Photoconversion of carbon dioxide in zinc-copper-gallium layered double hydroxides: The kinetics to hydrogen carbonate and further to CO/methanol

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1. Introduction

Carbon dioxide is one of the major greenhouse gases, and methods to reduce its concentration in the atmosphere require urgent attention [1–10]. It is advantageous to capture CO2 from the atmosphere or factories/power stations and convert it to fuel using a sustainable source of energy such as sunlight. This option simultaneously solves the problems of global warming and sustainable energy shortage. Recently, many investigators have researched this topic; however, more efficient, inexpensive photocatalyst needs to be developed to achieve its practical application [2–4,8–10].

In this regard, a study of selective CO2 photoconversion to methanol (68 mol%) was reported using H2 and layered double hydroxides (LDHs) of [Zn1.5Cu1.5Ga(OH)8]2+2(CO3)2−·mH2O [11]. The inclusion of Cu ions in the cationic layers of the photocatalysts improved the selectivity for methanol formation compared to CO formation. The substitution of interlayer carbonate anions for [Cu(OH)4]2− anions further boosted the methanol selectivity to 88 mol% [12]. The conversion rate was higher by 3.1 times using [Zn1.5Cu1.5Ga(OH)8]2+2(CO3)2−·mH2O than that using [Zn1.5Cu1.5Ga(OH)8]2+2(CO3)2−·mH2O, but the Al analogue was more selective to CO formation (74%) [11].

Photoreduction of CO2 to CO with water was also reported using LDH compounds, for example, [Ni3In(OH)6]2+2(CO3)2−·mH2O and [Ni3Ga(OH)6]2+2(CO3)2−·mH2O [13] or the combination of [Zn1.5Cu1.5Ga(OH)8]2+2(CO3)2−·mH2O and WO3 (or TiO2) separated by proton-conducting film [14]. Studies of CO2 photoreduction have been intensively published [8,15,16]. In the case of CO2 photoreduction using LDHs, it also needs to be investigated that the CO2 conversion to fuels preceded photocatalytically rather than thermally for the intrinsic storage of solar energy as fuels [8]. It is also important to monitor the surface species derived from CO2 under the photocatalytic reaction conditions [15,16]. Furthermore, the photocatalytic reaction mechanism has rarely been clarified except for a few examples using TiO2, which include a mechanistic study of formic acid formation from supercritical CO2 based on electron spin resonance (ESR) [17,18], another study describing methane formation from gaseous CO2 and H2O based on ESR [19], and an unexpected result from an ESR–density functional theory (DFT) calculations-based investigation describing methane formation via C2-glyoxal (OHC–CHO) [20].

In this paper, an investigation of the site structure for a LDH [Zn1.5Ga(OH)8]2+2[Cu(OH)4]2−·mH2O as semiconductor photocatalyst used in the conversion of CO2 to hydrogen carbonate under light irradiation was performed by extended X-ray absorption fine structure (EXAFS). The kinetics of the conversion to hydrogen carbonate, initiated by charge separation in the LDH compounds under UV–visible light, was investigated in detail by X-ray absorption...
near-edge structure (XANES) and Fourier-transform infrared (FTIR) spectroscopy [21,22]. The relevance to the photocatalytic conversion of CO₂ into methanol is discussed.

2. Experimental

The LDH compound with the formula [Zn₁₋ₓCuxGa(OH)₆][CO₃]₂₋−mH₂O was synthesized from an aqueous solution of metal nitrates and sodium carbonate at a controlled pH (pH 8). Details of the synthetic procedure were described in Ref. [11]. LDH compounds with the formula [Zn₁₋ₓCuₓGa(OH)₆][Zn(CuOH)₆]₂₋−mH₂O (x = 0, 1.5) were synthesized from an aqueous solution of metal nitrates and ammonium tetrachlorocuprate dihydrate at the same pH (pH 8). The details of this procedure were described in Ref. [12].

The obtained precipitates were filtered using a membrane filter, washed with deionized water, and dried in ambient air at 290 K for 5 days. The purity of the deionized water used in the experiments was <0.06 μS cm⁻¹. No C-containing chemicals were used except for Na₂CO₃ for these LDH syntheses. For the latter LDH compounds, all synthetic steps up to the filtration and washing (water) of the LDHs were performed in an argon atmosphere.

The photocatalysts were evacuated (10⁻⁶ Pa) at 290 K for 2 h prior to kinetic tests. Photocatalytic CO₂ reduction tests and control tests in the dark were performed in a closed circulating system under CO₂ at 0.20–2.1 kPa and H₂ at 21.7 kPa using a quartz cell illuminated by a 500-W xenon arc lamp (Ushio, Model U1-502Q: 42 mW cm⁻²) [23]. The distance between the lamp exit window and the bottom of the cell was 20 mm. The products were analyzed using an online gas chromatograph equipped with a thermal conductivity detector (GC-TC-H; Shimadzu, Model GC-8A). The details are described in Refs. [11,12].

In situ XANES measurements were conducted in a transmission mode at the Photon Factory on beamline 7C (KEK, Tsukuba) and at Spring-8 on beamline 01B1 [24] for Cu, Zn, or Ga in LDHs. An LDH photocatalyst disk (φ = 2 cm) was set in an air-tight quartz batch cell equipped with polyethylene naphthalate windows (Q51-16, Tejin) [25,26] under CO₂ at 2.1 kPa and H₂ at 21.7 kPa and irradiation by UV–visible light from a 500-W xenon arc lamp (UL-502Q). The distance between the lamp exit window and the sample disk was 20 mm. The light intensity was 42 mW cm⁻² at the sample position.

