

Monitoring of Electron Flow in Layered Double Hydroxides to Photoreduce Carbon Dioxide into Fuels

Photocatalytic conversion of CO₂ into fuel would simultaneously solve the problems of global warming and shortage of sustainable energy. Layered double hydroxides (LDHs), especially comprising Cu^{II} sites, are advantageous to photoreduce CO₂ selectively into methanol using H₂. By monitoring the pre-edge peak due to 1s-3d transition for Cu sites in LDHs, electron diffusion rates to inlayer Cu sites (580 μmol h⁻¹ g_{cat}⁻¹) and to interlayer Cu sites (36 μmol h⁻¹ g_{cat}⁻¹) were evaluated and was sufficiently fast compared to photocatalysis of CO₂. The preferable interaction of CO₂ with Cu sites in LDHs was also demonstrated and suggested to control the photoreactivity with CO₂ based on multiple scattering peak intensity for Zn, Cu, and Ga in X-ray absorption near-edge structures.

Carbon dioxide is one of the major greenhouse gases and methods to reduce its concentration in the atmosphere and its emission to the environment require urgent attention [1]. It would be advantageous to capture CO₂ from the atmosphere or factories/power stations and convert it to fuel using natural light, as this approach would simultaneously solve the problems of global warming and shortage of sustainable energy. Recently, many researchers have investigated this topic.

A study of selective CO₂ photoconversion to methanol (68 mol%) was reported using H₂ and layered double hydroxide (LDH) of [Zn_{1.5}Cu_{1.5}Ga^{III}(OH)₈]₂(CO₃)₂·mH₂O (**1**) [2]. LDH is one of the families of clays, but is unusual in that the cationic layers intercalate anionic species, e.g. carbonates, whereas in the majority of clays the layers are anionic and intercalate cationic species. The inclusion of Cu ions in the LDH cationic layers improves the selectivity for methanol formation compared to CO formation. Methanol is more favorable as it can be directly used in the existing infrastructure as fuel whereas CO

needs to be converted to hydrocarbons or alcohols for use as an energy. The substitution of interlayer carbonate anions of LDH for [Cu(OH)₄]²⁻ anions further boosted the methanol selectivity to 88 mol% [3].

In principle, photocatalysis takes place starting from the charge separation in semiconductor/chemical bonds due to light irradiation. For compound **1**, ultraviolet (UV) light of energy greater than 3.5 eV excites electrons (e⁻s) at the valence band (major O 2p character) to the conduction band (metal d, s, p character) in the LDH. If the e⁻s on metal and holes on oxygen diffuse to the surface of photocatalysts, reduction and oxidation reactions take place independently, e.g. CO₂ reduction and H₂ oxidation [2, 3] or H₂O oxidation [4]. Thus, to understand the photoreduction mechanism of CO₂ into fuels (methanol, CO), it is necessary to monitor the e⁻ flow in LDH upon light irradiation and the interaction of CO₂ with LDH surface. In this study, these steps were monitored using X-ray absorption near-edge structure (XANES) spectroscopy [5].

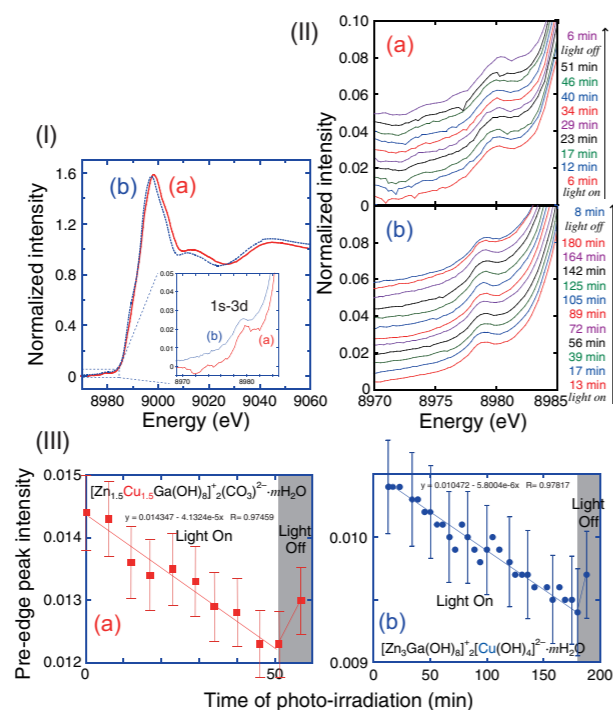


Figure 1: (I) Normalized Cu K-edge XANES spectra of compound **1** preheated at 423 K (a) and fresh compound **2** (b) and (II) under CO₂ + H₂ and UV-visible light irradiation and subsequent change after the light was turned off, and (III) time course of the 1s-3d peak intensity for the two LDH photocatalysts under CO₂ + H₂ and UV-visible light irradiation and subsequent change after the light was turned off.

