Photocatalytic conversion of carbon dioxide into methanol using optimized layered double hydroxide catalysts

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The photocatalytic reduction of carbon dioxide into methanol was enabled between the Zn–Ga or Zn–Cu–Ga hydroxide layers using hydrogen and was promoted by the partial desorption of structural water stuffed between the cationic layers. The photoreduction rate obtained using [Zn1.5Cu1.5Ga(OH)8]2+2(CO3)2−·mH2O was improved by replacing interlayer carbonate anions with [Cu(OH)]2− to 0.49 μmol h−1 gcat−1, and the methanol selectivity was 88 mol%. At the molar level, interlayer Cu species was 5.9 times more active than the octahedral Cu sites in the cationic layers. The bandgap value was evaluated as 3.0 eV for the semiconductors [Zn1.5Cu1.5Ga(OH)8]2+[Cu(OH)4]2−·mH2O. Direct electronic transition from 0 2p to metal 3d, 4s, or 4p was responsible for the photocatalysis excited largely by ultraviolet (UV), and to a lesser extent by visible light.

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1. Introduction

There has been growing interest in the development of novel artificial methods that capture and concentrate large quantities of atmospheric carbon dioxide for subsequent conversion into fuels. Use of these methods is considered to have the potential to help alleviate major environmental problems relating to global warming and the scarcity of sustainable and secure energy sources [1,2]. Employing similarities that exist with the reaction of light during photosynthesis in green plants, phytoplankton, and algae, many researchers [3–5] have tried to attempt the photoreduction of CO2 coupled with water. However, due to thermodynamic limitations, the conversion of CO2 into fuels (such as methanol and Fischer–Tropsch) is extremely unfavorable [6]. In contrast, the conversion of CO2 and hydrogen into fuel shows promise for application in the near future if H2 can be obtained from water using sunlight.

Recently, the photoreduction of CO2 and H2 into methanol was reported for the first time using semiconductor layered double hydroxide (LDH) photocatalysts that were formulated as [Zn1−x−yAlxMiy(OH)2]x+y:[CO3]y−·2xH2O (M = Ga, Al; 0 ≤ x ≤ 1/3; 0 ≤ y ≤ 1/2; m~1/2) [6]. The methanol selectivity (26 mol%) obtained using Zn–Cu–Al LDH catalysts was improved to 68 mol% using Zn–Cu–Ga LDH catalysts. For practical applications, the catalytic rates of CO2 photoreduction are essential. Overall photocatalytic rates (250 mmol h−1 gcat−1) obtained using Zn–Cu–Ga catalysts [6] need to be accelerated by the optimization of their electronic state, concentrating the number of active sites, and the design of their interlayer reaction space.

In the interlayer space of LDH photocatalysts, CO2 was suggested for the reaction with the hydroxy group bound to the Cu sites to form a hydrogen carbonate intermediate [6]. Under UV–visible light, the Cu ions in the cationic layer facilitated charge separation utilizing the reduction–oxidation (redox) of Cu0 ↔ Cu1. Hydrogen carbonate species were gradually reduced to formic acid, formaldehyde, and finally to methanol utilizing the trapped photogenerated electrons as Cu1 ions [6]. Therefore, the interlayer space of these LDH photocatalysts served as an active pocket for the reduction of CO2 to methanol. An increase in the available reaction space would lead to enhanced photocatalytic activity.

The shape and size controls of ordered one dimensional nano/mesopores of metal oxides [7] and ordered two dimensional spaces between clay layers [8] were reported to lead to improved catalysis. The LDH compounds are advantageous in that they increase the available reaction space between cationic layers by the desorption of structural water molecules and carbonate anions while maintaining the regular stacked layer structure at 423–473 K [9,10]. As the quantity of Cu0 sites in the cationic layers increased, the photocatalytic formation rates of methanol were enhanced [6]. If photoactive Cu sites can also be accommodated as anion species of LDHs between the cationic layers, the photocatalytic rates per unit amount of catalyst would be further optimized.

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In this study, the available interlayer reaction space was increased by the pretreatment of LDH catalysts. Also, [Cu(OH)₄]²⁻ anion species was introduced between the cationic layers of LDHs. The effects of these modifications on the structure, physical properties, and photocatalytic performance were studied. In addition, we demonstrated the feasibility of CO₂ reduction coupled with water.

2. Methods

2.1. Catalyst syntheses

\[ [\text{Zn}3\text{Ga(OH)}_6]^{2+} \cdot (\text{CO}_3)_{3:2} \cdot m\text{H}_2\text{O} \text{ and } [\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga(OH)}_{8}]^{1+} \cdot (\text{CO}_3)_{3:2} \cdot m\text{H}_2\text{O} \]
LDH compounds were synthesized using a reported procedure [6]. They are abbreviated as Zn₉Ga/CO₃ and Zn₃₋₅Cu₃₋₅Ga/CO₃, respectively. Corresponding LDH samples consisting of anionic copper species between the [Zn₉Ga(OH)₆]³⁺ or [Zn₃₋₅Cu₃₋₅Ga(OH)₈]¹⁺ cationic layers were synthesized following a similar procedure, in order to use (NH₄)₂CuCl₄·2H₂O as the source of [CuCl₄]²⁻ anions.

