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Speciation of Cu species in Cu–ZSM-5 after calcination

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Introduction

The state of Cu in Cu–ZSM-5 has been widely investigated using various experimental techniques because of its usefulness for the direct decomposition and the selective catalytic reduction of NO. The EXAFS spectroscopy is the most powerful technique to determine the local structure around the metal center and it is adoptable under *in-situ* conditions. In this study, the local structure around the Cu center in Cu–ZSM-5 has been determined by the highly-precise EXAFS measurements.

Experiments

The Cu–ZSM-5 sample was prepared by an ion-exchange method at ambient temperature and pH 5.2–5.8 using an aqueous solution of $Cu(NO_3)_2$ suspended by ZSM-5 (Tosoh, Si/Al = 11.9). The ZSM-5 powder adsorbed Cu(II) was filtered, washed by distilled water, dried at 393 K for 12 h in air, and calcined at 773 K in air for 1–2 h.

The conventional EXAFS spectra at the Cu K edge were measured at BL-NW2 at 298 and 773 K. The incident and transmitted X-ray intensities were measured by ionization chambers. The higher-order reflections at an Si(111) double-crystal monochromator were removed by a Rh-coated focusing mirror (2.8 mrad) and a Rh-coated double mirror (5.5 mrad). The X-ray energy was calibrated using the spectrum of a Cu foil. The EXAFS spectra of CuO were also measured for comparison.

The EXAFS oscillation functions were extracted by a usual procedure and the data over the range of $2 \leq k$ / $Å^{-1} \leq 20$ were used for the analysis. The FEFF-generated scattering amplitudes, the phase shifts, and the mean free paths of the photoelectron were used in the R-space curve fitting ($0.7 \leq R$ / Å ≤ 6), in which all the direct interactions and the multiple scatterings with the path length less than 6 Å were taken into account.

Results and Discussion

The k^3-weighted EXAFS oscillation function and the Fourier transform magnitude of Cu–ZSM-5 after the calcination are plotted in Figure 1 together with those of CuO at the same temperature. The EXAFS data of CuO at 298 K are excellently reproduced by the known structure model with four nearest-neighboring O atoms (1.96 Å), two distant O atoms (2.82 Å), total 10 Cu atoms, etc. The CuO structure is mainly retained at 773 K with the slight modification of interaction distances. The Cu–ZSM-5 powder shows a very similar EXAFS data to that of CuO at 298 K except for a small difference at R ~ 4–6 Å, which can be explained by an additional broad contribution from the Cu–Si interaction ($N = 12 \pm 4$ and $R = 4.6 \pm 0.8$ Å at 298 K and $N = 25 \pm 10$). These results indicate that the CuO-like cluster is incorporated in the intersection channel of the ZSM-5 framework.

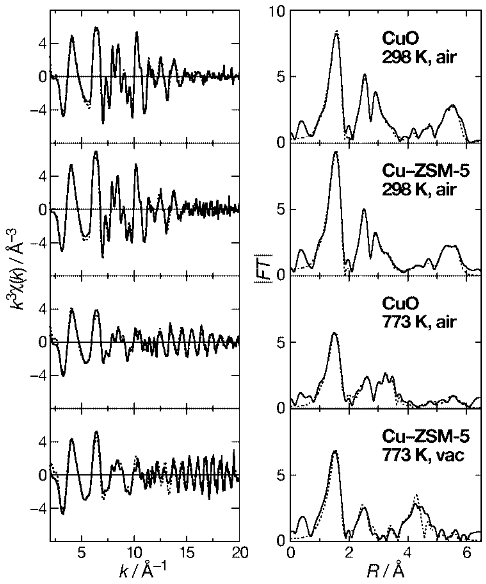

Figure 1: The k^3-weighted EXAFS oscillations and the Fourier transform magnitudes. The solid and dotted lines denote the observed and fitted values, respectively.

The elevation of temperature to 773 K drastically modifies the EXAFS data of Cu–ZSM-5 especially at R ~ 3–6 Å. The interactions with first and second neighboring atoms, O and Cu, respectively, are however unchanged, and the 4+2 O and 10 Cu atoms are well reproduce the observed data, strongly indicating that the local structure around the Cu center in Cu–ZSM-5 is quite similar to that of CuO within the distance range shorter than 3.5 Å. A peak observed at around 4.2 Å can be explained by the additional broad Cu–Si interaction ($N = 25 \pm 10$ and $R = 4.4 \pm 0.6$ Å). These structural aspects are first obtained by the wide-range precise EXAFS measurements.

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