

# Photocatalytic Conversion of CO<sub>2</sub> in Water over Layered Double Hydroxides\*\*

Kentaro Teramura,\* Shoji Iguchi, Yuto Mizuno, Tetsuya Shishido, and Tsunehiro Tanaka\*

Conversion of the greenhouse gas CO<sub>2</sub> into carbon and useful carbon sources such as CO, HCOOH, HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub> (the corresponding reactions and reduction potentials are reported elsewhere)<sup>[1]</sup> is a potential method of solving both energy and environmental problems. Photocatalytic conversion of CO<sub>2</sub> is attractive from the viewpoint of sustainable energy production and greenhouse gas reduction. A few decades ago, some groups attempted the photocatalytic conversion of CO<sub>2</sub> using heterogeneous and homogeneous photocatalysts.<sup>[1,2]</sup> However, interest in the photocatalytic conversion of CO<sub>2</sub> by water over heterogeneous photocatalysts decreased because of competition from overall water splitting (decomposition of water into H<sub>2</sub> and O<sub>2</sub>). Further, complexes that function as homogeneous photocatalysts in aqueous media have not yet been identified. Kudo and co-workers<sup>[3]</sup> reported that CO<sub>2</sub> underwent reduction into CO and HCOOH more rapidly in the presence of silver-cocatalyst-loaded BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> than did H<sub>2</sub>O (with the reduction of H<sup>+</sup> into H<sub>2</sub>), although in the absence of cocatalyst overall water splitting predominantly occurred over BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>. Their finding indicated that novel photocatalysts can be designed by creating active sites on typical photocatalyst surfaces. Our group found that CO is generated in the photocatalytic conversion of CO<sub>2</sub> over ZrO<sub>2</sub>,<sup>[4]</sup> MgO,<sup>[5]</sup> ATaO<sub>3</sub> (A = Li, Na, or K),<sup>[6]</sup> and Ga<sub>2</sub>O<sub>3</sub>,<sup>[7]</sup> which have the properties of solid-base catalysts, in the presence of H<sub>2</sub> or CH<sub>4</sub> (reductants). Acidic substances such as CO<sub>2</sub> can be adsorbed on a solid base, indicating that solid bases determine, alter,

and control the structure of CO<sub>2</sub> on their surface. The nonlinear CO<sub>2</sub> molecule generated on the surface of solid bases is more destabilized than the linear CO<sub>2</sub> molecule. Distortion of CO<sub>2</sub> upon adsorption onto a solid base and subsequent conversion into the active species show the high reactivity of the photocatalyst for CO<sub>2</sub> conversion.

Layered double hydroxides (LDHs; [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O) are synthetic or natural crystalline clays that consist of brucite (Mg(OH)<sub>2</sub>)-like positively charged two-dimensional sheets in which some divalent cations such as Mg<sup>2+</sup> are substituted by trivalent cations; further, water and exchangeable charge-compensating anions are present in the interlayer.<sup>[8]</sup> Infinite two-dimensional sheets consist of several edge-sharing octahedral units in which divalent and trivalent cations are sixfold coordinated to OH<sup>-</sup>. The positive charge on the sheets is compensated by anions such as CO<sub>3</sub><sup>2-</sup> intercalated in the interlayers. Although LDHs are well-known catalyst supports (e.g. Mg-Al hydrotalcite), they have rarely been used as photocatalysts. LDHs show photocatalytic activity for the degradation of organic compounds<sup>[9]</sup> and O<sub>2</sub> evolution from water in the presence of AgNO<sub>3</sub>.<sup>[10]</sup> Subsequently, Hwang and co-workers developed visible-light-responsive nanohybrids of LDHs and a layered metal oxide.<sup>[11]</sup> A copper-modified LDH was reported to show activity for the photocatalytic conversion of CO<sub>2</sub> in the presence of H<sub>2</sub> gas.<sup>[12]</sup> In that study, LDH was used only as a CO<sub>2</sub> adsorbent because the Cu species acted as active sites, as is the case for Cu/TiO<sub>2</sub>, a photocatalyst for CO<sub>2</sub> conversion.<sup>[13]</sup> Mg-Al hydrotalcite anionic clay catalyzes the aldol reaction of carbonyl compounds in aqueous solution because of the high water tolerance of the surface base sites.<sup>[14]</sup> If CO<sub>2</sub> is first adsorbed on the photocatalyst surface and then activated under photoirradiation, most LDHs would function as photocatalysts in water. In this study, we carried out the photocatalytic conversion of CO<sub>2</sub> in water in the presence of various LDHs such as Mg-Al hydrotalcite.

