Preparation of transition metal-containing layered double hydroxides and application to the photocatalytic conversion of CO₂ in water

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Abstract

Layered double hydroxides (LDHs) have been paid great attention in the field of the photocatalysis due to their interesting physicochemical properties such as positively charged hydroxide sheet, compositional flexibilities, and large surface area. We previously reported that the use of Ni–Al LDH as a photocatalyst enabled us to achieve the maximum conversion of CO₂ to CO with high selectivity among a series of synthesized LDHs, and chloride ions (Cl[−]) in the reaction solution enhanced the amount of CO evolved. In this study, we attempted to prepare 16 different kinds of transition metal containing M²⁺–M³⁺ LDHs (M²⁺ = Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺; M³⁺ = V³⁺, Cr³⁺, Mn³⁺, and Fe³⁺) and applied them to the photocatalytic conversion of CO₂ in an aqueous solution of NaCl. Ni–V LDH, which has large specific surface area, exhibited the highest activity for the CO evolution among these LDHs; however the formation of H₂ as a reduction product of protons (H⁺) was totally suppressed. It is estimated that a combination of V³⁺ and Cl[−] plays a significant role for the high photocatalytic activity and the high selectivity toward CO formation.

- 1 **Keywords**
- 2 Photocatalysis
- 3 CO₂ conversion
- 4 Layered double hydroxide (LDH)
- 5 Ni–V LDH

1 Introduction

2 Layered double hydroxides (LDHs) with a general formula of
 3 $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ are known as anionic clays that have highly
 4 ordered layer structures in the *c*-axis direction, where M^{2+} and M^{3+} are divalent and
 5 trivalent cations, respectively[1,2]. The value of *x* represents the molar ratio of
 6 $M^{3+}/(M^{2+} + M^{3+})$, whereas A^{n-} is the interlayer anion of valence *n*. Generally, the value
 7 of *m* indicates the extent of hydration, which is highly influenced by the surrounding
 8 environment such as atmosphere, temperature, and humidity. The natures of M^{2+} , M^{3+} , *x*,
 9 and A^{n-} can vary over a wide range; hence, a series of isostructural materials with
 10 various chemical properties can be synthesized[3]. When the *x* value is outside of the
 11 0.2–0.4 range, hydroxides or other compounds can form as impurity phases. The
 12 best-known LDH material is hydrotalcite, which has a structural formula of
 13 $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Various LDHs can be formed by fully or partially replacing
 14 Mg^{2+} or Al^{3+} with divalent ($M^{2+} = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+},$ and Ca^{2+}) or
 15 trivalent cations ($M^{3+} = Co^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, Cr^{3+}, In^{3+}, V^{3+}, Y^{3+},$ and La^{3+}),
 16 respectively [4–20]. Moreover, tetravalent cations ($M^{4+} = Ti^{4+}, Zr^{4+},$ and Sn^{4+}) are also
 17 reported to form LDH structures[21–28]; however, M^{4+} cations sometimes form
 18 amorphous oxides instead of incorporating within the hydroxide sheets. Recently,
 19 various LDHs have been applied to photocatalytic reactions such as degradation of
 20 organic compounds, water splitting, and conversion of CO_2 . For example, García et al.
 21 reported that various Zn^{2+} -containing LDHs (Zn–Cr, Zn–Ti, and Zn–Ce LDHs)
 22 exhibited photocatalytic activity for O_2 evolution from an aqueous solution of $AgNO_3$
 23 under visible light irradiation[18]. On the other hand, photocatalytic H_2 production from
 24 water, with lactic acid as a sacrificial electron donor, was demonstrated using Ni–Ti,

1 Zn–Ti, and Mg–Al–Ti LDHs under visible light irradiation[26]. In addition,
 2 photocatalytic degradations of dyes and organic compounds using a series of LDHs as
 3 photocatalystshavealso been recently introduced [9,24,25,29–37].

4 Photocatalytic conversion of CO₂ into valued chemicals such as CO, HCHO,
 5 HCOOH, CH₃OH, and CH₄ is one of the most promising methods to construct a
 6 sustainable carbon cycling system. We have previously reported that ZrO₂[38–41],
 7 MgO[42,43], and Ga₂O₃[44], on which basic surface sites were suitable for the
 8 adsorption of CO₂ molecules, showed photocatalytic activity for the conversion of CO₂
 9 to CO in gas phase using H₂ as a reductant. CO₂ molecules that are adsorbed on the
 10 basic sites of these materials can be altered into active species, which is necessary for
 11 the photocatalytic conversion of CO₂, as shown in previous literature [43,44].
 12 Accordingly, solid base materials are promising candidates to developa photocatalytic
 13 system for the conversion of CO₂. From this viewpoint, we attempted to apply
 14 synthesized LDHs to the photocatalytic conversion of CO₂into CO in water, and found
 15 that various M²⁺–M³⁺ LDHs (M²⁺ = Mg²⁺, Ni²⁺, and Zn²⁺; M³⁺ = Al³⁺, Ga³⁺, and In³⁺)
 16 exhibited photocatalytic activity[45]. For the case of LDH photocatalyst, large specific
 17 area and high affinity for CO₂ molecules might facilitate the selective conversion of
 18 CO₂ under illumination. Similarly, Izumi et al. and Katsumata et al. also reported the
 19 photocatalytic conversion of CO₂ using Cu-containing LDHs[46–48] and noble
 20 metal-loaded LDHs[49], respectively. In our previous study, Ni–Al LDH,in particular,
 21 showed high activity and selectivity for CO formation among a series of LDHs; the
 22 amount of H₂ evolved as a reduction product of protons (H⁺) derived from water was
 23 much smaller than those of the other LDHs[50]. Isotopic experiments using ¹³CO₂ as a
 24 substrate revealed that the CO evolved in the photocatalytic reaction over these LDHs

