Time-resolved study on the change of the state of copper ions in CuMFI zeolite in the hydration process

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Introduction
A copper-ion-exchanged MFI zeolite (CuMFI), which exhibits high levels of catalytic activity for the direct decomposition of NO, strongly adsorbs N₂ molecules, even at room temperature[1]; monovalent copper ions (Cu⁺) formed in CuMFI by the heat treatment in vacuo act as the active centers. More recently, we have elucidated for the first time on the coordination environment around copper ion before and after N₂ adsorption by employing a conventional X-ray absorption fine structure (XAFS) spectroscopy[2,3]. In the NO decomposition or N₂ adsorption process, the catalytic activity and adsorption capability of CuMFI are known to be lower in the presence of water vapor; the effect of water vapor on the state of copper ions in CuMFI is considered. The disproportionation reaction (2Cu⁺ → Cu²⁺ + Cu⁰) has thus far been reported to occur when the sample is exposed to water vapor under a certain pressure[4,5]. Furthermore, the formed metallic copper species have been transformed into the monovalent copper ions after reevacuation at high temperatures. However, their details have not yet been clarified completely.

In this study, we examined the change of the state of copper ions in CuMFI in the hydration process by the Dispersive XAFS (DXAFS) method.

Experimental
CuMFI (Si/Al=11.9; copper-ion-exchange level: 126%) was prepared in a mixture of each of aqueous solution of Cu(CH₃COO)₂ and of NH₄CH₃COO at room temperature[2]. The measurement of DXAFS spectra was performed at the same time when the 873 K-treated CuMFI sample was exposed to water vapor of 2.4 kPa at room temperature. The spectra were obtained every 120 ms after exposure to water vapor. The detailed setup for the DXAFS measurement is shown in Figure 1.

Results and discussion
The DXAFS spectra are represented in Figure 2. For the 873 K-treated sample, the band ascribed to the 1s-4p electronic transition due to the Cu⁺ ions is observed at 8.983 keV. When the sample is exposed to water vapor, the intensity of this band starts to decrease, and concomitantly, the band at 8.997 keV, which is assigned to the 1s-4p electronic transition of the Cu²⁺ ions, increases in its intensity. The position of 8.997 keV band is shifted to the position of 8.999 keV in the photon energy with an increase in the exposure time, suggesting that the metallic copper species were formed. From these results, it was shown that in the initial exposure process the Cu⁺ ions are oxidized into Cu²⁺ followed by the formation of metallic copper. The detailed analysis of the change of the state of copper ions and the investigation of the correlation between the formation of Cu²⁺ and Cu⁰ to the exposure time are in progress.

Figure 2: DXAFS spectra (a) and difference spectra (b) for CuMFI after exposure to water vapor. The difference spectra were subtracted the spectrum at 0 ms of (a) from other spectra.

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References
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