NW10A/2012G597

Model study on the efficient CO_2 adsorption site in BaMFI by applying an in situ XAFS method

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1 Introduction

Since a carbon dioxide (CO_2) gas has been well-known to be one of greenhouse gases having a potential to cause global warming, many efforts have so far been made on the CO_2 reduction in the atmosphere by using various types of the sorption materials, such as zeolite, MOF, and so on. However, CO_2 reduction is not so easy because the CO_2 molecule is chemically stable; as far as we know, the CO_2 sorption material which meets today's worldwide demands has not been designed. Under such circumstances, recently, we have found that divalent barium ion modified MFI-type zeolite (BaMFI) has an excellent CO_2 adsorption feature at low pressure region (P_e= 0.1 kPa) and at room temperature as compared with other metal ion modified MFI samples. However, there is no understanding of the origin of the excellent sorption feature; the state of the active species in BaMFI is unclear. Clarification of this behavior is very important for the development of the today's chemical design for the CO_2 sorption material. In the present work, we intended to clarify the state of the active barium species in BaMFI by applying a XAFS method.

2 Experiment

The BaMFI sample was prepared by treating sodium-form MFI (Si/Al= 11.9), which was purchased from Tosoh Co., Japan, in an aqueous solution of $Ba(NO_3)_2$ with stirring at 353 K for 1 h. Barium-ion-exchange level for the obtained sample was estimated to be 149%. The sample was evacuated at 873 K, and CO_2 adsorption isotherms or XAFS study were carried out in an in situ condition at 298 K. In situ XAFS measurements were performed at KEK-AR (NW10A) on the Ba K edge.

3 Results and Discussion

CO_2 adsorption property of the prepared BaMFI sample was examined by measurement of CO_2 adsorption isotherms at 298 K. As a result, a Langmuir type adsorption isotherm was obtained, which indicates that the BaMFI sample interacted strongly with the CO_2 molecule even at low pressure. Interestingly, quantification of the adsorbed CO_2 molecule at low pressure (P_e= 0.1 kPa) definitely suggested that respective barium ions interacted with a single CO_2 molecule; proportion of the total number of the ion-exchanged Ba^{2+} to adsorbed amount of CO_2 was evaluated to be almost one. These mean that the barium species which have superior CO_2 adsorption feature is selectively formed in the MFI pore.

To identify the state of the barium species with superior CO_2 adsorption feature, X-ray absorption fine structure (XAFS) spectroscopy which is an excellent technique for the studying the coordination structure around a target atom was used. Figure 1 shows the EXAFS spectrum for the BaMFI sample. The BaMFI sample exhibits two prominent bands at 2.05 Å and 3.09 Å (no-phase shift correction). Curve fitting analysis by the least-squares method clearly revealed that the band at 2.05 Å is due to the backscattering from the first nearest oxygen atoms that exist at an ion-exchangeable site, and the band at 3.09 Å is due to the second nearest barium ions. The coordination number (CN) of O and Ba for the first and second shells are almost three and one, which indicates the $[BaOBa]^{2+}$ species, as shown in Figure 2, is formed in the prepared BaMFI sample. Our claim (i.e., formation of the $[BaOBa]^{2+}$ species) was also strongly supported by other spectroscopic studies, such as the IR measurement using a probe molecule. Considering these experimental data, we may say that the $[BaOBa]^{2+}$ species encapsulated in MFI shows an excellent CO_2 adsorption feature.

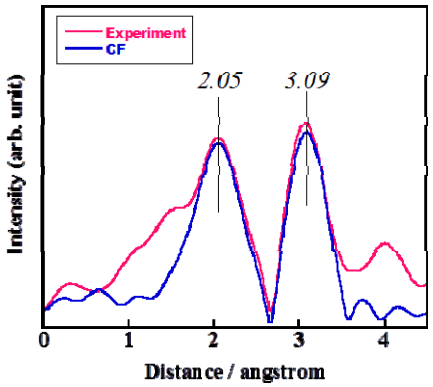

Figure 1. EXAFS spectrum for the BaMFI: (pink) experimental data; (blue) curve fitting data.

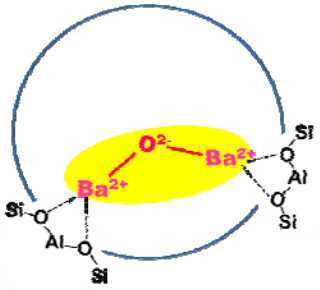

Figure 2. Active site for CO_2 adsorption in BaMFI.

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