1 originated from the introduced CO₂ substrate. The addition of chloride ions(Cl⁻) to the
2 reaction solution promoted the conversion of CO₂ to CO, and we confirmed that during
3 the photocatalytic reaction,a stoichiometric amount of hypochlorous acid (HClO) was
4 produced as an oxidation product of Cl⁻ in the reaction solution, which was quantified
5 by*N,N'*-diethyl-*p*-phenylenediamine (DPD) tests[51,52]. This indicated that Cl⁻ can act
6 as a hole scavenger and is oxidized into chlorine (Cl₂), which is immediately
7 transformed into HClO in water[53]. In this study, wesynthesized various transition
8 metal-containing M²⁺-M³⁺ LDHs (M²⁺ = Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺; M³⁺ = V³⁺, Cr³⁺,
9 Mn³⁺, and Fe³⁺) and investigated their photocatalytic activities for the conversion of
10 CO₂ in an aqueous NaCl solution under UV light irradiation.

11

Experimental Section

Catalyst preparation

Various M^{2+} – M^{3+} layered double hydroxides (M^{2+} – M^{3+} LDHs, M^{2+} = Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} ; M^{3+} = V^{3+} , Cr^{3+} , Mn^{3+} , and Fe^{3+}) were synthesized by a typical co-precipitation method, unless otherwise noted, with that the ratio of M^{2+} to M^{3+} (M^{2+}/M^{3+}) was fixed at 2. A mixed aqueous solution of precursors ($M^{2+}Cl_2$ and $M^{3+}Cl_3$) was slowly dropped to an aqueous solution of Na_2CO_3 at room temperature with a vigorous stirring. The pH was kept stable by adding an aqueous solution of NaOH during the precipitation using a liquid feeding pump (NRP-76, Nissin Rika) connected to a pH controller (NPH-660NDE, Nissin Rika). The resulting suspension was aged at 333 K for 24 h with the stirring. The solid was collected by the suction filtration and rinsed with 1.0 L of ultra-pure water, and then dried at 333 K in a vacuum oven. Organic chemicals and solvents were not used throughout each step of the LDH preparation procedure to prevent a contamination of carbon residue in the photocatalytic reaction.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns of prepared M^{2+} – M^{3+} LDHs were measured by an X-ray diffractometer (Ultime IV, Rigaku), using Cu K_α radiation (λ = 0.154 nm) at a scan rate of $4.0^\circ \text{ min}^{-1}$. The morphology of these as-synthesized samples were investigated from SEM images, which were captured by using a field emission scanning electron microscope (SU-8220, Hitachi High-Technologies) at an acceleration voltage of 3.0 kV. The specific surface areas of LDHs were estimated from their N_2 adsorption isotherms at 77 K via BET method using an adsorption analyzer

(BELSORP-miniII, BEL Japan). Prior to the measurements, each sample was evacuated at 383 K for 1 h using a pretreatment system (BELPREP-vacII, BEL Japan). The thermal analysis for the prepared LDHs were performed using athermobalance (Thermo Plus 2, Rigaku). A certain amount of sample powder was set in the furnace, and the change of sample weight was recorded with the increasing temperature under a dried air flowing at a flow rate of 80 mL min⁻¹. UV/Vis diffuse reflectance spectra of LDHs were obtained using a UV-Vis Spectrometer (V-670, JASCO) equipped with an integrated sphere accessory.

Photocatalytic conversion of CO₂ in an aqueous solution

The photocatalytic conversion of CO₂ in an aqueous solution of NaCl was carried out using an inner-irradiation type reaction vessel under CO₂ gas flow. 0.5 g of as-synthesized photocatalyst powder was dispersed in 1.0 L of an aqueous solution of NaCl (0.1 M), and He or CO₂ gas was bubbled into the suspension to degas the dissolved air. The suspension was illuminated with a 400 W high-pressure mercury lamp through a quartz filter equipped with a cooling water system under a flow of CO₂ gas at a flow rate of 15 mL min⁻¹. The products such as CO, H₂, and O₂ were analyzed by a barrier discharge ionization detector (BID) gas chromatograph (GC-2010 Tracera, Shimadzu Corp.), which was connected to the reactor online, equipped with a MICROPACKED ST column using He gas as a carrier. Amount of metal ions in the reaction solution which were eluted from the photocatalyst powder during the photocatalytic reaction was estimated by the elemental analysis using an ICP-OES (iCAP7400 Duo, Thermo Fisher Scientific, Inc.).

Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of powder samples synthesized via the coprecipitation method using each of the metal chlorides as precursors ($M^{2+}/M^{3+} = 2$, if not otherwise specified). A series of LDHs (Co–Cr, Co–Fe, Ni–V, Ni–Cr, Ni–Mn, Ni–Fe, Zn–Cr, Zn–Mn, and Zn–Fe LDH) exhibited characteristic diffraction peaks corresponding to the LDH structure[1], which are presented as asterisks (*) in **Figure 1(a-d)**. Two sharp diffraction peaks assigned to (003) and (006) phase reflections, were located around $11\text{--}12^\circ$ and $22\text{--}24^\circ$, respectively. The broadened (009) phase diffraction peak around $33\text{--}35^\circ$ was difficult to separate from the (012) phase. The (003), (006), and (009) phase diffraction peaks are related to the structure layered toward the *c*-axis direction. The existence of a layer structure is commonly determined by the reflection peak of the (003) phase. The other two intense peaks around $60\text{--}63^\circ$, which sometimes occur as a single broad peak, are indexed as (110) and (113) phases with respect to the hexagonal unit. These reflections can be utilized for calculating parameter *a* ($a = 2d_{(110)}$); the value of *a* depends on the nature of the metal cations of the hydroxide sheets and the ratio of the metal components. These results indicated that Ni– M^{3+} ($M^{3+} = V^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}), Co–Cr, Co–Fe, and Zn–Cr LDHs have relatively advanced layer structures along the *c*-axis direction, whereas Zn–Mn, and Zn–Fe LDHs have layer structures with impurity phases. On the other hand, the other precipitated samples in this study, Cu– M^{3+} ($M^{3+} = V^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}), Co–V, Co–Mn, and Zn–V, did not form LDH structures. Diffraction peaks assigned to Co_3O_4 (◇) were found in the Co–Mn sample, as shown in **Figure 1(a)**. In addition, $CuFeO_2$ (●) and CuO (○) phases were confirmed in the XRD patterns of Cu–Fe and Cu–Cr precipitates, respectively, which are presented in **Figure 1(c)**. The impurity

phases, as marked with white triangles (∇) and black triangles ($\blacktriangledown$) in **Figure 1(d)**, correspond to rhodochrosite (MnCO_3) and $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, respectively. Moreover, the MnCO_3 phase reflection (∇) was also confirmed in the diffraction pattern of Ni-Mn LDH, as shown in **Figure 1(b)**, indicating that MnCO_3 crystals formed as an impurity phase in the Ni-Mn LDH structure. None of the peaks in the XRD patterns of Co-V and Cu-V precipitates could be assigned to any reported crystal phases.

Table 1 summarizes the existence of the LDH structure determined from the XRD patterns, specific surface area (S_{BET}), and full width at half maximum of the (003) phase reflection ($\text{FWHM}_{(003)}$) for each of the synthesized samples in this study. As mentioned above, the characteristic layer structure of Co-Cr, Co-Fe, Ni-V, Ni-Cr, Ni-Mn, Ni-Fe, Zn-Cr, Zn-Mn, and Zn-Fe LDHs were confirmed using the XRD patterns. On the other hand, Co-V, Co-Mn, Cu-M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}), and Zn-V precipitates had no LDH structure, although it was previously reported that Co-Mn[11,14], Cu-Cr[10], and Cu-Fe[19] LDHs were successfully synthesized. In order to achieve the LDH structure for these precipitates, it is necessary to optimize the detailed preparation procedure, such as the precursor concentration in the solution, the conditions during co-precipitation (pH, temperature, and atmosphere), and the conditions of aging, rinsing, and drying. In this study, all samples were prepared via a unified procedure, as presented in the experimental section. Among the successfully synthesized LDHs, Ni-M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}) LDHs exhibited relatively small $\text{FWHM}_{(003)}$ values, indicating that Ni-M^{3+} LDHs have an advanced characteristic layer stacking along the c -axis. Co-Cr, Co-Fe, Ni-V, Zn-Cr, and Zn-Fe LDHs exhibited particularly large specific surface areas, whereas it was known that the specific surface areas of a series of LDH materials were less than $100 \text{ m}^2 \text{ g}^{-1}$ [1,50].

