CO₂ Photoreduction with Water Vapor by Ti-Embedded MgAl Layered Double Hydroxides

Huilei Zhao^a, Jinye Xu^b, Lianjun Liu^b, Guiying Rao^a, Cunyu Zhao^b, Ying Li^{a*}

^a Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA

^b Mechanical Engineering Department, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

* Corresponding author. Tel.: +1-979-862-4465, E-mail address: yingli@tamu.edu

Abstract

Photocatalytic reduction of CO₂ into value-added fuels (e.g., CO and CH₄) is a promising approach of storing solar energy and mitigating greenhouse gas emissions simultaneously. In this work, a novel material of crystallized titanium-embedded magnesium-aluminum layered double hydroxides (MgAlTi-LDHs) is developed and tested for CO₂ photoreduction with water. Three different materials synthesis methods were explored: (1) coprecipitation, (2) coprecipitation + hydrothermal, and (3) coprecipitation + calcination + reconstruction. The coprecipitation method alone only produced amorphous TiO_x species in the LDHs, while the latter two methods resulted in the formation of crystalline anatase TiO₂ when appropriate treatment temperatures were applied but the specific surface area was decreased due to the thermal treatment. Compared with commercial TiO₂-P25 nanoparticles, all MgAlTi-LDHs prepared in this work demonstrated two to four times higher catalytic activities in CO₂ photoreduction to CO. Among the MgAlTi-LDHs, the CO₂ photoreduction activity was affected by both the crystallinity of TiO₂ and the specific surface area. Consequently, the material hydrothermally treated at 150 to 200 °C demonstrated the highest CO production due to a well-balanced TiO₂ crystallinity and specific surface area. Findings in this work contribute to the development of efficient photocatalysts for CO₂ reduction and advance the understanding of the catalyst property-activity relationships.

Keywords

Layered double hydroxides (LDHs), TiO₂, Crystallinity, CO₂ photoreduction, Photocatalyst

1. Introduction

Photocatalytic reduction of carbon dioxide (CO_2) to fuels or value-added chemicals (carbon monoxide, methane, methanol, etc.) has become an attractive approach to solve the problem of increasing CO_2 concentration in the atmosphere resultant from fossil fuels consumption.¹ TiO_2 is one of the most extensively studied photocatalysts for CO_2 photoreduction because TiO_2 is earth abundant, inexpensive, chemically stable, and environmentally benign.² TiO_2 has three naturally existing crystal structures: anatase (A), rutile (R), and brookite (B). Anatase is widely believed to be the most active phase for photocatalysis. Our previous work demonstrated that the photocatalytic activity of TiO_2 for CO_2 photoreduction was in the order of $\text{A} > \text{B} > \text{R}$ on defect-free surfaces while oxygen-deficient brookite also showed superb activity.³ It remains controversial in the literature whether amorphous TiO_2 is photocatalytic active. Amorphous TiO_2 has a larger band gap (3.3-3.5 eV)⁴ than anatase (3.2 eV)³, and it is generally believed to be inactive for photochemical reaction due to large number of defects, which lead to fast recombination of electrons and holes.⁵⁻⁷ Meanwhile, some studies have demonstrated the photoactivity of amorphous TiO_2 for decomposition of stearic acid⁸ and for hydrogen production from water⁹. Krylova et.al¹⁰ reported that amorphous TiO_2 was active for photocatalytic water reduction and methyl blue oxidation but the crystallization to rutile TiO_2 further enhanced its photocatalytic activity.

