Applied Surface Science 447 (2018) 687-696

Contents lists available at ScienceDirect

## **Applied Surface Science**

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

# Optimized photoreduction of CO<sub>2</sub> exclusively into methanol utilizing liberated reaction space in layered double hydroxides comprising zinc, copper, and gallium



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Applied Surface Science

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#### ARTICLE INFO

Article history: Received 11 September 2017 Revised 26 February 2018 Accepted 5 April 2018 Available online 6 April 2018

Keywords: Layered double hydroxide CO<sub>2</sub> Methanol Photoconversion Interlayer XANES

#### ABSTRACT

Layered double hydroxides (LDHs), typically comprising Zn, Cu, and Ga, photoreduce CO<sub>2</sub> into methanol and CO, however, selective methanol synthesis using CO<sub>2</sub> and heterogeneous photocatalyst is very rare. In this study, the amount of interlayer water molecules is reduced to 31% of that for as-synthesized LDHs by preheating the LDHs at 423 K in vacuum, and the performance for CO<sub>2</sub> photoreduction using 0–0.28 MPa of CO<sub>2</sub> and 0–0.56 MPa of H<sub>2</sub> was investigated. If the LDHs are preheated in vacuum and never in contact with air prior to the photoreduction tests, methanol was produced exclusively in all experiments of this study. LDHs comprising inlayer Cu sites were more active compared to [Zn<sub>3</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>CO<sub>3</sub>·*m*H<sub>2</sub>O, [Zn<sub>3</sub>Ga (OH)<sub>8</sub>]<sub>2</sub>Cu(OH)<sub>4</sub>·*m*H<sub>2</sub>O, and [Zn<sub>3</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>Pd(OH)<sub>4</sub>·*m*H<sub>2</sub>O LDHs. A contour plot for methanol formation rates was drawn for the most active [Zn<sub>1.5</sub>Cu<sub>1.5</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>CO<sub>3</sub>·*m*H<sub>2</sub>O and the volcano top positioned at 0.12 MPa of CO<sub>2</sub> and 0.28 MPa of H<sub>2</sub>: 2.8 µmol-methanol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> and the selectivity was >97 mol%methanol. <sup>13</sup>CH<sub>3</sub>OH formation in the presence of <sup>13</sup>CO<sub>2</sub> and [Zn<sub>1.5</sub>Cu<sub>1.5</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>CO<sub>3</sub>·*m*H<sub>2</sub>O confirmed photocatalytic methanol synthesis. Under 0.12 MPa of CO<sub>2</sub> and 0.28 MPa of H<sub>2</sub>, the intensity of the Cu K preedge peak progressively decreased at the rate of 170 µmol-Cu h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> upon the UV-visible light irradiation for the [Zn<sub>1.5</sub>Cu<sub>1.5</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>CO<sub>3</sub>·*m*H<sub>2</sub>O LDH, demonstrating photogenerated electron accumulation at the Cu<sup>11/1</sup> sites for subsequent CO<sub>2</sub> reduction.

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#### 1. Introduction

Photocatalytic conversion of CO<sub>2</sub> into fuels explores one of the routes to carbon–neutral fuels [1,2], avoiding the net increase in atmospheric CO<sub>2</sub> concentrations associated with fossil-derived alternatives [2,3]. Layered double hydroxide (LDH), a kind of clay families, comprising Zn and Cr was originally reported to generate O<sub>2</sub> from water at a rate of 1.1 mmol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> using a sacrificial oxidant (AgNO<sub>3</sub>) [4]. Then, LDHs comprising Zn, Cu, and Ga/Al were reported to form methanol and CO at 2.3 kPa of CO<sub>2</sub> and 21.7 kPa of H<sub>2</sub> as a new type of photocatalysts for the CO<sub>2</sub> photoconversion [5]. The highest formation rate and selectivity to methanol were 0.49 µmol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> and 88 mol%, respectively, using LDH with a formula [Zn<sub>1.5</sub>Cu<sub>1.5</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>Cu(OH)<sub>4</sub>·mH<sub>2</sub>O irradiated by Ultraviolet (UV)–visible light [6]. The Refs. [5] and [6] assume that H<sub>2</sub> is obtained via photosplitting of water for the following reaction with CO<sub>2</sub>, and the overall reaction is the combination of CO<sub>2</sub> with water

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to form methanol and oxygen ( $\Delta G_r^{\circ} = 689 \text{ kJ mol}^{-1}$ ) [5]. LDHs have been also reported to photoproduce methane [7,8], CO [9–16], and methanol [15–18] starting from CO<sub>2</sub> and water/hydrogen. Ultrathin LDHs are defect-rich and expected to be better photocatalysts [12].

In a practical point of view, it is highly expected to boost the methanol formation rates from CO<sub>2</sub> and H<sub>2</sub> by the optimization of LDH composition, pretreating conditions, and reaction pressure. Methanol is advantageous to handle and transport. Recently, new semiconductor-based photocatalysts reducing CO<sub>2</sub> were developed, however, most of them formed methane [19] and/or CO [20] at the rates as high as 0.63 mmol  $h^{-1}$  g<sub>cat</sub><sup>-1</sup> using triethanol amine [20]. In this study, owing to both the liberation of interlayer reaction space in LDHs (31% removal of structural water) and high reactant pressure (0.40 MPa), the formation rate and selectivity to methanol were significantly improved using [Zn<sub>1.5</sub>Cu<sub>1.5</sub>Ga(OH)<sub>8</sub>]<sub>2</sub> CO3·mH2O LDH irradiated by UV-visible light. Furthermore, the effects of interlayer carbonates and inlayer Cu ions in LDHs are critically evaluated. These results are comparable to the best activities among literature reporting selective methanol formation in the absence of sacrificial reductant [2,3]. Furthermore, pressure dependence of photocatalysis rates, blank tests of CO2 photoreduction, synthesis and the performance using LDH comprising



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interlayer  $[Pd(OH)_4]^{2-}$ , isotope-labeled test using  ${}^{13}CO_2$ , and the Zn and Ga K-edge X-ray absorption near-edge structure (XANES) under high pressure of CO<sub>2</sub> and H<sub>2</sub> irradiated by the UV-visible light are reported.

#### 2. Experimental section

#### 2.1. Syntheses of LDH photocatalysts

Throughout the syntheses of LDHs in this study, no C-containing compounds including organic solvents were used except for sodium carbonate. Deionized water (conductivity <0.055  $\mu$ S cm<sup>-1</sup>, total organic C <10 ppb) supplied by a RFU424TA system (Advatec) was used and special care was taken not to include any contaminations. [Zn<sub>3</sub>Ga(OH)<sub>8</sub>]<sub>2</sub>CO<sub>3</sub>·*m*H<sub>2</sub>O and [Zn<sub>3</sub>Ga (OH)<sub>8</sub>]<sub>2</sub>CU<sub>3</sub>(OH)<sub>4</sub>·*m*H<sub>2</sub>O were synthesized via previously reported procedures [5,6]. The color of LDHs are white and light turquoise and the LDHs are denoted as Zn–Ga–CO<sub>3</sub> and Zn–Ga–Cu(OH)<sub>4</sub>, respectively, in the following (Table 1A).