1 Previously, we have reported that Ni–Al LDH, which has a large surface area, can
 2 produce large amounts of CO as a reduction product of CO₂ in an aqueous solution
 3 under UV light irradiation. This indicates that the adsorption of CO₂ molecules on the
 4 surface of the Ni–Al LDH photocatalyst is a significant process for the selective
 5 conversion of CO₂. **Table 1** also lists the amounts of products evolved in the gas phase
 6 and the selectivity toward CO₂ reduction in the photocatalytic conversion of CO₂ in an
 7 aqueous NaCl solution using 16 different precipitated samples as photocatalysts for 5 h
 8 of photoirradiation. Each sample showed photocatalytic activity without pretreatment or
 9 modification. Reduction products such as CO, CH₄, and H₂ were produced in the gas
 10 phase. The photocatalytic activities presented in this study did not correspond with the
 11 magnitude of the specific surface areas of the LDH photocatalysts. Ni–V LDH, Co–Fe
 12 LDH, and Co–Mn precipitate (no LDH structure) evolved larger amounts of CO than
 13 that evolved by Ni–Al LDH, which was previously reported by our group as a good
 14 photocatalyst for this reaction [53]. The amount of H₂ produced over these
 15 photocatalysts as a reduction product of H⁺ was less than that of CO, indicating that these
 16 photocatalysts achieved a selective reduction of CO₂ to CO and CH₄ under UV light
 17 irradiation. In particular, Ni–V LDH evolved 147.1 μmol of CO after 5 h of
 18 photoirradiation, and the selectivity toward CO formation among the reduction
 19 products was 97%. Moreover, Co–Cr LDH, Co–Fe LDH, Ni–Fe LDH, and Co–V
 20 precipitate enabled the production of a certain amount of CH₄, which is known as an
 21 eight-electron reduction product of CO₂.

22 **Figure 2** exhibits the weight loss profiles of Ni–M³⁺ (M³⁺ = V³⁺, Cr³⁺, Mn³⁺, and
 23 Fe³⁺) LDHs measured by thermogravimetric analysis (TGA), which is typically used to
 24 characterize the LDH structure in the prepared samples. Several weight losses were

1 present in the TGA profiles of these as-prepared LDHs. It has been reported that LDHs
 2 show characteristic two-step weight losses with increasing temperature[1]. The initial
 3 step at <473 K was caused by the desorption of water molecules preserved on the
 4 surface and in the interlayer. The second step above 473 K was caused by the collapse of
 5 the layer structure, accompanied by dehydration of the hydroxyl groups and
 6 decomposition of the charge compensating interlayer anions. As shown in **Figure 2**,
 7 Ni-V, Ni-Cr, and Ni-Fe LDHs exhibited two-step weight loss curves with the increase
 8 in temperature. It is expected that the LDH structures of these samples were converted
 9 into mixed oxide phases above 700 K. In the case of Ni-Mn LDH, however, another
 10 weight loss occurred after the second step. It is presumed that this third weight loss
 11 was due to the decomposition of MnCO_3 into Mn_2O_3 [54], indicating that the layer
 12 structure of Ni-Mn LDH would collapse at the second step to form MnCO_3 , and then
 13 became a mixed oxide phase at the third step. The morphologies of the synthesized
 14 Ni-M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}) LDHs were investigated using scanning
 15 electron microscopy (SEM) images, as displayed in **Figure S1**. The assembly of many
 16 platelet structures was observed in the SEM images of Ni-Fe, Ni-Mn, and Ni-V LDHs.
 17 Ni-Cr LDH did not show the sheet structure, although characteristic diffraction peaks
 18 due to the layer structure were clearly confirmed in the XRD pattern. The platelet
 19 structure of the Ni-V LDH was much smaller than those of the other LDHs, which is
 20 consistent with the BET surface area results showing that the Ni-V LDH has the largest
 21 specific surface area among the Ni-M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}) LDHs.

22 UV/Vis diffuse reflectance spectra of Ni-M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+})
 23 LDHs are presented in **Figure 3**. Absorption peaks due to the d-d transition of Ni^{2+} and
 24 each M^{3+} were found in the visible region. The photocatalytic reaction did not proceed

thoroughly using a Pyrex jacket equipped with a cooling system, whereas the use of a quartz jacket helped achieve suitable photocatalytic activity. It can be speculated that UV light irradiation < 280 nm is necessary to induce the photocatalytic reaction over Ni-M³⁺ LDHs.

Figure 4(a) displays the formation rates of CO and H₂ evolved in the photocatalytic conversion of CO₂ in an aqueous NaCl solution after 1 h of photoirradiation using Ni-M³⁺ (M³⁺ = V³⁺, Cr³⁺, Mn³⁺, and Fe³⁺) LDHs, Ni-Al LDH, and Ni(OH)₂ as photocatalysts. The amount of H₂ evolved was less than that of CO in all cases, indicating that selective CO₂ reduction was achieved under UV light irradiation. Ni-Cr and Ni-Mn LDHs showed lower CO evolution activities than Ni(OH)₂, which has no characteristic LDH structure. On the other hand, the CO formation rates for Ni-V, Ni-Fe, and Ni-Al LDH were higher than that of Ni(OH)₂. This result is consistent with the previous assertion that incorporation of M³⁺ into Ni(OH)₂ to construct the LDH structure clearly enhances the photocatalytic activity for the conversion of CO₂ in an aqueous NaCl solution. In particular, the CO formation rate over Ni-V LDH was 49.9 $\mu\text{mol h}^{-1}$ after 1 h of photoirradiation, which is much greater than that of the other Ni-M³⁺ (M³⁺ = Cr³⁺, Mn³⁺, Fe³⁺, and Al³⁺) LDHs and Ni(OH)₂. The time course of the products evolved in the photocatalytic conversion of CO₂ in an aqueous NaCl solution using Ni-V LDH as a photocatalyst is shown in **Figure 4(b)**. CO was continuously produced as a reduction product of CO₂ during the 8 h of photoirradiation, and the total (accumulated) amount of CO evolved was ~ 200 μmol , whereas the amount of H₂ formed was < 10 μmol . Accordingly, the Ni-V LDH is considered a promising material for the photocatalytic selective conversion of CO₂ to CO in an aqueous NaCl solution. In addition, none of the Ni-M³⁺ (M³⁺ = V³⁺, Cr³⁺, Mn³⁺, Fe³⁺, and Al³⁺) LDHs showed