For the synthesis of [Zn₉Ga(OH)₆]³⁺ LDH consisted of anionic Cu species, 20 mL solution consisting of both 0.75 M Na₂CO₃·6H₂O and 0.25 M Ga(NO₃)₃·mH₂O was dropped at a rate of 0.6 mL min⁻¹ into 100 mL of a 0.025–0.075 M (NH₄)₂CuCl₄·2H₂O solution in a flask at 290 K under argon atmosphere while stirring at a rate of 900 rpm. The pH was adjusted to 8 by adding 1.0 M NaOH (~40 mL total), after which the mixture was continuously stirred at the same rate of 290 K for 2 h. The pH was maintained at 8 by adding 1.0 M NaOH (~1 mL total). Then, the mixture of the temperature was raised to 353 K and stirred continuously for an additional 22 h, during which time the pH of the solution remained at 8. The precipitates that were obtained were filtered using a polytetrafluoroethylene based membrane filter (OmegaPro JGWPO7400, Millipore) with a pore size of 0.2 μm and washed well with deionized water. The slurry of the precipitates was maintained under an Ar atmosphere until the end of washing. The precipitates that were obtained were dried in ambient air at 290 K for 5 days.

During the catalyst synthesis, the [CuCl₄]²⁻ ions were hydrolyzed in the alkaline solution to form [Cu(OH)₄]²⁻ ions (see Section 3.1). The LDH compound obtained using 0.025 M (NH₄)₂CuCl₄·2H₂O solution is [Zn₉Ga(OH)₆]³⁺[Cu(OH)₄]₂⁻·mH₂O and abbreviated as Zn₉Ga/Cu(OH)₄. When 0.075 M (NH₄)₂CuCl₄·2H₂O solution was used, the molar quantity of [CuCl₄]²⁻ had increased by three times to form Zn₃₋₅Cu₃₋₅Ga/Cu(OH)₄. The compound that was obtained is denoted as [Zn₉₋₅Cu₅₋₅Ga(OH)₆]³⁺[Cu(OH)₄]₂⁻·mH₂O·3 x ex and abbreviated as Zn₉₋₅Ga/Cu(OH)₄·3·ex.

Cu atoms were substituted at the Zn₈ sites of cationic layers and were also intercalated as hydroxy anions following a similar procedure to obtain [Zn₉₋₅Cu₅₋₅Ga(OH)₈]¹⁺ LDH consisting of anionic Cu species. In order to set the molar ratio of Zn₈, Cu₅, and Ga₀ ions to 3:3:2, a mixed acid solution (20 mL) was prepared as 0.375 M Zn(NO₃)₂·6H₂O, 0.375 M Cu(NO₃)₂·3H₂O, and 0.25 M Ga(NO₃)₃·mH₂O. The 20 mL solution was dropped at a rate of 0.6 ml min⁻¹ into 100 mL of a 0.025–0.075 M (NH₄)₂CuCl₄·2H₂O solution in a flask at a temperature of 290 K and under an Ar atmosphere while stirring at a rate of 900 rpm. The subsequent steps in the procedure were identical to those for Zn₉Ga/Cu(OH)₄. The stoichiometric product starting from 0.025 M of (NH₄)₂CuCl₄·2H₂O is [Zn₉₋₅Cu₅₋₅Ga(OH)₆]³⁺[Cu(OH)₄]₂⁻·mH₂O and abbreviated as Zn₉₋₅Cu₅₋₅Ga/Cu(OH)₄. In the case where three times the quantity of (NH₄)₂CuCl₄·2H₂O (0.075 M) was used, the compound that was obtained is denoted as [Zn₉₋₅Cu₅₋₅Ga(OH)₆]³⁺[Cu(OH)₄]₂⁻·mH₂O·3 x ex and abbreviated as Zn₉₋₅Cu₅₋₅Ga/Cu(OH)₄·3·ex.

2.2. Characterization

Nitrogen adsorption isotherm measurements were performed at 77 K within the pressure range 1–90 kPa in a vacuum system that was connected to diffusion and rotary pumps (10⁻⁶ Pa) and equipped with a capacitance manometer (Modells CCMT-1000A and GM-2001, ULVAC). The Brunauer–Emmett–Teller (BET) surface area (S BET) was calculated on the basis of the eight-point measurements between 10 and 46 kPa (P/P₀ = 0.10–0.45) in the adsorption isotherm. As-synthesized samples were evacuated at 383 K for 2 h or at 423 K for 1 h before the measurements were taken.

X-ray diffraction (XRD) data were obtained using a MiniFlex diffractometer ( Rigaku) at a Bragg angle of 2θ = 5–70° with a scan step of 0.01° and a scan rate of 7 s per step for the sample powders. The measurements were performed at 30 kV and 15 mA using Cu Ka emission and a nickel filter.

Optical spectrosopic measurements were performed using a UV–visible spectrophotometer (JASCO, Model V-650). D₂ and halogen lamps were used for wavelengths below and above 340 nm, respectively, and an integrating sphere (JASCO, Model ISV-469) was used for the diffuse reflectance measurements. Measurements were performed at 290 K for wavelengths in the range 200–900 nm using 100 mg of fresh samples. Diffuse reflectance spectra were converted to absorption spectra on the basis of the Kubelka–Munk function [11,12]. The bandgap (Eg) value was evaluated on the basis of either simple extrapolation of the absorption edge or the fit to the Davis–Mott equation [12], given by

\[ a \times h \nu \propto (h \nu - E_g)^n \]

where a, h, and ν are the absorption coefficient, Planck's constant, and wavenumber, respectively, and n is 1/2, 3/2, 2, and 3 for allowed direct, forbidden direct, allowed indirect, and forbidden indirect transitions, respectively.

