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XAFS analysis of the states of copper ions in mesoporous silica

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Introduction

Copper-planted mesoporous silica MCM-41 (Cu-M41) was found to show high catalytic activity for enantioselective cyclopropanation of styrene derivatives and diazo compounds. In this reaction, the Cu-M41 catalysts must be evacuated at elevated temperatures for the appearance of the catalytic activity, indicating that some specialized states of copper ion would be the active species. The states of copper ions were characterized as a function of evacuation temperature by using XAFS spectroscopy.

Experimental

The parent mesoporous silica MCM-41 (M41) was prepared from colloidal silica and $C_{12}H_{25}N(CH_3)_3Br$ by hydrothermal treatment as mentioned in the literature [1]. The template-ion exchange (TIE) method was employed to prepare Cu-M41. In the TIE method, the as-synthesized M41 without the calcination was treated with an aqueous solution of copper nitrate at 353 K for 20 h, in which the copper ion was ion-exchanged with the template ion. The resulting powder was calcined at 873 K for 6 h in air to remove the templates. The Si/Cu ratios of the resulting sample were 17, 110, and 255. The XAFS spectra of Cu K-edge were recorded on beam line 9C of PF-KEK.

Results and discussion

Figure 1 shows the XANES spectra of Cu-M41 after evacuation at various temperatures. For all samples evacuated at room temperature (r.t.), a weak XANES band was observed at 8.978 keV. This band is assignable to the 1s–3d electronic transition of the Cu^{2+} ions [2]. With increasing evacuation temperature, two bands appeared at 8.983 and 8.993 keV, which are ascribed to the $1s–4p_{\pi}$ and $1s–4p_{\sigma}$ electronic transitions of the Cu^{+} ions, respectively [2]. The changes in these spectra indicated the reduction of Cu^{2+} to Cu^{+}. The intensities of the band at 8.983 keV in each spectrum at 473–873 K increased with increasing the Si/Cu ratio. It was found that the copper ions in Cu-M41 with lower copper content are easily reduced upon the evacuation at high temperature.

In the Fourier transforms of k^3-weighted EXAFS spectra (Figure 2), two bands were observed at around 1.5 and 2.6 Å (no phase-shift correction) for the r.t.-evacuated samples. The former band was assigned to back-scattering from the nearest neighboring oxygen atoms, and the latter one to back-scattering from the second nearest neighboring copper and oxygen atoms. For Cu-M41 with Si/Cu ratio of 17 the intensities of the bands at around 1.5 and 2.6 Å hardly changed by evacuating the samples at higher temperatures, while for Cu-M41 with higher Si/Cu ratios those greatly decreased. In particular, the latter band was remarkably decreased by the evacuation at 673 K and almost disappeared at 873 K. It was suggested that the supported-copper cluster is transformed to isolated Cu^{+} ions [2].

From these results, it was found that the reduction behavior of the copper ions in Cu-M41 significantly depends on copper content. In another experiment we have already found that the 673 K-evacuated Cu-M41 with lower copper content shows high catalytic activity for the above-mentioned reaction. Therefore, it was considered that the isolated Cu^{+} ions formed by heat treatment *in vacuo* could be the active sites. The detailed analysis of the coordination structure around copper ion and the estimation of the reduction mechanism are now in progress.

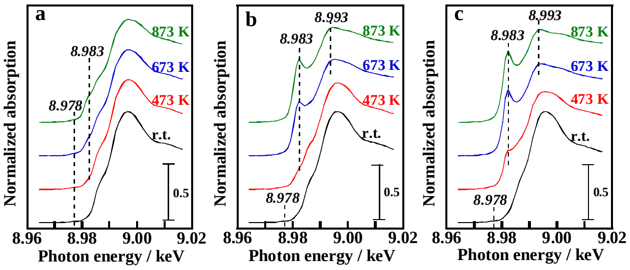

Figure 1: XANES spectra of Cu-M41. (a) Si/Cu=17, (b) 110, and (c) 255.

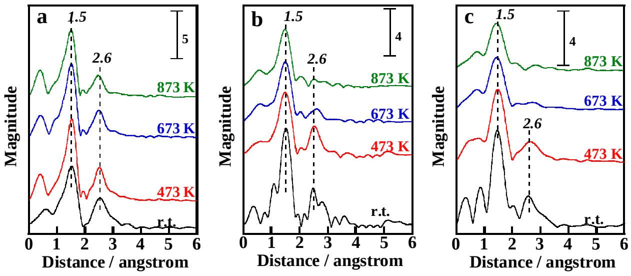

Figure 2: Fourier transforms of k^3-weighted EXAFS spectra of Cu-M41. (a) Si/Cu=17, (b) 110, and (c) 255.

References

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[2] G. T. Palomino et al., J. Phys. Chem. B 104, 4064 (2000).

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