 $\label{eq:constraint} \begin{array}{ll} [Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2Cu_3\cdot mH_2O, & [Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2Cu(OH)_4\cdot mH_2O, and [Zn_3Ga(OH)_8]_2Pd(OH)_4\cdot mH_2O, denoted as Zn-Cu-Ga-CO_3, Zn-Cu-Ga-Cu(OH)_4, and Zn-Ga-Pd(OH)_4, respectively, were synthesized by adding an aqueous solution (20 mL) of 0.75 M Zn (NO_3)_2\cdot 6H_2O and 0.25 M Ga(NO_3)_3\cdot nH_2O (for Zn-Ga-Pd(OH)_4) or 0.375 M Zn(NO_3)_2\cdot 6H_2O, 0.375 M Cu(NO_3)_2\cdot 3H_2O and 0.25 M Ga (NO_3)_3\cdot nH_2O (for the two LDHs comprising inlayer Cu) to an aqueous solution (100 mL) of 0.075 M Na_2CO_3 (for Zn-Cu-Ga-CO_3), 0.025 M (NH_4)_2CuCl_4\cdot 2H_2O (for Zn-Cu-Ga-Cu(OH)_4), or 0.025 M \end{array}$ 

 $Na_2PdCl_4$  (for Zn–Ga–Pd(OH)<sub>4</sub>) dropwise under rapid stirring at the rate of 900 rotations per minute. Thereby, the pH value was continuously adjusted to 7.6–7.9 except for 6.5 for Zn–Ga–Pd (OH)<sub>4</sub> to prevent Pd(OH)<sub>2</sub> falling out by the addition of aqueous NaOH solution (1.0 M, 40–44 mL in total). Then, the pH value was increased to 8 and the mixture was stirred for 2 h at 300 K. Subsequently, the temperature was raised to 333–353 K and the suspension was kept stirring for 22 h, yielding light turquoise, light turquoise, and light brown precipitates, respectively (Table 1A).

Filtering through a polytetrafluoroethene-based membrane filter (Omnipore JVWP04700, Millipore; pore size 0.1  $\mu$ m) followed by washing with deionized water for five times (5 × 50 mL) afforded the crude LDH product, which was wetly casted as thin film on a Pyrex glass plate and dried in a glove box under ambient air for Zn–Ga–CO<sub>3</sub> and Zn–Cu–Ga–CO<sub>3</sub> and Ar for Zn–Ga–Cu(OH)<sub>4</sub>, Zn–Cu–Ga–Cu(OH)<sub>4</sub>, and Zn–Ga–Pd(OH)<sub>4</sub> LDHs for 5 d.

#### 2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer for  $5.0^{\circ} \le 2\Theta \le 60^{\circ}$  with a scan step of 0.01° and a scan rate of 5 s per step. The measurements were performed under the conditions at 40 kV and 40 mA using Cu K $\alpha$  emission ( $\lambda$  = 0.15419 nm) and a Ni filter. The crystalline size (*t*) was evaluated based on Scherrer equation:

$$t = \frac{0.9\lambda}{(\text{Full width at half maximum})\cos\theta_{\text{B}}}$$
(1)

Table 1

(**D**)

(A) Basic physicochemical properties and (B) the analysis of elemental metal composition of LDH photocatalysts synthesized in this study.

(A) LDHs	Color	Interlayer distance (nm) <sup>a</sup>	Mean crystalline size (nm) <sup>a</sup>	$E_{\rm g}$ (eV) or <i>n</i> value <sup>b</sup>					
				Extrapolation of abs. edge E <sub>g</sub> n		$\alpha h v^{1/n}$ plot versus $h v$			
						$\frac{1}{2}$ Eg	<u>3</u> 2	2	3
Zn-Ga-CO3	White	0.753	59.5	5.5	0.95	5.7	5.3	5.2	5.0
Zn-Cu-Ga-CO3	Light turquoise	0.749	45.9	3.9	0.95	4.3	3.0	2.8	2.7
Zn-Ga-Cu(OH) <sub>4</sub>	Light turquoise	0.783	25.7	4.4	0.99	5.0	3.0	2.9	2.7
Zn-Cu-Ga-Cu(OH) <sub>4</sub>	Light turquoise	0.772	24.0	3.3	1.03	4.0	2.9	2.8	2.5
Zn-Ga-Pd(OH) <sub>4</sub>	Light brown	0.777	21.3	3.8	1.00	4.7	3.0	2.8	2.6

Absorption edge	Zn K-edge	Cu K-edge	Ga K-edge	Pd K-edge
Change of mass attenuation coefficient $\Delta(\mu/\rho)$ at the edge (cm <sup>2</sup> g <sup>-1</sup> ) [21]	218.6	240.1	190.4	49.0
(1)	Edge jump $\Delta(\mu t)$	) observed <sup>c</sup>		
Zn-Ga-CO <sub>3</sub>	4.02	-	0.765	-
Zn-Cu-Ga-CO <sub>3</sub>	2.01	2.30	0.783	-
Zn-Ga-Cu(OH) <sub>4</sub>	3.20	0.587	0.633	-
Zn-Cu-Ga-Cu(OH) <sub>4</sub>	1.34	2.05	0.537	-
$Zn-Ga-Pd(OH)_4$	3.85	-	0.702	0.287
(2)	Atomic ratio in sample based on $\Delta(\mu t)$ listed in (1) <sup>a</sup>			
Zn-Ga-CO <sub>3</sub>	1	-	0.21	-
Zn-Cu-Ga-CO <sub>3</sub>	0.50	0.54	0.21	-
Zn-Ga-Cu(OH) <sub>4</sub>	1	0.17	0.21	-
Zn-Cu-Ga-Cu(OH) <sub>4</sub>	0.5	0.72	0.22	-
$Zn-Ga-Pd(OH)_4$	1	-	0.20	0.20
(3)	Atomic ratio of introduced metal salts for the LDH synthesis			
Zn-Ga-CO <sub>3</sub>	1	-	0.33	-
Zn-Cu-Ga-CO <sub>3</sub>	0.50	0.50	0.33	
Zn-Ga-Cu(OH) <sub>4</sub>	1	0.17	0.33	-
Zn-Cu-Ga-Cu(OH) <sub>4</sub>	0.50	0.67	0.33	-
Zn-Ga-Pd(OH) <sub>4</sub>	1	-	0.33	0.17

<sup>a</sup> Based on XRD pattern.

<sup>b</sup> Based on UV-visible spectra.

<sup>c</sup> The evaluation error was within 4%.

where  $\lambda$  is wavelength for Cu K $\alpha$  emission and  $\Theta_{\rm B}$  is the Bragg angle of the peak.