A general pathway for TiO_2 assisted CO_2 photoreduction with H_2O was described as follows: reactants adsorbed on the surface of TiO_2 , photogeneration of electrons and holes, activation of the adsorbed reactants by charge carriers, formation of intermediates adsorbed on the surface of TiO_2 , conversion of intermediates to products, desorption of products from catalyst surface, and regeneration of the catalyst.¹¹ However, fast recombination rate of photogenerated electrons and holes, and poor CO_2 adsorption capability on the surface of TiO_2 limit its photocatalytic activity. Surface modification of TiO_2 with stronger CO_2 adsorbent could improve CO_2 adsorption and reduction on TiO_2 . Xie et al.¹² added a variety of metal oxides to Pt-loaded TiO_2 for CO_2 photoreduction and discovered a linear correlation between the amount of chemisorbed CO_2 on metal oxides and the CH_4 yield. Our recent study demonstrated that CO_2 photoreduction was significantly improved by using a hybrid adsorbent–photocatalyst (i.e., MgO/TiO_2 microspheres) due to great CO_2 adsorption ability of MgO .^{13,14}

Layered double hydroxides (LDHs), known as a class of anionic clays or hydrotalcite (HT)-like materials, and their derivatives, e.g. layered double oxides (LDOs) obtained upon calcination of LDHs have both been applied as CO_2 adsorbents.¹⁵⁻¹⁸ LDOs can be reconstructed to LDHs upon rehydration.¹⁹ Our recent work reported an integrated CO_2 capture and photocatalytic reduction process by a hybrid $\text{TiO}_2/\text{MgAl-LDO}$ material where captured CO_2 on MgAl-LDO can be converted to CO by TiO_2 under UV light

irradiation.²⁰ Hong et al.²¹ assembled MgAl-LDHs nanosheets with carbon nitride (C₃N₄) photocatalyst, which was demonstrated to yield more CH₄ from photoreduction of CO₂ than C₃N₄ alone in aqueous solution with Pd as the cocatalyst. The main reason was identified to be the enrichment of CO₂ adsorption on the catalyst surface by MgAl-LDHs. Other LDHs like ZnAl-LDHs, ZnCr-LDHs and NiAl-LDHs did not make significant improvement of CH₄ production since they have very limited CO₂ adsorption capacity.²¹

LDHs themselves have also been demonstrated as photocatalysts thanks to their highly tunable chemical compositions. Silva et al.²² reported O₂ evolution from water under visible light on ZnTi, ZnCr and ZnCe-LDHs. Parida et al.²³ reported photocatalytic H₂ generation from water by a MgAlFe-LDH. Ti-containing LDHs (NiTi, ZnTi and MgAlTi-LDHs) have been reported to enhance H₂ production from photocatalytic water splitting by providing highly dispersed TiO₆ units in the LDHs structure.²⁴ In general, Ti species in MgAlTi-LDHs remain as amorphous phase in LDHs prepared by a conventional coprecipitation method.¹⁹ However, reconstructed LDHs, prepared by calcination at 400 °C and subsequent rehydration in water showed crystalline TiO₂ in MgAlTi-LDHs.¹⁹ While both MgAlTi-LDHs (with amorphous Ti species) and crystalline TiO₂ embedded in MgAl-LDH are demonstrated as photocatalysts, it is not clear in the literature which material is more active, particularly for CO₂ photoreduction with water.

In this work, we have prepared three types of MgAlTi-LDHs photocatalyst materials with different Ti species and structures and compared their activities in CO₂ photoreduction with water. The first type is prepared using a conventional coprecipitation method. The second method is coprecipitation followed by hydrothermal treatment to increase the crystallinity of TiO₂. This method has not been reported in the literature before and is inspired by the idea that amorphous TiO_x species can be transformed to crystalline TiO₂ by hydrothermal treatment.^{25,26} The third method is to reconstruct LDHs by calcination and rehydration, which was anticipated to crystallize TiO₂ while maintaining the layered structure. We have carefully characterized the three types of materials and correlated their materials properties with their photocatalytic activities in CO₂ reduction.

2. Experimental

2.1 Materials Preparation

Fig. 1. Schematic diagram showing the three methods of preparing MgAlTi-LDHs: coprecipitation, hydrothermal treatment, and reconstruction.