Cu K-edge X-ray absorption fine structure (XAFS) spectra were measured at 290 K in transmission mode in the Photon Factory at the High Energy Accelerator Research Organization on the beamlines of 9C or 7C. The storage-ring energy was 2.5 GeV, and the top-up ring current was 450 mA. A Si(1 1 1) double-crystal monochromator was inserted into the path of the X-ray beam. The X-ray intensity was maintained at 65% of the maximum flux using a piezo translator to suppress higher harmonics. The size of the slit opening in front of the l₀ ionization chamber was 1 mm (vertical) × 2 mm (horizontal). The l₀ and l₂ mm ionization chambers were purged with N₂ and Ar gases, respectively. The data accumulation time was 1 s for each data point. The Cu K absorption edge energy value was calibrated to 8980.3 eV for the spectrum of Cu metal [13,14]. The energy position of the monochromator was reproduced with an error of ±0.1 eV.

The XAFS data were analyzed using an X-ray absorption spectroscopy data analysis program (XDDAP) package [15]. The pre-edge background was approximated by a modified Victoreen function C₁/E² + C₂/E + C₀. The background of the post-edge oscillation was approximated by a smoothing spline function and calculated by an equation for the number of data points, where k is the wavenumber of photoelectrons.

\[ \sum_{i=1}^{n} \frac{(\mu x_i - B G_i)^2}{\exp(-0.075k^2)} \leq \text{smoothing factor} \]

2.3. Photocatalytic conversion tests for CO₂

As-synthesized and preheated samples of LDHs were tested for the photocatalytic conversion of CO₂ [6]. The tests were conducted in a closed circulating system (186 mL) equipped with a photoaction quartz cell that had a flat bottom (23.8 cm²) [16]. 100 mg
of the LDH catalyst was uniformly spread in the photoreaction cell and was evacuated by rotary and diffusion pumps (10−6 Pa) at 290 K for 2 h until the desorbed gas was detected by an online gas chromatograph (GC).

Reaction tests were also performed for samples of Zn1.5Cu1.5Ga3Ga(CO3) and Zn1.5Cu1.5Ga2Ga(CO3) preheated at 423 K. The LDH sample was evacuated at 290 K and the temperature was elevated to 423 K at a rate of 4 K min−1. The sample was kept at 423 K for 1 h, cooled, and transferred to the photoreaction cell using an argon filled glove box to prevent contact with air.

2.3 kPa of CO2 (0.177 mmol) and 21.7 kPa of H2 (1.67 mmol) were introduced to both intact and pretreated LDH photocatalysts and were allowed to circulate for 30 min in contact with the catalyst to attain sorption equilibrium before illumination. The photocatalyst was then illuminated with UV–visible light from the 500-W xenon arc lamp (Ushio, Model UJ-502Q) from downward through the flat bottom of the quartz reactor for 5 h. The distance between the bottom of the reactor and the lamp house exit window was set to 20 mm. The light intensity at a wavelength of 555 nm was 110 mW cm−2 at the center of the sample cell and 73 mW cm−2 at the periphery of the bottom plate of the sample cell. The intensity was measured at 555 nm, but the Xe arc lamp irradiated in a wide spectrum between 200 and 1100 nm. The temperature was within the range 305–313 K at the catalyst position during the illumination for 5 h [6]. The durability test for 20 h was also performed for the Zn1.5Cu1.5Ga2Cu(OH)2 photocatalyst.

Products and reactants were analyzed using packed columns of molecular sieves 13X-S and polyethylene glycol (PEG-6000) supported on Fluisin P (GL Sciences) set in the online GC equipped with a thermal conductivity detector (Shimadzu, Model GC-8A).

3. Results

3.1. Nitrogen adsorption, XRD, UV–visible spectra, and Cu K-edge EXAFS

The S BET values were measured by the N2 adsorption at 77 K for LDH compounds treated at 383 K in a vacuum (Table 1). The S BET value for Zn1.5Ga3Ga(CO3) was 23% greater than that for Zn1.5Cu1.5Ga3Ga(CO3). On increasing the preheating temperature to 423 K for these LDHs, S BET values increased by 18–19% (67–83 m2 g−1) due to the partial desorption of interlayer water and carbonate ions.

When compared with the S BET value for Zn1.5Ga3Ga(CO3), the values for Zn1.5Ga2Cu(OH)2 and Zn1.5Ga(Cu(OH))2×3 ex decreased by 50–53% because of the substitution of carbonate ions with [Cu(OH)]2− ions. On the other hand, when compared with the S BET value for Zn1.5Cu1.5Ga3Ga(CO3), the values for Zn1.5Cu1.5Ga2Cu(OH)2 and Zn1.5Cu1.5Ga(Cu(OH))2×3 ex did not change significantly (±8.8%). The contribution of impurity phases (see Section 3.1) may not be negligible.

The XRD spectra measured for as-synthesized LDH samples are shown in Fig. 1. The diffraction peaks exhibited typical patterns due to the diffraction of layer planes showing intense and sharp peaks at 2θ = 10–35°, and also showing weak and broad peaks at 2θ values greater than 35° [17]. There was a downward shift in several peaks at 2θ = 11.7–11.8°, 23.5°, 34.3°, 36.9–37°, 38.9°, 43.6–43.7°, 46.4°, 52.6°, 56.0°, 59.4°, 60.8°, and 66.8° for Zn1.5Cu1.5Ga3Ga(CO3) (spectrum a) and Zn1.5Cu1.5Ga2Ga(CO3) (spectrum d) by 0.4–1.5° to 11.2–11.4°, 22.5–22.7°, 33.9–34.1°, 36.4–36.5°, 38.2–38.6°, 43.1–43.2°, 45.3–45.5°, 51.1–51.4°, 54.5°, 59.0–59.2°, 60.3–60.5°, and 64.0–64.1° for Zn1.5Ga2Cu(OH)2 (spectrum b), Zn1.5Cu1.5Ga2Cu(OH)2 (spectrum c), and their 3 ex analogues (c and f) that were assigned to (003), (006), (009), (104), (015), (107), (018), (1010), (0111), (110), (113), and (116) diffractions, respectively [18,19].