UV-visible spectra were recorded on a JASCO V-650 spectrophotometer equipped with an integrated JASCO ISV-469 sphere for diffuse reflectance detection within the range of 200 and 800 nm. The spectra were used to evaluate the band gap values ( $E_g$ ) based on the extrapolation of the absorption edge to the *x*-axis and then *n* value is evaluated as the slope of the plot of log( $\alpha hv$ ) versus ( $hv - E_g$ ) value derived from Davis–Mott equation (Tauc plot), given by

$$\alpha h \nu \propto \left( h \nu - E_{g} \right)^{n} \tag{2}$$

where  $\alpha$ , h, and v are the absorption coefficient, the Planck constant, and the frequency of light for n value of  $\frac{1}{2}$ ,  $\frac{3}{2}$ , 2, or 3 for allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively [22]. Alternatively, the  $E_g$  value was also evaluated by extrapolation of the  $(\alpha hv)^{1/n}$  plot versus hvas the interpolation to x-axis based on Eq. (2).

#### 2.3. Temperature programed desorption (TPD)

48.6 mg of Zn–Cu–Ga–CO<sub>3</sub> were charged in a Pyrex glass reactor connected to a closed circulating line connected to vacuum using rotary and diffusion pumps ( $10^{-6}$  Pa). The temperature at the sample was elevated starting from 303 K to 773 K with a ramping rate of 4 K min<sup>-1</sup>. The desorbed gas mixture was trapped using a loop section cooled to 77 K and analyzed every 7.5 min using a gas chromatograph (GC) equipped with thermal conductivity detector (TCD) (model 8A, Shimadzu) equipped with a packed column of polyethylene glycol (PEG)-6000 supported on Flusin P (GL Sciences Inc.). The system was evacuated for 30 s after sampling at every 7.5 min. Another TPD test was also performed prior to every photoconversion test following a similar procedure, but by elevating the temperature from 303 K to 423 K in 30 min and keeping the temperature at 423 K for 1 h.

#### 2.4. Photocatalytic CO<sub>2</sub> conversion tests

LDH catalyst powder was suspended in deionized water and agitated by ultrasound (430 W, 38 kHz, 303 K) for 3 min. The suspension was casted on a Pyrex glass plate ( $25 \text{ mm} \times 25 \text{ mm} \times 1 \text{ mm}$ ) and dried overnight at 373 K. The mass of the films was  $9 \pm 2 \text{ mg}$ , the area that covers the plate was adjusted to  $20 \text{ mm} \times 20 \text{ mm}$ , and the film thickness was  $\sim 10 \,\mu\text{m}$  according to crosssectional scanning electron microscopy (SEM) images [8]. Prior to photocatalytic test, the film on Pyrex plate was heated to 423 K with a ramping rate of  $4 \text{ K min}^{-1}$  and kept at 423 K for 1 h at  $10^{-6}$  Pa using rotary and diffusion pumps (Fig. 1). The film on Pyrex plate was then introduced into a homemade high-pressure stainless-steel reactor (double quartz windows, effective internal volume of 98.4 mL) under Ar [8,23].

The reactor and the stainless metal lines were purged with the reaction gas of  $CO_2$  and  $H_2$  for 15 min [8,23]. The gas was previously mixed in cylinders with the molar ratio of 2:8, 3:7, 4:6, or 5:5. Pure  $CO_2$  (Purity >99.995%),  $H_2$  (Purity >99.99%), or He (Purity >99.999%) was used for the blank tests. Subsequently, the pressure was elevated to the respective reaction pressure and the catalyst was irradiated through double quartz windows by UV–visible light emitted from a 500-W xenon arc lamp (Ushio, model OPM2-502) for 5 h at 300 K. The light intensity was 90.2 mW cm<sup>-2</sup> at the center of the photocatalyst. Thereby, the pressure increased by 1.7% within the first 10 min, however, gradual pressure decrease later than that was slower. Therefore, first pressure increase is exclusively due to the temperature change by light irradiation. Assuming ideal gas behavior, temperature inside the reactor

should increase by 5 K within the first 10 min and negligibly changed later than that during photocatalytic tests of 5 h.

Thereafter, the reaction gas was analyzed using columns packed with 13X-S molecular sieves (GL Sciences Inc.) for the separation and quantification of  $O_2$ ,  $N_2$ ,  $CH_4$ , and CO and PEG-6000/Flusin P for those of  $CO_2$ , methanol, water, and formic acid both set in a GC-TCD using helium (Purity >99.9999%) as a carrier gas. The amounts of methanol and water were analyzed by concentrating those gases in a trap cooled to 195 K with a mixture of diethyl ether and dry ice to separate them from  $H_2$  and vast bulk of  $CO_2$  [8,23,24].

#### 2.5. Preliminary isotope-labeled photoreaction tests

Preliminary isotope-labeled photoreaction tests were performed using a GC-mass spectrometry (GCMS; model JMS-Q1050GC, JEOL) equipped with quadrupole mass spectrometer to investigate the reaction mechanism into methanol. The sampling loop in a Pyrex glass system connected to model JMS-Q1050GC using 1.5 m of deactivated fused silica tube (model 160-2845-10, Agilent;  $\Phi = 250 \,\mu\text{m}$ ) was vacuumed using rotary and diffusion pumps ( $10^{-6}$  Pa). The fused SiO<sub>2</sub> tube was maintained at 393 K during the analysis to avoid gas adsorption inside the tube.

<sup>13</sup>CO<sub>2</sub> exchange (1.27 kPa; <sup>13</sup>C 99%, chemical purity >99.5%) with Zn–Cu–Ga–CO<sub>3</sub> LDH (100 mg) was monitored at 300 K using a quartz reactor [2,5] connected to a closed circulating Pyrex glass system connected to the rotary and diffusion pumps ( $10^{-6}$  Pa). The exchange with interlayer carbonates was monitored using a PEG-6000/Flusin P column set in model JMS-Q1050GC.

## 2.6. Cu, Zn, Ga, and Pd K absorption edge for metal composition analyses and XANES under high-pressure of $CO_2$ and $H_2$

Zn and Ga K-edge XANES spectra were measured in the Photon Factory on beamline 12C at the High Energy Accelerator Research Organization (KEK), Tsukuba. The storage ring energy was 2.5 eV and the ring current was between 450.2 and 324.8 mA. A Si (1 1 1) double-crystal monochromator and a pair of bent cylindrical mirrors were inserted into the X-ray beam path. Cu, Zn, Ga, and Pd K-edge XANES spectra were also measured in the Photon Factory Advanced Ring on beamline NW10A at KEK. The storage ring energy was 6.5 eV and the ring currents were between 47.3 and 36.2 mA. A Si (3 1 1) double-crystal monochromator, bent cylindrical mirror, and double flat mirror were inserted into the X-ray beam path. The details for beam control and X-ray detection system were described previously [5,18,24–28].

