Carbon Sequestration

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Photocatalytic Conversion of CO_2 in Water over Layered Double Hydroxides**

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

Conversion of the greenhouse gas CO_2 into carbon and useful carbon sources such as CO, HCOOH, HCHO, CH_3OH, and CH_4 (the corresponding reactions and reduction potentials are reported elsewhere)[1] is a potential method of solving both energy and environmental problems. Photocatalytic conversion of CO_2 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_2 using heterogeneous and homogeneous photocatalysts.[1,2] However, interest in the photocatalytic conversion of CO_2 by water over heterogeneous photocatalysts decreased because of competition from overall water splitting (decomposition of water into H_2 and O_2). Further, complexes that function as homogeneous photocatalysts in aqueous media have not yet been identified. Kudo and co-workers[3] reported that CO_2 underwent reduction into CO and HCOOH more rapidly in the presence of silver-cocatalyst-loaded $BaLa_4Ti_4O_{15}$ than did H_2O (with the reduction of H^+ into H_2), although in the absence of cocatalyst overall water splitting predominantly occurred over $BaLa_4Ti_4O_{15}$. 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_2 over ZrO_2,[4] MgO,[5] $ATaO_3$ (A = Li, Na, or K),[6] and Ga_2O_3,[7] which have the properties of solid-base catalysts, in the presence of H_2 or CH_4 (reductants). Acidic substances such as CO_2 can be adsorbed on a solid base, indicating that solid bases determine, alter, and control the structure of CO_2 on their surface. The nonlinear CO_2 molecule generated on the surface of solid bases is more destabilized than the linear CO_2 molecule. Distortion of CO_2 upon adsorption onto a solid base and subsequent conversion into the active species show the high reactivity of the photocatalyst for CO_2 conversion.

Layered double hydroxides (LDHs; $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot m\,H_2O$) are synthetic or natural crystalline clays that consist of brucite ($Mg(OH)_2$)-like positively charged two-dimensional sheets in which some divalent cations such as Mg^{2+} are substituted by trivalent cations; further, water and exchangeable charge-compensating anions are present in the interlayer.[8] Infinite two-dimensional sheets consist of several edge-sharing octahedral units in which divalent and trivalent cations are sixfold coordinated to OH^-. The positive charge on the sheets is compensated by anions such as CO_3^{2-} 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[9] and O_2 evolution from water in the presence of $AgNO_3$.[10] Subsequently, Hwang and co-workers developed visible-light-responsive nanohybrids of LDHs and a layered metal oxide.[11] A copper-modified LDH was reported to show activity for the photocatalytic conversion of CO_2 in the presence of H_2 gas.[12] In that study, LDH was used only as a CO_2 adsorbent because the Cu species acted as active sites, as is the case for Cu/TiO_2, a photocatalyst for CO_2 conversion.[13] 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.[14] If CO_2 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_2 in water in the presence of various LDHs such as Mg-Al hydrotalcite.

LDHs with an M^{2+}/M^{3+} ratio of 3 were synthesized ($M^{2+} = Mg^{2+}$, Zn^{2+}, Ni^{2+}; $M^{3+} = Al^{3+}$, Ga^{3+}, In^{3+}). Each sample, except the one prepared using Zn^{2+} and In^{3+}, 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_3^{2-} to

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[*] 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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CO_2. This decomposition caused collapse of the layer structure. All M^{2+}-M^{3+} LDHs, including Zn-In compounds, showed activity for the photocatalytic conversion of CO_2 in water (Figure 1). With these LDHs, CO_2 reduction afforded only CO and a considerable amount of O_2. Interestingly, H_2 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_2 in water, H_2 would be evolved at a much higher rate. In addition, the usual CO_2 reduction products would be formed. Therefore, in the presence of these photocatalysts, reduction of H^+ to H_2 proceeds competitively with CO_2 reduction. In our case, only CO_2 reduction occurs on the reducing side. Possibly, CO_2 is reduced to CO by two electrons, and water is oxidized to O_2 by four holes.

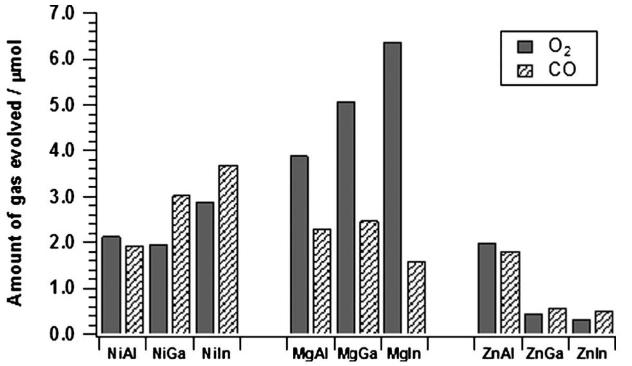

Figure 1. Yields of O_2 and CO for the photocatalytic conversion of CO_2 in water, over various LDHs ($M^{2+}/M^{3+} = 3$) after 10 h of photoirradiation (light intensity is adjusted constantly).

