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Structural Analysis of the Adsorbed Dioxygen Species on Copper Ion-Exchanged MFI Zeolite at Room Temperature

Yuusuke Sogawa, Atsushi Itadani, Hiroe Torigoe, Akira Oda, Mitsuhiro Ushio, Masayasu Nishi, Takahiro Ohkubo, and Yasushige Kuroda*
Okayama University, Okayama 700-8530, Japan

1 Introduction

Copper ion-exchanged MFI zeolite (CuMFI) has been well-known to exhibit high levels of catalytic activity for the direct decomposition of NO [1]. This material also has surprising adsorption features for N_2, H_2, and Xe; CuMFI strongly interacts with these gases, even at room temperature [2]. The active center in CuMFI for such phenomena has been accepted to be the monovalent copper ion (Cu^+) which is formed by the evacuation at high temperatures [1,2]. Recently, Groothaert et al. have reported that CuMFI interacts with O_2 and consequently works as the oxidation catalyst for CH_4; the methanol synthesis through the reaction of CH_4 with the adsorbed O_2 is achieved [3]. However, the state of the adsorbed O_2 species on CuMFI and the reaction mechanism are not completely clarified, although some reports have so far been made on them [4]. We believe that the elucidation of the interaction between CuMFI and O_2 is essential to understand the above subject. In this work, we examined the interaction of CuMFI with O_2 at room temperature by the X-ray absorption fine structure (XAFS) measurement.

2 Experiment

CuMFI (Si/Al = 11.9; ion-exchange level = 131%) was prepared at room temperature in a mixed aqueous solution of $Cu(CH_3COO)_2$ and NH_4CH_3COO. The XAFS spectra were collected in transmission mode at the beamline PF-9C equipped with a double crystal monochromator of Si(111). The self-supporting disk was placed into an in situ sample cell which is capable of pre-treatment of sample and gas introduction in situ.

3 Results and Discussion

Fig. 1 shows the X-ray absorption near edge structure (XANES) spectra and the Fourier transform of the extended X-ray absorption fine structure (EXAFS) oscillations at the K-edge of the copper-ion exchanged in CuMFI under various atmospheres. For the 873 K-treated sample, two characteristic bands are observed at 8.983 and 8.993 keV, which are due to the 1s–4p_π and 1s–4p_σ electronic transitions of Cu^+ in the sample, respectively. Appearance of these bands is explained by considering that the Cu^+ ions are in a linear or a planar coordination state. When the CuMFI sample was exposed to O_2 gas at room temperature, the intensity of the band at 8.983 keV is considerably smaller than that of the band for the sample evacuated at 873 K, being interpreted that a linear or a planar coordination structure around Cu^+ in CuMFI was deformed by the interaction with O_2. The intensity of the 8.983 keV-band for the sample re-evacuated at room temperature hardly changes. The result clearly indicates the existence of the strong interaction between Cu^+ and O_2. In the EXAFS spectrum of the 873 K-treated sample, a band is observed at around 1.6 Å (no phase-shift correction), which is due to the backscattering from the nearest neighboring oxygen atoms. The analysis of the EXAFS data clarified that the Cu^+ ions are in the two- or three-coordination state with lattice oxygen atoms (Cu–O distance: 1.95 Å). In addition, in the case of the present CuMFI sample, a peculiar backscattering at around 2.2 Å (no phase-shift correction) attributed to the Cu^+–Cu^+ interaction is confirmed (analysis data: coordination number ($N_{Cu–Cu}$) = 0.8; distance ($r_{Cu–Cu}$) = 2.65 Å). For CuMFI adsorbing O_2 strongly, the band at 1.6 Å increases in its intensity and width, compared with that for the sample evacuated at 873 K. Simultaneously, an additional band clearly appears at around 2.5 Å (no phase-shift correction). For the band at 1.6 Å, the analysis values were evaluated to be $N_{Cu–O}$ = 4.2 and $r_{Cu–O}$ = 1.94 Å (including lattice oxygen). For the band at 2.5 Å, the fitting result of Cu^+–Cu^+ was better than that of Cu–O ($N_{Cu–Cu}$ = 0.8; $r_{Cu–Cu}$ = 2.90 Å). The distance of Cu–Cu was found to be longer after the interaction with O_2 than that before one. These results suggest the existence of the species composed of two Cu^+ ions bridging O_2. Taking into other experimental and calculational data consideration, further discussion will be necessary. The details are in progress.

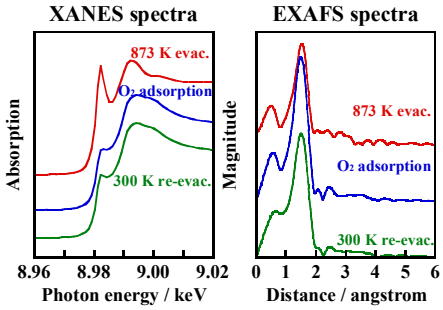

Fig. 1. XANES and EXAFS spectra for CuMFI.

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* kuroda@cc.okayama-u.ac.jp