photocatalytic activity without NaCl in the reaction solution. We have previously reported that Cl^- in the reaction solution can act as a hole scavenger and improves the photocatalytic conversion of CO_2 into CO over Ni–Al LDH photocatalysts[53]. We presume that Cl^- promotes the selective conversion of CO_2 for the photocatalytic system using Ni– M^{3+} ($\text{M}^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}) LDHs via the same mechanism as that of Ni–Al LDH. In other words, Cl^- is oxidized by the photogenerated holes into Cl_2 , which is immediately converted into HClO in water.

Figure 5 displays the XRD patterns of (a) Ni–V LDH with various Ni/V ratios ($\text{Ni}/\text{V} = 2, 3, 4$, and 5) and (b) $\text{Ni}_2\text{--V}_x\text{--Al}_{1-x}$ LDH ($x = 0, 0.1, 0.5, 0.7, 1.0$). The positions of the characteristic diffraction peaks around 11° (black circle), 23° (white circle), and 61° (triangle), which are assigned to the (003), (006), and (110) phase reflections, respectively, did not alter with the change in the Ni/V ratio of Ni–V LDH, as shown in **Figure 5(a)**. This result indicates that the hydroxide sheet thickness and the cation to cation distance within the hydroxide sheets is not influenced by the ratio of Ni^{2+} to V^{3+} since there is little difference in the reported ionic radii of the 6-fold coordinated Ni^{2+} and V^{3+} (69.0 pm and 64.0 pm, respectively) [55]. However, the specific surface areas of the Ni–V LDHs were affected by the Ni/V ratio within the hydroxide sheets; the observed S_{BET} values of $\text{Ni}/\text{V} = 2, 3, 4$, and 5 were 200, 120, 130, and $87 \text{ m}^2 \text{ g}^{-1}$, respectively. On the other hand, **Figure 5(b)** shows that the XRD patterns were obviously influenced by the V/Al ratio in the $\text{Ni}_2\text{--V}_x\text{--Al}_{1-x}$ LDH (the ratio of Ni/M^{3+} is fixed at 2, $x = 0, 0.1, 0.5, 0.7$, and 1.0). The intense peaks $>60^\circ$ are attributed to the (110) and (113) phase reflections. These peaks, which sometimes overlap because of broadening, shifted to a higher angle with a decrease in the V/Al ratio. This change can be explained by the incorporation of Al^{3+} , which has a much smaller ionic radii (53.5

pm[55]) than V^{3+} , that decreases the average cation-to-cation distance within hydroxide sheets. In addition, the peak intensity and FWHM value of the (003) phase reflection were altered by the V/Al ratio; the increase in the (003) peak intensity and the decrease in the $FWHM_{(003)}$ indicated that the layer stacking along the c -axis direction was advanced by the substitution of V^{3+} with Al^{3+} within the hydroxide sheets.

Table 2 displays the amount of products evolved in the photocatalytic conversion of CO_2 in an aqueous NaCl solution using Ni–V LDHs with various Ni/V ratios, $Ni(OH)_2$, and V_2O_5 . Ni–V LDHs exhibited much higher CO formation activities than $Ni(OH)_2$ and V_2O_5 , which were used as reference photocatalysts. On the other hand, none of the photocatalysts showed H_2 evolution activity via the reduction of H_2O . The CO formation rate was clearly affected by the Ni/V ratio in the Ni–V LDH, with Ni/V = 2 showing the largest amount of CO evolution. The incorporation of V^{3+} into $Ni(OH)_2$ to construct the LDH structure obviously enhanced the CO formation activity. Furthermore, high V^{3+} content in the Ni–V LDH (which is synonymous with a small Ni/V ratio) afforded good photocatalytic activity for the conversion of CO_2 in an aqueous NaCl solution. However, the formation rate of CO gradually decreased with the photoirradiation time, and dropped to about a third of the initial rate after 5 h of photoirradiation. It can be estimated that the Ni–V LDH photocatalyst is deactivated during the photocatalytic reaction, as is described later. **Figure 6** exhibits the CO formation rate in the photocatalytic conversion of CO_2 in an aqueous NaCl solution using $Ni_2-V_x-Al_{1-x}$ LDHs ($x = 0, 0.1, 0.5, 0.7$, and 1.0). The photocatalytic activities were clearly influenced by the V^{3+} to Al^{3+} ratio, and the increase in the V^{3+} concentration improved the CO formation rate under UV light irradiation. This result is consistent with that of Ni–V LDH case; the use of a low Ni/V ratio achieved the high photocatalytic activity for

CO₂ conversion in an aqueous NaCl solution. The V³⁺ specie in the LDH hydroxide sheets is expected to play an important role in this reaction. However, the low Ni–V LDH stability during the photocatalytic reaction was not restituted by the incorporation of Al³⁺ into the Ni–V LDH to assemble the Ni₂–V_x–Al_{1-x} LDH, which was found to have a relatively advanced layer structure.