In addition to characteristic LDH diffraction patterns, peaks derived from the Cu impurity phase appeared at 2θ = 32.4–32.5°, 35.5°, and 57.0–57.1° [20,21] in the spectra of Zn1.5Cu1.5Ga2Cu(OH)2 and the 3 ex analogue (Fig. 1e and f). Peaks derived from the Cu(OH)2 impurity phase appeared at 2θ = 16.2–16.3°, 39.4°, 50.1–50.2°, 53.5–53.6°, and 62.6–62.7° [22,23] for Zn1.5Ga2Cu(OH)2−3 x ex, Zn1.5Cu1.5Ga2Cu(OH)2, and Zn1.5Cu1.5Ga2Cu(OH)2−3 ex (spectra c, e, and f). The low index diffraction peaks derived from CuO or Cu(OH)2 were detectable for Zn1.5Ga2Cu(OH)2(b), which suggested a limited population of impurity phase(s). Diffraction peaks due to CuO and Cu(OH)2 were not found for Zn1.5Cu1.5Ga2Ga(CO3) (d).

The interlayer interval was evaluated as 0.751 and 0.753 nm on the basis of the (003) diffraction angle for Zn1.5Ga3Ga(CO3) and Zn1.5Cu1.5Ga3Ga(CO3) (Table 1A and B) [24]. The values were nearly consistent with the values of 0.756 and 0.758 nm, which were evaluated based on the (006) diffraction angle. The interlayer interval values on the basis of the (009) diffraction were 0.784 and 0.785 nm. The overlap of (012) peaks on (009) peaks may be the reason for the discrepancy (0.032–0.033 nm), when compared with the corresponding values based on (003) diffraction.

On the basis of the (003) diffraction angle (Table 1A, C, and E), the interlayer interval increased from 0.751 nm for Zn1.5Ga3Ga(CO3) to 0.792–0.784 nm for Zn1.5Ga2Cu(OH)2 and Zn1.5Ga2Cu(OH)2−3 ex. This reflected the greater size of [Cu(OH)]2− ions when compared to that of (CO3)2− [25,26]. In a similar manner, by substituting (CO3)2− with [Cu(OH)]2− (Table 1B, D, and F), the interlayer interval increased from 0.753 nm for Zn1.5Cu1.5Ga3Ga(CO3) to 0.782–0.772 nm.

The in-plane (1 1 0) diffraction angle (0.155–0.156 nm, Table 1) within a layer corresponds to R(Zn–O) of 0.219 nm if the complete ZnO octahedra are assumed and remained unchanged for all of the LDH samples. In this study, the value did not change for the Zn-based LDHs [24].

The UV–visible absorption spectra for synthesized LDH compounds are depicted in Fig. 2. The Ey values were estimated by extrapolation of the absorption edge to the x-axis. For Zn1.5Ga3Ga(CO3), the intersection with the x-axis was at 222 nm (spectrum a), which corresponded to an Ey value of 5.6 eV (Table 1A). The Ey values were also estimated based on the fit to the Davis–Mott equation, and they were similar to 5.6 eV when n was 1/2 or 3/2 (Table 1A), suggesting direct electronic transition from oxygen 2p to 4s or 4p levels of Zn and Ga.

When the interlayer (CO3)2− ions were replaced with [Cu(OH)]2−, the UV absorption edge shifted by 60–75 nm towards the lower energy side (Fig. 2a and b). The absorption edge was extrapolated to 297 nm, corresponding to the Ey value of 4.2 eV (Table 1C). In addition, a shoulder peak near the base that extended...
close to the visible light region (Fig. 2b) was extrapolated to 390 nm (Eg = 3.2 eV). The absorption edge further shifted by 40–50 nm towards the lower energy side for Zn1.5Cu1.5Ga(OH)3−3 × ex compared to that for Zn1.5Cu1.5Ga(OH)4−3 × ex (spectrum b–c). The absorption edge was extrapolated to 348 nm (Eg = 3.6 eV; Table 1E). For spectrum c, the edge overlapped with the larger shoulder peak between 300 and 430 nm. The extrapolation of the larger shoulder resulted in an estimated Eg value of 3.1 eV (397 nm) (Table 1B).

The fits to the Davis–Mott equation resulted in similar Eg values of 4.2 and 3.6 eV, which were based on simple extrapolation (Fig. 2b and c), for Zn1.5Cu1.5Ga(OH)4−3 × ex, respectively, when n was 1/2 or 3/2 (Table 1C and E), suggesting direct electronic transition from oxygen 2p to Cu 3d, 4s, or 4p levels and Zn/Ga 4s or 4p levels.

The shoulder corresponded to Eg values of 3.1–3.2 eV for Zn1.5Cu1.5Ga(OH)4−3, and the 3 × ex analogue appeared to originate from the Cu(OH)2 and/or CuO impurity phases (l) in the XRD spectra (Fig. 1b and c). The Eg values estimated by the fit to the Davis–Mott equation were very similar to the values that were based on simple extrapolation when n was 3/2 (Table 1C and E). This demonstrates the forbidden direct electronic transition from oxygen 2p to Cu 3d, 4s, or 4p levels of Cu(OH)2 and/or CuO phases.

