Photocatalytic conversion of CO₂ in an aqueous solution using various kinds of layered double hydroxides

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1 **Keywords**

- 2 CO₂ conversion,
3 photocatalyst,
4 layered double hydroxides,
5 aqueous solution,
6 chloride ion

1 **Abstract**

2 We found that various layered double hydroxides (LDHs) showed good activity for
3 the photocatalytic conversion of CO₂ in an aqueous solution. Isotope experiments using
4 ¹³CO₂ as a substrate clearly revealed that CO was generated as a main reduction product
5 of CO₂. Ni-Al LDH (Ni/Al = 4) exhibited the largest amount of CO evolved among the
6 various kinds of LDHs. Especially, Ni-Al LDHs fabricated from chlorides showed the
7 higher conversion of CO₂ to CO than those from nitrates. The amount of CO evolved
8 was increased by the addition of chloride ions into the reaction solution, on the other
9 hand, the addition of carbonate and hydrocarbonate ions did not enhance the conversion
10 of CO₂ but promoted the selectivity to H₂ evolution for water splitting.

1 **Introduction**

2 Over the past a few decades, the amount of CO₂ in air has been increased to a
3 critical level owing to high consumption rates of fossil fuels such as coal, oil, and
4 natural gas. The fixation of CO₂ in a chemical process is attracted by many scientists
5 and engineers because the increasing atmospheric concentration of CO₂ would cause the
6 global warming. The conversion of CO₂ into valuable chemicals such as CO and CH₄
7 using solar energy is one of the most suitable ways from the point of view of energy
8 problem. The photocatalytic conversion of CO₂ using several kinds of heterogeneous
9 photocatalysts including TiO₂ were first reported by Honda and his co-workers in 1979
10 [1]. However, TiO₂ possesses a fatal weak point that the conduction band is located at
11 the more positive potential than that required to reduce CO₂. For this reason, it is of
12 interest to explore other photocatalysts which show the activity for the photocatalytic
13 conversion of CO₂ [2]. Some research groups have been trying to apply non-titanium
14 metal oxides to the photocatalytic conversion of CO₂ [2], such as CdS [3], NiO/InTaO₄
15 [4], ZnGa₂O₄ [5], Bi₂WO₆ [6], ZnO [7], etc. Recently, Kudo et al. reported that Ag
16 cocatalyst-modified ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) exhibits the photocatalytic activity
17 for the conversion of CO₂ into CO and HCOOH [8]. It was the first report that O₂ gas
18 was also evolved stoichiometrically, indicating that H₂O functions as a reductant (an
19 electron donor) for the photocatalytic conversion of CO₂.

20 Our group found that CO was generated as a result of the photocatalytic conversion
21 of CO₂ over ZrO₂ [9-12], MgO [13,14], ATaO₃ (A = Li, Na, and K) [15], and Ga₂O₃ [16],
22 which are known as solid base materials, in the presence of H₂ or CH₄ as a reductant. It
23 is known that CO₂, which is one of acidic substrates, can be easily adsorbed and then,
24 monodentate, bidentate, and bridging carbonates are generated together with surface
25 oxygen atoms on the surface of the solid base materials. These nonlinear CO₂ molecules

1 formed on the surface of the photocatalysts are more destabilized than the typical linear
2 CO₂ molecule, which indicates that the distorted CO₂ molecules are expected to be
3 activated under photoirradiation easily in the conversion of CO₂. Those photocatalysts,
4 however, did not work in an aqueous solution because the base sites were poisoned by
5 H₂O. Layered double hydroxides (LDHs) are well known as natural or synthetic
6 crystalline clays. Ebitani et al. reported that Mg-Al LDH (hydrotalcite) catalyzed the
7 aldol condensation of carbonyl compounds in an aqueous solution because their surface
8 base sites show high water tolerance property [17]. This result indicates that the LDHs
9 including Mg-Al LDH can function as solid base catalysts and CO₂ can be adsorbed on
10 the surface of LDHs in an aqueous solution. Previously, we found that LDHs which
11 were prepared using nitrates as precursors of hydroxide sheets exhibited the activity for
12 the photocatalytic conversion of CO₂ in H₂O [18]. It is well-known that LDHs can be
13 fabricated using not only nitrates but also chlorides, and that their surface properties and
14 morphology would be changed by residual anions derived from the precursors. We
15 expect that the photocatalytic activity of LDHs should be also affected by their
16 precursors. In this study, we have tried to apply various kinds of LDHs synthesized from
17 chlorides to the photocatalytic conversion of CO₂ in an aqueous solution, and the effect
18 of anions existing in the reaction solution on the selectivity of products evolved was
19 investigated.

