Selective Photoconversion of Carbon Dioxide into Methanol Using Layered Double Hydroxides at 0.40 MPa

Masaya Miyano, Hongwei Zhang, Mao Yoshiba, and Yasuo Izumi*

CO₂ photoconversion is a promising method to reduce atmospheric CO₂ concentrations and mitigate energy problems simultaneously. Among the various efficient and stable semiconductor photocatalysts used for this purpose, layered double hydroxides (LDHs) have attracted attention as catalysts for CO₂ photoconversion into CO and/or methanol. In this study, various LDHs of the formula [M₃⁺,Ga₄⁺(OH)₆]ₐ Å·mH₂O (M²⁺ = Zn²⁺, Cu²⁺; Å²⁺ = CO₂⁻, [Cu(OH)₂]²⁻) were synthesized and used for CO₂ photoconversion at a reaction pressure of 0.40 MPa in the presence of H₂ to result in the exclusive production of methanol. Furthermore, the pretreatment of carbonate-type LDHs at 423 K boosted the reaction rates by a factor of 7.5–20. Interestingly, [Zn,Ga(OH)₃]ₐ CO₂·mH₂O was the only LDH that produced methanol primarily by an eight-electron reduction (rather than the production of methanol by a six-electron reduction) at a total formation rate of 2.7 µmol h⁻¹ gcat⁻¹ after it was pre-heated at 423 K and protected by an Ar atmosphere.

Introduction

The photocatalytic conversion of CO₂ into fuels is a method to reduce atmospheric CO₂ concentrations and mitigate energy problems simultaneously. A further advantage of this process is the generation of methanol as a product for further transportation and storage. The major products reported for CO₂ photoconversion are methane, CO, the formate ion, and methanol. The selective production of methanol has few precedents, particularly for semiconductor-based photocatalysts.

Layered double hydroxides (LDHs) of the formula [M₃⁺,M₄⁺(OH)₆]ₐ Å·mH₂O (Å²⁺ = CO₂⁻, [Cu(OH)₂]²⁻) produce methanol and CO photocatalytically from CO₂ and H₂, and the combination of Cu²⁺ and Ga₄⁺ ions favors methanol formation. The selective formation of methanol was preserved for a Zn–Ga LDH exposed to CO₂ and UV/Vis light (cathode), and a proton-conducting film was used to separate it from a WO₃ moisture photo-oxidation catalyst (anode). The doping of LDHs by Ag or Au nanoparticles and phthalocyanines can boost the visible-light-only photocconversion of CO₂ into methanol and CO effectively.

In contrast, Ni-Al LDH; LDHs with M³⁺ = Ni, Mg, Zn and M₄⁺ = Al, Ga, In; and Zn–Al LDH produced mainly CO, CO₃⁻ and formic acid, formaldehyde, and methanol, respectively, from CO₂ in liquid water or moisture. The diffusion of photocogenerated electrons to CO₂-derived species in LDHs was monitored by using X-ray absorption fine structure analysis (XAFS) and FTIR spectroscopy; however, the origin of selective methanol production over the Zn–Ga LDH from CO₂ and H₂ is still unclear.

In this study, the photocatalytic conversion of CO₂ over Zn–Ga and Zn–Cu–Ga LDHs was investigated at 0.40 MPa of CO₂ and H₂ (Figure 1). Following the water photo-oxidation step [Eq. (1)], H₂ acted as a reductant for CO₂ photoconversion [Eq. (2)]. The metal ion profile of the cationic layers and the type of interlayer anions were varied, and the mechanism of selective methanol formation is discussed below.

\[ \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  \hspace{1cm} (1)

\[ \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  \hspace{1cm} (2)

Results

Characterization of photocatalysts

The XRD patterns of Zn–Ga–CO₃ and Zn–Cu–Ga–CO₃ LDHs are depicted in Figures 2a and b. The diffraction peaks at 2θ = 11.7, 23.5, 34.2, 37.0, 38.8–38.9, 43.3–43.6, 46.4,

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The XRD patterns measured for as-synthesized Zn–Ga–Cu(OH)$_3$ and Zn–Cu–Ga–Cu(OH)$_3$, as shown in Figure 2c,d. A shift to lower angles (by 0.3–1.6°) was detected for several peaks in the patterns of Zn–Ga–CO$_3$, Zn–Cu–Ga–CO$_3$, and Zn–Cu–Ga–Cu(OH)$_3$ to result in peaks at 2θ = 11.2, 22.6, 33.9, 36.5, 38.3, 42.8, 45.4, 51.3, 54.4, and 59.1° for Zn–Ga–Cu(OH)$_3$, Zn–Cu–Ga–Cu(OH)$_3$, and Zn–Cu–Ga–Cu(OH)$_4$. These peaks were assigned to the (003), (006), (009), (104), (015), (017), (018), (010), (011), and (110) lattice plane diffractions, respectively.[4] The interlayer interval for Zn–Ga–Cu(OH)$_3$ and Zn–Cu–Ga–Cu(OH)$_3$, was determined to be 0.785 nm from their (003) peaks (Table 1).

The mean thickness of the Zn–Ga–Cu(OH)$_3$ and Zn–Cu–Ga–Cu(OH)$_3$ LDH crystallites was 60 and 59 nm, respectively [determined from Eq. (3) and the width of the (003) peak]. In addition to the characteristic LDH diffraction patterns, impurity peaks appeared at 2θ = 16.3, 32.5, and 39.9–39.9°, which originate from CuO and Cu(OH)$_2$ impurity phases in both Zn–Ga–Cu(OH)$_3$ and Zn–Cu–Ga–Cu(OH)$_3$ LDHs (Figures 2c and d).