The EXAFS measurements were also conducted in a transmission mode for LDH photocatalyst powder pretreated in vacuum (10⁻⁶ Pa) at 290 K for 2 h with Data analysis software XDAP version 2.2.7 (XAFS Services International, Woudenberg, the Netherlands) was used. EXAFS spectra were also generated theoretically using ab initio multiple scattering calculation code FEFF version 8.4 [27] for comparison to the experimental spectra.

The surface species over a 2-cm-φ self-supporting pressed LDH disk (50 mg) placed under a CO₂ atmosphere in a quartz photoreaction cell [28] equipped with NaCl windows on both sides was monitored by an FTIR instrument (JASCO, Model FT/IR-4200) equipped with a mercury–cadmium–tellurium–M detector. The LDH sample disk was evacuated (10⁻⁶ Pa) at 290 K for 2 h prior to taking spectral measurements. The spectrum acquired for each freshly evacuated sample was set as a reference spectrum. The energy resolution was set to 2 cm⁻¹. The in situ FTIR measurements were basically performed at 290 K. The sample was irradiated by UV–visible light from a 500-W xenon arc lamp (Ushio, Model SX-U1D502XAM) via quartz fiber light guide (San−ei Electric Co., Model 5d−28−1000L; the length: 1075 mm). The distance between the fiber light exit and sample disk was 90 mm. The light intensity at the sample position was 88 mW cm⁻². During illumination, the temperature of the sample reached as high as 310 K. The

![Fig. 1. Structure of [Zn₁₋ₓCuₓGa(OH)₆][CO₃]₂₋−mH₂O (A) and structure of [ZnGa(OH)₆][Zn(CuOH)₆]₂₋−mH₂O as determined by XAFS analyses (B). Interlayer carbonates are not drawn in (A) for clarity.](image)

### 3. Results

#### 3.1. Copper site structures

The LDH compounds consist of cationic layers with anions such as carbonates and structural water molecules, both in interlayer space (Fig. 1A) [11,29]. For the compound [Zn₁₋ₓCuₓGa(OH)₆][Zn(CuOH)₆]₂₋−mH₂O, Zn, Cu, and Ga cations were in the Mo₆ octahedra linked at the edge to form a cationic layer, and the cations distribute statistically [30] to exhibit a similar XANES pattern at the Zn, Cu, and Ga K-edges [11].

The structure of the anions in the LDH compound [Zn₁₋ₓGa(OH)₆][Zn(CuOH)₆]₂₋−mH₂O was studied by Cu K-edge EXAFS [31]. The experimental Fourier transform (FT) (Fig. 1A) was compared to theoretically generated data using FEFF version 8.4 (Fig. 1B–f). As a result, a (μ−O)₃Cu(OH)(H₂O)₂ model accompanied by the coordination of two water molecules (Fig. 1B) [31] was most likely being covalently anchored to cationic layer: Zn₆Ga₂(OH)₁₃[(μ−O)₃Cu(OH)(H₂O)₂]mH₂O (Supplementary data).

#### 3.2. Rates of photogenerated electron trapping at the Cu sites

Next charge separation in the LDH compounds under CO₂ + H₂ and UV–visible light irradiation was monitored by Cu K-edge XANES spectroscopy as the reduction of Cu⁰ sites (Fig. 2). Assuming the wavelength of 354 nm, near the activity maximum as a function of excitation wavelength for the CO₂ photoreduction using LDH [11], the photon number at the sample disk position was on the order of 10 mmol–photons h⁻¹ g⁻¹. A pre-peak at 8979 eV because of a 1s–3d transition was used to evaluate the population of Cu⁰ sites [32,33] in the LDH compounds (Fig. 2). When the electrons separated from holes under UV–visible light diffused to the Cu⁰ sites in the LDH, Cu⁰ sites were reduced to Cu⁰. The pre-peak does not appear for the Cu¹ sites with d¹⁰ configuration.

The reduction of inlayer sites of Cu⁰ to Cu¹ was monitored for the LDH compound [Zn₁₋ₓCuₓGa(OH)₆][Zn(CuOH)₆]₂₋−mH₂O under CO₂ and H₂ and UV–visible light irradiation. The pre-peak intensity for 170 mg of incipient LDH (Cu¹: 0.55 mmol) monotonously decreased by 15% within 50 min of irradiation (Fig. 2I-(a) and III-a). The occurrence of reduction suggests that photogenerated electrons in the LDHs diffused and were trapped at Cu sites. The e⁻ trapping rate was 580 mmol h⁻¹ g⁻¹ (Table 1A). This rate was lower than reported Cu²⁺ photoreduction rate (2.2 mmol h⁻¹ g⁻¹ TiO₂) suspension and sacrificial reducing
agent HCO\textsuperscript{2-} Na\textsuperscript{+} (0.1 mol L\textsuperscript{-1}) \cite{34}, but higher than the Cu\textsuperscript{II} photoreduction rate (4.1 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1} for a Cu–ZnO photocatalyst (0.5 wt% of Cu) in the presence of CO\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2} gas \cite{28}).