1 **Experimental Section**

2 **Catalyst preparation**

3 Various LDHs ($[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$); Mg-Al, Ni-Al, Zn-Al, Mg-In,
4 and Ni-In, were synthesized by the following coprecipitation method; an aqueous
5 solution of nitrates or chlorides of M^{2+} and M^{3+} was slowly added to an aqueous
6 solution of Na₂CO₃ at room temperature. The pH was kept constant at 10 by adding an
7 aqueous solution of NaOH. The resulting suspension was transferred into a stainless
8 steel autoclave with an inner Teflon vessel and aged at 383 K for 20 h under
9 hydrothermal condition. The solid was collected by filtration and washed with
10 ultra-pure water, and dried at 383 K in air atmosphere. M^{2+} - M^{3+} LDH(NO₃⁻) and
11 M^{2+} - M^{3+} LDH(Cl⁻) mean M^{2+} - M^{3+} LDH prepared from nitrates and chlorides as
12 precursors of hydroxide sheets, respectively.

13

14 **Catalyst characterization**

15 The powder XRD patterns of various LDHs were collected on a X-ray
16 diffractometer (Rigaku, Multiflex), using Cu K_α radiation ($\lambda = 0.154$ nm) at a scan speed
17 of 4.0 degree min⁻¹. The thermo gravimetric analysis for LDHs was performed using
18 Rigaku, Thermo Plus 2. The certain amount of sample was set in the furnace, and the
19 temperature was increased by 3 K min⁻¹ under flow condition of dried air. **Specific**
20 **surface areas of various LDHs were evaluated by BET method at 77 K (liquid nitrogen**
21 **temperature) using a surface area and pore size analyzer (BELSORP-miniII, BEL Japan,**
22 **Inc.). Before the measurement, LDHs were heated at 383 K under vacuum condition**
23 **using a pretreatment instrument (BELPREP-vacII, BEL Japan, Inc.).** Temperature
24 programmed desorption profiles were recorded using TPD-1-AT (BEL Japan, Inc.)
25 equipped with a quadrupole-type mass spectrometer (M-QA100F, ANELVA) as a

1 detector. 50 mg of sample powder was set in a quartz glass tube and the temperature
2 was increased by 5 K min⁻¹ under He flow. Q-Mass profile in $m/z = 44$ and 45 were
3 monitored during increasing temperature to confirm the desorption of ¹²CO₂ and ¹³CO₂,
4 respectively.

6 **Photocatalytic activity test for the CO₂ conversion in H₂O**

7 Photocatalytic conversion of CO₂ in H₂O was carried out in a closed circulating
8 system with 220 mL of total dead space volume. 500 mg of photocatalyst (LDH)
9 powder was dispersed in 350 mL of ultra-pure water in the glass reactor, and the
10 suspension was degassed. Gaseous CO₂ purified by vacuum distillation at liquid
11 nitrogen temperature was introduced into the free gas space, and the circulating was
12 performed for 1 hour before photoirradiation. Then, the suspension was illuminated
13 from within the reactor with a 400 W high pressure Hg lamp (HL400BH-9, SEN
14 LIGHTS CORPORATION, Japan) through the quartz water jacket. The products were
15 analyzed by thermal conductivity detector gas chromatography (TCD-GC) using a
16 GC-8A chromatograph (Shimadzu Corporation, Japan) equipped with a MS-5A packed
17 column. A quadruple-type mass spectrometer (BEL Mass, BEL Japan, Inc.) was used for
18 isotope experiments.