LDHs with an M<sup>2+</sup>/M<sup>3+</sup> ratio of 3 were synthesized (M<sup>2+</sup> = Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>; M<sup>3+</sup> = Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>). Each sample, except the one prepared using Zn<sup>2+</sup> and In<sup>3+</sup>, showed a characteristic X-ray diffraction (XRD) pattern and thermogravimetry-differential thermal analysis (TG-DTA) curve of an LDH (Supporting Information, Figure S1–S2 for Mg-In LDH). In addition, the absorption edges for Mg-In LDH appeared at wavelengths less than 250 nm (Figure S3). The (003) and (006) peaks in the XRD patterns were attributed to layer formation. The two-stage weight loss pattern in the TG-DTA curve could be explained by the desorption of molecular water preserved in the interlayer and the condensation of neighboring OH groups with the decomposition of CO<sub>3</sub><sup>2-</sup> to

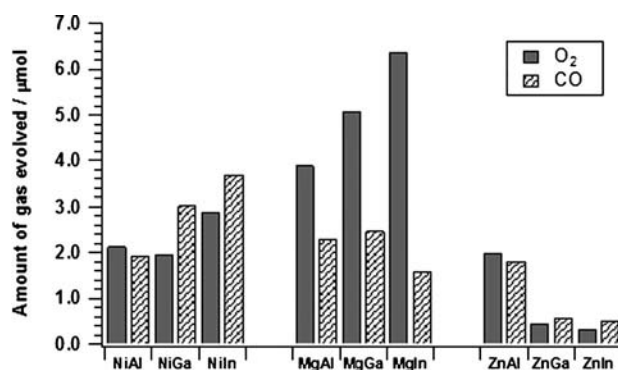
[\*] Dr. K. Teramura, S. Iguchi, Y. Mizuno, Prof. Dr. T. Shishido, Prof. Dr. T. Tanaka  
Department of Molecular Engineering, Graduate School of Engineering, Kyoto University  
Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)  
E-mail: teramura@moleng.kyoto-u.ac.jp  
tanakat@moleng.kyoto-u.ac.jp

Dr. K. Teramura  
Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST)  
4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)

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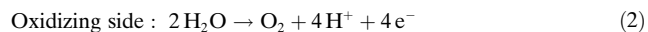
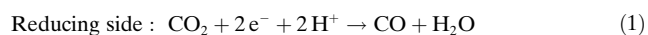
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CO<sub>2</sub>. This decomposition caused collapse of the layer structure. All M<sup>2+</sup>-M<sup>3+</sup> LDHs, including Zn-In compounds, showed activity for the photocatalytic conversion of CO<sub>2</sub> in water (Figure 1). With these LDHs, CO<sub>2</sub> reduction afforded only CO and a considerable amount of O<sub>2</sub>. Interestingly, H<sub>2</sub>



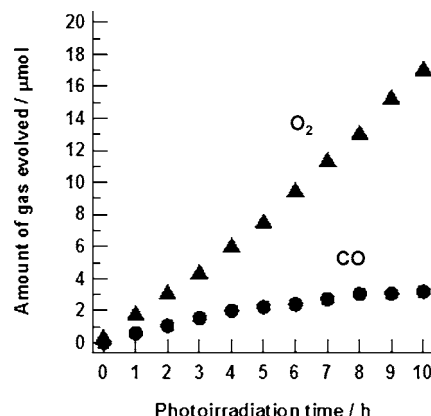
**Figure 1.** Yields of O<sub>2</sub> and CO for the photocatalytic conversion of CO<sub>2</sub> in water, over various LDHs (M<sup>2+</sup>/M<sup>3+</sup> = 3) after 10 h of photoirradiation (light intensity is adjusted constantly).

was not formed, indicating a lack of overall water splitting. If a photocatalyst that shows suitable activity for overall water splitting is used for the photocatalytic conversion of CO<sub>2</sub> in water, H<sub>2</sub> would be evolved at a much higher rate. In addition, the usual CO<sub>2</sub> reduction products would be formed. Therefore, in the presence of these photocatalysts, reduction of H<sup>+</sup> to H<sub>2</sub> proceeds competitively with CO<sub>2</sub> reduction. In our case, only CO<sub>2</sub> reduction occurs on the reducing side. Possibly, CO<sub>2</sub> is reduced to CO by two electrons, and water is oxidized to O<sub>2</sub> by four holes.