In total, only 0.38% of the trapped electrons should be available for photocatalytic six – \textsuperscript{e}\textsuperscript{-} reduction to methanol (0.31 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1} and two – \textsuperscript{e}\textsuperscript{-} reduction to CO (0.18 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}) \cite{12} (Table 1A), suggesting the rate of lateral \textsuperscript{e}\textsuperscript{-} diffusion to Cu sites within the cationic layers was sufficient (Fig. 1A) in contrast to that of subsequent \textsuperscript{e}\textsuperscript{-} transfer from Cu sites to substrates/intermediates.

When the UV–visible light was turned off, the Cu\textsuperscript{I} sites oxidized back to Cu\textsuperscript{II} (Fig. 2II-a and III-a) at a rate of 1600 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}, higher than the \textsuperscript{e}\textsuperscript{-} trapping rate (580 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}) at the Cu sites under light (Table 1A).

The 1s–3d pre-edge peak intensity for 170 mg of incipient [Zn\textsubscript{3}Ga(OH)\textsubscript{8}]\textsuperscript{2+}[Cu(OH)\textsubscript{4}]\textsuperscript{2-} - mH\textsubscript{2}O (Cu\textsuperscript{II}, 0.17 mmol) also monotonously decreased by 11% within 180 min of irradiation (Fig. 2II-b and III-b). In contrast to that of the LDHs consisting of interlayer Cu sites, the reduction rate of Cu\textsuperscript{II} (Fig. 2I-b) to Cu\textsuperscript{I} at interlayer Cu sites (Fig. 1B) was 36 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1} for [Zn\textsubscript{3}Ga(OH)\textsubscript{8}]\textsuperscript{2+}[Cu(OH)\textsubscript{4}]\textsuperscript{2-} - mH\textsubscript{2}O (Table 1A). The rate was essentially the slower \textsuperscript{e}\textsuperscript{-} diffusion rate in the perpendicular direction to interlayer Cu sites later than the faster \textsuperscript{e}\textsuperscript{-} diffusion in the cationic layers. Even though the interlayer Cu sites were covalently bonded to O atoms in the cationic layers (Fig. 1B), the \textsuperscript{e}\textsuperscript{-} diffusion rate in the perpendicular direction (36 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}) was smaller than that in the parallel, interlayer direction (580 μmol h\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}). In total, 5.7% of the trapped electrons were used for photocatalysis to form

![Table 1](https://example.com/table1.png)

**Table 1** Comparison of the rates of photocatalytic conversion of CO\textsubscript{2} with those of the elementary step measured by FTR and Cu-K-edge XANES. (A) CO\textsubscript{2} (2.1 kPa) and/or H\textsubscript{2} and/or CO (0.20 kPa) or CO (0.20 kPa) + H\textsubscript{2} (21.7 kPa).

![Diagram](https://example.com/diagram.png)

**Fig. 2** (I) Normalized Cu K-edge XANES spectra of [Zn\textsubscript{3}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}[CO\textsubscript{3}]\textsuperscript{3-} - mH\textsubscript{2}O preheated at 423 K (a) and fresh [Zn\textsubscript{3}Ga(OH)\textsubscript{8}]\textsuperscript{2+}[Cu(OH)\textsubscript{4}]\textsuperscript{2-} - mH\textsubscript{2}O (b) ([Inset] Expanded view of the 1s–3d pre-edge peak region) and (II) under CO\textsubscript{2} (2.1 kPa) + H\textsubscript{2} (21.7 kPa) and UV–visible light irradiation: (a) 6–51 min; b: 13–180 min) and subsequent change after the light was turned off (a: 6 min; b: 8 min), and (III) time course of the 1s–3d pre-edge intensity for the two LDH photocatalysts under CO\textsubscript{2} (2.1 kPa) + H\textsubscript{2} (21.7 kPa) and UV–visible light irradiation and subsequent change after the light was turned off. The amount of the LDH photocatalyst charged in the photoelectron cell was 170 mg.
methanol (0.30 $\mu$mol h$^{-1}$ g$^{-1}$cat) and CO (0.13 $\mu$mol h$^{-1}$ g$^{-1}$cat)$^{12}$ (Table 1A). When the UV–visible light was turned off, the Cu$^+$ sites quickly oxidized back to Cu$^0$ (Fig. 2II-b and III-b) at a rate of 2200 $\mu$mol h$^{-1}$ g$^{-1}$cat$^{-1}$.

The Zn and Ga K-edge XANES spectra for [Zn$_{3.3}$Cu$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O were already reported in Ref. [11]. The photogenerated electron trap was only observed in Cu K-edge in situ XANES (Fig. 2) due to the reduction of Cu$^+$ sites to Cu$^0$. However, partially reduced state from Zn$^0$ or Ga$^{	ext{III}}$ was not successfully detected in the Zn or Ga K-edge in situ XANES spectra.

3.3. Monitoring carbonate, hydrogen carbonate, and hydroxy species for [Zn$_2$Ga(OH)$_8$]$_2$[Cu(OH)$_4$]·mH$_2$O

Next, the interactions of [Zn$_{3.3}$Ga$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O with CO$_2$($^{13}$CO$_2$ (2.1–0.20 kPa) were monitored by FTIR at 290 K.

Under CO$_2$ at 2.1 kPa for 3–62 min, two peaks (1655 and 1570 cm$^{-1}$) gradually increased, while a sharp peak at 3671 cm$^{-1}$ gradually weakened (Fig. 3A). A weak shoulder peak was also observed at 1511 cm$^{-1}$. Under $^{13}$CO$_2$ at 2.1 kPa for 3–62 min, three overlapping peaks (1629, 1530, and 1474 cm$^{-1}$) gradually increased and a sharp peak at 3673 cm$^{-1}$ gradually weakened (Figs. 3B and 4B).