1 **Results and Discussion**

2 **Figure 1** shows XRD patterns of various kinds of M²⁺-M³⁺ LDHs(Cl⁻). All of
3 these patterns correspond to a typical structure of LDH-like compounds [19]. As for
4 Ni₃-Al₁ LDH(Cl⁻) (**pattern a**), two sharp diffraction peaks at 11.4 and 23.1 degree are
5 assigned to (003) and (006) phase reflections, which are related to interval of each
6 hydroxide sheets and distance from hydroxide sheets to interlayer anions, respectively.
7 The other intense peak at 60.8 degree is indexed as a (110) phase reflection with respect
8 to hexagonal axes. The parameter *a* of layered double hydroxides corresponding to the
9 cation-cation distance within the hydroxide sheet can be calculated as follow: *a* = 2*d*₍₁₁₀₎.
10 The (110) reflection of Mg-In LDH(Cl⁻) appeared at lower angle than that of Mg-Al
11 LDH(Cl⁻), indicating that the cation-cation distance of Mg-In LDH(Cl⁻) was longer
12 than that of Mg-Al LDH(Cl⁻). This peak shift is due to the difference of ionic radii of
13 trivalent cation, Al³⁺: 53.5 pm and In³⁺: 80.0 pm [20], existing in the hydroxide sheet of
14 LDHs. On the other hand, the position of these sharp diffraction peaks were not changed
15 by Ni/Al ratio of Ni-Al LDH(Cl⁻) (**pattern f–i**). The value of full width at half
16 maximum (FWHM) of (003) phase reflection was the smallest at Ni/Al = 3, indicating
17 that the stacking of hydroxide sheets along with *c* axis has been advanced at Ni/Al = 3.
18 **Specific surface areas of Mg-Al, Ni-Al, Zn-Al, Mg-In, and Ni-In LDHs evaluated by a**
19 **BET method were 59.4, 88.5, 15.2, 35.0, and 56.8 m² g⁻¹, respectively. Figure 2** shows
20 the weight loss curve of Ni-Al LDH(Cl⁻) recorded by thermo gravimetric analysis. It
21 was known that LDHs exhibit the characteristic two steps weight loss with increasing
22 temperature in the TG curve [19]. The first step at less than 473 K is due to desorption
23 of water molecules kept on the surface and in the interlayer. The second step between
24 473 – 673 K is caused by collapse of the layer structure accompanied with the

1 dehydration of hydroxyl groups and the decomposition of charge compensating
2 interlayer anions.

3 **Figure 3** shows the amount of products evolved for the photocatalytic conversion
4 of CO₂ in H₂O over various M²⁺-M³⁺ LDHs(Cl⁻) after 8 h of photoirradiation. All kinds
5 of M²⁺-M³⁺ LDHs(Cl⁻) were active for the photocatalytic conversion of CO₂ and the
6 photocatalytic H₂ evolution from water simultaneously, and CO was evolved as a main
7 reduction product of CO₂. No product was evolved without the photoirradiation and in
8 the absence of LDHs, respectively. The selectivity to CO obviously depended on the
9 metal components of hydroxide sheets of LDHs. Ni-Al LDH(Cl⁻) showed the highest
10 selectivity to CO among various LDHs(Cl⁻). Mg-In LDH(Cl⁻) and Ni-In LDH(Cl⁻),
11 which contained indium as trivalent cation in the hydroxide sheet, exhibited the high
12 efficiency for the H₂ production, but the amount of CO evolved was small. In the case
13 of Ni-Al LDH(Cl⁻), the amount of H₂ evolved was much lower than those of others
14 LDHs. It is important to suppress the formation of H₂ in order to obtain more high
15 selectivity to the conversion of CO₂ because the photocatalytic reduction of H⁺ derived
16 from H₂O into H₂ competitively takes place in the photocatalytic conversion of CO₂ in
17 H₂O. We expect that Ni species in Ni-Al LDH(Cl⁻) which function like a cocatalyst
18 cause the selective formation of CO. The yields of CO, CH₄, and H₂ were 21.0, 1.2, and
19 12.3 μmol over Ni-Al LDH(Cl⁻), respectively, and the selectivity to CO (CO / CO +
20 CH₄ + H₂ × 100) was 67% after 8 h of photoirradiation. **The formation rate of CO in the**
21 **photocatalytic conversion of CO₂ in an aqueous solution over Ni-Al LDH(Cl⁻)**
22 **decreased with the photoirradiation time as shown in **Figure S1**. The color of Ni-Al**
23 **LDH(Cl⁻) changed from green to gray after the photocatalytic reaction. On the contrary,**
24 **the structure, which was identified by the XRD pattern, did not change as compared to**
25 **that before the reaction (**Figure S2**).**

