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Role of copper in the CO_2 photo-reduction to fuels using Zn-Cu-Al/Ga layered double hydroxides

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Introduction

Layered double hydroxides formulated as $[Zn_{3-x}Cu_xM^{III}(OH)_8]_2(CO_3)\cdot mH_2O$ (M^{III} = Al, Ga; x = 0 – 1.5) were synthesized and applied to the CO_2 photo-conversion to fuels. The interlayer carbonate ions were reduced to methanol under UV-visible light and gaseous CO_2 was further photo-converted to interlayer carbonate-like species and finally to methanol. In this study, the Cu site structure and its photo-catalytic role to produce methanol were investigated using XAFS.

Experimental section

For the synthesis of $[Zn_3M^{III}(OH)_8]_2(CO_3)\cdot mH_2O$ (M = Al, Ga), a mixed solution of 0.75 M $Zn(NO_3)_2\cdot 6H_2O$ and 0.25 M $M(NO_3)_3\cdot mH_2O$ was added to 0.075 M Na_2CO_3 at 290 K, keeping the pH value 8 by the NaOH addition. It was aged at 353K for 1 d. Obtained precipitates were filtered, washed, and dried. For the synthesis of $[Zn_{1.5}Cu_{1.5}M^{III}(OH)_8]_2(CO_3)\cdot mH_2O$ (M = Al, Ga), the molar ratio of Zn, Cu, and M^{III} nitrates was set to 3:3:2 for the initial mixed solution of 0.75 M Zn+Cu nitrates and 0.25 M M^{III} nitrate.

Zn, Cu and Ga K-edge XAFS measurements were performed at beamline 7C, 9C and 10A in a transmission mode at 30 – 290 K.

Results and Discussion

In the Cu K-edge XANES for $[Zn_{1.5}Cu_{1.5}Al(OH)_8]_2(CO_3)\cdot mH_2O$, an intense peak at 8998.8 eV appeared accompanied with three weak, broad peaks at 9015, 9043, and 9051 eV (Figure 1b). This spectrum pattern resembled well with those of Zn K-edge spectrum for the same sample and of theoretically generated XANES for complete O_h layer structure model $CuZn_{44}Al_{12}(OH)_{72}$ (spectrum d). In the XANES for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2(CO_3)\cdot mH_2O$ (spectrum c), a first intense peak at 8999.2 eV and two weak, broad peaks at 9016 and 9047 eV were observed. The pattern resembled well with those of Zn and Ga K-edge spectra for the same sample and of theoretically generated XANES for complete O_h layer structure model $CuZn_{56}(OH)_{72}$ (spectrum e). Note that the scattering of photoelectrons should be very similar for $_{30}Zn$ and $_{31}Ga$. Thus, predominant occupation of Cu on the O_h sites in the LDH layers was confirmed.

On heating $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2(CO_3)\cdot mH_2O$ sample, the intensity of post-edge peak at 9016 eV for fresh sample (Figure 2c) decreased (spectrum c-383), suggesting the loss of photoelectron scattering atoms, *e.g.* interlayer H_2O molecules and CO_3^{2-} ions. This behavior was supported by theoretical calculations of XANES spectra for $CuZn_{56}(OH)_{72}\cdot 38H_2O$ model and corresponding model to lose all of interlayer water molecules by FEFF 8.4 (Figure 2f→e). Upon introduction of CO_2 to 383 K-heated sample, the peak intensity increased back (spectrum c-CO_2-290, c-CO_2-423). This reversible trend was observed only for LDH samples containing the Cu sites in the layers, not for $[Zn_3Al(OH)_8]_2(CO_3)\cdot mH_2O$ or $[Zn_3Ga(OH)_8]_2(CO_3)\cdot mH_2O$. Thus, the Cu sites act to bind CO_2 molecules and lead to photo-catalytically reduce to methanol.

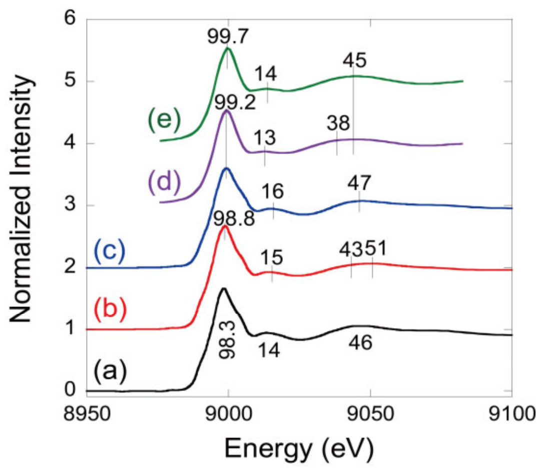

Figure 1. Normalized Cu K-edge XANES for CuO (a), $[Zn_{1.5}Cu_{1.5}Al(OH)_8]_2(CO_3)\cdot mH_2O$ (b), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2(CO_3)\cdot mH_2O$ (c), $CuZn_{44}Al_{12}(OH)_{72}$ model (d), and $CuZn_{56}(OH)_{72}$ model (e).

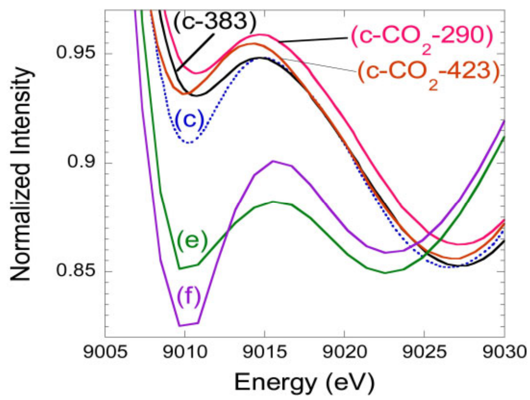

Figure 2. Normalized Cu K-edge XANES of $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2(CO_3)\cdot mH_2O$. Fresh sample (c), heated at 383 K (c-383), c-383 in CO_2 at 290 K (c-CO_2-290) or 423 K (c-CO_2-423), $CuZn_{56}(OH)_{72}$ model (e), and $CuZn_{56}(OH)_{72}\cdot 38H_2O$ model (f).

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