2.1.1 Coprecipitation synthesis of MgAlTi-LDHs

The first type of MgAlTi-LDH was fabricated with a coprecipitation method reported by Lu et al.¹⁹ In a typical preparation process (**Fig. 1**), solution A containing 1.6 M NaOH and 0.16 M Na₂CO₃ and solution B containing 0.6 M Mg(NO₃)₂•6H₂O, 0.2 M Al(NO₃)₃•9H₂O, and 0.3 M TiCl₄ were prepared in two separated beakers. Then solution A was added dropwise into solution B with rigorous stirring until pH 10. The resultant white mixture was aged in a silicon oil bath of 60°C for 18 h. The precipitates were then collected by vacuum filtration and dried overnight at 80°C. The powders were finally grinded and sieved. The atomic ratio of Mg: Al: Ti was 6:2:3. The as synthesized Ti-containing MgAl-LDHs from coprecipitation was denoted as **MgAlTi(CP)** or simply **CP**.

2.1.2 Hydrothermal treatment of MgAlTi-LDHs

The MgAlTi(CP) powders were re-dispersed in water (1wt%) and stirred for 30 min (**Fig. 1**). Then the mixture was transferred into a hydrothermal vessel and heated at varies temperature (100, 150, or 200°C) for 24 h. After the hydrothermal reaction, powders were obtained by filtration, vacuum drying and grinding. The samples were denoted as **MgAlTi(HT100)**, **MgAlTi(HT150)**, and **MgAlTi(HT200)** or simply **HT100**, **HT150** and **HT200**, where the number designates the hydrothermal temperature.

2.1.3 Calcination and reconstruction of MgAlTi-LDHs

The MgAlTi(CP) powders were first calcined in a muffle furnace at 400, 500, or 600°C for 2 h and then dispersed in water and rigorously stirred at room temperature for 24 h for reconstruction (**Fig. 1**). Powders were collected after filtering and drying at 80°C. The samples were denoted as **MgAlTi(R400)**, **MgAlTi(R500)**, and **MgAlTi(R600)** or simply **R400**, **R500** and **R600**, where the number designates the calcination temperature.

2.2 Material Characterization

Crystal structures of samples were characterized with X-ray diffraction (XRD, Scintag XDS 2000) using Cu K α irradiation ($\lambda=0.1540562$ nm) at 45 kV and a diffracted beam monochromator at 40 mA in the 2 θ range of 5°-70° at a scan rate of 2°/min. UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained by an UV–visible spectrometer (Ocean Optics) using BaSO₄ as the background. Scanning electron microscopy (SEM) (Hitachi S4800) was used to visualize the catalyst morphology. Porous textual characterization was performed with nitrogen adsorption–desorption at 77 K using the Brunauer–Emmett–Teller (BET) method for surface area estimation and Barrette-Joynere-Halenda (BJH) method for cumulative pore volume analysis (Micrometrics, ASAP 2020). CO₂ adsorption capacity of different samples were investigated by CO₂ adsorption isotherms taken with the thermogravimetric analyzer (TGA-DAT-2960 SDT). For each test, 15-20 mg of sample was loaded in an Al₂O₃ container and heated to 150°C at a ramp of 10°C/min under an argon flow (100 ml/min). After the weight was stabilized, the argon flow was replaced with a moisturized CO₂ flow (120 ml/min). The weight versus time was recorded and analyzed for a period of 60 minutes.

Thermal stability analysis of the MgAlTi(CP) material was also carried out on the same thermogravimetric analyzer (TGA) at a heating ramp of 10°C/min from room temperature to 800°C in air flow. Temperature programed desorption (TPD) of CO₂ (10°C/min) was recorded with a mass spectrometer (MS). To characterize the surface chemistry of the MgAlTi(CP) under thermal treatment, Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 spectrometer (Thermo Electron) equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector. The sample was loaded in a

reaction chamber (Harrick Scientific, HVCDRP) equipped with a heater and a programmed temperature controller, as well as cooling water circulation.

