

Electron Diffusion Rates in the Cationic Layers and to the Interlayer Sites of Zinc–Copper–Gallium Layered Double Hydroxide Photocatalysts

Naveed Ahmed,¹ Motoharu Morikawa,² and Yasuo Izumi^{1,*}

¹Graduate School of Science and ²Graduate School of Advanced Integration Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

1 Introduction

It is advantageous to capture CO₂ from the atmosphere or factories/power stations and convert it to fuel using a sustainable source of energy. Selective CO₂ photoconversion to methanol (68 mol%) was reported using H₂ and layered double hydroxides (LDHs) of [Zn_{1.5}Cu_{1.5}Ga^{III}(OH)₈]₂(CO₃)₂·mH₂O [1]. The substitution of interlayer carbonate anions for [Cu(OH)₄]²⁻ anions further boosted the methanol selectivity to 88 mol% [2]. In this paper, the electron transfer rates in the cationic layers and to the interlayer sites of Zn–Ga LDH compounds under UV-visible light, was investigated by XANES.

2 Experiments

In-situ XANES measurements were conducted in a transmission mode at the Photon Factory 7C, 9C and at SPring-8 01B1. An LDH photocatalyst disk was set in quartz batch cell equipped with PEN windows under CO₂ at 2.1 kPa and H₂ at 21.7 kPa and irradiation by UV-visible light.

3 Results and Discussion

A pre-edge peak at 8979 eV because of a 1s–3d transition was used to evaluate the population of Cu^{II} sites in the LDH compounds (Fig. 1I). When the electrons separated from holes under UV-visible light diffused to the Cu^{II} sites, Cu^{II} sites were reduced to Cu^I. The pre-edge peak does not appear for the Cu^I sites with d¹⁰ configuration.

The reduction of inlayer sites of Cu^{II} to Cu^I was monitored for [Zn_{1.5}Cu_{1.5}Ga(OH)₈]₂(CO₃)₂·mH₂O. The pre-edge peak intensity for 170 mg of incipient LDH monotonously decreased by 15% within 50 min of irradiation (Fig. 1II-a). The reduction suggests that photogenerated electrons in the LDHs diffused and were trapped at Cu sites at the rate of 580 μmol h⁻¹ g_{cat}⁻¹.

In total, only 0.38% of the trapped electrons should be available for photocatalytic reduction to methanol and reduction to CO [2], suggesting the rate of lateral e⁻ diffusion to Cu sites within the cationic layers was sufficiently fast in contrast to that of subsequent e⁻ transfer from Cu sites to substrates/intermediates.

The 1s–3d pre-edge peak intensity for 170 mg of incipient [Zn₃Ga(OH)₈]₂[Cu(OH)₄]₂·mH₂O also monotonously decreased by 11% within 180 min of irradiation (Fig. 1II-b). The reduction rate of Cu^{II} (Figure 3I-b) to Cu^I at interlayer Cu sites was 36 μmol h⁻¹ g_{cat}⁻¹. The rate was essentially the slower e⁻ diffusion rate in the perpendicular direction to interlayer Cu sites, *i.e.* (μ–O)₃Cu(OH)(H₂O)₂ sites, later than the faster e⁻ diffusion in the cationic layers. In total, 5.7% of the trapped

electrons were used for photocatalysis to form methanol and CO [2].

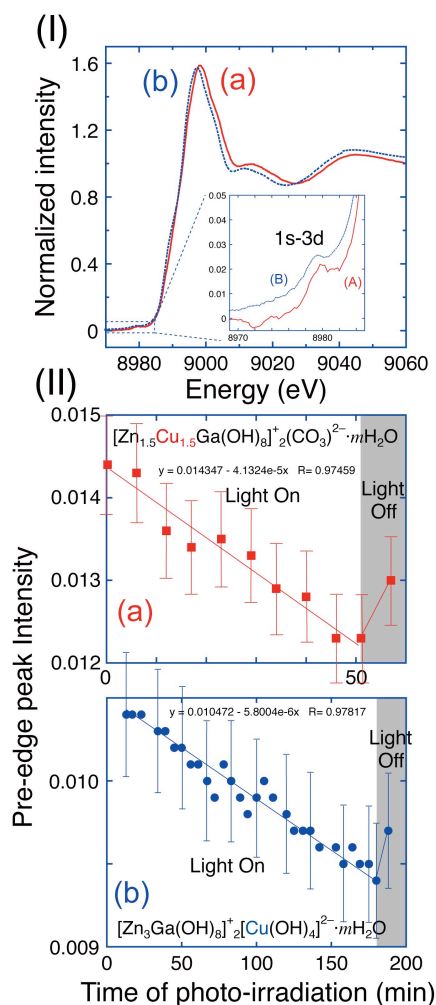


Fig. 1. (I) Normalized Cu K-edge XANES spectra of [Zn_{1.5}Cu_{1.5}Ga(OH)₈]₂(CO₃)₂·mH₂O (a) and [Zn₃Ga(OH)₈]₂[Cu(OH)₄]₂·mH₂O (b). (Inset) Expanded view of the 1s–3d peak region. (II) Time course of the 1s–3d peak intensity under CO₂ + H₂ and UV-visible light irradiation and subsequent change after the light off.

References

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* yizumi@faculty.chiba-u.jp