The extrapolation of the absorption edges in the UV/Vis absorption spectra (Figures 3Aa–d) yielded x intercepts of λ = 221, 370, 295, and 428 nm for Zn–Ga–CO$_3$, Zn–Cu–Ga–CO$_3$, Zn–Ga–Cu(OH)$_3$, and Zn–Cu–Ga–Cu(OH)$_3$ LDHs, which correspond to band gap ($E_g$) values of 5.5, 3.4, 4.2, and 2.9 eV, respectively (Table 1). The $E_g$ values of the above samples, calculated from Equation (4) (Experimental Section) by applying different n values, were 5.8–5.9, 3.9–2.7, 5.0–4.0, and 3.6–2.7 eV, respectively (Table 1). In the case of n = 1/2 and 3/2, the obtained values were similar to those obtained by simple absorption edge extrapolation (Table 1).

Alternatively, log–log plots of Equation 4 were constructed using $E_g$ values obtained by simple extrapolation (Table 1) to give n values between 0.85 and 1.02. As these values were between 1/2 (allowed direct transition) and 3/2 (forbidden transition), n = 0.85 was assigned as the transition probability of the direct transition for these LDHs.

### Table 1. Basic physicochemical properties of the LDH samples used in this study.

<table>
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<tr>
<th>Sample</th>
<th>Color</th>
<th>$E_g$ [eV]</th>
<th>$n^3$</th>
<th>Interlayer distance $[\text{nm}]^3$</th>
<th>Crystallite thickness $[\text{nm}]^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn–Ga–CO$_3$</td>
<td>white</td>
<td>5.5</td>
<td>5.8</td>
<td>5.4</td>
<td>0.85</td>
</tr>
<tr>
<td>Zn–Cu–Ga–CO$_3$</td>
<td>gray</td>
<td>3.4</td>
<td>3.9</td>
<td>2.7</td>
<td>0.97</td>
</tr>
<tr>
<td>Zn–Cu–Ga–Cu(OH)$_3$</td>
<td>pale blue</td>
<td>4.2</td>
<td>5.0</td>
<td>4.0</td>
<td>1.02</td>
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<tr>
<td>Zn–Cu–Ga–Cu–Cu(OH)$_3$</td>
<td>light blue</td>
<td>2.9</td>
<td>3.6</td>
<td>2.7</td>
<td>0.95</td>
</tr>
<tr>
<td>Zn(OH)$_2$</td>
<td>white</td>
<td>3.2</td>
<td>3.2</td>
<td>3.1</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>light blue</td>
<td>2.9</td>
<td>3.0</td>
<td>2.8</td>
<td>0.99</td>
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<tr>
<td>CuO</td>
<td>black</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>white</td>
<td>4.6</td>
<td>4.7</td>
<td>4.5</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Zn–Ga–CO$_3^-$ could exhibit a direct electronic transition from O2p to Zn/Ga 4s or 4p levels, and Zn–Cu–Ga–CO$_3^-$, Zn–Ga–Cu(OH)$_4^-$, and Zn–Cu–Ga–Cu(OH)$_4^-$ could exhibit direct transitions from O2p to Zn/Ga 4s or 4p levels or Cu 3d, 4s, or 4p levels.

The interlayer CO$_3^{2-}$ ions of Zn–Ga–CO$_3^-$ LDH were replaced with [Cu(OH)$_2$]$_2^{2-}$ (which results in Cu/Zn = 1:6 mol/mol), the UV absorption edge shifted to longer wavelengths by 74 nm (Figure 3A a,c). Accordingly, $E_g$ decreased from 5.5 to 4.2 eV, mostly because of an electronic transition to the Cu 3d level. Additionally, a d–d transition was observed as a weak feature between $\lambda = 560$ and 800 nm (Figure 3A c).

If half of the Zn$^{2+}$ sites in the cationic layers of Zn–Ga–CO$_3^-$ LDH were replaced with Cu$^{2+}$ sites (Cu/Zn = 1:1 mol/mol), the UV absorption edge was further shifted to longer wavelengths by 149 nm (Figures 3A a and b), and $E_g$ decreased from 5.5 to 3.4 eV, mostly because of electronic transitions to the Cu 3d level. Thus, the amount of Cu was a primary factor to determine the extent of the $E_g$ shift (Figures 2a–c). In other words, the density of states for Cu 3d in Zn–Cu–Ga–CO$_3^-$ was more diffuse than that in Zn–Ga–Cu(OH)$_4^-$.

Finally, if we replaced both the interlayer and cationic layer sites in Zn–Ga–CO$_3^-$ LDH with Cu to produce Zn–Cu–Ga–Cu(OH)$_4^-$ (Cu/Zn = 4:3 mol/mol) the UV absorption edge shifted to longer wavelengths by 207 nm, and $E_g$ decreased from 5.5 to 2.9 eV, mostly because of electronic transitions to the Cu 3d level at inter- and in-layer sites. The observed decrease (2.6 eV) was greater than that obtained by replacing interlayer sites with [Cu(OH)$_2$]$_2^{2-}$ (1.3 eV) or by replacing half of the Zn$^{2+}$ sites in cationic layers (2.1 eV). In accord with the increasing Cu content, the intensity of the d–d transition between $\lambda = 560$ and 800 nm increased in comparison to that observed for Zn–Ga–Cu(OH)$_3^-$ (Figures 3A c and d).