2.3 Photocatalytic Activity Test of MgAlTi-LDHs for CO₂ photoreduction

CO₂ photoreduction tests were performed in a system as shown in **Fig. 2**. For each test, 50 mg of samples were dispersed on a clean glass fiber filter paper and loaded on the inner wall of a quartz tube reactor. CO₂ (99.999%, Praxair) controlled by mass flow controller (MFC) was continuously passed through a water bubbler to allow a mixture of CO₂ and 2.3 vol% H₂O vapor to flow through the photoreactor. A 400 W UV lamp (Oriel) was used as the light source, and the light intensity is about 420 mW cm⁻² in the range of 200-1000 nm. Our previous studies found that slightly increasing the reaction temperature could aid desorption of the surface intermediates and thus promote the photocatalytic reduction of CO₂ with water vapor.^{13,14} Therefore, in this work two 250 W infrared lamps were applied to heat up the photoreactor to a temperature of 150°C, the optimal temperature found in our previous work.¹³ The photoreactor was operated in a continuous-flow mode, and the gaseous products in the reactor effluent were continuously analyzed by a gas chromatograph (GC, Agilent 7890A) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Fig. 2. Schematic diagram showing the experiment setup for measuring the activity of photocatalytic CO₂ reduction with water vapor

3. Results and Discussion

3.1 Crystal Structures

Crystal structures of MgAlTi-LDH samples were examined by XRD as shown in **Fig. 3**. The XRD pattern of MgAlTi(CP) sample shows peaks at 2θ around 12° (003), 23° (006), 35° (009)/(102), 61° (110) and 64° (113) that match the typical rhombohedral structure of MgAl-LDHs reported in literature.^{21,27} The basal spacing corresponding to (003) plane is calculated to be 0.759 nm using Bragg's equation.²⁸ Assuming 3-layer rhombohedral (3R) stacking sequence²⁹ of MgAlTi-LDHs, the unit cell parameter c was calculated to be 2.276 nm, three times that of the layer-to-layer distance. By applying Bragg's equation to (110) plane, the unit cell parameter a was obtained to be 0.305 nm, which is the averaged metal-to-metal distance within the layers. These calculated parameters were comparable to those reported in the literature.^{30,31} By applying the Scherrer equation on the (003) peak, the crystallite size, i.e. disk diameter³² in the stacking direction of the MgAlTi(CP) sample was determined to be 8.3 nm. **Fig. 3** also shows the crystal structure changes of MgAlTi(CP) treated with hydrothermal or calcination/reconstruction. The (101) diffraction peaks for anatase type TiO_2 (JCPDS no. 21-1272) appeared for HT150, HT200 and R600 samples at $2\theta=25.3^\circ$, 25.2° and 25.7° , respectively. Hydrothermal at lower than 150°C or calcination lower than 600°C did not result in anatase TiO_2 formation. Yanagisawa et al.²⁵ attributed the reason that crystallization temperature required in hydrothermal condition was lower than that in calcination in air to the acceleration of nucleation by water. At a higher hydrothermal temperature, the nucleation by structural rearrangement of the TiO_6 octahedral units in the amorphous TiO_2 might proceed quickly and heterogeneously followed by immediate growing, leading to larger anatase crystals.³³ That explains why the anatase crystallite size for HT(200), 12.3 nm, is larger than that of HT(150) 8.4 nm. Reconstructed LDHs generally preserved the original LDH structure, as seen in the R400, R500 and R600 samples; however, reflection peaks of impurities like Al_2O_3 and spinel MgAl_2O_4 ³⁴⁻³⁶ were identified on the R600 sample, indicating permanent structure change due to high temperature calcination.

Crystal structural parameters of MgAlTi-LDHs samples calculated from XRD results were summarized in **Table 1**. The lattice parameters of LDHs structures remained similar after hydrothermal and reconstruction treatments, basal spacing $d(003) = 0.751\sim 0.767$ nm and unit cell parameter $a = 0.303\sim 0.306$ nm, consistent with the literature.¹⁹ But the crystallinity changed significantly (disk diameter = 4.8~19.9 nm). Hydrothermal treatment at 100, 150, and 200°C increased the crystallite size of LDHs from 8.3 nm to 11.9, 14.4 and 19.9 nm, respectively. Whereas, reconstructed samples at 400, 500, and 600°C calcination have a decreased crystallite size to 4.8, 5.5 and 6.0 nm. It is highly possible that during hydrothermal treatment, LDHs crystallites prong to grow larger via ostwald ripening.³⁷ This phenomenon