Figure 7(a) shows the time course of the products evolved and the amount of metal ions in the reaction solution eluted from the Ni–V LDH photocatalyst during the photocatalytic conversion of CO₂ in an aqueous NaCl solution. As mentioned previously, the CO formation rate gradually decreased with the photoirradiation time: 49.9 μmol h⁻¹ after 1 h of photoirradiation diminished to 14.5 μmol h⁻¹ after 8 h of photoirradiation. The H₂ formation rate also declined from 1.4 μmol h⁻¹ after 1 h of photoirradiation to 0.3 μmol h⁻¹ after 8 h of photoirradiation. In contrast, the amount of Ni ions in the reaction solution increased with the photocatalytic reaction time. **Actually**, amorphous Ni(OH)₂ was completely eluted into the reaction solution within 5 h of photoirradiation under the same reaction conditions, whereas the Ni–Al LDH, which forms a rigid layer structure, was sufficiently stable. **Therefore**, the pregnable layer structure of the Ni–V LDH and the existence of the amorphous Ni(OH)₂ phase would facilitate the elution during the photocatalytic reaction. **After 8 h of photoirradiation, partial collapse of the layer structure was found in the XRD patterns, shown in Figure S2, because FWHM₍₀₀₃₎ was increased as compared with before the photoirradiation.** It can be estimated that the non-crystalline phase, e.g., Ni(OH)₂ was preferentially dissolved in the reaction solution. Hence, after 8 h of photoirradiation, the amount of V ions in the reaction solution was much lower than that of Ni ions. As shown in **Figure 7(b)**, which represents an elongated time course, V ions in the Ni–V LDH began elution into the reaction solution

1 after almost half of the Ni ions have leached out. The formation rates of CO and H₂
 2 continuously decreased, and less than 0.3 μmol h⁻¹ of CO was evolved after 200 h of
 3 photoirradiation. Almost all of the Ni-V LDH powder has disappeared during that
 4 time; in other words, the powder sample of photocatalyst could not be collected by the
 5 filtration of the reaction solution. In addition, the leaching of Ni-V LDH was clearly
 6 suppressed under a flow of He instead of CO₂ gas. These results indicated that Ni-V
 7 LDH consisting of mixed hydroxide sheets afforded surface properties suitable for the
 8 photocatalytic conversion of CO₂ in an aqueous solution; however, this photocatalyst
 9 easily leached under UV light irradiation in a CO₂ atmosphere. When Ni-Al LDH was
 10 used as a photocatalyst, as described in previous literature, a stoichiometric amount of
 11 HClO was produced in the reaction solution as an oxidation product of Cl⁻ during the
 12 photocatalytic conversion of CO₂ in an aqueous NaCl solution [53]. In contrast, the
 13 amount of HClO produced in the photocatalytic reaction using Ni-V LDH,
 14 as demonstrated in this study, was much lower than the stoichiometric amount. Although
 15 the reason why the incorporation of V³⁺ enhanced the photocatalytic activity for
 16 CO₂ conversion is still not clear, we estimate the oxidation reaction pass as presented
 17 below.

22 Cl⁻ was oxidized to chlorine (Cl₂) by capturing the photogenerated holes, as shown in
 23 formula (1). This reaction is considered to trigger the subsequent process, because the
 24 photocatalytic activity of Ni-V LDH is completely diminished in the absence of NaCl. It

1 is known that Cl_2 is immediately converted to HClO and HCl via
 2 disproportionation reaction in water (formula (2)). It can be approximated that HCl
 3 produced in the reaction solution by the disproportionation of HClO causes Ni-V LDH
 4 to be more easily leached. Meanwhile, HClO has strong oxidation power due to the
 5 reaction shown in formula (3), according to the reported value of $E^\circ(\text{HClO}/\text{Cl}_2) = 1.630$
 6 V vs. SHE[56], indicating that HClO can oxidize the V^{3+} present in the hydroxide sheets
 7 and/or in the reaction solution. Considering the oxidation potential from V^{3+} to
 8 VO^{2+} ($E^\circ(\text{VO}^{2+}/\text{V}^{3+}) = 0.337$ V vs. SHE[56]), the whole formula for HClO consumption in
 9 the reaction solution can be described by formula (5).