On inclusion of Cu ions in the cationic layers of Zn1.5GaCO3, the UV absorption edge shifted towards the lower energy side for Zn1.5Cu1.5GaCO3 (Fig. 2d) when compared to the corresponding LDH free from Cu (spectrum a). Simple extrapolation yielded an Eg value of 3.5 eV (354 nm; Table 1B). Upon further replacing interlayer (CO3)2− ions with [Cu(OH)4]2− ions, the UV absorption edge shifted by 65–75 nm towards the lower energy side (Fig. 2e).

Simple extrapolation of the absorption edge resulted in an intersection with the x-axis at 417 nm (Eg = 3.0 eV; Table 1D).

The absorption edge for the LDH sample for which three times the amount of [CuCl4]2− was used for the synthesis (Fig. 2f) was extrapolated to 407 nm (Eg = 3.0 eV; Table 1F). For the case of n ranging from 1/2 or 3/2, the fits of the spectrum to the Davis–Mott equation resulted in very similar estimates of the Eg values based on simple extrapolation for Zn1.5Cu1.5GaCO3 and Zn1.5Cu1.5GaCu(OH)4−3 × ex (Table 1D and F).

In summary, the Eg value (5.6 eV) for Zn1.5GaCO3 that is free from copper decreased to 4.2 and 3.5 eV on the inclusion of Cu between and within layers, respectively, and decreased further to 3.0 eV on the inclusion of Cu at both locations. The electronic transition was considered to be directly from O 2p to metal (n−1)d, ns, or np. In addition, the forbidden direct electronic transition (3.1–3.2 eV) from oxygen 2p to Cu 3d, 4s, or 4p levels of Cu(OH)2 and/or CuO impurity phase(s) was observed.

The Cu K-edge EXAFS spectrum was tentatively measured for the Zn1.5Cu1.5Ga(OH)4−3 × ex sample (Fig. 3). In the Fourier transform (panel B), two intense peaks appeared at 0.16 and 0.27 nm (phase shift uncorrected). The peak that was derived from Cu–Cl bond(s) would appear at 0.195 nm [27] (phase shift uncorrected; true bond distances 0.2270–0.2287 nm) [28,29], but no peak appeared at the distance in Fig. 3B. Therefore, no Cu–Cl peaks were found in the Fourier transform for this LDH photocatalyst (Fig. 3B), demonstrating the complete hydrolysis of [CuCl4]2− into [Cu(OH)4]2−.

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>S_{ext} (m² g⁻¹)</th>
<th>Extrapolated</th>
<th>Eg (eV)</th>
<th>Fit to $\alpha \times hν - (hν - E_g)^n$</th>
<th>Interlayer Distance (nm)</th>
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<tr>
<td>A</td>
<td>[Zn1.5Ga(OH)3]2+[Zn1.5Ga(OH)3]2− + H2O (Zn1.5Ga(OH)3)</td>
<td>70* (83*) 2.0</td>
<td>5.6</td>
<td>5.9</td>
<td>5.4</td>
<td>5.2</td>
</tr>
<tr>
<td>B</td>
<td>[Zn1.5Cu1.5Ga(OH)3]2+[Zn1.5Cu1.5Ga(OH)3]2− + H2O (Zn1.5Cu1.5Ga(OH)3)</td>
<td>57* (87*) 2.0</td>
<td>3.5</td>
<td>4.2</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>C</td>
<td>[Zn1.5Ga(OH)3]2+[Cu(OH)4]2− + H2O (Zn1.5Ga(CuOH)4)</td>
<td>35* 2.0</td>
<td>4.2</td>
<td>4.8</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>D</td>
<td>[Zn1.5Cu1.5Ga(OH)3]2+[Cu(OH)4]2− + H2O (Zn1.5Cu1.5Ga(CuOH)4)</td>
<td>33* 2.0</td>
<td>3.6</td>
<td>4.2</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>E</td>
<td>[Zn1.5Ga(OH)3]2+[Cu(OH)4]2− + H2O (Zn1.5Ga(CuOH)4)</td>
<td>34* 2.0</td>
<td>3.6</td>
<td>4.2</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>F</td>
<td>[Zn1.5Cu1.5Ga(OH)3]2+[Cu(OH)4]2− + H2O (Zn1.5Cu1.5Ga(CuOH)4)</td>
<td>52* 2.0</td>
<td>3.1</td>
<td>4.1</td>
<td>2.9</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*Preheated at 383 K for 2 h or 423 K for 1 h under vacuum.

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**Fig. 3.** Cu K-edge EXAFS spectra for Zn1.5Cu1.5Ga(CuOH)4−3 × ex sample. (A) k²-weighted EXAFS $\chi$-function and (B) its associated Fourier transform. The solid and dotted lines represent the magnitude and the imaginary part in (B).

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While Zn1.5GaCO3 was CO selective (80 nmol h⁻¹ gcat⁻¹) in 2.3 kPa of CO₂ and 21.7 kPa of H₂ under the illumination of UV–visible light (Fig. 4A and Table 2A), Zn1.5Cu1.5GaCO3 was methanol selective (170 nmol h⁻¹ gcat⁻¹ and 68 mol%; Fig. 4B and Table 2B).
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Zn1.5GaCO3

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was

negligible

(Fig.

4C and A). In contrast, when Zn1.5Cu1.5GaCO3 was preheated at 423 K (Fig. 4D), the methanol formation rate increased by a factor of 1.8 (310 nmol h⁻¹ gcat⁻¹; Table 2D and B). The availability of interlayer sites bound to Cu was considered to be critical for CO2

photeruaction.

