

Dynamic change in framework structures of Cu-complex material

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Introduction

Coordination polymers with designated frameworks are of interest due to their characteristic structural properties. Their frameworks with nanopores are suitable for the storage of a wide range of molecules such as methane or hydrogen. Li and Kaneko have found that the Cu-complex material $[\text{Cu}(\text{bpy})(\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{bpy})]_n$ (LPC) shows a gate effect on CO_2 adsorption that means the steep increase of the amount adsorbed at specific relative pressure[1]. Although the characteristic adsorption properties can be found after the heat treatment to remove the water molecules, the LPC cannot retain its single-crystallinity upon the removal of water molecules. These results suggest that the dynamic change in the coordination structures will be occurred by the removable of water molecules. In this work, we have characterized the dynamic behavior of the frameworks in the LPC by XAFS techniques.

Experimental

The LPC materials were prepared by the addition of an aqueous solution of copper(II) tetrafluoroborate to a methanol solution of 4,4'-bipyridine (bpy). The detail preparation methods are described elsewhere [2]. The LPCs were heated at 378 K in *vacuo* to remove water molecules in their frameworks. The LPCs were kept in XAFS cell with Kapton film windows. The XAFS spectra were recorded in transmission mode at BL-10B beam line.

Results and Discussion

Figure 1 shows the Fourier transforms (FTs) of $\chi(k)$ extracted from the EXAFS spectra of the as synthesis and the heat-treated LPCs. The changes in the FT were observed after the heat-treatment to give the dehydrated forms. In order to investigate the coordination structures, the structural parameters have been calculated by curve fitting method. The results of best-fitted data for atomic distances of the first shell were tabulated in Table 1. The results of the local structures for the as synthesis LPC are almost consistent with those calculated from XRD data of the single crystal. The XANES spectra of the as synthesis and the heat-treated LPC show main peaks at the energy range from 8980 to 9000 eV. These peaks are assigned to the dipole-allowed transition from $1s$ to $4p$ states in molecular orbital. The XANES spectra of the heat-treated LPC did not drastically change compared with that of the as synthesis LPC, indicating the heat-treated

LPC retain the O_h symmetry around a Cu atom irrespective of the removal of water molecules. These results suggest that the bpy pillar ligands coordinate to Cu ions instead of water molecules. The nearest-neighbor atomic distances of the heat-treated LPC were also shown in Table 1. The curve fitting results also suggest that the Cu ions are coordinated by the bpy units to form the 2D square grid layers and that the BF_4^- ions act as pillars to hold tow layers together.

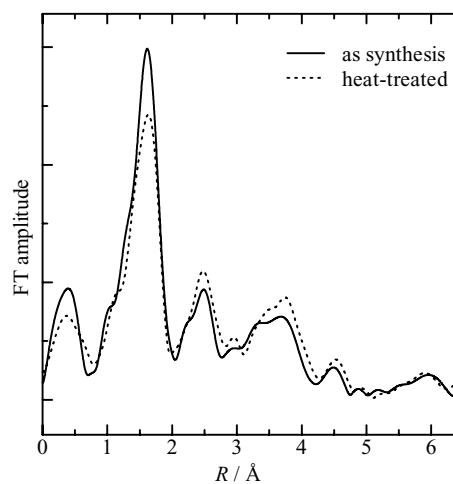


Figure 1. The Fourier transforms of $\chi(k)$ extracted from EXAFS spectra for as synthesis and heat-treated LPCs.

Table 1. Nearest-neighbour atomic distances of as synthesis (R_{LPC}) and heat-treated (R_{HT}) LPCs. The R_{XRD} denotes the distances calculated from the single-crystal XRD analysis.

	$R_{\text{LPC}} / \text{\AA}$	$R_{\text{XRD}} / \text{\AA}$	$R_{\text{HT}} / \text{\AA}$
Cu-O	1.97	1.97	-
Cu-N	1.99	1.99	1.99
Cu-F	2.41	2.39	2.19

References

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