Electronic transitions between the O2p and metal energy levels were observed for reference Zn(OH)$_2$ and Ga$_2$O$_3$ samples in the UV region with no absorption detected in the visible region (Figures 3B e and h). Consistently, these samples were white (Table 1). In contrast, the reference CuO sample was black and absorbed in the whole UV/Vis region (Figure 3B g). Thus, the gray color (Table 1) and broad absorption peak between $\lambda = 330$ and 800 nm (Figure 3A b) observed for Zn–Cu–Ga–CO$_3^-$ was because of the presence of a Cu O impurity, as evidenced by using XRD (Figure 2 b).

The Cu(OH)$_2$ reference material was light blue (Table 1) and its d–d transitions and the absorption edge caused by O2p to Cu 3d transitions lay in the visible and UV light regions, respectively. Cu(OH)$_2$ exhibits a flat, sheetlike[17] structure that is somewhat similar to that of LDHs. The absorption edge of Cu(OH)$_2$ was extrapolated to $\lambda = 433$ nm (Figure 3B f), which is shifted significantly to longer wavelengths in comparison to those of Zn–Cu–Ga–CO$_3^-$ and Zn–Ga–Cu(OH)$_4^-$ (Figures 3A b and c and Table 1). Therefore, the weak shoulders at $\lambda = 310–330$ and 300–400 nm observed for Zn–Cu–Ga–CO$_3^-$ and Zn–Ga–Cu(OH)$_4^-$ (Figures 3A b and c), respectively, can be ascribed to a Cu(OH)$_2$ impurity. However, the concentrations of this impurity are very low, as estimated from the XRD peak intensity of Cu(OH)$_2$ (Figures 2 b–d). Accordingly, the contribution of this impurity to the d–d transition is marginal (Figures 3A c and d).

Based on Equation (4), $E_v$ values of 2.9–4.6 eV were determined for Zn(OH)$_2$, Cu(OH)$_2$, and Ga$_2$O$_3$, for which $n$ values between 1/2 and 3/2 demonstrated direct O–to-metal electronic transitions (Table 1).

The replacement of CO$_3^{2-}$ with [Cu(OH)$_2$]$_2^{2-}$ was confirmed by the dramatic intensity decrease observed by using FTIR spectroscopy for symmetric and antisymmetric stretches of CO$_3^{2-}$.[15] The Cu/Zn molar ratios of Zn–Cu–Ga–CO$_3^-$, Zn–Ga–Cu(OH)$_4^-$, and Zn–Cu–Ga–Cu(OH)$_4^-$ (1:1, 1:6, and 4:3, respectively) were confirmed by using X-ray absorption spectroscopy. Interestingly, the octahedral coordination of Cu$^{2+}$ and O atoms was common in these LDHs, as observed by using X-ray absorption near-edge and extended X-ray absorption fine structure spectroscopy. Cu exhibited Cu(OH)$_2$ motifs in the cationic layers of Zn–Cu–Ga–CO$_3^-$ and Zn–Cu–Ga–Cu(OH)$_4^-$, whereas ($\mu$-O)$_2$Cu(OH)$_4$(H$_2$O)$_2$ ($n = 1, 2, 3; \mu$-O from the cationic layer; H$_2$O from interlayer water) units were present in the interlayer sites of Zn–Ga–Cu(OH)$_4^-$ and Zn–Cu–Ga–Cu(OH)$_4^-$.[15]

The SEM and TEM images of Zn–Ga–CO$_3^-$ (Figure 4A 1 and 6) show flake-like thin layers. The thickness distribution of a single layer (e.g., Figure 4A 5) centered at 30–40 nm (Figure 4A, histogram) and the mean value of (42 ± 2) nm were not consistent with the thickness of 68 nm obtained by using XRD (Table 1) as electron-transparent layers were chosen for TEM measurements, which are thinner than those characterized by using XRD. The observed hexagonal crystallites and outlines (perimeters) with thinner contrast are depicted in Figure 4A 2–4 and the outline (perimeter) width
was centered at 4–6 nm (Figure 4A, histogram). The side face of a single thin layer (thickness ≈ 42 nm) was observed at a nearly parallel angle.

TEM images of Zn–Ga–Cu(OH)₄ (Figure 4B) displayed flake-like thin layers (Figure 4B1). The thickness distribution of a single layer (e.g., Figure 4B5) centered at 30–40 nm (Figure 4B, histogram) with a mean of (43 ± 22) nm was fairly consistent with the value of 60 nm determined by using XRD (Table 1). In analogy to the images of Zn–Ga–CO₃, outlines (perimeters) of crystallites with a thinner contrast were observed, and the width distribution was centered at 2–4 nm (Figure 4B2–4, histogram).

**Photocatalytic tests using LDHs at 0.40 MPa**

CO₂ photoconversion tests were performed at a total pressure of 0.40 MPa using four LDH catalysts and H₂. The photocatalyst film formed on a Pyrex plate was dried at 373 K for 12 h and transferred to the high-pressure reactor (Figure 1B and C) under ambient conditions (Table 2A). Methanol was formed as the only the C-containing product, and the observed activity order was: Zn–Cu–Ga–Cu(OH)₄ > Zn–Ga–CO₃ > Zn–Ga–Cu(OH)₄ > Zn–Cu–Ga–CO₃.

The selectivity trend at 0.40 MPa contrasted with the results of LDH low-pressure photoconversion tests performed under 2.3 kPa of CO₂ + 22 kPa of H₂, in which both CO and methanol were obtained as major products (Table 2E1–4).

Water was also formed (Table 2A), however, its formation rate was a factor of 780–5500 higher than that of methanol, which demonstrates that it originated exclusively from desorbed interlayer water molecules and was not produced from the reactants. The rates of water formation among LDH photocatalysts varied by a factor of 5.6 (Table 2A), which suggests that the LDH film preheated at 373 K (Figure 1A) absorbed atmospheric moisture into the interlayer space before it was introduced into the reactor (Figure 1C).