The e⁻ excitation and flow in compound **1** and [Zn₃Ga(OH)₈]₂[Cu(OH)₄]²⁻·mH₂O (**2**) under CO₂ + H₂ and UV-visible light irradiation was monitored by Cu K-edge XANES spectroscopy (Fig. 1). 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 [6]. When the Cu^{II} sites trap diffused e⁻s, they are reduced to Cu^I. The pre-edge peak does not appear for the Cu^I sites with d¹⁰ configuration.

The pre-edge peak intensity for incipient compound **1** monotonously decreased by 15% within 50 min of irradiation [Fig. 1(II)-(a) & (III)-(a)]. As 0.55 mmol of Cu sites were included in 170 mg of LDH disk, the e⁻ trap rate was 580 μmol h⁻¹ g_{cat}⁻¹. The e⁻s flow was within the cationic layer [Fig. 2(A)].

The 1s-3d pre-edge peak intensity of incipient compound **2** also monotonously decreased by 11% within 180 min of irradiation [Fig. 1(II)-(b) & (III)-(b)]. Based on Cu K-edge extended X-ray absorption fine structure analysis, the [Cu(OH)₄]²⁻ anions dehydrated with hydroxy groups of the cationic layer to form (μ-O)₃Cu(OH)(H₂O)₂ [Fig. 2(B)] [5]. “μ-O” means an O atom bound to the cationic layer. The reduction rate of 0.17 mmol of out-of-layer Cu^{II} sites in 170 mg of LDH disk was 36 μmol h⁻¹ g_{cat}⁻¹. The rate was essentially slower diffusion in the perpendicular direction to interlayer Cu sites later than the faster e⁻ diffusion in the cationic layer (580 μmol h⁻¹ g_{cat}⁻¹).

Monitored e⁻ trap (36–580 μmol h⁻¹ g_{cat}⁻¹) was fast enough compared to photocatalytic CO₂ conversion into methanol & CO using compounds **1** and **2** (2.1–2.2 μmol e⁻s_{used} h⁻¹ g_{cat}⁻¹) irradiated under light. The interaction of CO₂ with Cu sites of LDHs was also

monitored using Cu K-edge XANES spectroscopy [2]. For compound **1**, a post-edge peak intensity at 9016 eV decreased to 76% by heating in vacuum at 383 K. Upon introduction of CO₂, the peak intensity increased back to 87% of the fresh sample at 290 K and 91% of the fresh one at 423 K. As a hydroxy group shares three metal atoms in LDHs (Fig. 2), the post-edge peak intensity at 9689 and 10398 eV above Zn and Ga K-edge, respectively, also exhibited a similar semi-reversible trend. The reversible in-situ peak intensity changes were not observed for the post-edge peaks at 9688 and 10397 eV for Cu-free [Zn₃Ga(OH)₈]₂CO₃²⁻·mH₂O. Thus, Cu sites adsorbed CO₂ and transferred the trapped e⁻s to CO₂ during the photoconversion to fuel.

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BEAMLINES

BL-7C, BL-9C and BL-01B1 (SPring-8, Priority Program for Disaster-Affected Quantum Beam Facilities)

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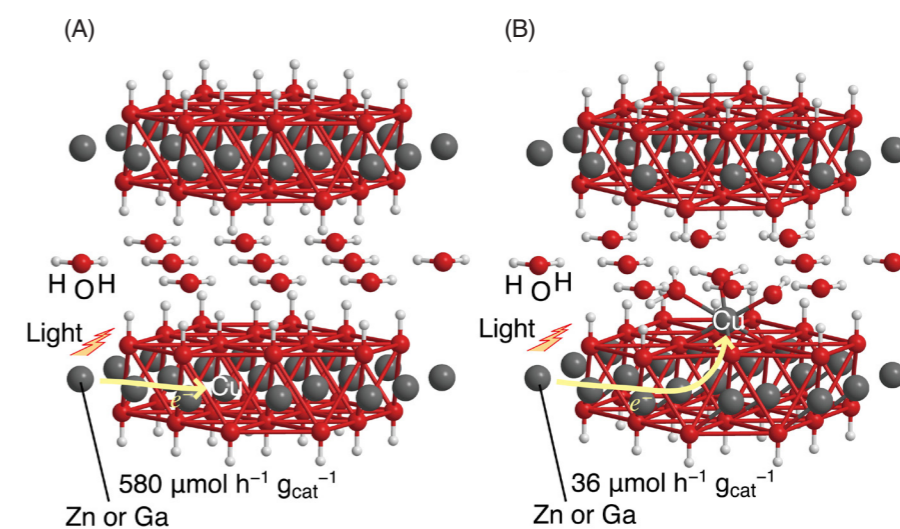


Figure 2: Structure of compound **1** (A) and structure of compound **2** (B). Interlayer carbonates are not drawn in (A) for clarity.