The Zn1.5GaCu(OH)4 photocatalyst was then tested (Fig. 4E). The methanol formation rate was enhanced by a factor of 5.9 compared to that using Zn1.5GaCO3 (Table 2E and A). The methanol selectivity was nearly the same as that obtained using Zn1.5Cu1.5GaCO3 (71–68 mol%). Cu sites between interlayers and within cationic layers may work similarly in photocatalysis. On the other hand, the interlayer Cu sites boosted the methanol formation rates by a factor of 5.9 as opposed to the promotion of Cu sites in [Zn1.5Cu1.5Ga(OH)3]⁺ layers, which boosted the methanol formation rates by a factor of 3.3 (Table 2E, B and A).

When the Zn3GaCO3 sample was preheated at 423 K in a vacuum, the change in the photocatalytic performance was negligible (Fig. 4C and A). In contrast, when Zn1.5Cu1.5GaCO3 was preheated at 423 K (Fig. 4D), the methanol formation rate increased by a factor of 1.8 (310 nmol h⁻¹ gcat⁻¹; Table 2D and B). The availability of interlayer sites bound to Cu was considered to be critical for CO2

photeruaction.

The Zn1.5GaCu(OH)4 photocatalyst was then tested (Fig. 4E). The methanol formation rate was enhanced by a factor of 5.9 compared to that using Zn1.5GaCO3 (Table 2E and A). The methanol selectivity was nearly the same as that obtained using Zn1.5Cu1.5GaCO3 (71–68 mol%). Cu sites between interlayers and within cationic layers may work similarly in photocatalysis. On the other hand, the interlayer Cu sites boosted the methanol formation rates by a factor of 5.9 as opposed to the promotion of Cu sites in [Zn1.5Cu1.5Ga(OH)3]⁺ layers, which boosted the methanol formation rates by a factor of 3.3 (Table 2E, B and A).

Using Zn1.5Cu1.5GaCu(OH)4 (Fig. 4F), the methanol formation rate and selectivity were further improved to 490 nmol h⁻¹ gcat⁻¹ and 88 mol% (Table 2F) owing to the combination of Cu sites within layers and Cu sites between layers.

In addition, photocatalysis using Zn1.5GaCu(OH)4-3 × ex was compared with an exact stoichiometric Zn1.5GaCu(OH)4 sample to evaluate the effects of Cu impurities. The decrease in the product formation rates was only 5.6–8.6% (Table 2E and G). The catalytic effects of Cu impurities were greater for Zn1.5Cu1.5GaCu(OH)4-3 × ex compared to its stoichiometric analogue (12–31%; Table 2H and F). However, the effect was still relatively small.

In the kinetic tests (Fig. 4), the formation rates of water were between 0.3 and 3.0 μmol h⁻¹ gcat⁻¹. These rates exceeded the quantity of water that was catalytically formed as the products of the following equations:

CO2 + H2 → CO + H2O

CO2 + 3H2 → CH3OH + H2O

This discrepancy is due to the desorption of interlayer water molecules of LDHs [30,31].

Finally, the durability of the Zn1.5Cu1.5GaCu(OH)4 photocatalyst (100 mg) was tested for 20 h in CO2 (2.3 kPa)+ H2 (21.7 kPa) illuminated with UV–visible light from the 500-W xenon arc lamp. In the test, methanol formation continued and the selectivity was 76–84 mol% (Fig. 5). After every 5 h, the methanol formation rate gradually decreased from 145 to 101, 61, and subsequently to 26 nmol h⁻¹ gcat⁻¹, while the CO formation rate decreased from 28 to 23, 15 and finally 8.2 nmol h⁻¹ gcat⁻¹. Throughout the test, the only products that were identified were methanol, CO, and water.

Table 2
 Rates of photocatalytic conversion of CO2 with H2 into CH3OH and CO over LDH photocatalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Formation rate (nmol h⁻¹ gcat⁻¹)</th>
<th>Conversion (%)</th>
<th>Selectivity to CH3OH (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH3OH</td>
<td>CO</td>
<td>Σ</td>
</tr>
<tr>
<td>A</td>
<td>Zn3GaCO3</td>
<td>51±4</td>
<td>80±6</td>
<td>130</td>
</tr>
<tr>
<td>B</td>
<td>Zn1.5Cu1.5GaCO3</td>
<td>170±14</td>
<td>79±6</td>
<td>250</td>
</tr>
<tr>
<td>C</td>
<td>Zn1.5GaCO3</td>
<td>50±6</td>
<td>74±6</td>
<td>120</td>
</tr>
<tr>
<td>D</td>
<td>Zn1.5Cu1.5GaCO3</td>
<td>310±9</td>
<td>180±4</td>
<td>500</td>
</tr>
<tr>
<td>E</td>
<td>ZnGaCu(OH)4</td>
<td>300±9</td>
<td>130±10</td>
<td>430</td>
</tr>
<tr>
<td>F</td>
<td>Zn1.5Cu1.5GaCu(OH)4</td>
<td>490±15</td>
<td>70±6</td>
<td>560</td>
</tr>
<tr>
<td>G</td>
<td>Zn1.5GaCu(OH)4-3×ex</td>
<td>290±8</td>
<td>120±9</td>
<td>390</td>
</tr>
<tr>
<td>H</td>
<td>Zn1.5Cu1.5GaCu(OH)4-3×ex</td>
<td>430±13</td>
<td>48±4</td>
<td>480</td>
</tr>
</tbody>
</table>

* The catalyst amount was 100 mg. Values in the parentheses are experimental errors for evaluation.

b Preheated at 423 K for 1 h under vacuum.