Next, LDHs were pretreated at an elevated temperature (423 K) for 12 h to desorb approximately one third of the interlayer water. The LDH film on the Pyrex plate was preheated and transferred to the high-pressure reactor under ambient conditions (Table 2B). Again, methanol was observed as the only C-containing product; however, its formation rates were boosted by a factor of 7.5–20 compared to the values obtained for catalysts preheated at 373 K (Table 2A). Apparently, the photoconversion of CO₂ was accelerated by removing some of the interlayer water molecules to liberate reaction space (Scheme 1B).

Water desorption rates (Table 2B) decreased to 56–57% of the values obtained for catalysts preheated at 373 K (Table 2A). Despite this decrease, the partial adsorption of atmospheric moisture during sample transfer from the drying oven held at 423 K to the high-pressure reactor could not be excluded.

To address this issue, a preheated LDH film on a Pyrex plate was transferred to the high-pressure reactor in an atmosphere of Ar to avoid contact with air and thus ensure the partial removal of interlayer water molecules (Table 2C). Except for the Zn–Ga–CO₃ photocatalyst, which favored methane production over that of methanol, all LDHs produced methanol exclusively. The total formation rate of C-containing compounds (Σc) using Zn–Ga–CO₃ LDH was 2.7 μmol h⁻¹ g⁻¹ (Table 2C1). The more effectively liberated interlayer reaction space of the Zn–Ga–CO₃ catalyst transferred under Ar favored a further two-electron reduction (Scheme 1C). The catalytic activity based on total C-containing products was in the order: Zn–Ga–CO₃ > Zn–Cu–Ga–CO₃ > Zn–Cu–Ga–Cu(OH)₄ ≈ Zn–Ga–Cu(OH)₄.

The total formation rate of C-containing products for Zn–Ga–CO₃ transferred under Ar (Table 2C) was higher than
that obtained for the same catalyst transferred in air by a factor of 9.0 (Table 2B), which indicates that sample transfer under Ar preserved the interlayer reaction space of this LDH liberated by heating at 423 K.

However, the rate of exclusive methanol formation for Zn–Cu–Ga–CO\(_2\) transferred in air was similar to that of the photocatalyst transferred in Ar (Table 2B, C). The exclusive methanol formation rates for Zn–Ga–Cu(OH)\(_4\) and Zn–Cu–Ga–Cu(OH)\(_4\) preheated at 373 K were almost unchanged if these photocatalysts were preheated at 423 K and transferred under Ar (Table 2A, C). The reason behind these unimproved CO\(_2\) photoconversion rates is not known; however, two plausible reasons can be used to explain this observation: (1) the amount of water in the tests listed in Table 2A and B was not controlled well and was similar to that in the tests summarized in Table 2C and/or (2) the interlayer space of these LDHs was not utilized effectively for catalysis as the major active sites are located only on the outer surface (Scheme 1B).

The results of a blank test using Zn–Ga–CO\(_2\) in the dark at 303 K are shown in Table 2C. No CO and methane were detected; however, methanol was formed at a rate of 0.020 \(\mu\text{mol h}^{-1}\text{g}_{\text{cat}}^{-1}\). Thus, some methanol is formed thermally rather than photocatalytically if the catalyst activity is relatively low (Table 2A1–3, C3–4). In contrast, the thermal route is negligible for the entries in Table 2A4, B1–2, and C1–2, mainly because of the effect of the liberated LDH interlayer space.

The effects of Zn(OH)\(_2\), Cu(OH)\(_2\), CuO, and Ga\(_2\)O\(_3\) impurities in Zn–Cu–Ga–CO\(_2\) (Figure 2b) and Cu(OH)\(_2\) and CuO in Zn–Ga–Cu(OH)\(_4\) and Zn–Cu–Ga–Cu(OH)\(_4\) (Figures 2c and d) were evaluated. In photocatalytic tests under 0.40 MPa of CO\(_2\)+H\(_2\), the total formation rates of C-containing compounds for Zn(OH)\(_2\) and Ga\(_2\)O\(_3\) were low (0.048–0.059 \(\mu\text{mol h}^{-1}\text{g}_{\text{cat}}^{-1}\). Table 2D5 and 8), which indicates that the contribution of these impurities on the performance of Zn–Cu–Ga–CO\(_2\) (Table 2C2) was negligible.

In contrast, CuO photoconverted CO\(_2\) into methanol at a moderate rate (0.14 \(\mu\text{mol h}^{-1}\text{g}_{\text{cat}}^{-1}\); Table 2D7), which shows that a low concentration of this impurity may contribute to the lower rates observed for Zn–Ga–Cu(OH)\(_4\) and Zn–Cu–Ga–Cu(OH)\(_4\) (0.028–0.034 \(\mu\text{mol h}^{-1}\text{g}_{\text{cat}}^{-1}\); Table 2C3 and 4). As the photocatalytic performances of Zn–Cu–Ga–CO\(_2\) and CuO were similar (Table 2C2 and D7), the contribution of the CuO impurity to the rates observed for Zn–Cu–Ga–CO\(_2\) is marginal because of its low concentration.