Zn–Ga–CO<sub>3</sub> and Zn–Cu-Ga–CO<sub>3</sub> LDH samples were set in a homemade stainless reactor equipped with a pressure gauge, diamond windows (thickness 0.50 mm) for X-ray and a quartz window (thickness 4.0 mm) for UV–visible light (Fig. 2). 0.12–0.18 MPa of CO<sub>2</sub> and 0.28–0.42 MPa of H<sub>2</sub> were introduced to the reactor and the LDH sample was irradiated by UV–visible light provided by a 500-W Xe arc lamp (Ushio, model SX-UID502XAM). Obtained XANES data were analyzed using the XDAP software package [29].

#### 3. Results and discussion

#### 3.1. XRD patterns

The XRD patterns for five LDHs synthesized are depicted in Fig. 3. For carbonate-type LDHs (patterns a and b), peaks appeared at  $2\theta_{\text{Bragg}}$  = 11.7, 23.5, 34.3, 36.9, 38.9, 43.7, 46.4, 52.6, 56.0, and 59.4° those were assigned to diffractions by 0 0 3, 0 0 6, 0 0 9, 1



Fig. 1. A glass cell for heating the photocatalyst film (light turquoise) on Pyrex plate in vacuum.



Fig. 2. Homemade in-situ reaction cell for X-ray absorption fine structure measurements during high-pressure photocatalytic test.



**Fig. 3.** XRD patterns for LDHs. (a) Zn–Ga–CO<sub>3</sub>, (b) Zn–Cu–Ga–CO<sub>3</sub>, (c) Zn–Ga–Cu (OH)<sub>4</sub>, (d) Zn–Cu–Ga–Cu(OH)<sub>4</sub>, and (e) Zn–Ga–Pd(OH)<sub>4</sub>. Impurities: \* Cu(OH)<sub>2</sub>, + CuO, # Zn(OH)<sub>2</sub>, – Ga<sub>2</sub>O<sub>3</sub>, and  $\circ$  PdO. *y*-Scale: (a) <sup>1</sup>/<sub>2</sub>, (b) and (c) <sup>2</sup>/<sub>3</sub>.

04, 015, 107, 01, 1010, 0111, and 110 planes, respectively. The peak due to 012 diffraction overlaps with that due to 009 diffraction. The peaks for Cu/Pd hydroxide-type LDHs (pattern ce), peaks shifted downward to  $2\theta_{\text{Bragg}}$  = 11.3, 22.7, 34.0, 36.5, 38.3, 43.0, 45.5, 51.3, 54.2, and 59.1° especially for diffraction planes perpendicular to the *c*-axis due to the difference of anions, those were assigned to diffractions by 0 0 3, 0 0 6, 0 0 9, 1 0 4, 0 1 5, 107,018,011, and 110 planes, respectively. Based on the peak position of 0 0 3 diffraction, the interlayer distance was evaluated to 0.749-0.753 nm and 0.772-0.783 nm for carbonate-type LDHs and Cu/Pd hydroxide-type LDHs, respectively (Table 1A). These values fall almost within the range 0.751-0.753 nm and 0.772-0.792 nm, respectively, reported for the two types of LDHs [6]. It should be noted that formal Cu hydroxide-type  $[M_{1-x}^{II}M_{x}^{III}(OH)_{2}]_{2}[ Cu(OH)_4]_x \cdot mH_2O$  dehydrates into  $[M_{1-x}^{II}M_x^{III}O_{xy/2}(OH)_{2-xy/2}]_2[Cu$  $(OH)_{4-y}]_x \cdot mH_2O + xyH_2O (y = 1, 2, 3)$  during LDH synthesis in which Cu ions are bound to the O atoms bonded to M ions in cationic layers based on Fourier transform infrared and X-ray absorption fine structure analyses [18]. Namely, Cu hydroxide dehydrates with hydroxy groups of cationic layer and is bound to the cationic layer through Cu-O-M bonds. They are 'layered double hydroxide salts' [6,30] and the minor difference of interlayer distance ( $\Delta = 0.019 - 0.034$ nm) for carbonate-type LDHs and LDH salts is understandable to assume the LDH salt formation also for Zn-Ga-Pd(OH)<sub>4</sub>. Those values based on 006 or 009 peak width were in accord with those above.

Under application of the Eq. (1), the crystallite sizes were estimated at 59 and 46 nm for the carbonate-type LDHs, 26 and 24 nm for the tetrahydroxycuprate-type LDHs, and 21 nm for tetrahydroxypalladate-type LDH (Table 1A). Relatively greater crystallites were formed for the  $CO_3$ -type LDHs due to the higher thermodynamic stability compared to the  $Cu(OH)_4$ -type and Pd (OH)\_4-type counterparts.

Besides, peaks derived from CuO impurity phase appeared at 32.5 and 35.5° and those from Cu(OH)<sub>2</sub> impurity phase appeared at 16.3, 40.0, 50.2, and 53.6° in the pattern for Zn–Cu–Ga–Cu(OH)<sub>4</sub> (d) whereas the intensity of these peaks was quite weak for Zn–Ga–Cu(OH)<sub>4</sub> (c). Additionally, a peak appeared at 31.9° due to PdO impurity phase in the pattern for Zn–Ga–Pd(OH)<sub>4</sub> (e) and two small peaks at 12.8–13.7 and 17.7° in the pattern of Zn–Cu–Ga–CO<sub>3</sub> (b) indicate minor Zn(OH)<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> impurities, respectively.

#### 3.2. Metal ion elemental composition based on X-ray absorption edge jump

The metal ion elemental composition for LDH samples (Table 1A) was analyzed based on X-ray absorption edge jump  $\Delta(\mu t)$  at Zn, Cu, Ga, and Pd K-edge. Based on the changes of mass attenuation coefficient  $\Delta(\mu/\rho)$  at each absorption edge [21], the weight of each element  $m_{\text{element}}$  was calculated:

$$\Delta(\mu t) = \Delta(\mu/\rho) \times m_{\text{element}}/A = \Delta(\mu/\rho) \times m_{\text{element}}/0.50^2 \pi$$
(3)

where  $\mu$  is linear absorption coefficient and *t*, *A*, and  $\rho$  are thickness, area, and the density, respectively, for disk samples of  $\Phi$  = 1.0 cm. Then, the atomic ratios of Zn, Cu, Ga, and Pd in these LDH samples were evaluated (Table 1B2).