was also reported by Xu et.al.³⁸ that LDHs particles disaggregated at a lower temperature and followed by the growth of LDHs individual crystallite via 3-D process (dissolution, diffusion, and deposition). At a higher temperature, the development of LDHs accelerated could be due to the faster diffusion of ions, e.g. Mg^{II} , Al^{III} cations. Reconstructed samples were prepared by calcination and reconstruction method, using the memory effect of LDHs materials. Amorphous phase is often produced during the calcination-reconstruction process simultaneously,³⁹ which led to a smaller crystallite size compared with the unmodified LDH materials. Increasing calcination temperature of LDHs samples may boost the agglomeration of crystals, which could give rise to the growing of crystals in the reconstructed LDHs as well.

Fig. 3. XRD patterns of MgAlTi(CP), MgAlTi(HT100), MgAlTi(HT150), MgAlTi(HT200), MgAlTi(R400), MgAlTi(R500), and MgAlTi(R600) samples. (* refers to Al_2O_3 phase; S refers to spinel $MgAl_2O_4$; A refers to anatase TiO_2)

Table 1. Crystal structural parameters of samples

Sample	CP	HT100	HT150	HT200	R400	R500	R600
d(003) (nm)	0.759	0.751	0.753	0.767	0.751	0.758	0.759
(003) disk diameter (nm)	8.3	11.9	14.4	19.9	4.8	5.5	6
a (nm)	0.305	0.304	0.304	0.305	0.303	0.304	0.306
Anatase crystallite size (nm)	/	/	8.4	12.3	/	/	30.1

3.2 Morphologies of MgAlTi-LDHs

Morphologies of the samples obtained by SEM are shown in **Figs. 4-5**. The pristine CP sample (**Fig. 4**) was composed of densely aggregated small nanoflakes (~50 nm). Porous flower-like morphologies were observed for all the hydrothermal and reconstruction treated samples (**Fig. 5**). Increasing the hydrothermal temperature resulted in larger flakes with diameters of ~100, ~500 and ~1000 nm for HT100, HT150, HT200, respectively, which matches the increased crystallite size observed in the XRD results (Table 1). Whereas, the reconstructed samples (R400, R500, and R600) consisted of relatively small flakes (~100 nm) and no obvious change of flake size was observed with increased calcination temperature.

Fig. 4. SEM images of MgAlTi(CP)

Fig. 5. SEM images of MgAlTi-LDHs after hydrothermal treatment (HT100, HT150, and HT200) and calcination + reconstruction treatment (R400, R500, and R600)

3.3 Thermal stability of MgAlTi(CP)

To better understand the crystal structural change of the MgAlTi(CP) as a function of calcination temperature, the MgAlTi(CP) sample was calcined at 200, 400, 500, and 600 °C, respectively (without the reconstruction step), and the XRD patterns are shown in **Fig. 6A**. At a lower temperature (200 °C), broadened LDH characteristic peaks were observed, suggesting that LDH layered structure started to collapse upon thermal treatment.⁴⁰ When the calcination temperature was raised to 400-500 °C, the layered structure was completely lost, leaving mixed metal oxide (MMO) of MgO and Al₂O₃. When the calcination temperature further increased to 600 °C, crystal TiO₂ (anatase type, JCPDS no. 21-1272) and spinel phase MgAl₂O₄ appeared.

Fig. 6. XRD patterns of MgAlTi(CP) after calcined at 200~600°C for 2 h (A); TGA curve of MgAlTi(CP) (B), TPD profile of MgAlTi(CP) for CO₂ desorption (C); FTIR spectra of MgAlTi (CP) heated at different temperatures in air (D).

The XRD pattern change of the MgAlTi(CP) sample upon thermal treatment was consistent with TGA result, as shown in **Fig. 6B**. Three stages with a total weight loss of 34.4% were identified: 20-216 °C, 216-410 °C, and 410-800 °C. In the first stage, water molecules from the material surface and interlayer gallery were lost, but the layered structure was still preserved. In the second stage, dehydroxylation of the brucite-like sheet layers and decarbonation occurred,³² leading to gradual deformation of the layered structure. In the third stage, carbonates in the interlayer space were further eliminated.³⁰ Desorption of CO₂ as a result of decarbonation during the heating process (20 to 600 °C with a ramp of 10 °C/min) was recorded as the TPD profile shown in **Fig. 6C**. The peak centered at 420 °C coincided well with the transition from the second to the third stage weight loss shown in the TGA curve.