11 VO^{2+} is sufficiently soluble and shows slight blue color in aqueous solution. The filtrate
 12 solution after the photocatalytic reaction actually exhibited a slightly blue color. The
 13 reason why HClO , which was considered to be an oxidation product of Cl^- , was not
 14 detected at all by DPD test is that HClO produced in the reaction solution
 15 was continuously consumed by V^{3+} species. Unfortunately, quantitative balance between
 16 consumed electrons and holes could not be estimated because amount of the final
 17 product of oxidation reactions (maybe VO^{2+}) were not quantified
 18 experimentally. Regeneration of Cl_2 via the oxidation of V^{3+} (formula (5)) is considered
 19 to be converted to HClO and HCl again, as shown in formula (2), indicating that a
 20 combination of V^{3+} and Cl^- might play significant roles like a redox couple in the
 21 consumption of photogenerated holes during the photocatalytic conversion of CO_2 into
 22 CO . Therefore, the incorporation of V^{3+} into the LDH structure made the consumption
 23 of photogenerated electrons. On the other hand, the addition of Na_2CO_3 to the reaction
 24 solution as a second additive (0.1 M NaCl + 0.1 M Na_2CO_3) improved the stability of the

1 Ni–V LDH photocatalyst for the conversion of CO₂ to CO in an aqueous solution, as
2 shown in **Figure 8**. The increase of pH from 5.0 to 7.0 by adding Na₂CO₃ to the aqueous
3 NaCl solution effectively suppressed the leaching of Ni–V LDH during the
4 photocatalytic reaction. We conclude that the Ni–V LDH photocatalyst is substantially
5 active for the conversion of CO₂ in an aqueous NaCl solution, though its stability under
6 the reaction conditions is insufficient because of the oxidation of V³⁺ induced by HClO.
7 The co-presence of V³⁺ and Cl[−] might make it possible to achieve high photocatalytic
8 activity for the conversion of CO₂ into CO in an aqueous solution.

1 **Conclusion**

2 We found that Ni–V LDH showed the high photocatalytic activity for the
3 conversion of CO₂ in an aqueous solution of NaCl. Over 200 μmol of CO was evolved
4 as a reduction product of CO₂ after 8 h of photoirradiation when Ni–V LDH (Ni/V = 2)
5 was used as a photocatalyst. Through the investigation of photocatalytic activities for
6 different V³⁺ content of Ni–V LDH and Ni–V–Al LDH, the existence of V³⁺ afforded
7 good performance for the conversion of CO₂ into CO in an aqueous solution of NaCl.
8 The stability of Ni–V LDH was insufficient due to the leaching into the reaction
9 solution. It can be noted that the combination of V³⁺ and Cl[−] play a significant role in
10 the photocatalytic conversion of CO₂ to CO in an aqueous solution.

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- 22

Table 1 Summary of the characterizations and the photocatalytic activity test for the synthesized 16 different kinds of M^{2+} - M^{3+} LDHs ($M^{2+} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , and Zn^{2+} ; $M^{3+} = \text{V}^{3+}$, Cr^{3+} , Mn^{3+} , and Fe^{3+}). ^aLDH structure was judged from the XRD patterns. ^b S_{BET} was estimated from the N_2 absorption isotherms at 77 K. ^cAmounts of products evolved were evaluated by the photocatalytic reaction; photocatalyst weight 500 mg, water 1.0 L, additive 0.1 M NaCl, CO_2 supply 15 mL min^{-1} , light source 400 W high-pressure Hg lamp. ^dSelectivity to CO_2 reduction was calculated by using the formula; Selectivity to CO_2 reduction (%) = $100 \times ((\text{CO} + \text{CH}_4) / (\text{CO} + \text{CH}_4 + \text{H}_2))$.

Components		^a LDH structure	^b S_{BET} / $\text{m}^2 \text{ g}^{-1}$	FWHM ₍₀₀₃₎ / degree	^c Amounts of products evolved / μmol			^d Selectivity to CO_2 reduction (%)
divalent	trivalent				CO	CH_4	H_2	
Co	V	—	12	—	3.3	1.4	0.2	96
	Cr	○	140	3.1	40.2	1.0	3.0	93
	Mn	—	52	—	59.8	trace	2.0	97
	Fe	○	110	0.6	109.1	5.2	6.6	95
Ni	V	○	200	2.2	147.1	trace	4.2	97
	Cr	○	75	1.1	4.6	0.0	2.8	62
	Mn	○	27	0.6	4.6	0.0	17.0	21
	Fe	○	30	0.9	29.0	1.3	7.9	79
Cu	V	—	48	—	9.4	0.0	4.3	69
	Cr	—	60	—	2.0	trace	4.1	33
	Mn	—	39	—	2.4	0.0	0.2	92
	Fe	—	55	—	5.3	0.0	0.8	87
Zn	V	—	70	—	3.8	0.0	0.0	100
	Cr	○	260	1.7	34.0	0.0	7.1	83
	Mn	○	81	2.5	24.0	0.0	30.0	44
	Fe	○	140	—	3.3	0.0	27.0	11

Table 2 Formation rates of products evolved in the photocatalytic conversion of CO₂ in an aqueous solution of NaCl using Ni–V LDHs with various Ni/V ratio after 1 h and 5 h of photoirradiation. Photocatalyst weight 500 mg, water 1.0 L, additive 0.1 M NaCl, CO₂ supply 15 mL min^{−1}, light source 400 W high-pressure Hg lamp.