The values were basically consistent with the atomic ratios of Zn. Cu. and Pd introduced during LDH syntheses as their salts (Table 1B3, see Section 2.1), however, the evaluated atomic ratios for Ga K-edge (0.20-0.22) was inconsistent with introduced amount of  $Ga(NO_3)_3 \cdot nH_2O$  (0.33). Because Ga ion is more soluble compared to Zn and Cu at pH 6.5-7.9 during the LDH synthesis in this study [30],  $\sim 1/3$  of Ga ions would not be incorporated in LDHs and the actual formula of LDHs (neglecting hydration of interlayer Pd for simplicity) would be [Zn<sub>3</sub>Ga<sub>0.64</sub>(OH)<sub>7.28</sub>]<sub>2</sub>(CO<sub>3</sub>)<sub>0.64</sub>- $-mH_2O(1:0:0.21)$ ,  $[Zn_{1.5}Cu_{1.5}Ga_{0.64}(OH)_{7.28}]_2(CO_3)_{0.64} - mH_2O(0.5:$ 0.5: 0.21),  $[Zn_3Ga_{0.64}(OH)_{7.28}]_2[Cu(OH)_4]_{0.64} \cdot mH_2O(1:0.11:0.21)$ ,  $[Zn_{1.5}Cu_{1.5}Ga_{0.67}(OH)_{7.34}]_2[Cu(OH)_4]_{0.67} \cdot mH_2O (0.5 : 0.61 : 0.22),$ and [Zn<sub>3</sub>Ga<sub>0.61</sub>(OH)<sub>7.22</sub>]<sub>2</sub>[Pd(OH)<sub>4</sub>]<sub>0.61</sub>·mH<sub>2</sub>O (1 : 0.10 : 0.20) in which atomic ratio of Zn : Cu (or Pd) : Ga are also noted in the parenthesis. Minor inconsistency in the ratio of Cu and Pd for cuprate/palladate type LDHs (Table 1B2) suggested not negligible formation of Cu(OH)<sub>2</sub>, CuO, and PdO impurities with these LDHs as proved by XRD (Fig. 3c-e).

This evaluation is consistent with the color of filtrates during LDH syntheses. Any filtrates during the syntheses of LDHs in Table 1A were not colored, demonstrating all the Cu and Pd ions (Cu nitrate aqueous solution: blue; ammonium Cu chloride aqueous solution: yellow; sodium Pd chloride aqueous solution: brown) were incorporated in catalysts while a part of colorless Ga<sup>3+</sup> ions may be eluted during the washing step of LDH synthesis.

Furthermore, it was possible to distinguish inlayer Cu ion (present as octahedron in cationic sheet) and interlayer (dehydrated) Cu ion  $[Cu(OM)_y(OH)_{4-y}(OH_2)_2$  where M is a divalent/trivalent cation in the cationic layer and the Cu is coordinated to two structural water molecules] [18]. All coordination environment for inlayer Cu (Fig. 4A-b), Zn (Fig. 4B-b-d), and Ga (Fig. 4C-b-d), and accordingly all the XANES pattern well resembled each other. In contract, in Cu K-edge XANES for samples comprising interlayer (dehydrated) Cu sites (Fig. 4A-c and d), a shoulder peak appeared at 8991 eV and the peak at 9016 eV became weaker (Fig. 4A, arrows), strongly indicating the structural difference between octahedral Cu site in LDH cationic layer and dehydrated Cu(OM)<sub>y</sub> (OH)<sub>4-y</sub>(OH<sub>2</sub>)<sub>2</sub> sites.

#### 3.3. UV-visible spectra

To analyze the light absorption properties of the LDH catalysts, UV–visible diffuse-reflectance spectra were recorded, shown in Fig. 5. These spectra were used to evaluate the  $E_g$  value based on Eq. (2). The comparison of the  $E_g$  values based on simple absorption-edge extrapolation with the  $E_g$  values obtained from the  $(\alpha hv)^{1/n}$  plot versus hv indicates that the n value was between  $\frac{1}{2}$  and  $\frac{3}{2}$  (Table 1A), demonstrating that direct electronic transitions occurred. Additionally, n values were also evaluated based on the plot of log( $\alpha hv$ ) versus ( $hv - E_g$ ) value based on simple absorption edge extrapolation (Table 1A). The n values were in the range of



Fig. 4. (A) Cu K-edge, (B) Zn K-edge, and (C) Ga K-edge XANES for (b) Zn-Cu-Ga-CO<sub>3</sub>, (c) Zn-Ga-Cu(OH)<sub>4</sub>, and (d) Zn-Cu-Ga-Cu(OH)<sub>4</sub>.

0.95–1.03 and hence in agreement with the discussion above.  $Zn-Ga-CO_3$  sample exhibits direct electronic transitions from O 2p to Zn/Ga 4s and 4p levels; and  $Zn-Cu-Ga-CO_3$ , Zn-Ga-Cu (OH)<sub>4</sub>, and  $Zn-Cu-Ga-Cu(OH)_4$  exhibit direct electronic transitions from O 2p to Zn/Ga 4s and 4p and/or Cu 3d, 4s, and 4p levels. For  $Zn-Ga-Pd(OH)_4$  sample, transitions from O 2p to Zn/Ga 4s and 4p and/or Q 2p to Zn/Ga 4s and 4p and/or Q 2p to Zn/Ga 4s and 4p and/or Q 2p to Zn/Ga 4s and 4p and/or Pd 4d, 5s, and 5p levels occur.

If interlayer carbonate is replaced by  $Cu(OH)_{4}^{2-}$ , the UV absorption edge shifted to longer wavelength (59–90 nm) for both



**Fig. 5.** UV-visible spectra for LDHs. (a) Zn-Ga-CO<sub>3</sub>, (b) Zn-Cu-Ga-CO<sub>3</sub>, (c) Zn-Ga-Cu(OH)<sub>4</sub>, (d) Zn-Cu-Ga-Cu(OH)<sub>4</sub>, and (e) Zn-Ga-Pd(OH)<sub>4</sub>.

samples (Fig. 5, spectra a versus c, spectra b versus d). For Pd  $(OH)_4^{2-}$  replacement (spectra a versus e), the absorption edge also underwent a redshift for 101 nm. Additionally, inlayer Cu incorporation leads to an absorption edge shift of 63–95 nm towards higher wavelengths in comparison with Zn–Ga–CO<sub>3</sub> and Zn–Ga–Cu(OH)<sub>4</sub>, respectively (spectra a versus b, spectra c versus d).

Furthermore, a weak d-d transition peak appeared for Zn–Cu–Ga–CO<sub>3</sub>, Zn–Ga–Cu(OH)<sub>4</sub>, and Zn–Cu–Ga–Cu(OH)<sub>4</sub> LDHs between 500 and 800 nm (Fig. 5b–d). For the Zn–Ga–Pd(OH)<sub>4</sub> LDH, a d-d transition with a high absorption characteristic was observed in the region of 450–800 nm (Fig. 5e), mainly due to the presence of minor impurity PdO, as evidenced by XRD (Fig. 3e).

In summary,  $E_g$  values decreased from  $Zn-Ga-CO_3$  (5.5 eV) to  $Zn-Ga-Cu(OH)_4$  for 1.1 eV, to  $Zn-Cu-Ga-CO_3$  for 1.6 eV, to  $Zn-Ga-Pd(OH)_4$  for 1.7 eV, and then to  $Zn-Cu-Ga-Cu(OH)_4$  for 2.2 eV (Table 1A) due to the presence of Cu 3d levels or Pd 4d levels.