FTIR spectra of the sample heated to 50-500 °C (the sample was continuously purged with an air flow) were recorded in **Fig. 6D**. At 50 °C, the high frequency bands at 3550 and 3100 cm⁻¹ were ascribed to vibrations of H₂O and OH⁻ groups.³⁰ The band around 1643 cm⁻¹ was attributed to bending mode of interlayer water and the one around 1413 cm⁻¹ belonged to asymmetric stretching of the interlayer carbonate or bicarbonate.^{30,41} As the temperature increased, the 1643 and 1413 cm⁻¹ bands gradually decreased and finally disappeared at 300 °C, but new bands at 1566 and 1327 cm⁻¹ for bidentate carbonate (b-CO₃²⁻)⁴¹ appeared from 150°C and reached the maxima at 300°C. When the temperature was further raised to 500 °C, bands at 1731, 1450 and 1299 cm⁻¹ for bridged carbonate (d-CO₃²⁻)⁴¹ were observed. The FTIR results also agree with the TGA analysis on the structural transformation of the LDH material.

3.4 Textual Properties MgAlTi-LDHs

Nitrogen adsorption/desorption isotherms were taken at 77K to analyze textual properties of the samples. As shown in **Fig. 7A**, all of the samples display a type IV isotherm (IUPAC classification) and type H3 hysteresis loop,^{42,43} indicating mesoporous structures formed by aggregates of flakes or slit pores between edged flakes. The relative pressure (P/P₀) at the loop closing point for HT150 and HT200 (0.6-0.7) was higher than that for the rest of samples (~0.4), suggesting larger pore sizes for HT150 and HT200 samples. The BET surface area decreased from 169.9 m²/g for the CP sample to 117.0 and 78.3 m²/g at 150 and 200 °C hydrothermal treatment temperatures. However the HT100 sample had slightly increased BET surface area of 181.4 m²/g. A similar trend was also observed for the reconstructed samples, with the BET surface area decreased to 111.4, 102.1 and 73.8 m²/g as the calcination temperature raised from 400 to 500 and 600°C. The decreased specific surface area could be attributed to the increase in LDH crystallite size at higher calcination temperature.

Table 2. Textual parameters of samples.

Sample	CP	HT100	HT150	HT200	R400	R500	R600
S _{BET} (m ² /g)	169.9	181.4	117	78.3	111.4	102.1	73.8
Pore size (nm)	5.5	6.3	10.8	14.3	4.2	4.4	5.7
Pore volume (cm ³ /g)	0.25	0.3	0.38	0.33	0.14	0.16	0.2

Fig. 7. N₂ adsorption-desorption isotherms (A) and Pore size distribution (B)

Pore size distribution of the samples **Fig. 7B** were plotted using BJH desorption data. Average pore size and pore volume were summarized in **Table 2**. For the pristine CP sample, two peaks at 3.8 and 6.3 nm were observed, which was consistent with the values in the literature.⁴² Hydrothermal treatment at 100°C did not change the pore size distribution significantly, although the second peak was slightly broadened. When the hydrothermal temperature was raised to 150 and 200°C, the first peaks shrank significantly and the second peaks grew and shifted to 8.4 and 10.8 nm respectively. The average pore size for HT150 and HT200 was 10.8 and 14.3 nm, larger than that of 6.3 and 5.5 nm for the HT100 and CP samples. This increase in pore size could be the result of increased LDHs flake size due to hydrothermal treatment. Reconstructed samples had similar pore size distribution with the pristine CP sample. R400 and R500 had only the sharp peaks at 3.7 and 3.5 nm while the R600 sample had two peaks at 3.4 and 5 nm. Average pore sizes were 4.2, 4.4 and 5.7 nm for R400, R500 and R600 respectively. The increasing trend with temperature in pore size agreed well with the flake size changes observed in SEM analyses.