Fig. 5. Time course of photoreactions in CO2 (2.3 kPa)+ H2 (21.7 kPa) using 100 mg of Zn1.5Cu1.5GaCu(OH)4 for 20 h. Other reaction conditions and legends are the same as those for Fig. 4.
Table 3
Rates of photocatalytic formation of CH$_3$OH and CO per specific surface area and the quantity of Cu in the LDH photocatalysts.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Formulation rate per specific surface area (mmol h$^{-1}$ m$^{-2}$)</th>
<th>Formulation rate per amount of Cu (nmol h$^{-1}$ mmolCu$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH$_3$OH</td>
<td>CO</td>
</tr>
<tr>
<td>A</td>
<td>Zn$_2$GaCO$_3$</td>
<td>0.73</td>
<td>1.1</td>
</tr>
<tr>
<td>B</td>
<td>Zn$_2$Cu$_3$GaCO$_3$</td>
<td>3.0</td>
<td>1.4</td>
</tr>
<tr>
<td>C</td>
<td>Zn$_2$Ga(CO$_3$)$_2$</td>
<td>0.60</td>
<td>0.89</td>
</tr>
<tr>
<td>D</td>
<td>Zn$_2$Cu$_3$Ga(CO$_3$)$_2$</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>E</td>
<td>Zn$_2$Ga(CuOH)$_3$</td>
<td>8.6</td>
<td>3.6</td>
</tr>
<tr>
<td>F</td>
<td>Zn$_2$Cu$_3$Ga(CuOH)$_3$</td>
<td>7.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*a The catalyst amount was 100 mg. Values in the parentheses are experimental errors for evaluation.

b Preheated at 423 K for 1 h under vacuum.

4. Discussion

4.1. Improvement in photocatalysis by preheating of LDH photocatalysts

The layered structure of the synthesized compounds of the formula [Zn$_{3.5}$Cu$_{1.5}$Ga(OH)$_6$]$^{2-}$[2(CO)$_3$]$^{2-}$·mH$_2$O was confirmed by XRD. The interlayer distance of these compounds ranged from 0.751 to 0.753 nm, and the $S_{\text{BET}}$ values ranged from 57 to 70 m$^2$ g$^{-1}$. The $E_g$ value of Zn$_3$Ga(CO$_3$)$_2$ was 3.6 eV. Upon the addition of Cu sites in the layers to form Zn$_3$Cu$_3$Ga(CO$_3$)$_2$, the $E_g$ value decreased to 3.5 eV.

Heating these samples under vacuum conditions at 423 K resulted in the removal of one third of the water and interlayer carbonate ions [6], while the $E_g$ value increased by 18–19%. The $S_{\text{BET}}$ increase for Zn$_3$Cu$_3$Ga(CO$_3$)$_2$ does not adequately explain the increase of the methanol and CO formation rates by a factor of 1.8 and 2.3, respectively (Table 2D). The layered structure and the composition of the cationic layer did not change based on the XRD and UV-visible absorption pattern (Figs. 1 and 2). The available interlayer space that was created at 423 K is expected to facilitate the diffusion of CO$_2$ into the reaction space and the reaction with the surface hydroxy groups that are bound to the Cu sites (the Graphical abstract).

4.2. Role of in-layer and interlayer Cu in photocatalysis

Based on the tentative Cu K-edge EXAFS data, no chlorine coordination was observed for the Zn$_3$GaCu(CO$_3$)$_2$·3 nmol sample. Therefore, during catalysis synthesis, the following reactions (at least partially) took place.

\[
\text{[CuCl$_4$]}^{2-} + 4\text{NaOH} \rightarrow \text{[Cu(OH)$_4$]}^{2-} + 4\text{NaCl} \quad (1)
\]

\[2\text{[Zn$_3$Ga(OH)$_6$]}^{2+} + \text{[Cu(OH)$_4$]}^{2-} + \text{mH}_2\text{O} \rightarrow 2\text{[Zn$_3$Ga(OH)$_6$]}^{2+} \quad (2)
\]

\[\text{[Zn$_3$Ga(OH)$_6$]}^{2+} + \text{mH}_2\text{O} \Rightarrow \text{Zn$_6$Ga$_2$(OH)$_{15}$}^{\text{[(\mu-O)C$_3$Cu(OH)$_2$]}} \cdot \text{mH}_2\text{O} \quad (3)
\]

\[\text{Zn$_6$Ga$_2$(OH)$_{15}$}^{\text{[(\mu-O)Cu(OH)$_3$]}} \cdot \text{mH}_2\text{O} \Rightarrow \text{Zn$_6$Ga$_2$(OH)$_{15}$}^{\text{[(\mu-O)Cu(OH)$_2$]}} \cdot \text{mH}_2\text{O} + \text{H}_2\text{O} \quad (4)
\]

By substituting (CO$_2$)$_2^{2-}$ for [Cu(OH)$_4$]$^{2-}$, the $S_{\text{BET}}$ values decreased by 50–53% for Zn$_3$Ga(OH)$_6$ LDHs, and did not change significantly for Zn$_3$Cu$_1$Ga(OH)$_6$ LDHs (Table 1). The formation rates per specific catalyst surface area and the formation rates for specific quantities of Cu are summarized in Table 3. The methanol formation rates per specific surface area were greater for Cu containing LDHs, especially those which consisted of [Cu(OH)$_4$]$^{2-}$, whereas there was no significant variation in the CO formation rates per specific surface area. For the Zn$_3$Cu$_1$Ga(OH)$_6$ photocatalyst, the formation rates of methanol and CO were 51 and 24 nmol h$^{-1}$ mmolCu$^{-1}$, respectively. These values increased to 97 and 56 nmol h$^{-1}$ mmolCu$^{-1}$, respectively, when heated at 423 K in a vacuum. For the Zn$_2$Ga(CuOH)$_3$, the formation rates of methanol and CO were 300 and 130 nmol h$^{-1}$ mmolCu$^{-1}$, respectively. Therefore, the interlayer Cu sites were 5.3–5.9 times more effective than Cu sites in cationic layers, if we assume that the Cu atoms are primary active sites.