Surprisingly, the photoconversion of CO\(_2\) over Cu(OH)\(_2\) produced CO and methanol as the major and minor products, respectively, at a total formation rate of 7.8 \(\mu\text{mol h}^{-1}\text{g}_{\text{cat}}^{-1}\) (Table 2D6). As no CO formation was ob-

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**Table 2. Results of CO\(_2\) photoconversion and blank tests at elevated pressure using hydrogen and LDH photocatalysts (10 mg) and rates reported previously.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Reactant [MPa]</th>
<th>CO(_2)</th>
<th>CO</th>
<th>CH(_3)OH</th>
<th>CH(_4)</th>
<th>H(_2)O</th>
<th>(\Sigma)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Zn–Ga–CO(_2)</td>
<td>0.12 0.28</td>
<td>&lt;0.08</td>
<td>0.040</td>
<td>&lt;0.12</td>
<td>66</td>
<td>0.040</td>
<td>this work</td>
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</tr>
<tr>
<td></td>
<td>Zn–Cu–Ga–CO(_2)</td>
<td>0.12 0.28</td>
<td>&lt;0.08</td>
<td>0.011</td>
<td>&lt;0.12</td>
<td>61</td>
<td>0.011</td>
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<tr>
<td></td>
<td>Zn–Ga–Cu(OH)(_4)</td>
<td>0.12 0.28</td>
<td>&lt;0.08</td>
<td>0.023</td>
<td>&lt;0.12</td>
<td>18</td>
<td>0.023</td>
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</tr>
<tr>
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<td>Zn–Cu–Ga–Cu(OH)(_4)</td>
<td>0.12 0.28</td>
<td>&lt;0.08</td>
<td>0.087</td>
<td>&lt;0.12</td>
<td>100</td>
<td>0.087</td>
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<tr>
<td>B</td>
<td>Zn–Ga–CO(_2)</td>
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<td>&lt;0.08</td>
<td>0.30</td>
<td>&lt;0.12</td>
<td>37</td>
<td>0.30</td>
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<tr>
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<td>Zn–Cu–Ga–CO(_2)</td>
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<td>&lt;0.08</td>
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<td>&lt;0.12</td>
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<td>0.22</td>
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<tr>
<td>C</td>
<td>Zn–Ga–CO(_2)</td>
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<td>&lt;0.08</td>
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<td>2.6</td>
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<td>2.7</td>
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<tr>
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<td>Zn–Cu–Ga–CO(_2)</td>
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<td>&lt;0.08</td>
<td>0.19</td>
<td>&lt;0.12</td>
<td>59</td>
<td>0.19</td>
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<tr>
<td></td>
<td>Zn–Ga–Cu(OH)(_4)</td>
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<td>&lt;0.08</td>
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<td>&lt;0.12</td>
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<td>&lt;0.12</td>
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<td>D</td>
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<td>&lt;0.08</td>
<td>0.020</td>
<td>&lt;0.12</td>
<td>9.1</td>
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<td>Zn(OH)(_2)</td>
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<td>0.048</td>
<td>&lt;0.12</td>
<td>10</td>
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<td>34</td>
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<td>&lt;0.08</td>
<td>0.14</td>
<td>&lt;0.12</td>
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<tr>
<td></td>
<td>CaO</td>
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<td>&lt;0.08</td>
<td>0.059</td>
<td>&lt;0.12</td>
<td>19</td>
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<tr>
<td>E</td>
<td>Zn–Ga–CO(_2)</td>
<td>0.12 0.28</td>
<td>0.002</td>
<td>0.080</td>
<td>0.051</td>
<td>0.13</td>
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<td>Zn–Cu–Ga–CO(_2)</td>
<td>0.12 0.28</td>
<td>0.079</td>
<td>0.17</td>
<td>0.25</td>
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<td>Zn–Ga–Cu(OH)(_4)</td>
<td>0.12 0.28</td>
<td>0.11</td>
<td>0.30</td>
<td>0.43</td>
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<td>Zn–Cu–Ga–Cu(OH)(_4)</td>
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<td>0.070</td>
<td>0.49</td>
<td>0.56</td>
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<td>F</td>
<td>Ag/Zn–Ga–CO(_2)</td>
<td>0.12 0.28</td>
<td>0.05</td>
<td>0.10</td>
<td>2.1</td>
<td>5.3</td>
<td>3.2</td>
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<td></td>
<td>TiO(_2)</td>
<td>&lt;0.08 0.027</td>
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<td>56</td>
<td>4.0</td>
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<tr>
<td></td>
<td>g-C(_3)N(_4)</td>
<td>&lt;0.08 0.004</td>
<td>3.8</td>
<td>4.7</td>
<td>3.8</td>
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<td></td>
<td>BiOCl</td>
<td>1.9 &lt;0.004</td>
<td>1.1</td>
<td>37</td>
<td>3.0</td>
<td></td>
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</table>

[a] Total formation rates of C-containing products. [b] In the absence of UV/Vis light at 303 K.
Discussed for the LDHs studied, the effect of the Cu(OH)$_2$ impurity can be excluded. Only the reference catalyst Cu(OH)$_2$ was active because of the partial decomposition of bulk Cu(OH)$_2$ to CuO during pretreatment at 423 K, and the resulting mixture of Cu(OH)$_2$ and CuO phases is advantageous for CO$_2$ photoconversion.

