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Structural information on the states of acetylene adsorbed on CuMFI zeolite at 298 K

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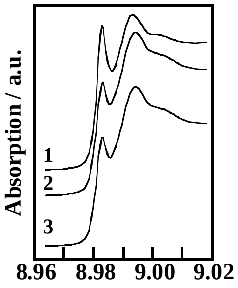
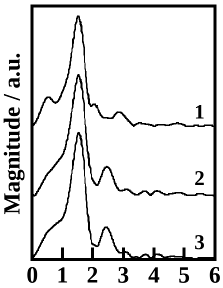
Introduction

A copper-ion-exchanged MFI zeolite (CuMFI) has been well-known to exert high levels of catalytic activity for the direct decomposition of NO into N_2 and O_2[1]. This material has also specific features for N_2, H_2, O_2, and CH_4 at temperatures around 300 K[2–4]; CuMFI strongly interacts with these gases, even at 298 K. The X-ray absorption fine structure (XAFS) technique is powerful method to know the electronic state and the coordination structure of the active species formed on the CuMFI sample. We have so far carried out evaluating the state of the active centers on CuMFI for the specific room-temperature adsorptions by utilizing the XAFS method[2,4,5]. It has consequently been found that the monovalent copper ions (Cu^+) formed in CuMFI by evacuating the sample at high temperatures act as the effective sites for the various gas-adsorptions. Although the specific adsorption properties of inorganic molecules at 298 K on CuMFI have thus far been examined by many researchers, including our group, it can be also considered to be important to investigate the interaction of organic molecules with CuMFI from the viewpoint of the activation of CH and/or CC bonds in their molecules. An acetylene, C_2H_2, gas (i.e., simple organic molecule), which has been used as a raw material for fine chemicals such as the fragrance and hydrocarbons in the field of petrochemistry, has been accepted to be hard to handle because of an explosive factor and an abundant reactivity and also to be difficult to extract one component among the mixed gases. Thus, the development of the substances adsorbing C_2H_2 selectively is hoped now. As mentioned above, CuMFI sample is splendid material adsorbing anything. In this short contribution, we examined the adsorption property of C_2H_2 on CuMFI at 298 K. The analysis of the state of active sites on CuMFI for C_2H_2, as well as the evaluation of the conformation of the C_2H_2 adsorbed on sample, were performed by using the XAFS technique.

Results and discussion

The X-ray absorption near edge structure (XANES) spectra and extended X-ray absorption fine structure (EXAFS) functions for CuMFI (Si/Al=11.9; Cu/Al=65) evacuated at 873 K (1), exposed to C_2H_2 gas (P_e=0.02 kPa) at 298 K (2), and then re-evacuated at 298 K (3) are shown in Figs. 1 and 2, respectively. For CuMFI evacuated at 873 K, two bands in the XANES spectra, which are attributed to the 1s–4p electronic transitions of Cu^+ in sample, are observed at 8.982 and 8.993 keV, respectively. The intensity of the former band markedly decreases after exposing the sample to C_2H_2 gas at 298 K, compared with that of the latter band. When the sample is re-evacuated at 298 K, the intensity of this band hardly changes. The results suggest the existence of the strong interaction between C_2H_2 molecules and Cu^+ ions in CuMFI. In the EXAFS function of the 873 K-treated sample, a band is observed at 1.52 Å (no phase-shift correction), which is due to the backscattering from the nearest neighboring oxygen atoms. Analysis of the EXAFS data clarified that the coordination number (N) and the distance (r) of oxygen around copper in sample are 2.6 and 1.95 Å, respectively. The band is also seen at around 2.87 Å. Appearance of this band is considered to be due to the copper existing in the neighborhood of the copper, and the $N_{Cu–Cu}$ and the $r_{Cu–Cu}$ were estimated to be 1.3 and 3.29 Å, respectively. By exposing the sample to C_2H_2 gas, the band observed at around 1.5 Å slightly shifts toward the longer distance in its maximum position and increases in its width, and the newly band also appears at 2.47 Å (no phase-shift correction). No the latter band has been observed for the adsorption of N_2. Furthermore, these bands hardly change by re-evacuation at 298 K. Therefore, the present results may give a hint for the conformation of C_2H_2 on CuMFI. The 1.5 Å band was analyzed using two shell (i.e., Cu–O and Cu–C) fitting technique: $N_{Cu–O}$=2.6 and $r_{Cu–O}$=1.97 Å; $N_{Cu–C}$=1.0 and $r_{Cu–C}$=1.88 Å. The parameters estimated for the 2.47 Å band were $N_{Cu–C}$=1.2, $r_{Cu–C}$=2.95 Å. The results of the analysis of spectral data suggest the presence of several types of the adsorbed C_2H_2 on Cu^+ in CuMFI. Taking accounts of the results of the density functional theory calculations, the further study on the conformation of the C_2H_2 adsorbed onto Cu^+ in CuMFI and the construction of the adsorption models are in progress.





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