Flow rate = 1000 mL min⁻¹; sample weight = 7.6 mg (Cu_{2.0}-CHA), 89.9 mg (Cu_{0.2}-CHA).

The oxidation half cycle was also investigated by *in situ* UV-vis at 200 °C (Figure 8). After reduction by NO + NH₃, different oxidation gas mixtures were fed to the Cu_{2.0}-CHA. The oxidation treatments increase the intensity of the d–d transition peak, indicating that Cu(I) is oxidized to Cu(II) using different oxidation gas mixtures: 500 ppm NO/500 ppm NO₂/10% O₂, 500 ppm NO/10% O₂, or 10% O₂. The intensity of the d–d band is slightly higher under NO/O₂ and NO/NO₂/O₂ than under O₂. The result suggests that O₂ acts as a primary important oxidant in the oxidation half cycle and NO_x promotes this step.

Figure 9 shows the kinetic curves for N₂ formation and the amount of Cu(II) species monitored by the *in situ* UV-vis experiment on Cu_{2.0}-CHA at 200 °C. When the feed gas was switched from NO + NH₃ + O₂ to NO + NH₃ (at $t = 0$ s), the relative rate of N₂ formation and relative amount of Cu(II) decreased with time and eventually dropped to a very low level (at 1000 s). When the feed gas was switched back to NO + NH₃ + O₂ (at 1320 s), the N₂ formation rate and the amount of Cu(II) increased significantly with time and recovered back to the level of standard SCR conditions. The coincidence of N₂ formation and the oxidation of Cu(I) to Cu(II) indicates that NH₃-SCR is driven by the Cu(II) ↔ Cu(I) redox cycle.

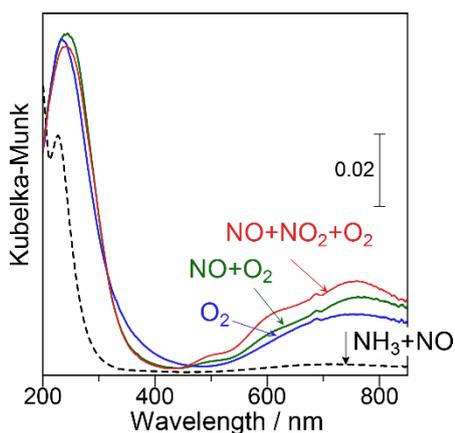


Figure 8. *In situ* UV-vis spectra of Cu_{2.0}-CHA at 200 °C after reduction by 500 ppm NH₃/ 500 ppm NO/Ar (100 mL min⁻¹) (dashed line), followed by reoxidation for 0.5 h under different oxidant mixtures (10% O₂/Ar, 500 ppm NO+10% O₂, or 250 ppm NO+250 ppm NO₂+10% O₂).

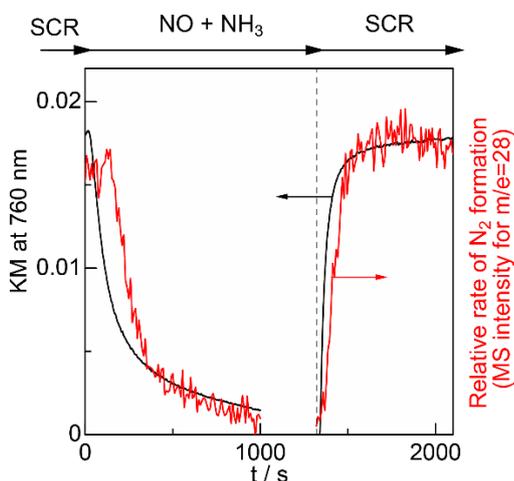


Figure 9. Time dependence of the UV-vis band intensity due to Cu(II) and MS intensity of N₂. The reaction system was changed from NH₃-SCR condition (500 ppm NH₃, 500 ppm NO, 10% O₂, Ar balance, 100 mL min⁻¹) to transient reduction condition (500 ppm NO, 500 ppm NH₃, Ar flow, 100 mL min⁻¹), and then back to the initial NH₃-SCR condition. Sample weight = 10 mg.