The methanol formation rate per unit amount of photocatalyst was optimum when using Zn$_3$Cu$_1$Ga(CuOH)$_3$, that consisted of both in-layer and interlayer Cu sites (Table 2F). The methanol formation rate per unit amount of Cu was 120 nmol h$^{-1}$ mmolCu$^{-1}$ (Table 3F), which is in close agreement with the calculated value of 110 nmol h$^{-1}$ mmolCu$^{-1}$, which was contributed by the in-layer Cu sites (2/4 × 51 nmol h$^{-1}$ mmolCu$^{-1}$) and the interlayer Cu sites (1/4 × 300 nmol h$^{-1}$ mmolCu$^{-1}$).

During the synthesis of LDH 3 × ex analogues, one third (2.5 mmol) of the (NH$_4$)$_2$CuCl$_2$2H$_2$O compound was used to produce 2.5 mmol of LDHs (2.5–2.51 g). Two thirds (5.0 mmol) of the (NH$_4$)$_2$CuCl$_2$2H$_2$O would produce 0.40–0.48 g of CuO & Cu(OH)$_2$, depending on the population ratio. Therefore, the contents of Cu impurity phases are 14–16 wt% in Zn$_3$GaCu(OH)$_3$·3 nmol and Zn$_3$Cu$_1$GaCu(OH)$_3$·3 nmol, which are in good agreement with the photocatalytic rate decrease of 5.6–8.6% and 12–31%, respectively (Table 2). The Cu impurity phases appear to be inactive.

The introduction of Cu in the interlayer space of LDHs accomplished two purposes. First, it resulted in an increase in the interlayer distance from 0.751 nm for Zn$_3$Ga(OH)$_3$ to 0.792 nm for Zn$_3$Ga(CO$_3$)$_2$, in effect expanding the interlayer reaction space. A similar change was observed for [Zn$_3$Cu$_1$Ga(OH)$_6$]$^{2-}$ layers where the increase was from 0.753 nm for carbonate containing LDH to 0.782 nm for [Cu(OH)$_4$]$^{2-}$ containing LDH. Secondly, the introduction of Cu resulted in the transformation to semiconductors as demonstrated by the decrease of the $E_g$ values to 3.0–4.2 eV (Table 1). The UV–visible absorption edge shifted towards the lower energy side and dramatically increased the excitation energy region for the photocatalysis.

It is interesting to compare the catalytic performance between interlayer Cu hydroxy anions and Cu octahedral sites surrounded by six oxygen atoms in the LDH cationic layers. Although the doped quantity of Cu was one third for the former sites, the methanol formation rates increased by a factor of 5.9 due to the replacement of
carbonates with \([\text{Cu(OH)}_2]^2-\) anions, as opposed to the increase by a factor of 3.3 due to the replacement of Zn sites with Cu (Table 2). The steric availability (accessibility) of \([\text{Cu(OH)}_2]^2-\) may be related to the reactivity difference (the Graphical abstract), but the exact speciation of doped Cu hydroxy groups (as in Eqs. (1)–(5)) is required for detailed discussion.

In this study, hydrogen was used to achieve CO₂ photoreduction, but we also demonstrated the feasibility of using LDH photocatalysts and water to achieve CO₂ photoreduction. 2.6 kPa of CO₂ was applied to 7 mg of \(\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga(OH)}_8\) and subsequently converted to methanol at a rate of 5.1 \(\mu\)mol h⁻¹ g⁻¹ and coupled with hydrogen species activated from water using 20 mg of Pt/C catalyst separated by a proton conducting polymer film. Currently, heating at 413 K is required to make the polymer proton-conductive. Also, the totally photocatalytic photoreduction of CO₂ using water is being researched.

5. Conclusions

The photoreduction of CO₂ into methanol with hydrogen using \([\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga(OH)}_8]^2-(\text{CO}_2)^2-\cdot\text{mH}_2\text{O}\) was improved by a factor of 1.8 by preheating at 423 K in a vacuum. The available interlayer space was created at 423 K and is expected to facilitate the diffusion of CO₂ to the reaction space and the reaction with the surface hydroxy groups that are bound to Cu sites.

By substituting the \((\text{CO}_2)^2-\) for \([\text{Cu(OH)}_2]^2-\), the methanol formation rates using \([\text{Zn}_{1.5}\text{Ga(OH)}_8]^2-(\text{CO}_2)^2-\cdot\text{mH}_2\text{O}\) and \([\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga(OH)}_8]^2-(\text{CO}_2)^2-\cdot\text{mH}_2\text{O}\) increased by a factor of 5.9 and 2.9, respectively. The hydroxy groups that were bound to Cu sites were important, and the effects of the interlayer \([\text{Cu(OH)}_2]^2-\) were greater than those of the in-layer octahedral Cu sites because of its steric availability (accessibility) and semiconductivity (\(E_g\) values of 3.0–4.2 eV).

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References