If we consider the isotope wavenumber shift based on the harmonic equation$^{[35]}$, the peaks at 1635, 1570, and 1511 cm$^{-1}$ under CO$_2$ (Fig. 3A) shift to 1618, 1535, and 1477 cm$^{-1}$, which is consistent with the values observed in $^{13}$CO$_2$ (1629, 1530, and 1474 cm$^{-1}$; Fig. 3B).

For Cu/TiO$_2$ in CO$_2$, the peaks at 1663 and 1554 cm$^{-1}$ were assigned to hydrogen carbonate (or carboxylate) and carbonate, respectively$^{[15]}$. For ZnO in CO$_2$, the peaks at 1635, 1595–1580, and 1522 cm$^{-1}$ were assigned to hydrogen carbonate, bisected carbonate, and polydentate carbonate, respectively$^{[36]}$. For MgO, the peaks at 1685 and 1526 cm$^{-1}$ were assigned to hydrogen carbonate and unidentate carbonate, respectively$^{[37]}$. Systematic vibration mode assignments for hydrogen carbonate, bisected carbonate, and polydentate carbonate have been well summarized pictorially$^{[38]}$. Thus, the peak at 1655 cm$^{-1}$ and the two peaks at 1570 and 1511 cm$^{-1}$ observed for [Zn$_{3.3}$Ga$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O in CO$_2$ (Fig. 3A) were assigned to antisymmetric vibrations of CO$_3$ ($v_{as}$(CO$_3$)) of hydrogen carbonate, $v_{as}$(CO$_3$) of bisected carbonate, and $v_{as}$(CO$_3$) of polydentate carbonate, respectively.

The peak intensity ratio at 1511 cm$^{-1}$ in CO$_2$ was inconsistent with the corresponding one at 1474 cm$^{-1}$ in $^{13}$CO$_2$. This was due to impurity carbonates included in the fresh LDH sample of [Zn$_{3.3}$Ga$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O. On closer inspection of the as-prepared, 2-h evacuated [Zn$_{3.3}$Ga$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O sample, the carbonate peak intensity at 1513 cm$^{-1}$ was 8.0% of that for the same molar amount of the [Zn$_{3.3}$Cu$_{1.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O disk, indicating that the exact formula was [Zn$_{3.3}$Ga$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O. Note that the interlayer anions $[\text{Cu}(\text{OH})_2]$$^-$ actually existed such as ($\mu$−O)$_2$Cu(OF)$_2$(H$_2$O)$_2$ (Fig. 1B) but were denoted as the species present before dehydration to avoid having a highly complicated composition formula. The impurity should originate from exposure to atmospheric CO$_2$ (remaining after the 2-h evacuation) during the drying sequence of the LDH synthesis at 290 K.

The amount of impurity carbonate in the LDH sample (4.0 $\mu$mol CO$_2$ per 50 mL LDH) was not negligible vs. the photocatalytic rate on the order of 1–10$^{-2}$ $\mu$mol h$^{-1}$ starting from CO$_2$+H$_2$ (Table 1). The impurity carbonates interfered with quantitative measurement of carbonate peaks in CO$_2$. In contrast, new carbonate peaks consisting of $^{13}$C could be clearly detected at 1530 and 1474 cm$^{-1}$ in $^{13}$CO$_2$. The change of impurity carbonate during pretreatment in vacuum (290 K) affected the FTIR data in CO$_2$, but the exchange between $^{12}$CO$_2$ and $^{13}$CO$_2$ seems slower than the reactions of $^{13}$CO$_2$ with surface. Fortunately in view of catalysis, the 8.0% of carbonate was quite inert in later steps than the pretreatment in vacuum and negligibly affected the photoreduction of CO$_2$.

The O atom source to form carbonate under CO$_2$ is unclear. The O atom formed by partial dehydration of hydroxy groups on the cationic layer during pretreatment (290 K, vacuum) is one potential source. Instead, the O atom of ($\mu$−O)$_2$Cu(OF)(H$_2$O)$_2$ species could react with CO$_2$ to form carbonates.

To evaluate the molar amount of hydrogen carbonate species, CO$_2$ uptake was volumetrically monitored for the LDH sample after the 2-h evacuation$^{39}$. The CO$_2$ uptake after 1 h (Fig. 4B) was equalized to the total peak area of hydrogen carbonate and

![Fig. 3. FTIR spectra for LDH compound [Zn$_{3.0}$Cu$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(Cu$_2$OH)$_4$·mH$_2$O under CO$_2$ at 2.1 kPa (A) and under $^{13}$CO$_2$ at 2.1 kPa (B) for 3 min (a), 17 min (b), 32 min (c), and 62 min (d), evacuated for 3 min (e) and 12 min (f), irradiated by UV–visible light for 3 min (g) and 12 min (h). FTIR spectra for LDH compound [Zn$_{3.0}$Cu$_{0.7}$Ga$_{0.0}$Ga$_{0.0}$]$_2$(CO$_3$)$_2$·mH$_2$O under $^{13}$CO$_2$ at 2.1 kPa (D) for 62 min (d). The amount of LDH was 50 mg.](image-url)
carbonate species identified by FTIR. We assumed that the molar absorption coefficients for hydrogen carbonate (1629 cm\(^{-1}\)) and carbonates (1530 and 1474 cm\(^{-1}\)) were identical. The result of this evaluation of the LDH sample of \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(CO\textsubscript{3})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) (0.52 mmol g\textsubscript{LDH}\(^{-1}\) for 12-h sorption) was in accord with reported CO\textsubscript{2} uptake values (0.5–1.4 mmol g\textsubscript{LDH}\(^{-1}\)) \cite{40,41} and the amount of interlayer Cu sites (0.99 mmol g\textsubscript{LDH}\(^{-1}\)) in the LDH.