Summarizing the experimental results, we provided comprehensive *in situ* spectroscopic and kinetic evidences on the standard NH₃-SCR reaction over Cu-CHA. Our model is basically consistent with the widely accepted model, where the reaction proceeds via the reduction of Cu(II) to Cu(I) and the subsequent reoxidation of Cu(I) to Cu(II).^[19–25] In the reduction half cycle, i.e. Eqn. (1), [Cu(NH₃)₃(OH)]⁺ exchanged to one [AlO₂]⁻ site or [Cu(NH₃)₄]²⁺ exchanged to two [AlO₂]⁻ site reacts with NO results in the reduction of Cu(II) to Cu(I) accompanied by the formation of N₂. Although previous studies have reported *in situ* XANES observation of Cu(II) → Cu(I) reduction by NO + NH₃,^[20,45] *in situ* IR result of the reaction of Cu(II)-NH₃ species in the presence of NO,^[37] and DFT-based detailed reaction coordinate for the reduction half cycle,^[20] the new contribution of this study is the comprehensive experimental evidences on the

reduction half cycle using different *in situ* (XANES) and *operando* (IR/MS and UV-vis/MS) spectroscopies with the same Cu-CHA sample. The *in situ* XANES results under steady-state NH₃-SCR conditions (Figure 1) show that NH₃-coordinated Cu(II) species is the dominant Cu species at low temperatures (100–150 °C), suggesting that the reduction half cycle is relatively slow step at low temperatures. At 150 °C, the initial rate of N₂ formation for the reduction half cycle is in the same order of magnitude as the N₂ formation rate under steady-state NH₃-SCR (Figure 6), suggesting that the reduction half cycle is the main N₂ formation step of NH₃-SCR. At higher temperatures, Cu(II) species and Cu(I) species coexist, suggesting that the rate of the Cu(II) → Cu(I) reduction step is comparable to that of the Cu(I) → Cu(II) oxidation step.

Compared with the reduction half cycle, rather few experimental evidences have been reported on the oxidation half cycle. This work provides *in situ* XANES (Figure 7) and *operando* UV-vis/MS (Figure 8) evidences on the dynamic changes of Cu species during oxidation half cycle and shows that [Cu(NH₃)₂]⁺ species is oxidized with O₂ even in the absence of NO_x. The *in situ* XANES result (Figure 7) suggests that higher density of Cu in CHA, or in other word shorter distance between the [Cu(NH₃)₂]⁺ species, results in higher efficiency in the oxidation half cycle. *In situ* XANES during steady-state SCR (Figure 2) indicates that lower Cu loading (Cu density) results in larger fractions of Cu(I) species. These results are consistent with the *in situ* XANES experiments by Paolucci et al.,^[22] suggesting that the oxidation half cycle is slow when the Cu(I) species are separated from each other as it is difficult for two [Cu(NH₃)₂]⁺ complexes to migrate inside the same cage and react with O₂ to give Cu(II) dimer species.

Conclusion

We have employed various *in situ* spectroscopic techniques to study the reaction mechanism of NH₃-SCR over Cu-CHA zeolites. By using the same Cu-CHA catalyst sample, *in situ* (XANES) and *operando* (IR/MS and UV-vis/MS) spectroscopic characterizations provided integrated experimental evidences on the reduction half cycle, showing that the Cu(II) → Cu(I) reduction is driven by the reaction of Cu(II)-NH₃ with NO to produce N₂ and H₂O, which is consistent with previous *in situ* XANES, *in situ* IR, and DFT studies.^{20,45,53} The transient rate of N₂ formation in the reduction half cycle is close to the steady-state SCR rate, which quantitatively shows that the reduction half cycle is the main N₂ formation step during steady-state SCR. *In situ* UV-vis spectra with online MS analysis of N₂ production indicate that the reaction rate of NH₃-SCR strongly depends on the O₂ pressure at low pressure region (<1%) due to the low rate of Cu(I) oxidation to Cu(II) species, but the reoxidation step does not limit the reaction rate under typical lean conditions (5–10% O₂) at 200 °C. Spectroscopic experiments on the oxidation half cycle suggest that a higher Cu density in CHA enhances the oxidation rate of Cu(I) species, and O₂ feed plays a key role in the oxidation half cycle of SCR reaction.