$$\text{Reducing side: } CO_2 + 2\,e^- + 2\,H^+ \rightarrow CO + H_2O \qquad (1)$$

$$\text{Oxidizing side: } 2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (2)$$

Photocatalytic conversion of CO_2 over the prepared M^{2+}-M^{3+} LDHs did not proceed stoichiometrically, as shown in Figure 1. The reason for the rate of CO evolution being lower than that of O_2 evolution is not clear. Because the reduction sites for H^+ on the LDH surface are identical to those on other photocatalysts, H^+ reduction competes with CO_2 reduction; this is confirmed from the small amount of H_2 formed. Because of their unique surface structure, LDHs can rapidly adsorb CO_2 as CO_3^{2-} in aqueous solution. H^+ ions are not directly reduced to H_2 but consumed in the reduction of CO_2. Accordingly, the photocatalyst used for CO_2 conversion must possess base sites for CO_2 adsorption. Ideally, on the oxidizing side, O_2 is generated with H_2, in addition to CO formation. However, in the overall water splitting and photocatalytic conversion of CO_2 over Mg-In LDH, O_2 was detected and H_2 was not evolved. Hence, it is unlikely that H^+ is reduced to H_2 on the reducing side and OH^- is oxidized to O_2 on the oxidizing side, after the dissociation of liquid-phase water into H^+ and OH^-. Water in solution and molecular water in the interlayer of the LDHs can be oxidized to O_2. However, O_2 would be formed only from the decomposition of the OH groups bound to M^{2+} and M^{3+}, 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_2 and CO evolution. When using Mg-In LDH for photocatalytic conversion, the amounts of CO and O_2 evolved increased slightly with the photoirradiation time (Figure 2).

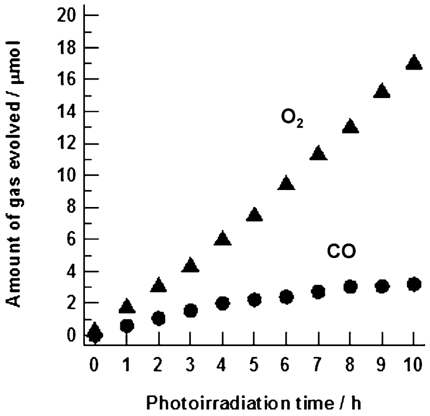

Figure 2. Time course of CO (circles) and O_2 (triangles) evolution in the photocatalytic conversion of CO_2 in water over Mg-In LDH fabricated by hydrothermal synthesis.

The photocatalytic conversion did not proceeded in the dark, but CO and O_2 were generated rapidly under illumination. After 10 h of photoirradiation, the yields of CO and O_2 from 100 mg of Mg-In LDH were 3.21 and 17.0 µmol, respectively (3.21 and 17.0 $\mu mol\,h^{-1}\,g\,cat^{-1}$). $Mg(OH)_2$ and $In(OH)_3$ exhibited much lower activity than did Mg-In LDH (Figure S4). In particular, 100 mg of $In(OH)_3$ afforded 7.25 µmol of H_2 after 10 h of photoirradiation, with small amounts of CO and O_2 evolved. Interestingly, photocatalytic conversion proceeded over Mg-In LDH (Mg/In = 3), but $Mg(OH)_2$ and $In(OH)_3$, which have the same constituent elements as Mg-In LDH, showed very low activity for CO and O_2 evolution.

Many groups have identified attractive materials that show activity for the photocatalytic conversion of CO_2.[3,12,15] However, it is unclear whether the carbon source of the reduction products—CO, HCOOH, HCHO, CH_3OH, and CH_4—is the introduced CO_2 or residual carbon species on the surface of the catalyst. Adding $^{13}CO_2$ would be the best way to demonstrate the source of the reduced products,[16] but residual $^{12}CO_2$ on the LDH surface and in the interlayer can pose a problem. When untreated Mg-In LDH was used, CO and O_2 were observed even in the absence of CO_2, indicating that the residual CO_2 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_3^{2-} 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_3^{2-}, we carried out the photocatalytic conversion of CO_2 using the reconstructed Mg-In LDH, in which there was hardly any pre-existing CO_3^{2-} 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 $^{13}CO_2$ in water over 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}CO because the peak position was consistent with that detected by GC. Some ^{12}CO was generated from the residual CO_3^{2-} ions in the interlayer after the heat treatment, but the predominant product was ^{13}CO. The sequence of processes could be summarized as follows: elimination of most of the CO_3^{2-} ions captured in the interlayer upon heat treatment→restoration of the interlayer (memory effect)→capture of $^{13}CO_2$ (as $^{13}CO_3^{2-}$) in the interlayer. Accordingly, CO was generated from CO_2 introduced in the gas phase, in the photocatalytic conversion of CO_2.