In contrast to the stable, inert carbonate peaks, the hydrogen carbonate peak at 1629 cm\(^{-1}\) grew at a rate of 400 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) under 2.1 kPa of H\textsubscript{2} (A) and decomposed at a rate of 110 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) under vacuum (Table 1A and Fig. 4B). The peak under \(^{13}\text{CO}_2\) for 62 min and under vacuum for 14 min further decreased at the rate of 11 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) during UV–visible irradiation (Figs. 3C–g, C–h and 5B and Table 1A). Alternatively, when H\textsubscript{2} at 4.3 kPa was added before UV–visible irradiation treatment, carbonate peaks still remained constant, while the decrease in the hydrogen carbonate peak was accelerated to 66 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) by hydrogen exposure (Figs. 3C–g’, C–h’ and 4B’ and Table 1A).

The isolated hydrogen peak at 3673 cm\(^{-1}\) in \(^{13}\text{CO}_2\) for \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(Cu(OH)\textsubscript{4})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) (Fig. 3B) was not observed for \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(CO\textsubscript{3})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) (Fig. 3D). Therefore, it was assigned to OH stretching vibrations \(v(\text{OH})\) of \((\mu\text{-O})\text{Cu}(OH)(H_2O)\text{O}\) species in \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(Cu(OH)\textsubscript{4})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) (Fig. 1B). The peak decrease under \(^{13}\text{CO}_2\) is plotted in Fig. 4B and B’ (180 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\); Table 1A). In this plot, the decreased molar amount of hydrogen carbonate was assumed to be equal to the molar quantity of hydrogen carbonate formed over 62 min. The hydrogen carbonate peak intensity (1629 cm\(^{-1}\)) at 62 min corresponded to 2.8% of that of the \((\mu\text{-O})\text{Cu}(OH)(H_2O)\text{O}\) site after being transformed to \((\mu\text{-O})\text{Cu}(O_2C\text{-OH})(H_2O)\text{O}\).

As soon as the gaseous \(^{13}\text{CO}_2\) was evacuated, the hydrogen peak recovered at the rate of 30 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) (Figs. 3B, 4B and B’ and Table 1A). The decrease/increase of hydrogen group did not coincide with the change observed for hydrogen carbonate, but it did correlate with 27–45% of the rate increase/decrease of hydrogen carbonate formation.

Then, under UV–visible light irradiation, the peak due to isolated hydroxy groups further recovered at the rate of 7.7 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) (Fig. 3C–g and C–h and Table 1A), similar to the rate of hydrogen carbonate decomposition (11 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\)) under this condition. Alternatively, when H\textsubscript{2} at 4.3 kPa was added before the UV–visible irradiation, the recovery of the peak associated with isolated hydroxy group did not change significantly (7.1 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\); Fig. 3C–g’ and C–h’ and Table 1A), suggesting hydrogen carbonate did not totally decompose back to initial CO\textsubscript{2} + surface hydroxy group, but it was further photoreduced by hydrogen.

FTIR monitoring was also performed at a lower pressure of \(^{13}\text{CO}_2\) (0.20 kPa). The rates of both hydrogen carbonate formation/decomposition and the decrease/recovery of Cu–OH species slowed by an order of magnitude (Table 1B). However, the rates of formation of Cu–OH species were again lower than those for hydrogen carbonate formation by a factor of 47–33% (Table 1B), comparable to the ratios for the test run under \(^{13}\text{CO}_2\) at 2.1 kPa (Table 1A).

### 3.4. Monitoring carbonate, hydrogen carbonate, and hydroxy species for \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(CO\textsubscript{3})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\)

For \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(CO\textsubscript{3})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) under 2.1 kPa of \(^{13}\text{CO}_2\), the signals from interlayer carbonate interfered with those of the additional minor carbonate and/or hydrogen carbonate and the spectra were less precise compared to those for \([Zn\textsubscript{1.5}Cu\textsubscript{1.5}Ga(OH)\textsubscript{8}]\textsuperscript{2+}(Cu(OH)\textsubscript{4})\textsubscript{2}^{-}\cdot m\text{H}_2\text{O}\) (Fig. 3D). A broad peak at 1647 cm\(^{-1}\) increased at the rate of 16 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) under \(^{13}\text{CO}_2\) and decreased at the rate of 1.3 \(\mu\text{mol h}^{-1}\text{ g}_{\text{cat}}^{-1}\) under vacuum (Fig. 4C). This peak can be assigned to hydrogen carbonate and quantified using the same criteria as that in Fig. 3B. The molar amount of hydrogen carbonate under \(^{13}\text{CO}_2\) exposure after 62 min corresponded to 0.12% of that of carbonate anion in the LDH.
compound. In the ν(OH) region, no peak due to isolated hydroxy group appeared (Fig. 3D, left).

