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Comparative studies of reduction behavior of copper ions in CuMFI, CuAlMCM-41, and CuMCM-41 via heat treatment in vacuo

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Introduction

Supported metal clusters inside the cages of molecular sieve hosts are expected to possess size-dependent electronic properties and non-linear optical features. The behavior of metal clusters in various reactions is dependent on their size and degree of homogeneous distribution in the host matrix. Moreover, the formation of Cu^{I} species during the reduction of zeolites containing Cu^{II} species is important for the catalytic activity, mainly for the selective reduction of NOx[1], and for their specific activity in N_2 adsorption at room temperature[2].

Despite the intensive research in catalysis, the formation process of various kinds of metal clusters and emergence of different species during the reduction process of metal ions confined in porous host materials is still not well understood. Detailed understanding of the reduction process of copper ion in the samples will be helpful in designing the other kinds of metal species in porous host materials, such as silver and gold ions, since these ions have the similar electronic structure in the outer shell and exhibit prominent catalytic features. In this report, the changes in the state of copper ions in four kinds of samples by heat treatment *in vacuo* have been studied by means of XAFS method. The samples used are as follows; CuMFI (Si/Al=11.9), CuAlMCM-41(IE) (Si/Al=11.5), CuAlMCM-41(TI) (Si/Al=11.5), and CuMCM-41, where we used the symbols of "IE" and "TI" signifying ion-exchange and template ion-exchange.

Results and discussion

Figure 1 shows the XANES and EXAFS spectra for CuMFI and CuAlMCM-41(IE) after evacuation at various temperatures. For both samples evacuated at 300 K, a weak XANES band is observed at 8.978 keV, and this band is assignable to the 1s–3d electronic transition of the divalent copper ion (Cu^{2+}). With increasing evacuation temperature, two bands appear at 8.983 and 8.993 keV, which are due to the 1s–$4p_\pi$ and 1s–$4p_\sigma$ electronic transitions of Cu^{+}, respectively: the reduction of Cu^{2+} to Cu^{+}. In the EXAFS spectra, a band due to back-scattering from the nearest neighboring oxygen atoms is observed at around 1.5 Å (no phase-shift correction) for the 300 K-treated samples, and the intensity of the band slightly decreases by evacuating the samples at higher temperatures. It was considered that the reduction properties of the exchanged copper ions in these samples are almost the same.

The XANES and EXAFS spectra of CuAlMCM-41(TI) and CuMCM-41(TI) evacuated at various temperatures are depicted in Fig. 2. For both samples evacuated at 300 or 473 K, the XANES band is observed at 8.978 keV; the exchanged copper ions take a divalent state. After evacuating these samples at above 673 K, quite prominent features of spectra were found, compared with those for CuMFI and CuAlMCM-41(IE); the new bands appear at 8.981 and 9.005 keV (especially in CuAlMCM-41(TI)), suggesting that the metallic copper species are formed in CuAlMCM-41(TI) and CuMCM-41(TI). This fact is supported from the EXAFS spectra; the band at 1.5 Å is drastically reduced in its intensity, and the first band assigned to the metallic copper species appears newly at 2.2 Å (no phase-shift correction). From these results, it was found that the Cu^{2+} species which were introduced by utilizing the template ion-exchange method are easily reduced to the metallic copper and the size of formed metal particles are different depending on the kinds of mother MCM-41 samples.

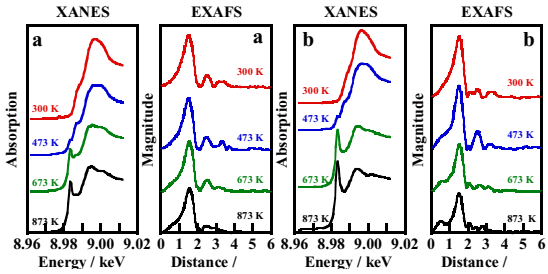

Figure 1: XANES and EXAFS spectra for (a) CuMFI and (b) CuAlMCM-41(IE).

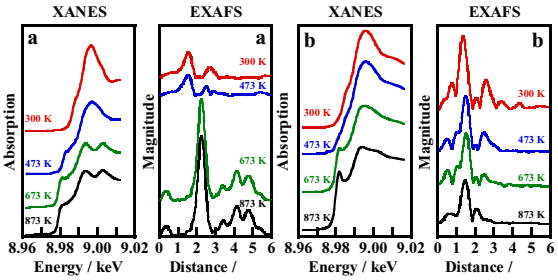

Figure 2: XANES and EXAFS spectra for (a) CuAlMCM-41(TI) and (b) CuMCM-41(TI).

Reference

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