KEK-PF 7C, 9C, SPring-8 01B1/2011G033, 2011A1977

Structure of Copper Hydroxy Anions in the Layered Double Hydroxides for the Photocatalytic Conversion of Carbon Dioxide to Methanol

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1. Introduction

The number of reports of CO_2 photoreduction has been dramatically increased in a couple of years [1] in expectations of reducing the atmospheric CO_2 concentration and also obtaining useful chemicals, *e.g.* formic acid and methanol. Layered double hydroxides (LDHs) of $[Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O$ photocatalytically converted CO_2 to methanol using hydrogen as a reducing agent [2,3]. The photocatalytic role of $[Cu(OH)_4]^{2-}$ sites should be essential and the structure was investigated using Cu K-edge XANES.

2. Methods

The synthesis of LDH samples starting from $[CuCl_4]^{2-}$ was described in literature [3]. Cu K-edge XAFS spectra were measured on a beamline 9C and 7C in KEK-PF and also on a beamline 01B1 at SPring-8. The sample disk was set in an in-situ cell equipped with PEN/Kapton film windows.

3. Results and Discussion

Cu K-edge EXAFS spectrum is shown in Figure 1A for $[Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O$. Two intense peaks in the Fourier transform (FT) at 0.16 and 0.27 nm (phase shift uncorrected) derived from Cu–O and Cu···Zn (or Cu···Ga) pairs, respectively, appeared in Figure 1B. But a peak derived from Cu–Cl bond(s) at ~0.195 nm (phase shift uncorrected) was not present. No Cu–Cl peaks were found in the FT for this LDH photocatalyst, demonstrating the complete hydrolysis of $[CuCl_4]^{2-}$ into $[Cu(OH)_4]^{2-}$ during the synthesis.

$$[CuCl_4]^{2-} + 4NaOH \rightarrow [Cu(OH)_4]^{2-} + 4NaCl \cdots(1)$$

$$2[Zn_3Ga(OH)_8]^+ + [Cu(OH)_4]^{2-} + mH_2O \rightleftarrows [Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O \cdots(2)$$

Based on the Cu K-edge X-ray absorption near-edge structure (XANES) spectra and the theoretical simulation, complex formation between cationic layer and $[Cu(OH)_4]^{2-}$ anion was suggested (Figure 2).

$$[Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O \rightleftarrows Zn_6Ga_2(OH)_{13}\{(\mu\text{–}O)_3Cu(OH)\}\cdot mH_2O + 3H_2O \cdots(3)$$

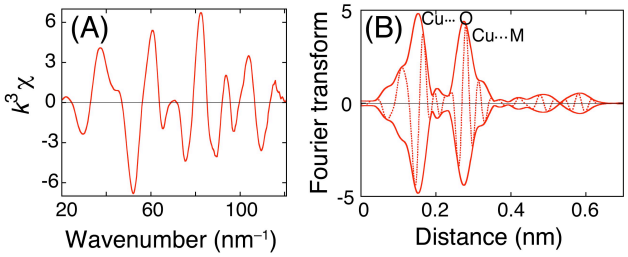

Figure 1. Cu K-edge EXAFS spectra for $[Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O$. (A) k^3-weighted EXAFS χ-function and (B) its associated FT. The solid and dotted lines represent the magnitude and the imaginary part in (B).

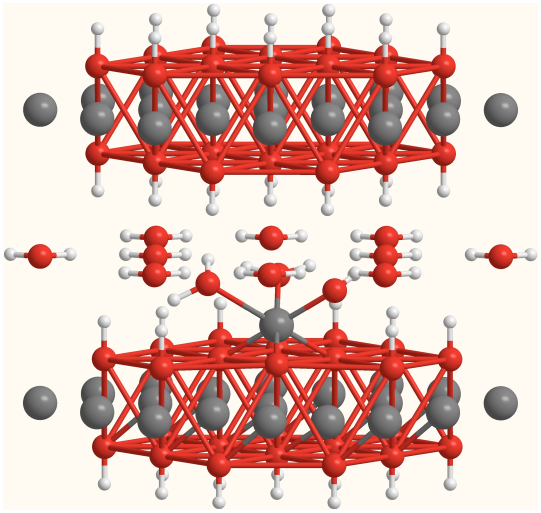

Figure 2. Proposed structure of $[Zn_3Ga(OH)_8]^+_2[Cu(OH)_4]^{2-}\cdot mH_2O$.

The interlayer $(\mu\text{–}O)_3Cu(OH)$ site was 5.9 times more active than the octahedral Cu sites in the octahedralCu sites in the cationic layers of $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+$ for the photocatalytic conversion of CO_2 to methanol.

References

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