3.5. CO2 conversion tests under light and in the dark at 313 K

Hydrogen carbonate observed in the FTIR spectra under CO2 can be reduced by the electrons trapped at the Cu site, as monitored by XANES. CO was formed (0.13 μmol h⁻¹ gcat⁻¹) using [Zn₃Ga(OH)₈]⁺₂[Cu(OH)]₄⁻·mH₂O [12] as resulting from the reaction of a reduced hydrogen carbonate with a proton and an e⁻ to form CO and water at the interlayer sites including the Cu sites [11]. On the other hand, methanol formation (0.30 μmol h⁻¹ gcat⁻¹) from a reduced hydrogen carbonate still requires multiple reduction steps. To obtain insight into the steps, kinetic tests under UV–visible light, and control tests in the dark at 313 K (maximum accessible temperature at the reactor under the test conditions [11]) were performed under CO2 and H2 using [Zn₁.₅Cu₁.₅Ga(OH)₈]⁺₂(CO₃)²⁻·mH₂O.

No products above the detection limit of GC–TCD were detected over a 5-h period in the dark at 313 K using [Zn₁.₅Cu₁.₅Ga(OH)₈]⁺₂(CO₃)²⁻·mH₂O (Table 1A and Fig. 5a). When UV–visible light was applied, the reactor was below 313 K, and a major amount of methanol and minor amount of CO were formed (Fig. 5b). Thus, hydrogen carbonate, which formed bound to inlayer Cu ions (Fig. 1A), should be reduced by multiple e⁻ transfer via the forbidden direct e⁻ transition from O 2p to M 3d (M = Zn, Cu, or Ga) in LDHs [11,12] and H⁺ transfer.

By contrast, in the dark at 313 K using [Zn₃Ga(OH)₈]⁺₂[Cu(OH)]₄⁻·mH₂O, CO was formed at the rate of 21 mmol h⁻¹ gcat⁻¹, but no methanol was found (Table 1A). The rate was 16% of that observed under UV–visible light [12]. Using [Zn₁.₅Cu₁.₅Ga(OH)₈]⁺₂(CO₃)²⁻·mH₂O, trace amounts of methanol and CO formed at the rates of 23 and 8.6 mmol h⁻¹ gcat⁻¹, respectively (Table 1A). The rates were 4.7% and 12%, respectively, of those observed under UV–visible light [12].

In addition, a photocatalytic test under CO2 at 0.20 kPa + H2 at 21.7 kPa was performed for comparison to the reported results under CO2 at 2.1 kPa + H2 at 21.7 kPa (Table 1A) [12] using [Zn₃Ga(OH)₈]⁺₂[Cu(OH)]₄⁻·mH₂O. The methanol and CO formation rates were only 0.90% and less than 3.9%, respectively, of those under CO2 at 2.1 kPa (Table 1B).

4. Discussion

4.1. Photogenerated electron trap

The Cu K-edge EXAFS analysis (Supplementary data) indicated that the structure of the interlayer Cu sites for the LDH compound [Zn₃Ga(OH)₈]⁺₂[Cu(OH)]₄⁻·mH₂O transformed into (μ–O)₃Cu(OH)(H₂O)₂ by reaction with hydroxy groups in the cationic layer (Fig. 1B). As determined by Cu K-edge in situ XANES monitoring, electron trapping (580 μmol h⁻¹ gcat⁻¹) at the Cu sites was 18–260 times faster than that observed for catalytic CO2 conversion into methanol + CO using [Zn₁.₅Cu₁.₅Ga(OH)₈]⁺₂(CO₃)²⁻·mH₂O (2.2 μmol·e⁻ h⁻¹ gcat⁻¹) and [Zn₂Ga(OH)₆]⁺₂[Cu(OH)]₄⁻·mH₂O (2.1 μmol·e⁻ h⁻¹ gcat⁻¹) under light (Table 1A). Furthermore, e⁻ trapping was 16 times faster for inlayer Cu sites in [Zn₁.₅Cu₁.₅Ga(OH)₈]³⁻ than for interlayer Cu sites as anchored (μ–O)₃Cu(OH)(H₂O)₂ (36 μmol·h⁻¹ gcat⁻¹; Table 1A).

In summary, photogenerated e⁻ trapping at the Cu sites of LDH samples in this study was fast enough compared to photocatalysis to afford CO2 conversion. Specifically, lateral e⁻ diffusion in the cationic sheets (Fig. 1A) was faster than diffusion in the direction perpendicular to the attached (μ–O)₃Cu(OH)(H₂O)₂ sites (Fig. 1B).

4.2. Dynamic equilibrium of CO2 with hydrogen carbonate

In the FTIR measurements of [Zn₂Ga(OH)₈]⁺₂[Cu(OH)]₄⁺·mH₂O under 13CO2, carbonate νas(CO3) peaks were observed at 1530 and 1474 cm⁻¹ (Fig. 3B). The peaks were stable in vacuum or an atmosphere of H2 and/or under irradiation with UV–visible light, suggesting bidentate/polydentate carbonate species were not incorporated during catalytic CO2 reduction under UV–visible light.

By contrast, for the LDHs, the hydrogen carbonate νas(CO3) peak was weaker (1629 cm⁻¹ under 13CO2, Fig. 3B) and the species were in equilibrium with CO2 and hydroxy groups. The rates of increase and decrease of the hydrogen carbonate peak under 13CO2 and vacuum (Fig. 3B) were 400 and 110 μmol·h⁻¹ gcat⁻¹, 930- and 260-fold higher, respectively, than those of catalytic CO2 conversion and slightly greater than the e⁻ trapping rates at the Cu sites (Table 1A).

