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XAFS study of specific methane adsorption at 298 K on CuMFI zeolite

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Introduction

Copper-ion-exchanged MFI-type zeolite (CuMFI) exhibits interesting property for an inert N_2 gas; this material adsorbs N_2, even at room temperature[1,2]. There are few materials that are capable of adsorbing N_2 molecules easily, safely, and rapidly at temperatures around 298 K since N_2 molecule is accepted to be inactive supercritical gas at such the temperatures. The CuMFI sample can be therefore considered to be outstanding and interesting material among various kinds of adsorbents developed so far. It is a great meaning to clarify the adsorption features against other gases associated with CuMFI. Recently, we have found that CuMFI is a good adsorbent for O_2 and activates adsorbed O_2 under irradiation, resulting in forming a certain species[3]. Groothaert et al. has reported that such a species plays an important role in methane (CH_4) activation[4]. The activation of C–H bond is very important from a fundamental point of view and for the conversion of common inexpensive alkanes into valuable substances. Thus, it may have become feasible to activate C–H bond in CH_4 molecule if the CuMFI sample is utilized as a catalyst. However, there seems to be few reports describing the interaction of CH_4 with CuMFI.

In this study, we examined the adsorption property of CH_4 at 298 K on CuMFI, and the conformation of the adsorbed CH_4 on the effective sites existing in sample was evaluated by using the X-ray absorption fine structure (XAFS) technique.

Results and discussion

The volumetric adsorption measurements of CH_4 at 298 K which were carried out in our laboratory elucidated that CuMFI sample (Si/Al=11.9; ion-exchange level: 112%) strongly interacts with CH_4, in comparison with other samples[5]. Moreover, the IR spectra for CuMFI exposed to CH_4 gas at 298 K suggested the possibility of the C–H activation in CH_4 by the use of the CuMFI catalyst; the stretching vibrations of C–H bond in CH_4 that are ordinarily IR inactive were observed. For such the specific interaction of CH_4 with CuMFI at 298 K, we intended to elucidate the coordination structure around the effective sites on the sample adsorbing CH_4.

The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) functions for CuMFI treated at various conditions are shown in Fig. 1. For the 873 K-treated CuMFI, two XANES bands due to the 1s–4p_z and 1s–4$p_{x,y}$ electronic transitions of Cu^+ that had been formed in sample by treatment at 873 K in vacuo are observed at 8.982 and 8.993 keV, respectively. When exposing the sample to CH_4 gas at 298 K, the intensity of the band at 8.982 keV slightly decreases, and the absorption maximum of the 8.993 keV band shifts toward the lower energy side. The spectra for the sample re-evacuated at 298 K recovered to its original one. These spectral changes suggest the interaction of CH_4 with Cu^+, considering that such the interaction with CH_4 exerts an influence on the energy state of 4p levels through the mixing with 3d, 4s, and 4p orbitals of copper ion. In the EXAFS function of the 873 K-treated sample, a band due to the backscattering from the nearest neighboring oxygen atoms is observed at 1.52 Å (no phase-shift correction). The parameters obtained by using the least-square method were as follows: $N_{Cu–O}$=2.57±0.18, $r_{Cu–O}$=1.95±0.01 Å, $\sigma^2_{Cu–O}$=0.0098±0.0001 $Å^2$. The band at around 1.5 Å observed after exposing the sample to CH_4 increases in its width and decreases in its intensity, compared with that for the 873 K-treated sample. Moreover, a new band appears at 2.35 Å (no phase-shift correction). The latter band disappeared by re-evacuation at 298 K, and the width of the band observed at around 1.5 Å recovered to its original state. The around 1.5 Å band for the sample interacting with CH_4 was analyzed by two shell (i.e., Cu–O and Cu–C) fitting technique: $N_{Cu–O}$=2.56±0.20, $r_{Cu–O}$=1.95±0.01 Å, $\sigma^2_{Cu–O}$=0.0128±0.0001 $Å^2$; $N_{Cu–C}$=0.89±0.20, $r_{Cu–C}$=2.09±0.03 Å, $\sigma^2_{Cu–C}$=0.0094±0.0006 $Å^2$. Furthermore, the parameters estimated for the band at 2.35 Å were $N_{Cu–C}$=1.4±0.9, $r_{Cu–C}$=2.62±0.06 Å, $\sigma^2_{Cu–C}$=0.0125±0.0025 $Å^2$. The results of the analysis of spectral data suggest the presence of at least two types of the adsorbed CH_4 on Cu^+ in CuMFI. These insights were supposed from the density functional theory calculations, and the adsorption models of CH_4 on CuMFI were proposed[5].

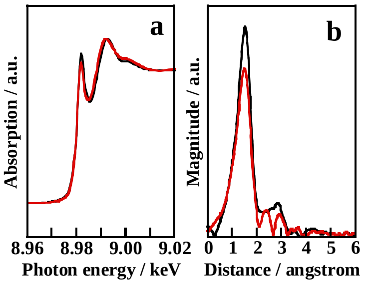

Fig. 1. (a) XANES spectra and (b) EXAFS functions for CuMFI. The black and red lines represent the spectra obtained for the sample evacuated at 873 K and exposed to CH_4 gas of 14.7 kPa, respectively.

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