Photocatalytic conversion of CO<sub>2</sub> over the prepared M<sup>2+</sup>-M<sup>3+</sup> LDHs did not proceed stoichiometrically, as shown in Figure 1. The reason for the rate of CO evolution being lower than that of O<sub>2</sub> evolution is not clear. Because the reduction sites for H<sup>+</sup> on the LDH surface are identical to those on other photocatalysts, H<sup>+</sup> reduction competes with CO<sub>2</sub> reduction; this is confirmed from the small amount of H<sub>2</sub> formed. Because of their unique surface structure, LDHs can rapidly adsorb CO<sub>2</sub> as CO<sub>3</sub><sup>2-</sup> in aqueous solution. H<sup>+</sup> ions are not directly reduced to H<sub>2</sub> but consumed in the reduction of CO<sub>2</sub>. Accordingly, the photocatalyst used for CO<sub>2</sub> conversion must possess base sites for CO<sub>2</sub> adsorption. Ideally, on the oxidizing side, O<sub>2</sub> is generated with H<sub>2</sub>, in addition to CO formation. However, in the overall water splitting and photocatalytic conversion of CO<sub>2</sub> over Mg-In LDH, O<sub>2</sub> was detected and H<sub>2</sub> was not evolved. Hence, it is unlikely that H<sup>+</sup> is reduced to H<sub>2</sub> on the reducing side and OH<sup>-</sup> is oxidized to O<sub>2</sub> on the oxidizing side, after the dissociation of liquid-phase water into H<sup>+</sup> and OH<sup>-</sup>. Water in solution and molecular water in the interlayer of the LDHs can be oxidized to O<sub>2</sub>. However, O<sub>2</sub> would be formed only from the decomposition

of the OH groups bound to M<sup>2+</sup> and M<sup>3+</sup>, because the LDH surface is packed with many OH groups. As expected, the Mg-In LDH fabricated by hydrothermal synthesis had much higher crystallinity than did that produced by the typical coprecipitation (Figure S1) and showed considerable activity for O<sub>2</sub> and CO evolution. When using Mg-In LDH for photocatalytic conversion, the amounts of CO and O<sub>2</sub> evolved increased slightly with the photoirradiation time (Figure 2).

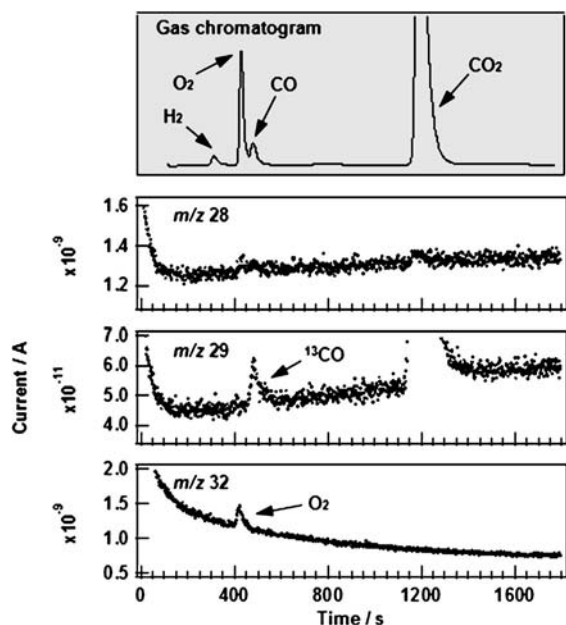


**Figure 2.** Time course of CO (circles) and O<sub>2</sub> (triangles) evolution in the photocatalytic conversion of CO<sub>2</sub> in water over Mg-In LDH fabricated by hydrothermal synthesis.

The photocatalytic conversion did not proceed in the dark, but CO and O<sub>2</sub> were generated rapidly under illumination. After 10 h of photoirradiation, the yields of CO and O<sub>2</sub> from 100 mg of Mg-In LDH were 3.21 and 17.0 μmol, respectively (3.21 and 17.0 μmol h<sup>-1</sup> g cat<sup>-1</sup>). Mg(OH)<sub>2</sub> and In(OH)<sub>3</sub> exhibited much lower activity than did Mg-In LDH (Figure S4). In particular, 100 mg of In(OH)<sub>3</sub> afforded 7.25 μmol of H<sub>2</sub> after 10 h of photoirradiation, with small amounts of CO and O<sub>2</sub> evolved. Interestingly, photocatalytic conversion proceeded over Mg-In LDH (Mg/In = 3), but Mg(OH)<sub>2</sub> and In(OH)<sub>3</sub>, which have the same constituent elements as Mg-In LDH, showed very low activity for CO and O<sub>2</sub> evolution.