Discussion

Carbonate-type Zn–Ga and Zn–Cu–Ga LDHs and their tetrahydroxycuprate-type counterparts were synthesized and their high purity was confirmed by XRD and UV/Vis spectroscopy (Figures 2 and 3). Traces of impurities such as Zn(OH)$_2$, Ga$_2$O$_3$, CuO, and Cu(OH)$_2$ were detected; however, their amounts were lower than those in materials prepared previously[3,4] because of the slow crystallization during drying on a wide Pyrex plate for five days. Notably, no impurities were detected in the most active Zn–Ga–CO$_3$ catalyst in this study, and these impurities were shown to be inert at a reactant pressure of less than 0.10 MPa.[3,4]

In this study, Zn(OH)$_2$ and Ga$_2$O$_3$ impurities were inactive at a reactant pressure of 0.40 MPa (Table 2D5, 8) and did not contribute to the rates observed for Zn–Cu–Ga–CO$_3$ (Figure 2b and Table 2C2). CuO exhibited a moderate activity toward methanol production (Table 2D7), which possibly affected the results of poorly performing Zn–Ga–Cu(OH)$_2$ and Zn–Cu–Ga–Cu(OH)$_2$, but had a negligible influence on Zn–Cu–Ga–CO$_3$ if we take the concentration of this impurity into account (Figures 2b–d). Bulk Cu(OH)$_2$ is probably activated by heating at 423 K to produce an interface between Cu(OH)$_2$ and CuO for the selective formation of CO (Table 2D6). Such effective CO$_2$ photoconversion sites were not formed in the LDHs studied herein, and no CO was produced (Table 2A–C).

The salient point of CO$_2$ photoconversion at 0.40 MPa (0.12 MPa of CO$_2$ and 0.28 MPa of H$_2$) is the exclusive selectivity toward methanol, whereas both CO and methanol were produced over these LDHs at 24 kPa (2.3 kPa of CO$_2$ and 22 kPa of H$_2$; Scheme 1A). Thus, above 0.40 MPa, the higher concentrations of reactants and/or intermediates in the reaction space of the LDHs facilitate the sequential six-electron reduction of CO$_2$ to methanol (Scheme 1B) rather than its two-electron reduction to CO.

For CO$_2$ photoconversion at 0.40 MPa, the catalyst activity depended critically on the pretreatment conditions of carbonate-type LDHs (Table 2A1, 2A2, 2B1, 2B2, 2C1, and 2C2), and the methanol formation rates increased by a factor of 7.5–20 as the pretreatment temperature increased from 373 to 423 K (Table 2A and B). In the special case of Zn–Ga–CO$_3$, the sample heated at 423 K and transferred to the high-pressure reactor under Ar (Table 2C) produced methane (eight-electron reduction) rather than methanol (six-electron reduction). The total formation rate of C-containing products reached 2.7 μmol h$^{-1}$g$_{cat}^{-1}$, which corresponds to a 9.0-fold increase compared to that observed for the same catalyst transferred in air (Table 2B1 and C1). This change can be understood by assuming a subsequent two-electron reduction path favored by the more efficient and open interlayer reaction space in the tests listed in Table 2C (Scheme 1C). Exclusive methane formation from CO$_2$ and moisture has been reported for Zn–Ce and Zn–Ti LDHs irradiated by UV light ($\lambda = 185$ nm).[19]

In clear contrast, the rates of methanol formation for tetrahydroxycuprate-type LDHs were suppressed to less than 0.1 μmol h$^{-1}$g$_{cat}^{-1}$ at 0.40 MPa (Table 2A3, 2A4, 2C3, and 2C4). The interlayer reaction space[19] created by the partial removal of water molecules and/or carbonate ions of LDHs is believed to be important for CO$_2$ photoconversion. For Zn–Ga–CO$_3$, the rate of water formation decreased progressively with the improvement of the pretreatment conditions (Table 2A →B →C) and the CO$_2$ photoconversion rate increased concomitantly. In the case of Zn–Cu–Ga–CO$_3$, the water formation rate did not decrease simply because of the improved pretreatment conditions; however, the extent of this decrease correlated well with the CO$_2$ photoconversion rate (Table 2A2, B2, and C2). In comparison to Zn–Ga–CO$_3$, Zn–Cu–Ga–CO$_3$ was destabilized by the inclusion of 3d$^9$ Cu$^{2+}$ ions in the cationic layer because of the Jahn–Teller effect,[19] and the desorption of interlayer water before/ during photocatalytic tests for 5 h was relatively difficult to reproduce quantitatively.

---

**Scheme 1.** Reaction space and products of CO$_2$ photoconversion at A) low pressure for LDHs pretreated at 373 K, B) high pressure for LDHs pretreated at 373 K, and C) high pressure for LDHs pretreated at 423 K.
The formation rates of C-containing products listed for Zn–Ga–CO₃ and Zn–Cu–Ga–CO₃ in Table 2B–C (0.40 MPa) are comparable to those obtained at 24 kPa (Table 2E1–4), except for the higher value of 2.7 μmol h⁻¹ g⁻¹ (Table 2C1). The rates observed for Zn–Ga–Cu(OH)₃ and Zn–Cu–Ga–Cu(OH)₄ (Table 2A and C, 0.40 MPa) were one order of magnitude lower than those obtained at 24 kPa (Table 2E–I–4). Thus, the reaction order was zero or even negative for most of the LDHs used in this study except for Zn–Ga–CO₃ in contrast to the reported TiO₂, g-C₃N₄, and BiOCl photocatalysts at 0.40 MPa, presumably because of the strong adsorption of reactants/intermediates in the interlayer reaction space of LDHs.

The photoconversion of CO₂ at 0.40 MPa over Ag-doped Zn–Ga–CO₃ was reported to produce methane, CO, and minor amounts of methanol at a total formation rate of 3.2 μmol h⁻¹ g⁻¹ (Table 2E1) and a similar value was observed for Ag-free Zn–Ga–CO₃ (2.7 μmol h⁻¹ g⁻¹, Table 2C1) by pretreatment at 423 K and sample transfer under Ar. The performance of Zn–Ga–CO₃ at 0.40 MPa (Table 2C1) was equivalent to that of BiOCl (Table 2E11) and close to that of TiO₂ and g-C₃N₄ (Table 2E9 and 10). Thus, the doping of LDHs with effective electron-trapping and/or surface plasmon resonance sites and the optimization of the pretreatment/transfer conditions (Table 2C) is expected to further improve the catalytic performance of CO₂ and H₂ at 0.40 MPa.

