

XAFS Analysis of Local Structure of Active Sites for Asymmetric Cyclopropanation on Copper Ion-planted Mesoporous Al-MCM-41

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1 Introduction

Copper ion-planted mesoporous Al-MCM-41 (Cu-AIM41) has been found to show high catalytic activity for asymmetric cyclopropanation of styrene derivatives and diazo compounds [1]. In this reaction, the Cu-AIM41 catalysts should be evacuated at elevated temperatures, such as 873 K, for the appearance of the catalytic activity. This result indicated that some specialized states of copper ion would be the active species. However, the states have little been clarified. In this study, the local structure of copper species on the Cu-AIM41 sample activated by the heat-treatment and subsequently modified by the addition of indane-derived bis(oxazoline) (IndaBOX) as chiral ligand were examined by using XAFS spectroscopy.

2 Experimental

AIM41 was synthesized by using high-purity colloidal silica (PL-3), aluminium nitrate, and $C_{12}H_{25}N(CH_3)_3Br$. The copper ion was planted in the as-synthesized AIM41 before organic template removal, according to the template-ion-exchange method [2]. The resulting powder was calcined at 873 K in air to remove the templates. The Si/Cu and Si/Al atomic ratios of the Cu-AIM41 sample obtained were 161 and 26, respectively. In the XAFS experiments, the Cu-AIM41 sample was evacuated at 873 K and was subsequently modified by adding CH_2Cl_2 solution of IndaBOX under an N_2 atmosphere. The dried sample at each process was pressed into self-supporting disk under an N_2 atmosphere. The XAFS spectra of Cu K-edge were recorded on beam line 9C of PF-KEK. The spectrum was treated by the REX2000 program. The curve-fitting analyses for Cu-O and Cu-N contributions were performed by using the FEFF6 code.

3 Results and Discussion

The XANES spectrum and Fourier transforms of k^3 -weighted EXAFS spectrum of Cu-AIM41 evacuated at 873 K are shown in Fig. 1. The XANES bands at 8.983 and 8.994 keV were observed. These bands were assignable to the 1s–4p electronic transitions of Cu^+ . Thus, it was clear that Cu^+ species are formed on Cu-AIM41 by the heat-treatment. In the EXAFS spectrum, a band due to back-scattering from the nearest neighboring oxygen atoms was observed at around 1.5 Å (no phase-shift correction). The structure parameters calculated from the EXAFS data using the least-square method are summarized in Table 1. The coordination number (CN) of Cu-O is 2.1 and the interatomic distance was 1.90 Å. It was found that Cu^+ species are coordinated with two lattice oxygen atoms in the AIM41.

When IndaBOX was added to the sample (Fig. 1a), the XANES band at 8.983 keV decreased in intensity. The band at around 1.5 Å (no phase shift correction) in the EXAFS spectra increased its intensity in comparison with the band obtained for the 873 K-treated sample. These results suggested that IndaBOX was coordinated to Cu^+ on AIM41. The curve-fitting analysis resulted in no changing CN of Cu-O but the elongation of Cu-O distance and the appearance of the contribution due to Cu-N. The CN of Cu-N was 2.1. Therefore, it was suggested the formation of the four-coordinate Cu^+ structure with two lattice oxygen atoms in the AIM41 and bidentate nitrogen atoms of IndaBOX. On the basis of the results, we propose that such four-coordinate Cu^+ species would act as active sites for asymmetric cyclopropanation.

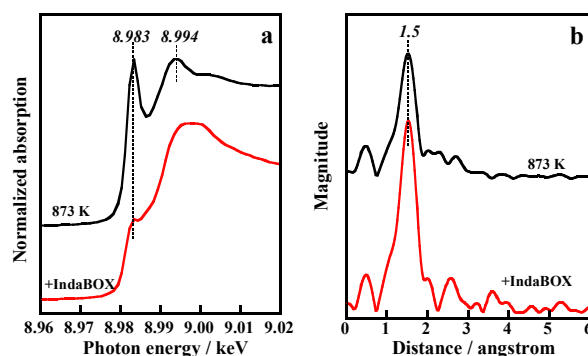


Fig. 1: (a) XANES spectra and (b) Fourier transforms of k^3 -weighted EXAFS spectra of Cu-AIM41 evacuated at 873 K and subsequently modified by adding IndaBOX.

Table 1: Structure parameters of Cu-AIM41 evacuated at 873 K and subsequently modified by the addition of IndaBOX

	shell	CN ^a	R (Å) ^b	σ^2 (Å ²) ^c
evac. at 873 K	Cu-O	2.1	1.90	0.0083
addition of IndaBOX	Cu-O	2.1	1.96	0.0104
	Cu-N	2.1	1.91	0.0058

^a Coordination number. ^b Interatomic distance. ^c Debye-Waller factor.

References

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