Table 1 shows the yields of CO, H₂, and CH₄ for the photocatalytic conversion of CO₂ in H₂O over a different Ni/Al ratio of Ni-Al LDH(Cl⁻). The largest amount of CO was evolved at Ni/Al = 4 after 10 h of photoirradiation. Photocatalytic H₂ production proceeded well over Ni-Al LDH(Cl⁻) with smaller Ni/Al ratio (Al rich). It is known that the ratio of metal components affects the surface property of LDHs, for example, Ebitani et al. insisted that the surface basic property of Mg-Al LDH depends on the Mg/Al ratio, and Mg-Al LDH (Mg/Al = 3) showed the highest activity for the aldol condensation [17]. In our case, the photocatalytic activity was also affected by the Ni/Al ratio of Ni-Al LDH(Cl⁻), and Ni/Al = 4 was the most effective ratio for the evolution of CO as mentioned above. The amounts of CO evolved over Ni(OH)₂ and Al(OH)₃, which does not have typical structure of LDHs, were less than that over Ni-Al LDH(Cl⁻) (Ni/Al = 2, 3, 4, and 5), indicating that Ni-Al mixed hydroxide gives suitable surface property for the photocatalytic conversion of CO₂ in H₂O.

Table 2 shows the difference of the activity between Ni-Al LDH(Cl⁻) and Ni-Al LDH(NO₃⁻) for the photocatalytic conversion of CO₂ in an aqueous solution. Larger amounts of CO and H₂ were evolved over Ni-Al LDH(Cl⁻) than those over Ni-Al LDH(NO₃⁻). On the other hand, Ni-Al LDH(NO₃⁻) showed the high efficiency for the formation of CH₄ and O₂. To investigate the origin of CO generated during the reaction, the photocatalytic conversion of ¹³C-labeled CO₂ was conducted over Ni-Al LDH(Cl⁻) (Ni/Al = 4) in an 0.1 M aqueous solution of NaCl. The GC-MS chromatogram for this isotope experiment is shown in **Figure 4**. The peak at 1000 second in GC chromatogram is assigned to CO in this case. There was a clear peak in the profile of *m/z* = 29 at the same retention time with GC chromatogram, and no peak was observed in the profile of *m/z* = 28. Therefore, only ¹³CO (*m/z* = 29) was evolved in the photocatalytic conversion of ¹³CO₂ over Ni-Al LDH(Cl⁻). This result clearly indicated that the carbon sources of

1 CO evolved were introduced CO₂; therefore, carbon species such as carbonate ions kept
2 in the interlayer of LDH and contaminated organics did not decompose into CO. **Figure**
3 **5** shows the temperature programmed desorption profile of Ni-Al LDH(Cl⁻) which was
4 used for the isotope experiment using ¹³CO₂ as substrate. ¹²CO₂ ($m/z = 44$) and ¹³CO₂
5 ($m/z = 45$) were desorbed from the used photocatalyst at around 573 K, indicating that
6 adsorbed ¹³CO₂ species such as carbonate or hydrocarbonate species existed on LDH.
7 This result showed that parts of the introduced CO₂ molecules were adsorbed on Ni-Al
8 LDH(Cl⁻) during the photocatalytic conversion of CO₂ in an aqueous solution.
9 Accordingly, we concluded that the adsorbed CO₂ species on the surface of LDH, which
10 are derived from the introduced gaseous CO₂ in the gas phase, are reduced into CO
11 under UV light photoirradiation..

12 The elemental analysis revealed that 1.2 wt% of chlorine atoms and 0.6 wt% of
13 nitrogen atoms derived from precursors of hydroxide sheets existed on Ni-Al LDH(Cl⁻)
14 and Ni-Al LDH(NO₃⁻), respectively. We have reported that Mg-In LDH(NO₃⁻)
15 exhibited the activity for the photocatalytic conversion of CO₂ in H₂O, 3.2 μmol of CO
16 as reduction product of CO₂ and 17.0 μmol of O₂ were evolved after 10 h of
17 photoirradiation [18]. **Figure 6** shows (a) TCD-GC chromatogram, Q-Mass profiles of
18 (b) $m/z = 29$ and (c) $m/z = 30$, in the photocatalytic conversion of ¹³CO₂ in H₂O over
19 Mg-In LDH(NO₃⁻). The peak at 480 seconds in the $m/z = 29$ profile was assigned to
20 ¹³CO, and the peak attributed to a fragment ion of ¹³CO₂ appeared at around 1200
21 seconds. Whereas, there was a peak at the same retention time as that of CO in the $m/z =$
22 30 profile, which can be ascribed to NO. This result indicates that residual nitrate ions
23 existed on Mg-In LDH(NO₃⁻) were decomposed into NO and O₂ under UV light
24 photoirradiation. Accordingly, the unpreventable photodecomposition of the residual
25 nitrate ions into NO and O₂ proceeded together with the photocatalytic conversion of

CO₂ into CO over LDHs fabricated using nitrates. The photodecomposition of nitrate ions during the reaction caused the evolution of excess amount of O₂, resulting in the formation of larger amount of O₂ over Ni-Al LDH(NO₃⁻) than that over Ni-Al LDH(Cl⁻) as shown in **Table 2**.

