

Further evidence supporting the existence of the dual-Cu⁺ sites in CuMFI zeolites being more effective for the adsorption of small organic molecules

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Introduction

Copper ion-exchanged zeolites exhibit the efficient adsorption and/or activation for the organic molecules such as methane[1], ethane[2], and ethyne[3]. The monovalent copper ions (Cu⁺) that had been formed in zeolites by the heat treatment *in vacuo* have so far been clarified to act as the active centers for these gases[1–3]. Very recently, we have found that by the interaction of Cu⁺ in the copper-ion-exchanged MFI zeolites (CuMFI) with ethyne at room temperature, new types of the adsorption complexes are formed in the samples[4]. Such the complexes consist of two Cu⁺ ions in CuMFI being bridged by ethyne: so-called, “dual species”. Furthermore, the dual-Cu⁺ sites in CuMFI have been suggested to contribute to the extremely strong adsorption of ethyne. The extent of the activation of the C≡C bond in ethyne molecule was confirmed to be larger on the dual-Cu⁺ sites than on the single-Cu⁺ site in CuMFI. However, our proposal has not been completely accepted yet since other groups have reported the different types of the adsorption complexes, namely, single types of the species[2,3,5]. The purpose of this work is to obtain the further evidence for the formation of the dual species composed of a small organic molecule with two carbon atoms (here, ethane (C₂H₆)) and two Cu⁺ ions in CuMFI by the Cu K-edge X-ray absorption fine structure (XAFS) measurements.

Results and discussion

The fourier transform of the EXAFS oscillations at the K-edge of the copper ion exchanged in CuMFI is shown in Figure 1. For the sample evacuated at 873 K, a band at 1.6 Å (no phase-shift correction) is observed, which is responsible for the back-scattering from the nearest neighboring zeolite-lattice oxygen atoms. The EXAFS datum obtained was analyzed through the least-square method using Cu₂O as the reference material for the oxygen around the copper to be the coordination number ($N_{\text{Cu-O}}$) = 2.6 and the distance ($r_{\text{Cu-O}}$) = 1.95 Å. It was considered from the $N_{\text{Cu-O}}$ = 2.6 value that the Cu⁺ ions in CuMFI are in the states coordinating two or three zeolite-lattice oxygen atoms. In addition to the band at 1.6 Å, other bands also appear at around 2.2 and 2.8 Å (no phase-shift correction). These bands are due to the copper–copper species in CuMFI, considering that the Cu⁺ ions in the sample are present at intervals of such distances. In practice, the analysis data obtained by the fitting of a Cu–Cu using the reference, copper metal were as follows: for the 2.2 Å-band, $N_{\text{Cu-Cu}}$ = 1.0 and $r_{\text{Cu-Cu}}$ =

2.63 Å; for the 2.8 Å-band, $N_{\text{Cu-Cu}}$ = 1.0 and $r_{\text{Cu-Cu}}$ = 3.29 Å. When a C₂H₆ gas was adsorbed onto CuMFI at room temperature, a characteristic band appears at around 2.5 Å (no phase-shift correction). This band almost disappears for the sample reevacuated at room temperature. The appearance of the 2.5 Å-band was also seen in the case of the C₂H₂ adsorption on CuMFI[4]. The EXAFS data were analyzed through the least-square method using Cu₂O and [KCu(CN)₂] as the reference materials for the oxygen and the carbon around the copper, respectively. For CuMFI adsorbing C₂H₆ gas, the $N_{\text{Cu-C}}$ and the $r_{\text{Cu-C}}$ were 1 and 1.96 Å, respectively, without any changes in the values of $N_{\text{Cu-O}}$ = 2.6 and $r_{\text{Cu-O}}$ = 1.95 Å by the fitting of two shells of Cu–O and Cu–C for the peak observed at around 1.6 Å. As for the characteristic band at around 2.5 Å, the $N_{\text{Cu-C}}$ and the $r_{\text{Cu-C}}$ were evaluated to be 0.8 and 2.94 Å, respectively. These results suggest the existence of the dual species

composed of two Cu⁺ ions in CuMFI being bridged by C₂H₆. The $r_{\text{Cu-O}}$ -value between copper and zeolite-lattice oxygen hardly changed before and after the adsorption of C₂H₆ (1.95 Å). The fact differs from the case of the C₂H₂ adsorption onto CuMFI; in C₂H₂ adsorption the distance of Cu–O lengthened from 1.95 and 1.97 Å by the strong interaction with C₂H₂[4]. Therefore, it was also evidenced from the XAFS measurements that the interaction of Cu⁺ with C₂H₆ is not so strong, in comparison with that with C₂H₂.

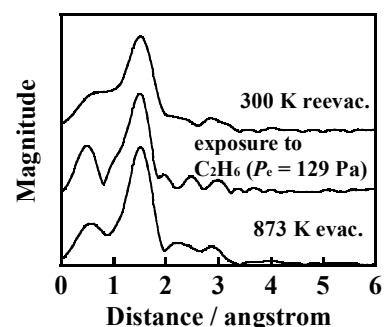


Figure 1. EXAFS spectra.

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