Many groups have identified attractive materials that show activity for the photocatalytic conversion of CO<sub>2</sub>.<sup>[3,12,15]</sup> However, it is unclear whether the carbon source of the reduction products—CO, HCOOH, HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub>—is the introduced CO<sub>2</sub> or residual carbon species on the surface of the catalyst. Adding <sup>13</sup>CO<sub>2</sub> would be the best way to demonstrate the source of the reduced products,<sup>[16]</sup> but residual <sup>12</sup>CO<sub>2</sub> on the LDH surface and in the interlayer can pose a problem. When untreated Mg-In LDH was used, CO and O<sub>2</sub> were observed even in the absence of CO<sub>2</sub>, indicating that the residual CO<sub>2</sub> on the LDH surface and in the interlayer was reduced to CO. The layer structure of the LDHs collapsed because of desorption of the interlayer water and CO<sub>3</sub><sup>2-</sup> upon mild heat treatment (at about 773 K); however, this layer was reconstructed in the presence of water (memory effect). To attenuate the effects of residual CO<sub>3</sub><sup>2-</sup>, we carried out the photocatalytic conversion of CO<sub>2</sub> using the reconstructed Mg-In LDH, in which there was hardly any pre-existing CO<sub>3</sub><sup>2-</sup> in the interlayers. Mg-In LDH was evacuated

at 773 K, and then decarbonized water was introduced (Figure S5–S6). Figure 3 shows the gas chromatogram and mass spectra ( $m/z$  28, 29, and 32) after 33 h of photoirradiation for the photocatalytic conversion of  $^{13}\text{CO}_2$  in water over



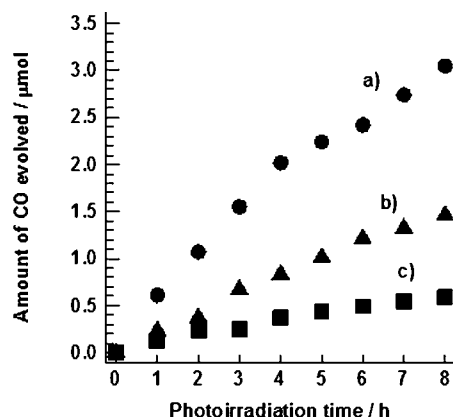
**Figure 3.** Gas chromatogram and mass spectra ( $m/z$  28, 29, and 32) after 33 h of photoirradiation in the photocatalytic conversion of  $^{13}\text{CO}_2$  in water over Mg-In LDH.

Mg-In LDH. Sampling gases were introduced into a mass spectrometer after segregation by a gas chromatograph. The peak at 480 seconds and  $m/z$  29 was assigned to  $^{13}\text{CO}$  because the peak position was consistent with that detected by GC. Some  $^{12}\text{CO}$  was generated from the residual  $\text{CO}_3^{2-}$  ions in the interlayer after the heat treatment, but the predominant product was  $^{13}\text{CO}$ . The sequence of processes could be summarized as follows: elimination of most of the  $\text{CO}_3^{2-}$  ions captured in the interlayer upon heat treatment → restoration of the interlayer (memory effect) → capture of  $^{13}\text{CO}_2$  (as  $^{13}\text{CO}_3^{2-}$ ) in the interlayer. Accordingly, CO was generated from  $\text{CO}_2$  introduced in the gas phase, in the photocatalytic conversion of  $\text{CO}_2$ .

To clarify the source of the evolved  $\text{O}_2$ , we carried out the photocatalytic conversion of  $\text{CO}_2$  in  $\text{H}_2^{18}\text{O}$  over the reconstructed Mg-In LDH. After photoirradiation, the peak at 440 seconds and  $m/z$  34 was assigned to  $^{16}\text{O}^{18}\text{O}$  (Figure S7). However,  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  were not found. This result implied that  $^{16}\text{O}$ -containing species different from those derived from  $\text{H}_2^{18}\text{O}$  were generated, which then reacted stoichiometrically with the  $^{18}\text{O}$ -containing species derived from  $\text{H}_2^{18}\text{O}$ . The  $^{16}\text{O}$  atom originated from  $\text{CO}_2$  dissolved in the solution or from the lattice oxygen (e.g. Mg-In mixed oxide) of the reconstructed Mg-In LDH. Signals at  $m/z$  44, 46, and 48—assigned to  $\text{C}^{16}\text{O}_2$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$ , and  $\text{C}^{18}\text{O}_2$ —were detected as soon as  $\text{C}^{16}\text{O}_2$  was introduced into the  $\text{H}_2^{18}\text{O}$  solution in the dark; this indicated there was oxygen exchange between  $\text{CO}_2$  and  $\text{H}_2^{18}\text{O}$  in the solution. Introduction of  $\text{H}_2^{18}\text{O}$  into the reconstructed

