

Photoreduction of Copper Sites of Semiconductor Layered Hydroxide Photocatalyst Monitored Using In Situ Cu K-edge XANES

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Introduction

Semiconductor layered hydroxides formulated as $[\text{Zn}_x\text{Cu}_x\text{Ga}^{III}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$ ($x = 0 - 1.5$) were found to convert CO_2 into methanol under UV-visible light by utilizing H_2 as reductant [1]. The methanol formation rates were enhanced from $51 \text{ nmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for $[\text{Zn}_3\text{Ga}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$ to $170 \text{ nmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$ due to the introduction of Cu sites in the cationic layers. The role of Cu sites was suggested to stabilize the hydrogen carbonate intermediate species formed by the reaction of CO_2 with surface hydroxy group bound to Cu (Scheme 1), leading to finally to methanol. In this study, in-situ Cu K-edge XAFS measurements were performed in the presence of CO_2 and H_2 under UV-visible light irradiation.

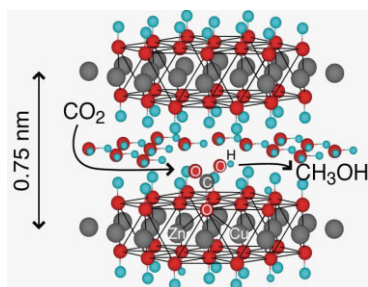
Methods

A mixed solution of 0.375 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.375 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 0.25 M $\text{Ga}(\text{NO}_3)_3 \cdot m\text{H}_2\text{O}$ was added to 0.075 M Na_2CO_3 solution at 290 K, keeping the pH at 8 by the addition of NaOH. Obtained slurry was kept at 353 K for 24 h, filtered, washed, and dried. Obtained $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$ powder was heated to 423 K for 1 h under vacuum as pre-treatment [2].

In-situ Cu K-edge XAFS measurements were performed at beamline 7C and 9C in a transmission mode at 290 K in the presence of 2.3 kPa of CO_2 and 21.7 kPa of H_2 under UV-visible light from xenon arc lamp (500 W, Ushio).

Results and Discussion

The pre-edge peak region of Cu K-edge XANES spectra in CO_2 and H_2 under UV-visible light for 20 s, 17 and 46 min, and 5 min after the illumination is depicted in Figure 1A. A pre-edge peak appeared at 8979.9–8980.3 eV, due to the electronic transition from Cu 1s to 3d,



Scheme 1. Proposed interlayer hydrogen carbonate intermediate species formed by the reaction of CO_2 with surface hydroxy group bound to Cu sites of LDH.

characteristic for d^9 divalent Cu sites, in all the spectra. As the UV-visible irradiation continued, the peak intensity gradually decreased. The peak intensity at 46 min was 72% of that at 20 s (Figure 1B), reflecting the reduction of Cu^{II} sites to Cu^I . When the UV-visible irradiation stopped, the intensity grew by 8% only in 5 min, demonstrating the reoxidation of Cu^I sites in the absence of UV-visible light.

Based on the in-situ XANES results (Figure 1A), Cu^{II} sites should trap electrons photogenerated in $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$. This effect would slow the charge recombination during the photocatalysis.

The rate of the reduction of Cu^{II} to Cu^I was $1.2 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ (Figure 1A) versus the photocatalytic reaction rate (methanol + CO) in the reaction condition of $0.50 \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. The reduction-oxidation of Cu sites was in faster dynamic equilibrium under UV-visible light and contributed to the photoreduction of CO_2 by increasing the surface concentration of available electrons.

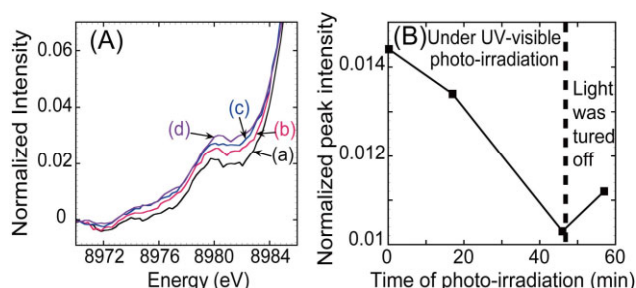


Figure 1. (A) The Cu K pre-edge peak region of $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]_2(\text{CO}_3) \cdot m\text{H}_2\text{O}$ in CO_2 and H_2 under UV-visible light for 20 s (a), 17 min (b), and 46 min (c), and 5 min after the illumination (d). (B) The pre-edge peak intensity change as a function of time.

References

- [1] N. Ahmed, Y. Shibata, T. Taniguchi, Y. Izumi, *J. Catal.* **279**(1), 123–135 (2011).
- [2] N. Ahmed, M. Morikawa, Y. Izumi, *Catal. Today*, under review.

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