#### 3.4. TPD

Two kinds of TPD data are shown in Fig. 6. The 48.6 mg of Zn– Cu–Ga–CO<sub>3</sub> used for this study corresponds to 52.2 µmol catalyst if the molar amount of structural water is a half of that of metal cations, i.e. m = 4 [30]. The total amount of CO<sub>2</sub> desorbed until 773 K was 85.8 µmol (Fig. 6A). The desorption centered at 690 K should be due to the decomposition of metal carbonates to oxides in agreement with literature [30,31]. The extra CO<sub>2</sub> in the TPD would be due to adsorbed CO<sub>2</sub> on the LDH surface leading to a shoulder peak centered at 560 K. In contrast, no clear peak was observed for water desorption, and total amount of H<sub>2</sub>O desorbed until 773 K was 120 µmol. The desorption temperature range was similar to reported thermogravimetric analysis data for [Mg<sub>2</sub>Al<sub>0.9</sub>-Ga<sub>0.1</sub>(OH)<sub>6</sub>]<sub>2</sub>CO<sub>3</sub>·mH<sub>2</sub>O [32]. Major part of interlayer water desorbs until 773 K, but metal hydroxides transformed from LDH also remain at the temperature.

The desorption during the pretreatment of Zn–Cu–Ga–CO<sub>3</sub> for photocatalytic tests using CO<sub>2</sub> and H<sub>2</sub> was also monitored. The desorption rate for both water and CO<sub>2</sub> increased until the 423 K were reached, and the desorption rate gradually decreased at 423 K for 1 h (Fig. 6B). The total amount of desorbed water during the pretreatment was 64.5 µmol corresponding to 31% of interlayer water removed. The total amount of desorbed CO<sub>2</sub> during the pretreatment was 7.47 µmol corresponding to 14% of carbonates in the LDH, however, CO<sub>2</sub> in Fig. 6B originates from both carbonates and adsorbed CO<sub>2</sub> on the LDH surface in comparison to peak pattern in Fig. 6A.

#### 3.5. Photocatalytic CO<sub>2</sub> conversion

Under reaction conditions of CO<sub>2</sub> 0.12 MPa and H<sub>2</sub> 0.28 MPa, the formation rates of C-containing products using LDH catalysts were monitored. Compared to previously-reported low-pressure experiments at CO<sub>2</sub> 2.3 kPa and H<sub>2</sub> 21.7 kPa [5,6], the formation rates were significantly improved by factors of 1.8–12 times (Table 2a–d).

Interestingly, the performances under reactant pressure of 0.40 MPa were highly selective for methanol formation: more than 90-97 mol% selectivity and rates of 0.78–2.8  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, mainly due to the advanced pretreatment conditions at 423 K under vacuum (Fig. 1). When the LDHs were exposed to air prior to the photoreduction tests of CO<sub>2</sub>, the methanol formation rates were as low as 0.011–0.30  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> [23]. One of the major reasons of this enhancement is the liberation of interlayer space by removing 31% of interlayer water (Fig. 6B). The rate difference among LDH catalysts (Table 2a-d) indicates that inlayer Cu(II) site accelerates the formation rates whereas dehydrated tetrahydroxy cuprate site attached to cationic sheet lowers them. The dehydrated tetrahydroxy palladate site was more effective as compared to cuprate counterpart for the methanol formation (Table 2c, e), however, it was less effective than inlayer Cu(II) site (Table 2b, e). Thus, inlayer Cu comprising LDH shows the highest methanol formation rate of 2.8  $\mu$ mol  $g_{cat}^{-1}$   $h^{-1}$ . This value is superior to CO formation rate of 1.7  $\mu$ mol  $g_{cat}^{-1}$   $h^{-1}$  using CO<sub>2</sub>, moisture, and Ce<sup>II</sup>–Ce<sup>III</sup> LDH [13]. Assuming homogeneous energy distribution in the whole wavelength range of the Xe arc light source and that the photons with the



**Fig. 6.** TPD of  $H_2O$  and  $CO_2$  using  $Zn-Cu-Ga-CO_3$  between 300 and 773 K with the ramping rate of 4 K min<sup>-1</sup> (A) and between 300 and 423 K with the ramping rate of 4 K min<sup>-1</sup> and keeping at 423 K for 1 h (B).

Table 2
Photocatalytic test results using 0.12 MPa of $CO_2$ and 0.28 MPa of $H_2$ and LDH photocatalysts irradiated by UV-visible light for 5 h.

Entry	Photocatalyst	Formation	Formation rate ( $\mu$ mol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )			Selectivity to methanol (mol%) <sup>b</sup>
		CH₃OH	СО	Σ	Ratio compared to corresponding low pressure test <sup>a</sup>	
a	Zn-Ga-CO <sub>3</sub>	1.5	<0.08	1.5	12	>95
b	Zn-Cu-Ga-CO <sub>3</sub>	2.8	<0.08	2.8	11	>97
с	Zn-Ga-Cu(OH) <sub>4</sub>	0.78	< 0.08	0.78	1.8	>90
d	Zn-Cu-Ga-Cu(OH) <sub>4</sub>	2.0	< 0.08	2.0	3.6	>96
e	Zn-Ga-Pd(OH) <sub>4</sub>	1.1	<0.08	1.1	-	>93

<sup>a</sup> Ratio of total C-containing product formation rate in comparison to that under 2.3 kPa of CO<sub>2</sub> and 21.7 kPa of H<sub>2</sub> using 100 mg of photocatalyst [5,6].

<sup>b</sup> Methane and formic acid were not detected above the detection limit of GC-TCD: 0.12 and 0.004  $\mu$ mol  $g_{cat}^{-1}$  h<sup>-1</sup>, respectively.



**Fig. 7.** Contour plot of methanol formation rates depending on the partial pressures of H<sub>2</sub> and CO<sub>2</sub> using Zn-Cu-Ga-CO<sub>3</sub> LDH photocatalyst (10 mg). The values in the plot are methanol formation rates in the unit of  $\mu$ mol  $g_{cat}^{-1}$  h<sup>-1</sup>.

energy of band gap (3.9 eV, Table 1A) are responsible for photocatalytic methanol synthesis using Zn–Cu–Ga–CO<sub>3</sub> (the formation rate 2.8  $\mu$ mol-CH<sub>3</sub>OH g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>, Table 2b), the quantum efficiency is calculated to 44 ppm.

We tried to detect C-containing products other than methanol throughout the tests in this study, however, CO, methane, and formic acid were not found above the detection limit of GC-TCD (Table 2). As the reason of exclusive formation of methanol in this study, longer residence time of CO<sub>2</sub>-derived intermediate(s) in the interlayer space of LDH is suggested during the multiple reduction steps to methanol [33].