Generally, carbonate ions as charge compensating anions are preserved in the interlayer of LDHs. Our fabricating LDHs in this study also keep large amount of carbonate ions with small amount of residual chloride ions derived from the precursor of hydroxide sheets. **Figure 7** shows the effect of anion addition to the reaction solution on the photocatalytic conversion of CO₂ in an aqueous solution over Ni-Al LDH(Cl⁻) (Ni/Al = 4). Amount of H₂ evolved as the reduction product of H⁺ derived from H₂O was increased by the addition of NaHCO₃ and Na₂CO₃, although the formation of CO was drastically suppressed. Sayama and Arakawa reported that the addition of carbonate ions or hydrocarbonate ions to an aqueous solution enhance the evolution of H₂ for water splitting [22]. In our case, on the other hand, amount of CO evolved was increased in the presence of NaCl and KCl in an aqueous solution as compared to that in a pure water. The formation of O₂ was not observed in all cases. This results indicated that chloride ions in the reaction solution promoted the photocatalytic conversion of CO₂ to CO over Ni-Al LDH(Cl⁻). We expect that chloride ion in an aqueous solution act as a hole scavenger in the photocatalytic reaction. Chloride ions should be oxidized by holes generated with the photoexcitation of electrons through two processes. One is that chloride ion is oxidized into chlorine (Eq.1), and chlorine (Cl₂) is disproportionately decomposed into chloride ion (Cl⁻) and hypochlorite ion (ClO⁻) (Eq. 2).

1 The other is that chloride ion is oxidized into hypochlorite ion directly (Eq. 3).
 2 (Eq.3) $\text{Cl}^- + 2\text{h}^+ + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O}$
 3 Standard redox potential of (Cl_2/Cl^-) and (ClO^-/Cl^-) are known as + 1.40 V and + 0.89
 4 V (vs. NHE at pH = 0), respectively [23]. In both cases, hypochlorite ion which can act
 5 as a strong oxidizing reagent in an aqueous solution would be formed finally. In
 6 addition, chlorate ion (ClO_3^-) and perchlorate ion (ClO_4^-) are generated through the
 7 disproportionation of hypochlorite ions in an aqueous solution. It is possible that the
 8 oxidation products of chloride ions such as ClO^- , ClO_3^- , and ClO_4^- are evolved
 9 instead of O₂ as an oxidation product of H₂O. The solution after the reaction was
 10 positive for the starch-iodine reaction, while the solution before the reaction (an 0.1 M
 11 aqueous solution of NaCl) and pure water were negative (**Figure S3**). This result
 12 indicated that ClO^- , ClO_3^- , and ClO_4^- whose redox potential are positive enough to
 13 oxidize iodide ion into iodine were formed in the aqueous solution during the
 14 photocataytic conversion of CO₂. We concluded that chloride ion in an aqueous solution
 15 act as a hole scavenger under UV light photoirradiation and it is oxidized into ClO^- ,
 16 ClO_3^- , and ClO_4^- in our system using Ni-Al LDH(Cl^-) as a photocatalyst.
 17

1 **Conclusion**

2 We found that Ni-Al LDH (Ni/Al = 4) prepared from chloride exhibited the
3 highest efficiency for the photocatalytic conversion of CO₂ into CO in an aqueous
4 solution among various kinds of LDHs. CO₂ introduced in the gas phase was adsorbed
5 on the surface of LDHs, and then reduced into CO under photoirradiation because only
6 ¹³CO was formed in the isotope experiment using ¹³CO₂ as a substrate. The addition of
7 chloride ions to the reaction solution enhanced the selectivity to CO. Chloride ion in an
8 aqueous solution act as a hole scavenger under UV light photoirradiation and it is
9 oxidized into ClO⁻, ClO₃⁻, and ClO₄⁻.