In this case, CO2 is in equilibrium with hydroxyl groups in the cation layers or interlayer (μ–O)₃Cu(OH)(H₂O)₂ species.

CO2 + H2O (catalytic layer) ⇌ HO–CO2 (catalytic layer)

CO2 + (μ–O)₃Cu(OH)(H₂O)₂ ⇌ (μ–O)₃Cu(O2C–OH)(H₂O)₂

The equilibrium of CO2 with Zn–OH sites to form hydrogen carbonate was calculated on the basis of Hartree–Fock and DFT to be exothermic by 33 kJ mol⁻¹ [42]. As in Ref. [42], hydrogen carbonate species in this study may also form hydrogen bonds with neighboring hydroxyl groups. The equilibrium of CO2 (and water) with CuO(1 1 1) surface species, as observed by DFT calculations, was also reported. Hydrogen carbonate was the major surface species and was suggested as the intermediate in the reduction of CO2 [43].

All the LDH compounds in this study were precipitated at pH 8 during the synthesis and have a basic nature. Near the basic surface in the interlayer space of the LDHs [44], the following equilibrium is also plausible.

CO2 + H2O (interlayer) ⇌ HO–CO2⁻ (interlayer) + H⁺ (interlayer)

The sharp peaks that appeared at 3671–3673 cm⁻¹ in CO2 (Fig. 3A) or 13CO2 (Panel B) were assigned to νOH for interlayer hydroxy group at (μ–O)₃Cu(OH)(H₂O)₂ sites (Fig. 1B). These were separated from the νOH peaks of interlayer water molecules (3348 cm⁻¹) and those of hydroxy groups in the cationic layers (3468 cm⁻¹) [45]. The rates of decrease and increase of the hydroxy peak were not equivalent to the rates of increase and decrease of the hydrogen carbonate peak in 13CO2; rather, the latter rates were greater by 2.2–3.7-fold. The situation was similar when a lower pressure (0.20 kPa) of 13CO2 was used (2.1–3.0-fold).

In summary, the hydroxy groups of the cationic layers and/or interlayer water reacted in the early stage of 13CO2 exposure, and
the slower diffusion of CO₂ into the interlayer space later led to the formation of (μ–O)₂CuO₂−C−OH(2H₂O). If the isolated hydroxy peak was because of an impurity (e.g., Cu(OH)₂) powder that coexisted with [Zn₃Ga(OH)₈]²⁺[Cu(OH)₄]²⁻·H₂O [12], this time delay cannot be rationalized.

Hydrogen carbonate formation was difficult to monitor for [Zn₅Cu₁.Ga(OH)₉]²⁺[CO₃]²⁻·H₂O under CO₂ or ¹³CO₂ owing to the strong IR absorption of the enormous amount of interlayer carbonates. Even so, the rates of formation and decomposition (16–1.3 μmol h⁻¹ g⁻¹ [Table 1A]) were significantly lower (4.0–12.1% of those for [Zn₃Ga(OH)₈]²⁺[Cu(OH)₄]²⁻·H₂O). The smaller interlayer spacing for [Zn₅Cu₁.Ga(OH)₉]²⁺[CO₃]²⁻·H₂O compared to that for [Zn₃Ga(OH)₈]²⁺[Cu(OH)₄]²⁻·H₂O (0.753 nm [11] vs. 0.792 nm [12]) may be the reason.

The hydrogen carbonate peaks at 1629 cm⁻¹ for [Zn₃Ga(OH)₈]²⁺[Cu(OH)₄]²⁻·H₂O increased under ¹³CO₂ at 2.1 kPa and quickly decreased under vacuum or UV–visible light (Fig. 4B and B'). The peak decrease under UV–visible light was further accelerated 6.0-fold in the presence of H₂ (Fig. 4B'). In clear contrast, the recovery of the isolated Cu–OH peak was not affected by the presence of H₂ (7.7 and 7.1 μmol h⁻¹ g⁻¹ [Table 3C] and Table 1A). This difference suggested that hydrogen carbonate dominantly decomposed back to initial CO₂− surface hydrogen under vacuum but was further reduced under H₂ and UV–visible light irradiation (Scheme 1).

The trend in the FTIR measurements under CO₂ and vacuum was similar to that under ¹³CO₂ at 0.20 kPa (Fig. 4A). As the amount of hydrogen carbonate in equilibrium decreased (from 28 to 2.3 μmol h⁻¹ g⁻¹), the rates of formation/decomposition were reduced by an order of magnitude by decreasing the ¹³CO₂ pressure from 2.1 to 0.20 kPa (Table 1A and B).

For [Zn₃Ga(OH)₈]²⁺[Cu(OH)₄]²⁻·H₂O under CO₂ at 0.20 kPa + H₂ at 21.7 kPa and UV–visible light, the photocatalytic rates of methanol and CO formation decreased by two orders of magnitude (Table 1A and B). Furthermore, when H₂ at 21.7 kPa was introduced to the LDH sample treated with CO₂ for 62 min followed by a 14-min evacuation and the sample was irradiated, methanol formation was confirmed by GC-TCD in addition to CO₂ and CO formation [11].

In summary, the rapid decomposition of the hydrogen carbonate species under vacuum and UV–visible light and its further promotion by the addition of H₂ as well as the critical catalytic rate dependence on the equilibrium concentration of the hydrogen carbonate species strongly suggested that hydrogen carbonate was the intermediate in the photocatalytic formation of methanol and CO from CO₂ using the LDH compounds.