Although methanol was formed exclusively under the described reaction conditions, the catalytic rate depended highly on the partial pressure ratio of  $CO_2$ :  $H_2$  and also on the total pressure (Fig. 7). A maximum rate of 2.8  $\mu$ mol g<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> was observed for hydrogen pressure  $P(H_2)$  of 0.28 MPa and CO<sub>2</sub> pressure  $P(CO_2)$  of 0.12 MPa. Shifting to higher P(CO<sub>2</sub>) of 0.19–0.28 MPa inhibited the methanol formation significantly by a factor of 0.089-0.14 shown as a slope in the contour plot (Fig. 7). Extra amount of  $CO_2$  should adsorb on/ in the LDH and would block the once-liberated interlayer reactive space and hamper the diffusion of reactant (H<sub>2</sub>) and/or product (methanol). In this context, the liberation of interlayer reactive space is primarily due to the removal of 31% of interlayer water, but the removal of 14% of carbonates (and adsorbed CO<sub>2</sub>) during the pretreatment is also critical. Once-removed CO<sub>2</sub> would be recovered to the LDH framework at the higher  $P(CO_2)$  regime of 0.19-0.28 MPa, and electrostatically stabilize it to possess less surface charging and be unreactive [34].

At lower  $P(CO_2)$  of 0–0.07 MPa, e.g. following on the straight line of  $P(H_2)$  of 0.28 MPa, the methanol formation rates became also lower by a factor of 0.39–0.68 (Fig. 7). It is evident that a *P* 

(CO<sub>2</sub>) higher than 0.19 MPa was even negative for the catalysis compared to lower  $P(CO_2)$  between 0 and 0.07 MPa. Especially, the relatively high conversion rate in the test under H<sub>2</sub> only is a specific feature of LDH catalysis (1.9 µmol  $g_{cat}^{-1}h^{-1}$ ), implying that interlayer carbonate can take part in the photocatalytic reaction.

Following along the straight line of  $P(CO_2) : P(H_2)$  ratio of 3:7 in Fig. 7, the rates were almost invariant at 1.0 ± 0.2 µmol  $g_{cal}^{-1}h^{-1}$  with exceptions of a lower rate at the origin (control test in 0.40 MPa of He; 0.73 µmol  $g_{cal}^{-1}h^{-1}$ ) and the volcano peak top region (2.8–1.9 µmol  $g_{cal}^{-1}h^{-1}$ ) of  $P(H_2)$  and  $P(CO_2)$  ranges of 0.28–0.35 MPa and 0.12–0.15 MPa, respectively. The region of almost invariant rates of 1.0 ± 0.2 µmol  $g_{cal}^{-1}h^{-1}$  further extends to the straight lines of P(CO<sub>2</sub>) of 0.12 MPa and lower  $P(CO_2)$  than 0.12 MPa forming relatively flat halfway region of the volcano (light green region in Fig. 7).

As already noted above, even at 0.40 MPa of He as a blank test, the observed methanol formation rate was not negligible: 0.73  $\mu$ mol g<sub>cat</sub>h<sup>-1</sup>. This result suggests that interlayer H<sub>2</sub>O is a reaction partner for methanol formation. Thus, it is necessary to further investigate the reaction mechanism to explain these results using isotope-labeled substrates.

#### 3.6. Preliminary <sup>13</sup>C-labeled tests

By the photocatalytic test using Zn–Cu–Ga–CO<sub>3</sub> film (10 mg), the best catalyst in this study (Table 2b), at a reactant pressure of 0.40 MPa (CO<sub>2</sub> : H<sub>2</sub> = 3:7) for 5 h, methanol formation was confirmed as the major peak of mass number (*m*/*z*) 31 (CH<sub>3</sub>O fragment, peak area  $5.7 \times 10^5$ ; Fig. 8A, top) and 32 (CH<sub>3</sub>OH, area 2.0  $\times 10^5$ ; Fig. 8A, bottom).

In 1.27 kPa of <sup>13</sup>CO<sub>2</sub> using Zn–Cu–Ga–CO<sub>3</sub> powder (100 mg) in the darkness for 1 h, no methanol peak was detected at m/z of 31 and 32 (Fig. 8B, top and bottom). In contrast, irradiated under UV-visible light for 1 h, methanol peaks appeared at m/z of 31 (area  $3.9 \times 10^3$ ) and m/z of 32 (area  $1.1 \times 10^4$ ) at the retention time of 11'05"-11'12" with the peak area ratio of 1:2.9 (Fig. 8C, top versus bottom). As in Fig. 8A, mass number for methoxy fragment is more pronounced for methanol detection in GCMS. It was observed that methanol retention time became progressively later as the amount decreased: from 8'39" (area  $2.3 \times 10^8$ , 0.501 kPa) to 9'16" (area  $1.5 \times 10^7$ , 0.016 kPa), 9'34" (area  $5.7 \times 10^5$ , Fig. 8A), and then 11'12'' (area  $2.9 \times 10^3$ , Fig. 8C). This result demonstrates that both gas-phase <sup>13</sup>CO<sub>2</sub> and interlayer carbonates photoreacted into methanol, however, gas-phase <sup>13</sup>CO<sub>2</sub> preferably reacted to form <sup>13</sup>CH<sub>3</sub>OH leading to greater peak of m/z = 32 due to 88% of <sup>13</sup>CH<sub>3</sub>O and 12% of <sup>12</sup>CH<sub>3</sub>OH fragments at the initial 1 h irradiated by UV-visible light. However, only 4.0% of carbonate exchanged with <sup>13</sup>CO<sub>2</sub> irradiated by UV-visible light for 24 h (data not shown). This fact suggested that only water near external LDH sites participated in the photocatalysis under low pressure of  ${}^{13}CO_2$  (1.27 kPa). The CO<sub>2</sub> exchange reaction with Mg-Al-<sup>13</sup>CO<sub>3</sub> LDHs via

$$CO_{2}(g) + H_{2}O(interlayer) + {}^{13}CO_{3}^{2-}(interlayer)$$
  

$$\rightarrow HCO_{3}^{-}(interlayer) + HO^{-}(interlayer) + {}^{13}CO_{2}$$
(4)



Fig. 8. Photocatalytic test using Zn-Cu-Ga-CO<sub>3</sub> LDH (10 mg), 0.12 MPa of CO<sub>2</sub>, and 0.28 MPa of H<sub>2</sub> (A) and CO<sub>2</sub> exchange test using Zn-Cu-Ga-CO<sub>3</sub> LDH (100 mg) and 1.27 kPa of <sup>13</sup>CO<sub>2</sub> (B, C) monitored using GCMS. Under dark for 1 h (B) and following irradiation by UV-visible light for 1 h (C). 500-W Xe arc lamp was used for tests A and C.