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1 Table 1 The yield of products in the photocatalytic conversion of CO₂ in an aqueous
2 solution of 0.1 M NaCl over different Ni/Al ratio of Ni-Al LDH(Cl⁻) after
3 photoirradiation for 10 h.
4 Photocatalyst weight: 500 mg, CO₂: 7.7 mmol, aqueous solution: 350 mL, light source:
5 400 W Hg lamp

6

Ni/Al ratio	Ni content (%)	Products evolved / μmol			Selectivity (CO+CH ₄)/(CO+CH ₄ +H ₂)
		CO	CH ₄	H ₂	
2	67	20.6	4.4	18.8	0.57
3	75	21.0	1.2	12.3	0.64
4	80	36.6	0.7	12.2	0.75
5	83	29.5	0.7	0.0	1.00
Ni(OH)₂	100	13.0	3.1	22.0	0.42

7

1 Table 2 The difference of the activity for the photocatalytic conversion of CO₂ in
2 aqueous solution between Ni-Al LDH(Cl⁻) and Ni-Al LDH(NO₃⁻).
3 Ni/Al = 3, photocatalyst weight: 500 mg, CO₂: 7.7 mmol, aqueous solution: 350 mL,
4 light source: 400 W Hg lamp, photoirradiation time: 10 h.
5

Photocatalyst	Products evolved / μmol			
	H ₂	O ₂	CH ₄	CO
Ni-Al LDH(NO ₃ ⁻)	trace	25.5	5.7	8.1
Ni-Al LDH(Cl ⁻)	12.3	trace	1.2	21.0

Figure captions

- Figure 1 XRD patterns of various kinds of M²⁺-M³⁺ LDH(Cl⁻); (a) Ni₃-Al₁, (b) Mg₃-Al₁, (c) Zn₃-Al₁, (d) Ni₃-In₁, (e) Mg₃-In₁, (f) Ni₅-Al₁, (g) Ni₄-Al₁, (h) Ni₃-Al₁, and (i) Ni₂-Al₁.
- Figure 2 The weight loss curve of Ni-Al LDH(Cl⁻) in thermo gravimetry analysis. Rate of temperature increase: 5 K min⁻¹, atmosphere: air.
- Figure 3 The amount of products evolved in the photocatalytic conversion of CO₂ in H₂O over various M²⁺-M³⁺ LDH(Cl⁻) after 8 h of photoirradiation. ■: CO, ■: CH₄, □: H₂, M²⁺/ M³⁺ = 3, photocatalyst weight: 500 mg, CO₂: 7.7 mmol, H₂O: 350 mL, light source: 400 W Hg lamp.
- Figure 4 The GC-MS chromatogram for the isotopic experiment; photocatalytic conversion of ¹³CO₂ in an aqueous solution of 0.1 M NaCl over Ni-Al LDH(Cl⁻) with Ni/Al = 4 after 26 h of photoirradiation. Photocatalyst weight: 500 mg, ¹³CO₂: 7.7 mmol, aqueous solution: 350 mL, light source: 400 W Hg lamp.
- Figure 5 The temperature programmed desorption profiles of Ni-Al LDH(Cl⁻) which was used for the isotopic experiment using ¹³CO₂ as substrate. Solid line: *m/z* = 44 (¹²CO₂), dot line: *m/z* = 45 (¹³CO₂), rate of temperature increase: 5 K min⁻¹, atmosphere: He.
- Figure 6 The GC-MS chromatogram in the photocatalytic conversion of ¹³CO₂ in H₂O over Mg-In LDH(NO₃⁻) after 26 h of photoirradiation. (a) TCD-GC chromatogram, (b) *m/z* = 29 profile, (c) *m/z* = 30 profile. Photocatalyst weight: 100 mg, ¹³CO₂: 500 μmol, H₂O: 4 mL, light source: 200 W Hg-Xe lamp.
- Figure 7 The yield of products in the photocatalytic conversion of CO₂ in various

1 aqueous solutions over Ni-Al LDH(Cl⁻) with Ni/Al = 4 after
2 photoirradiation for 10 h.

3 ■: CO, ■: CH₄, □: H₂, photocatalyst weight: 500 mg, CO₂: 7.7 mmol,
4 aqueous solution: 350 mL, concentration of additive: 0.1 M, light source:
5 400 W Hg lamp.

6

7

Figure 1

Figure2

Figure3

Figure 4

Figure 5

Figure 6

Figure7