Conclusions

The photoconversion of CO₂ was studied for various layered double hydroxides (LDHs). With H₂ as a reductant, methanol production over the LDHs was achieved at less than 0.1 MPa and became exclusive at 0.40 MPa. The CO₂ photoconversion rates observed for carbonate-type LDHs Zn–Ga–CO₃ and Zn–Cu–Ga–CO₃ were improved by increasing the pretreatment temperature from 373 to 423 K (0.19–2.7 μmol h⁻¹ g⁻¹), which suggests the liberation of the interlayer reaction space by the removal of approximately one third of the interlayer water molecules. For Zn–Ga–CO₃ heated at 423 K and transferred to the reactor under Ar, methane was formed selectively rather than methanol, which suggests that the liberation of further interlayer sites enabled the electron-reduction of CO₂ to methane. In contrast, tetrahydroxycarbonate-type LDHs Zn–Ga–Cu(OH)₃ and Zn–Cu–Ga–Cu(OH)₄ showed suppressed rates of 0.023–0.087 μmol h⁻¹ g⁻¹, probably because only the outer surface contributed to CO₂ photoconversion for this type of LDH.

Experimental Section

Synthesis of LDH photocatalysts

Two carbonate-type LDHs [Zn₉Ga(OH)₁₈]₄[CO₃₃]·mH₂O and [Zn₉Cu₃Ga(OH)₁₈]₄[CO₃₃]·mH₂O were synthesized according to procedures reported previously. An aqueous solution (20 mL) of 0.75M Zn(NO₃)₂·6H₂O (>99.9%, Wako Pure Chemical) and 0.25M Ga(NO₃)₃·nH₂O (n=7–9, >99.9%, Wako Pure Chemical) or 0.375M Zn(NO₃)₂·6H₂O, 0.375M Cu(NO₃)₂·3H₂O (>99.9%, Wako Pure Chemical), and 0.25M Ga(NO₃)₃·nH₂O was dropwise added to a 0.075M sodium carbonate (>99.8%, Wako Pure Chemical) aqueous solution (100 mL) at a rate of 0.24 mL min⁻¹ at 290 K under stirring at 900 rpm. The mixture was stirred at 290 K for 2 h, and the solution pH was adjusted to 8 by adding 1.0M NaOH (≈30 mL total; >93%, Wako Pure Chemical). Subsequently, the temperature was increased to 353 K, and the reaction solution was stirred for 22 h. The obtained precipitates were filtered through a polytetrafluoroethylene membrane filter (Omnipore JWP04700) with a pore size of 0.1 μm and washed with deionized water. In the drying step after the final washing step, a very thin intermediate product layer on a flat wide-area Pyrex glass plate was produced in a glovebox over 5 days to improve the purity of the crystalline LDHs. The produced LDHs were denoted as Zn–Ga–CO₃ and Zn–Cu–Ga–CO₃, respectively, in which n was generally equal to half of the total amount of metal cations.

Two tetrahydroxycarbonate-type LDHs [Zn₉Ga(OH)₁₈]₄[CO₃₃]·mH₂O and [Zn₉Cu₃Ga(OH)₁₈]₄[CO₃₃]·mH₂O were synthesized according to procedures described previously. An aqueous solution (20 mL) of 0.75M Zn(NO₃)₂·6H₂O and 0.25M Ga(NO₃)₃·nH₂O or 0.375M Zn(NO₃)₂·6H₂O, 0.375M Cu(NO₃)₂·3H₂O and 0.25M Ga(NO₃)₃·nH₂O was dropwise added to a 0.025M aqueous solution (100 mL) of (NH₄)₂CuCl₂·2H₂O (>98%, Wako Pure Chemical) at a rate of 0.32 mL min⁻¹ at 290 K under stirring at 900 rpm. The mixture was stirred at 290 K for 2 h, and the solution pH was adjusted to 8 by adding 1.0M NaOH (≈44 mL total). Subsequently, the temperature was increased to 353 K, and the reaction solution was stirred for 22 h. The obtained precipitates were filtered through a JWP04700 filter and washed with deionized water. In the drying step after the final washing step, a very thin intermediate product layer on a flat wide-area Pyrex glass plate was produced in a glovebox over 5 days to improve the purity of crystalline LDHs. The produced LDHs were denoted as Zn–Ga–Cu(OH)₃ and Zn–Cu–Ga–Cu(OH)₄, respectively. Notably, the interlayer [Cu(OH)₃]⁻ reacted with the hydroxy groups of the cationic layer in a dehydration reaction to result in Cu ion coordination by oxo and hydroxy groups, similar to the coordination environment of Cu₄⁺ in the cationic layer.

Zn(OH)₂ was synthesized according to a procedure reported previously from ZnO (1.0 g; >99%; Wako Pure Chemical) and 20 wt% aqueous NaOH (20 mL). Cu(OH)₂ (>90%, Wako Pure Chemical), CuO (>99.9%, Wako Pure Chemical), and Ga₂O₃ (>99.9%, Wako Pure Chemical) were used as received. The light-blue color of the as-received Cu(OH)₂ turned to dark brown at 423 K during the preparation of the photocatalyst film, which indicates its (partial) transformation into CuO.