Fig. 9. In situ normalized XANES spectra at (A) Zn K-edge and (B) Ga K-edge for Zn-Ga-CO<sub>3</sub> LDH under CO<sub>2</sub> (0.18 MPa) and H<sub>2</sub> (0.42 MPa) and UV-visible light irradiation at beamline (Fig. 2).



Fig. 10. (A) In situ normalized Cu K-edge XANES spectra for Zn-Cu-Ga-CO<sub>3</sub> (25 mg) under CO<sub>2</sub> (0.12 MPa) and H<sub>2</sub> (0.28 MPa) and UV-visible light irradiation for 0 min, 62 min, and 120 min at beamline. (Inset) Expanded view of 1s-3d preedge peak region. (B) Time course of the intensity of 1s-3d preedge peak for 2 h.

in air was reported. Most of  ${}^{13}\text{CO}_3^{2-}$  exchanged in 10 weeks, 7 h, and 1 h when the molar ratio of Mg: Al was 2, 3, and 4, respectively, in the LDHs [35]. This fact suggests that the population of positive charge in layer critically affects the exchangeability of carbonates.

#### 3.7. XANES for LDHs under 0.60–0.40 MPa of $CO_2$ and $H_2$

First, the Zn K-edge and Ga K-edge XANES spectra of Zn–Ga– $CO_3$  during  $CO_2$  photoreduction test at 0.18 MPa of  $CO_2$  and 0.42 MPa of H<sub>2</sub> are shown in Fig. 9A and B, respectively. Under similar conditions,  $CO_2$  is photoconverted into methanol (Table 2a). Corresponding to the performance, the whiteline peak intensity at 10379 eV near the Ga K-edge decreased by 2.1% when the sample was irradiated by UV–visible light compared to that in darkness (Fig. 9B, Right). In contrast, the whiteline peak intensity at 9671 eV near the Zn K-edge decreased only by 1.2% when the UV–visible light was irradiated as compared to that in darkness (Fig. 9A, Right). This change of whiteline peak intensity under UV–visible light irradiation was only observed at elevated total pressure of 0.60 MPa, but not at 0.10 MPa.

The decrease of whiteline intensity should be related to the partial occupancy of 4s and 4p states by the photogenerated electrons. Preferable  $CO_2$  adsorption on Ga ions is known [32,36]. The possibility of partially-reduced Ga ions adsorbed with intermediate species, e.g. carbonate and/or hydrogen carbonate, at elevated pressure needs to be verified.

In-situ Cu K-edge XANES of the most active Zn-Cu-Ga-CO<sub>3</sub> (Table 2b) was monitored under reactant pressures of 0.12 MPa CO<sub>2</sub> and 0.28 MPa H<sub>2</sub> irradiated by UV-visible light during measurement at beamline for 2 h (Fig. 2). The 1s-3d preedge peak appeared at 8980.6 eV (Fig. 10A, inset). The peak intensity progressively decreased (Fig. 10B) due to the reduction of Cu(II) (3d<sup>9</sup> configuration) to Cu(I) (3d<sup>10</sup> configuration) by the diffusion of photogenerated electrons to the Cu sites. 1s-3d electronic transition is impossible to fully occupied 3d<sup>10</sup> Cu(I) site. The peak decreasing rate corresponds to 170 µmol-Cu h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> for 25 mg-disk sample of  $\Phi$  = 1.0 cm.

Under 2.1 kPa of CO<sub>2</sub> and 21.7 kPa of H<sub>2</sub>, Cu site reduction rate of 580 µmol-Cu h<sup>-1</sup>  $g_{cat}^{-1}$  was reported under similar conditions for 170 mg-disk Zn–Cu–Ga–CO<sub>3</sub> sample of  $\Phi$  = 2.0 cm [18]. The reduction rate of Cu at 0.40 MPa was 10 times greater compared to its methanol formation rate (Table 2b), taking the electron number (s) needed for each reaction (Cu(II)/(I) redox versus six electron reduction to methanol) into account. Thus, the inlayer Cu sites once accumulate photogenerated and diffused electrons. However, the electrons transfer to CO<sub>2</sub> (or CO<sub>2</sub>-derived species) more easily under pressurized conditions (Fig. 10) in comparison to that at a lower pressure (23.8 kPa) [18]. Thereby the net Cu reduction rate during this experiment (Fig. 10B) seemed to be lower in comparison to that in Ref. [18].

#### 4. Conclusions

LDHs comprising Zn, Cu, and/or Ga in the cationic layers and carbonates,  $[Cu(OH)_4]^{2-}$ , or  $[Pd(OH)_4]^{2-}$  as anions were synthesized and applied for the photoreduction of CO<sub>2</sub> at total reactant pressures of 0-0.80 MPa. By the pretreatment in vacuum at 423 K for 1 h, 31% of interlayer water desorbed to liberate the interlayer reaction space for Zn-Cu-Ga-CO<sub>3</sub> LDH. The highest methanol formation rate in this study was observed at 0.40 MPa of CO<sub>2</sub> and H<sub>2</sub> with the molar ratio 3:7 using Zn-Cu-Ga-CO<sub>3</sub>. The liberation effects of interlayer space are apparent: methanol formation rate of 2.8  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> versus 0.011–0.30  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> using assynthesized versus air exposed LDHs [23] tested under similar reaction conditions. The pressure dependence of methanol photosynthesis rates on  $P(CO_2)$  and  $P(H_2)$  constituted a volcano-like contour peaked at  $P(CO_2)$  of 0.12 MPa and  $P(H_2)$  of 0.28 MPa using Zn-Cu-Ga-CO<sub>3</sub>. The reason of volcano-like pressure dependence is complicating because carbonates and interlayer water potentially react to form methanol under the photocatalytic reaction conditions. However,  $P(CO_2)$  above 0.12 MPa led to excessive CO2-derived species to block the diffusion of reactant and/or product to/from the interlayer reaction space liberated by the pretreatment at 423 K in vacuum. Major <sup>13</sup>CH<sub>3</sub>OH formation from <sup>13</sup>CO<sub>2</sub> was observed by GCMS analysis in addition to minor <sup>12</sup>CH<sub>3</sub>-OH formation from carbonate of the LDH catalysts. In-situ XANES study indicated complex formation of CO<sub>2</sub>-derived species with occupied Ga ion sites rather than Zn ion sites in Zn-Ga-CO<sub>3</sub> LDH and also the accumulation of photogenerated electrons at Cu ion sites for subsequent CO<sub>2</sub> reduction in Zn-Cu-Ga-CO<sub>3</sub> LDH.

#### Acknowledgments

The authors are grateful for the financial supports from the Grant-in-Aid for Scientific Research C (17K05961, 26410204) from Japan Society for the Promotion of Science and Leading Research Promotion Program (2015–) from the Institute for Global Prominent Research, Chiba University. X-ray absorption experiments were conducted under the approval of the Photon Factory Proposal Review Committee (2016G577). The authors thank Akane Kawashima for the technical support of TPD data acquisition.

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