Photocatalyst	Formation rate / $\mu\text{mol h}^{-1}$			
	CO		H ₂	
	1 h	5 h	1 h	5 h
Ni/V = 2	49.9	16.5	1.4	0.5
Ni/V = 3	23.0	7.6	1.3	0.2
Ni/V = 4	15.6	4.6	0.9	0.1
Ni/V = 5	12.9	8.4	0.0	0.1
Ni(OH) ₂	3.1	4.6	1.1	0.5
V ₂ O ₅	0.2	Trace	Trace	Trace

1 **Figure captions**

2 **Figure 1** XRD patterns of (a) Co-M³⁺ LDHs, (b) Ni-M³⁺ LDHs, (c) Cu-M³⁺
3 LDHs, and (d) Zn-M³⁺ LDHs. M³⁺ = V³⁺, Cr³⁺, Mn³⁺, and Fe³⁺ are given as (i), (ii), (iii),
4 and (iv) in the figures, respectively. The characteristic peaks are marked with asterisk
5 (*), diamond (◇), white triangle (Δ), black circle (●), white circle (○), and black triangle
6 (▼), which are respectively assigned to LDH structure, Co₃O₄, rhodochrosite (MnCO₃),
7 CuFeO₂, CuO, and Zn₃(OH)₂V₂O₇·2H₂O.

8 **Figure 2** Weight loss profiles of Ni-M³⁺ LDHs (M³⁺ = (i) V³⁺, (ii) Cr³⁺, (iii) Mn³⁺,
9 and (iv) Fe³⁺) in a thermal gravimetric analysis. Atmosphere: dried air flow at a rate of
10 80 mL min⁻¹, temperature increasing rate: 5 K min⁻¹.

11 **Figure 3** UV/Vis diffuse reflectance spectra of Ni-M³⁺ LDHs (M³⁺ = (i) V³⁺, (ii)
12 Cr³⁺, (iii) Mn³⁺, and (iv) Fe³⁺).

13 **Figure 4(a)** Formation rates of CO (red bar) and H₂ (blue bar) evolved in the
14 photocatalytic conversion of CO₂ in an aqueous solution of NaCl after 1 h of
15 photoirradiation using Ni-M³⁺ LDHs (M³⁺ = V³⁺, Cr³⁺, Mn³⁺, and Fe³⁺), Ni-Al LDH,
16 and Ni(OH)₂. (b) Time course of the total amounts of products evolved (accumulated)
17 in the photocatalytic conversion of CO₂ in an aqueous solution of NaCl using Ni-V
18 LDH. Red circle: CO, blue circle (outlined): H₂. Photocatalyst weight: 500 mg, water:
19 1.0 L, additive: 0.1 M NaCl, CO₂ supply: 15 mL min⁻¹, light source: 400 W
20 high-pressure Hg lamp.

21 **Figure 5(a)** XRD patterns of Ni-V LDH with Ni/V = (i) 2, (ii) 3, (iii) 4, and (iv) 5). (b)
22 XRD patterns of Ni₂-V_x-Al_{1-x} (x = (i) 0, (ii) 0.1, (iii) 0.5, (iv) 0.7, and (v) 1.0, the ratio
23 of Ni/(V + Al) was fixed at 2.). x = 0 in Figure 5(b) was same as Ni-V LDH with Ni/V
24 = 2. The characteristic peaks which are marked with black circle (●), white circle (○),

and triangle (Δ) are attributed to (003), (006), and (110) phase reflections of LDH structure.

Figure 6 Formation rate of CO in the photocatalytic conversion of CO₂ in an aqueous solution of NaCl using Ni₂-V_x-Al_{1-x} ($x = 0, 0.1, 0.5, 0.7$, and 1.0) after 1 h (red circle) and 5 h (blue circle) of photoirradiation. Photocatalyst weight: 500 mg, water: 1.0 L, additive: 0.1 M NaCl, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp.

Figure 7 Time courses of the formation rates of gas phase products (left axis) and the amounts of metal ions eluted from Ni-V LDH into the reaction solution (right axis) in the photocatalytic conversion of CO₂ in an aqueous solution of NaCl for (a) 8 h and (b) 30 h of photoirradiation. Red circle: CO, blue circle: H₂, green diamond: Ni ions, and black diamond: V ions. Photocatalyst weight: 500 mg, water: 1.0 L, additive: 0.1 M NaCl, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp. Amounts of metal ions eluted from Ni-V LDH into the reaction solution were evaluated by using ICP-OES at each photoirradiation time.

Figure 8 Time course of the total amounts of CO evolved (accumulated) in the photocatalytic conversion of CO₂ using Ni-V LDH in an aqueous solution of (a) NaCl (0.1 M) + Na₂CO₃ (0.1 M) and (b) NaCl (0.1 M). Photocatalyst weight: 500 mg, water: 1.0 L, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp.

Figure 1(a)

Figure 1(b)

Figure 1(c)

Figure 1(d)

Figure 2

Figure 3

Figure 4(a)

Figure 4(b)

Figure 5(a)

Figure 5(b)

Figure 6

Figure 7(a)

Figure 7(b)

Figure 8