Characterization

XRD patterns were recorded by using a diffractometer (model D8 ADVANCE, Bruker) at the Center for Analytical Instrumentation, Chiba University, at 2θ = 5.0–60° with a scan step of 0.01° and a scan rate of 5 step⁻¹. Measurements were performed at 40 kV and 40 mA using CuKα emission (λ = 0.15419 nm) and a Ni filter. Crystallite sizes (t) were estimated using the Scherrer equation [Eq. (3)].
\[
t = \frac{0.9\lambda}{(\text{Full width at half maximum}) \times \cos \theta_h} \tag{3}
\]

UV/Vis spectra were recorded by using a model V-650 (JASCO) spectrophotometer equipped with an integrating sphere (ISV-469, JASCO) for diffuse reflectance measurements at 200–800 nm. The \( E_g \) values were estimated by a simple extrapolation of the absorption edge or by fitting to the Davis–Mott equation [Eq. (4)]:

\[
\alpha h \nu \propto (h \nu - E_g)^n \tag{4}
\]

in which \( \alpha, h, \) and \( \nu \) are the absorption coefficient, Planck’s constant, and the frequency of light, respectively, and \( n \) is 1/2, 3/2, 2, or 3 for allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively [1–9].

SEM imaging was performed by using a JSM-6510A instrument (JEOL) at the Center for Analytical Instrumentation, Chiba University. A W filament was used in the electron gun, and the electron accelerating voltage was 3.0 kV. Au particles were coated by using a JFC-1100 instrument (JEOL). The employed magnification was 10000–20000x.

TEM imaging was performed by using a model H-7650 transmission electron microscope (Hitachi) at an accelerating voltage of 100 kV. The samples were mounted on a carbon-coated Cu grid mesh (150 mesh per inch) coated with a copolymer film of polyvinyl alcohol and formaldehyde (Formvar, Monsanto). A W filament was used in the electron gun. The employed magnification was 6000–100000x.

**CO\(_2\) photoconversion tests**

LDH catalysts were immersed in deionized water (<0.055 µS cm\(^{-1}\)) produced by using an RFU424TA water purification system (Advantec) and agitated by ultrasound (430 W, 38 kHz) for 3 min. The suspension was cast on a Pyrex glass plate (25 mm x 25 mm x 1 mm) and dried for 12 h at 373 or 423 K. The mass and area of the obtained films were 10 mg and 20 mm x 20 mm, and their thickness was \( \approx 12 \mu \text{m} \) (Figure 1A). These films were introduced into a homemade high-pressure stainless-steel reactor with quartz double windows, a pressure gauge, and Swagelok valves (Figures 1B, C) for photoconversion tests. The effective internal volume of the reactor was 98.4 mL.

Subsequently, 0.40 MPa of a CO\(_2\)/H\(_2\) mixture (3:7 v/v) was introduced into the reactor. The photocatalyst (Table 1) was irradiated by UV/Vis light emitted by a 500 W Xe arc lamp (model OPM2-502, Ushio) through quartz windows in the reactor chamber for 5 h (Figure 1C). The distance between the light exit point and the photocatalyst surface was 82.7 mm. Light transmission was checked by using a photosensor and a counter (model PCM-01, Prede; and model KADEC-UP, North One, respectively). The light intensity at the center of the photocatalyst was 90.2 mW cm\(^{-2}\). The quartz windows of the high-pressure reactor composed of reflective/diffused/absorbed 95.9% of incident light, whereas 10 mg of our standard photocatalyst film (Pd/TiO\(_2\)) on the Pyrex glass plate absorbed/diffused/reflect/diffrae 49% of incident light.

After 5 h of irradiation, the gas mixture was analyzed by using columns packed with 13X-S molecular sieves and polyethylene glycol (PEG-6000) supported on Flusin P (GL Sciences) set in a GC equipped with a thermal conductivity detector (model GC-8A, Shimadzu)[5–9]. He (>99.999 99.5%) was used as a carrier gas. The amounts of produced methanol and moisture were checked by concentrating them in a trap cooled by a mixture of diethyl ether and dry ice (192 K) to achieve separation from H\(_2\) and most of the CO\(_2\) (Figure 1D).

Typically, the initial pressure of 0.400 MPa at 295 K increased gradually to 0.407 MPa in approximately 10 min during the CO\(_2\) photoconversion tests. As the critical pressures of H\(_2\) and CO\(_2\) are relatively high (1.30 and 7.38 MPa, respectively), the reaction gas in this study (0.28 MPa H\(_2\), 0.12 MPa CO\(_2\)) can be approximated to be an ideal gas. Therefore, the temperature of the reaction gas reached 300 K. We confirmed that the external surface of the high-pressure reactor (Figure 1C) reached the same temperature, which is in thermal equilibrium with the reaction gas.

The thin photocatalyst film (10 mg) on Pyrex glass and the reactor were in contact during photocatalytic tests. Even if we assume that the catalyst film retained all the heat of methanol or methane formation (15 and 130 nmol maximum), the maximum temperature increase is calculated as 0.10 and 2.9 K, respectively, based on Equations (5) and (6), with the catalyst heat capacity approximated to that of Zn(OH)\(_2\) (72.4 J mol\(^{-1}\) K\(^{-1}\)). Thus, we chose 303 K as a blank test temperature for LDH photocatalysts under 0.40 MPa of CO\(_2\) + H\(_2\) (Table 2C).

\[
\text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \Delta H^\circ_i = -50 \text{kJ mol}^{-1} \tag{5}
\]

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}, \Delta H^\circ = -165 \text{kJ mol}^{-1} \tag{6}
\]

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**Keywords:** copper • layered double hydroxides • photochemistry • reduction • zinc