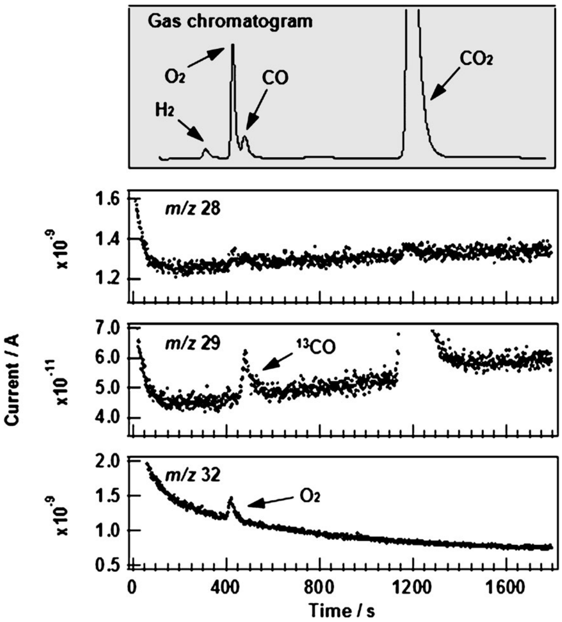

Figure 3. Gas chromatogram and mass spectra (*m*/*z* 28, 29, and 32) after 33 h of photoirradiation in the photocatalytic conversion of $^{13}CO_2$ in water over Mg-In LDH.

To clarify the source of the evolved O_2, we carried out the photocatalytic conversion of CO_2 in $H_2{}^{18}O$ over the reconstructed Mg-In LDH. After photoirradiation, the peak at 440 seconds and *m*/*z* 34 was assigned to $^{16}O^{18}O$ (Figure S7). However, $^{16}O_2$ and $^{18}O_2$ were not found. This result implied that ^{16}O-containing species different from those derived from $H_2{}^{18}O$ were generated, which then reacted stoichiometrically with the ^{18}O-containing species derived from $H_2{}^{18}O$. The ^{16}O atom originated from 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 $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$—were detected as soon as $C^{16}O_2$ was introduced into the $H_2{}^{18}O$ solution in the dark; this indicated there was oxygen exchange between CO_2 and $H_2{}^{18}O$ in the solution. Introduction of $H_2{}^{18}O$ into the reconstructed Mg-In LDH afforded Mg-In LDH containing the same amount of ^{18}O as ^{16}O: $Mg^{16}O + H_2{}^{18}O \rightleftarrows Mg(^{16}OH)(^{18}OH)$. No species containing only ^{16}O or ^{18}O was present in the solution, but a peak corresponding to $^{16}O^{18}O$ was detected in the mass spectrum. Although the exact mechanism of O_2 evolution still unclear, it has been confirmed that 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 activity in the absence of CO_2 (in this case, Ar was introduced as a substitute for CO_2), this was probably owing to residual CO_2 after heat treatment. The rates of CO and O_2 evolution were improved when 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 CO_2 when using the reconstructed Mg-In LDH (Figure S8). This result indicated that 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 CO_2 into CO in water (this process is similar to photosynthesis).

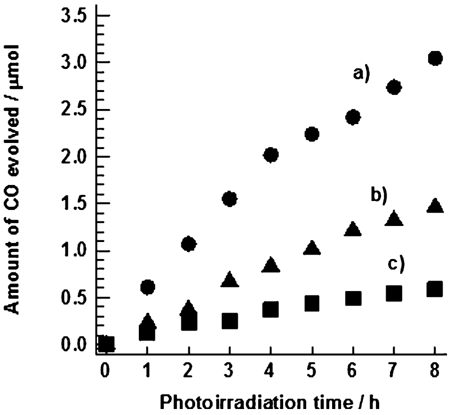

Figure 4. CO evolution in the photocatalytic conversion of CO_2 over a) bare Mg-In LDH (circles), b) reconstructed Mg-In LDH in the presence of CO_2 (triangles), and c) reconstructed Mg-In LDH in the absence of CO_2 (squares).

Experimental Section

Layered double hydroxides (LDHs) were synthesized by coprecipitation and hydrothermal synthesis. An aqueous solution of metal nitrates (e.g. $Mg(NO_3)_2$ and $In(NO_3)_3$; $[M^{2+}]+[M^{3+}]=0.64$ M) and an aqueous NaOH solution (1.0 M) were slowly added to an aqueous Na_2CO_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_2 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_2 (500 μmol), purified by vacuum distillation at liquid-N_2 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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