Mg-In LDH afforded Mg-In LDH containing the same amount of  $^{18}\text{O}$  as  $^{16}\text{O}$ :  $\text{Mg}^{16}\text{O} + \text{H}_2^{18}\text{O} \rightleftharpoons \text{Mg}^{16}\text{O}^{18}\text{O} + \text{H}_2^{16}\text{O}$ . No species containing only  $^{16}\text{O}$  or  $^{18}\text{O}$  was present in the solution, but a peak corresponding to  $^{16}\text{O}^{18}\text{O}$  was detected in the mass spectrum. Although the exact mechanism of  $\text{O}_2$  evolution still unclear, it has been confirmed that  $\text{O}_2$  evolved in the gas phase is derived from water introduced into the LDH.

The difference between the properties of the LDH before and after reconstruction is explicitly depicted in Figure 4. The reconstructed Mg-In LDH exhibited very low photocatalytic



**Figure 4.** CO evolution in the photocatalytic conversion of  $\text{CO}_2$  over a) bare Mg-In LDH (circles), b) reconstructed Mg-In LDH in the presence of  $\text{CO}_2$  (triangles), and c) reconstructed Mg-In LDH in the absence of  $\text{CO}_2$  (squares).

activity in the absence of  $\text{CO}_2$  (in this case, Ar was introduced as a substitute for  $\text{CO}_2$ ), this was probably owing to residual  $\text{CO}_2$  after heat treatment. The rates of CO and  $\text{O}_2$  evolution were improved when  $\text{CO}_2$  was introduced into the water solution containing the reconstructed Mg-In LDH. However, the activity of the reconstructed Mg-In LDH was much lower than that of bare Mg-In LDH because of the incomplete restoration of the LDH structure. The rate of CO evolution increased slightly after the introduction of  $\text{CO}_2$  when using the reconstructed Mg-In LDH (Figure S8). This result indicated that  $\text{CO}_2$  from the gas phase dissolved in water and was reduced to CO under photoirradiation. In conclusion, LDHs in which the surface base sites have high water tolerance show superior activity than does a simple metal hydroxide for the photocatalytic conversion of  $\text{CO}_2$  into CO in water (this process is similar to photosynthesis).

## Experimental Section

Layered double hydroxides (LDHs) were synthesized by coprecipitation and hydrothermal synthesis. An aqueous solution of metal nitrates (e.g.  $\text{Mg}(\text{NO}_3)_2$  and  $\text{In}(\text{NO}_3)_3$ ;  $[\text{M}^{2+}] + [\text{M}^{3+}] = 0.64\text{ M}$ ) and an aqueous NaOH solution (1.0 M) were slowly added to an aqueous  $\text{Na}_2\text{CO}_3$  solution (1.0 M) at room temperature and pH 10.0. The resulting solution was aged for 24 h at 333 K and ambient pressure. In hydrothermal synthesis, the aforementioned solution was allowed to mature in a stainless-steel pressure vessel (inner vessel made of Teflon) at 383 K for 24 h. The solution was filtered, and the filtrate

was washed with distilled water and dried at 383 K for 24 h in an oven. The dried sample was ground to a powder size of smaller than 100 mesh. LDH formation was confirmed by powder X-ray diffraction (Rigaku, Multiflex) and differential thermal analysis (Rigaku, Thermo Plus 2 TG-DTA TG8120). Photocatalytic reduction of CO<sub>2</sub> was carried out in a closed circulating system connected to a vacuum line, with a quartz glass ceiling for illumination. The synthesized LDH (100 mg) was dispersed in water (4 mL). CO<sub>2</sub> (500  $\mu$ mol), purified by vacuum distillation at liquid-N<sub>2</sub> temperature, was introduced into the reactor and irradiated by a 200 W Hg-Xe lamp (San-Ei Electric Co., Ltd., UVF-204S Type B) equipped with fiber optics, a collective lens, and a mirror. Bare LDH was evacuated at 773 K for 2 h, and then decarbonized water was introduced, in the case where the reaction was carried out using the reconstructed LDH. The products were analyzed by thermal conductivity detector-gas chromatography (TCD-GC) using a GC-8A chromatograph (Shimadzu Corp.) equipped with an active-carbon-packed column (carrier gas: Ar) and by mass spectroscopy using a quadrupole-type mass spectrometer (BEL Japan, Inc., BEL Mass).

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