Experimental Section

Preparation of the Catalysts

CHA zeolite (Si/Al = 14) was prepared according to the previous report.^[46] Sodium hydroxide, dealuminated FAU zeolite, *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAda, 25 wt%, Sachem Asia Co., Ltd., Japan), and distilled water were mixed to obtain a gel with the composition 1:0.0625:0.3:0.1:7.5 of Si/Al/TMAda/NaOH/H₂O. The resulting gel was transferred into a 100 cm³ Teflon-lined stainless-steel autoclave (stirring-type hydrothermal synthesis reactor, R-100, Hiro Company, Japan) and heated at 150 °C for seven days with tumbling at 10 rpm. After crystallization, the solid product was collected by centrifugation, washed thoroughly with distilled water until it was almost neutral, and then dried overnight at 70 °C. To remove organic molecules, the obtained as-synthesized CHA zeolite was calcined in air at 600 °C for 10 h. Cu-CHA catalysts were prepared by aqueous-phase Cu ion exchange using a Cu(NO₃)₂ solution at a pH 5.5. After the ion exchange, the sample was filtered, rinsed with distilled water (200 mL) three times, and dried at 100 °C for 24 h, followed by calcination under air at 600 °C for 1 h. Energy-dispersive X-ray fluorescence (EDX) spectrometry (EDX-700HS, Shimadzu Corp.) was used to determine the Cu loading amount, and the results gave Cu/Al ratios of 0.03 and 0.29 depending on the concentration of Cu in the solution during Cu exchange. The catalysts are designated as Cux-CHA, where *x* denotes Cu loading in wt%.

In situ XAFS

Cu K-edge quick XAFS measurements were performed 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. Spectra were recorded in transmission mode with the ionization chambers using gas mixtures to give 10% absorption in the incident X-ray detector and

70% absorption in the transmission X-ray detector. *In situ* XANES data were collected in a quick-scanning mode; the Si(111) monochromator was continuously moved from 12.985° to 12.450° in 10.14 s. The energy of the X-ray was calibrated using a Cu foil as the reference. A self-supported wafer form of the sample with ca. 7 mm diameter was placed in a quartz *in situ* cell available at the beamline (dead volume = approximately 20 mL) 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 software.^[47] XAFS 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-CHA (Z-[Cu²⁺]; Z = zeolite framework) or prepared as solution-phase complexes according to the literature.^[19,30] The brief preparation procedure is as follows. The Cu-CHA (Si/Al = 14) with 2.0 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. The [Cu(H₂O)₆]²⁺ solution was prepared by adding 0.50 g of copper(II) acetate to 50 mL of ion-exchanged water.

***In situ* 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 Cu2.0-CHA (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 same type of mass spectroscopy apparatus used for the XAFS measurements. 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.

***In situ* IR**

In situ 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.

Catalytic reactions

The NH₃-SCR (NO + NH₃ + O₂) reaction was performed in a fixed-bed flow reactor with 10 mg Cu2.0-CHA catalyst at a flow rate of 100 mL min⁻¹. The composition of the feed gas was NO/NH₃/O₂/He = 500

ppm/500 ppm/10%/balance, respectively. The effluent gas was analyzed by IR spectroscopy and GC-TCD (Agilent 490 micro-GC). Note that the N₂O yield was below the detection limit.

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Keywords: Selective catalytic reduction • Cu-CHA zeolite • *In situ* spectroscopy • XAFS • Reaction mechanism

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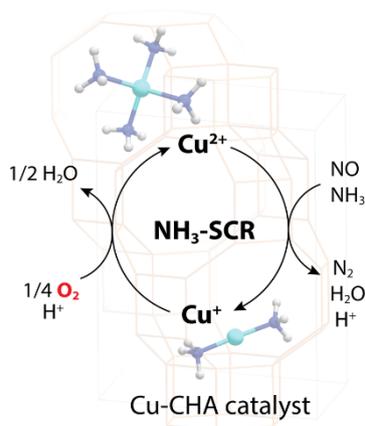
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Entry for the Table of Contents

FULL PAPER

The selective catalytic reduction of NO with ammonia (NH₃-SCR) over Cu-CHA zeolites is investigated using in situ spectroscopic XANES, IR, and UV-vis experiments. The transient kinetics of reduction and oxidation half cycles is studied in combination with the analysis of gas-phase product formation.



Dr. C. Liu, H. Kubota, T. Amada, Dr. K. Kon, Dr. T. Toyao, Dr. Z. Maeno, Dr. K. Ueda, Dr. J. Ohyama, Prof. A. Satsuma, T. Tanigawa, Dr. N. Tsunoji, Prof. T. Sano, Prof. K. Shimizu**

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In Situ Spectroscopic Studies on the Redox Cycle of NH₃-SCR over Cu-CHA Zeolites