4.3. Photocatalytic reaction mechanism from CO₂

On the basis of our study by Cu K-edge in situ XANES and in situ FTIR, we postulate the following initial reaction steps for the CO₂ photoconversion at the LDH interlayer sites including the interlayer Cu sites (Scheme 1): (Step 1) the reaction of CO₂ with hydroxy group bound to interlayer Cu₃ to form hydrogen carbonate. (Step 2) the forbidden direct e⁻ transition from O 2p to M 3d (M = Zn, Ga) [11], (Step 3) the diffusion of electrons and holes in the LDHs to Cu₆ sites and H atom, respectively, at the surface, and (Step 4) the transfer of trapped electrons from Cu⁺ to hydrogen carbonate forming anionic hydrogen carbonate. Steps 1 and 2 occurred at a sufficient rate (Table 1), and Step 4 (or possibly an event later than Step 4) should be rate-determining.

The direct e⁻ transition of LDHs in this study was considered as forbidden, based on the fit [11,12] of UV–visible absorption data to the equation of Davis and Mott. This is forbidden due to the symmetry of the Bloch functions of valence band and conduction band. Even so, minor term in the perturbation Hamiltonian does not diminish due to the symmetry, and weaker absorption was observed experimentally [46].

In this study, no C-containing intermediate/adsorbed species was observed in the FTIR spectra except for carbonate and hydrogen carbonate (Fig. 3), and the bidentate and polydentate carbonates were inert. For TiO₂, the photooxidation of carbonate to CO₃− radicals was detected by ESR at 4.5 K, but the photocatalytic reaction mechanism was proposed to proceed via a formate species [CO₂ + H²⁺ e⁻ → HCOO⁻ (surface)] followed by conversion to methane [47]. The surface concentration of hydroxy groups was 1.7–4.5 groups nm⁻¹ over TiO₂ vs. 1.7 × 10⁵ groups nm⁻¹ for [Zn₅Cu₁.Ga(OH)₉][CO₃][H₂O] (specific surface area, 57 m² g⁻¹) [11]. Because of this difference, hydrogen carbonate was preferentially observed for the LDH compounds in this study.

Although the e⁻ diffusion rate to Cu₆ sites (Step 3) was 16 times greater for [Zn₅Cu₁.Ga(OH)₉][CO₃][H₂O] than for [Zn₅Ga(OH)₈][CO₃][H₂O] as determined by Cu K-edge in situ XANES (Fig. 2 and Table 1A), the molar ratio of hydrogen carbonate species in ¹³CO₂ for 62 min was 0.12% and 2.8%, respectively, to the anion ([CO₃]²⁻ or [Cu(OH)₄]²⁻) of LDHs. In addition to hydrogen carbonate population (23 times greater for [Zn₅Ga(OH)₈][Cu(OH)₄][H₂O] effects, e⁻ transfer at the interface (Step 4) may be more effective between a Cu atom and hydrogen carbonate species (μ–O)₂CuO₂−C−OH(2H₂O) formed at the interlayer Cu–OH sites (Fig. 1B) than between a Cu atom and the hydrogen carbonate species formed at inlayer (M–)OH sites (M = Cu, Zn, or Ga; Fig. 1A).

By these effects, with [Zn₅Ga(OH)₈][Cu(OH)₄][H₂O], an important improvement in the utilization efficiency of trapped electrons at the Cu sites is observed (5.7% vs. 0.38% at inlayer (M–)OH sites). Because of the compensating effects of Steps 3 and 4, the photocatalytic CO₂ conversion rates into methanol and CO were similar for [Zn₅Cu₁.Ga(OH)₉][CO₃][H₂O] [0.49 μmol(CO₂) h⁻¹ g⁻¹] and [Zn₅Ga(OH)₈][Cu(OH)₄][H₂O] [0.43 μmol(CO₂) h⁻¹ g⁻¹] (Table 1A).

4.4. Verification of photocatalysis from CO₂ + H₂ using LDHs

Using the LDH compound [Zn₅Cu₁.Ga(OH)₈][CO₃][H₂O], no products were detected after 5 h at 313 K in the dark under CO₂ and H₂ (Fig. 5A). The Zn–Cu–Al LDH was reported to be stable as high as 573 K [48].

Unfortunately, the purity of [Zn₅Cu₁.Ga(OH)₈][CO₃][H₂O] was lower than that of [Zn₅Ga₁.Ga(OH)₈][CO₃][H₂O] in this study; minor CuO and Cu(OH)₂ were included for the LDH compounds.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.07.065.

References

[23] The light intensity was measured using a spectroradiometer Model USR-40D (Ushio). The xenon arc lamp irradiated in a wide spectrum between 200 and 1000 nm.
[35] Wavenumber $\tilde{\nu} = 1/2\pi c \sqrt{\kappa/\mu}$ was based on harmonic equation in which $c$ is the speed of light, $k$ is the force constant, and reduced mass $\mu$ satisfies $1/\mu = 1/M_1 + 1/M_2$. Thus, $\tilde{\nu}_{\text{CO}}/\tilde{\nu}_{\text{CO}_2} = \sqrt{13 + 16}/(13 + 16) = 0.97778$ and $\tilde{\nu}_{\text{CO}}/\tilde{\nu}_{\text{CO}_2} = \sqrt{13 + 1)/(13 + 1)}/(12 + 1)/(12 + 1) = 0.99704$.
[39] The CO$_2$ uptake was measured using a capacitance manometer (ULVAC, Models CCMT–1000A and GM–2001).