3.5 Optical property of MgAlTi-LDHs

Band gaps of the samples measured from UV-Vis absorption spectra are listed in **Table 3**. The CP sample had a band gap of 3.40 eV, in consistent with the reported value for amorphous TiO₂.⁴ Hydrothermal treatment at 100 °C (HT100) did not change the band gap. But when the hydrothermal temperatures were raised to 150°C and 200°C, the band gaps were slightly narrowed down to 3.32 and 3.31 eV, which could be attributed to the presence of anatase TiO₂ in the two samples. Band gaps of reconstructed samples were determined to be 3.42, 3.35 and 3.30 eV at calcination temperatures of 400, 500 and 600°C. The results indicate that all the treatments did not significantly change the band gap of the MgAlTi-LDH materials.

3.6 CO₂ Adsorption Capacity of MgAlTi-LDHs

CO₂ adsorption capacities were measured from CO₂ isotherms obtained by the TGA instrument and shown in **Table 3**. The CP sample had a CO₂ adsorption capacity of 2.07 wt% or 0.47 mmol/g, the highest among all samples tested. The decrease in CO₂ adsorption capacity for the HT150, HT200, R400, and R600 was probably caused by the decreased surface area after hydrothermal and reconstruction treatment. All MgAlTi-LDHs have a much higher CO₂ adsorption capacity than commercial TiO₂-P25 nanoparticles, which is a mixture of anatase and rutile crystal phases^{44,45}.

Table 3. Optical and CO₂ adsorption parameters of MgAl-Ti-LDHs

Sample	CP	HT100	HT150	HT200	R400	R500	R600	P25
Band gap (eV)	3.40	3.40	3.32	3.31	3.42	3.35	3.30	3.20
CO₂ adsorption capacity (wt%)	2.07	N/M*	0.66	0.62	0.85	N/M*	0.59	0.11
CO₂ adsorption capacity (mmol/g)	0.470	N/M*	0.150	0.141	0.193	N/M*	0.134	0.025
CO₂ adsorption capacity per unit surface area (μmol/m²)	2.77	N/M*	1.28	1.80	1.73	N/M*	1.82	0.5

*N/M: not measured

3.7 CO₂ Photocatalytic Reduction Activity of MgAlTi-LDHs

The photocatalytic activity of MgAlTi-LDHs were tested for CO₂ photoreduction by UV light irradiation for 5 h with continuous moisturized CO₂ feeding. Baseline experiments were first carried out in the dark with the photocatalyst or in the absence of photocatalyst under light irradiation, and CO₂ reduction products were observed. Under light irradiation in the presence of photocatalyst, CO was identified as the

major product with only trace amount of CH₄ detected, which was consistent with our previous reports on TiO₂ based photocatalysts for CO₂ reduction^{3,46}.

The amounts of CO production evolved within 5 h with moisturized CO₂ feeding were compared for all the MgAlTi-LDHs samples and commercial TiO₂-P25 nanopowders. The experiments were repeated two to three times for each material and the results (average and deviation) of CO production per unit gram of active photocatalyst material (TiO₂) are shown in **Fig. 8**. P25 had the lowest CO production at around 10 $\mu\text{mol/g}$. The CP sample, with amorphous TiO₂, produced 33 $\mu\text{mol/g}$ CO, more than two times of that by P25. This result indicates that amorphous TiO₂ in MgAlTi-LDH is photocatalytically active. The much higher activity of CP than that of P25 is likely due to the much large surface area (BET specific area of CP and P25 are 169.9 and 50 m²/g, respectively) and thus better dispersion of Ti species, as well as the facilitated CO₂ adsorption capacity due to the MgAl-LDH. All the hydrothermal treated (HT) samples showed enhanced photoactivity compared to the CP sample. HT150 showed the highest CO production at around 50 $\mu\text{mol/g}$, 50% higher than that of the CP sample and four times higher than that of P25. Either lower (100 °C) or higher (200 °C) hydrothermal temperature did not improve photocatalytic activity significantly compared with the CP sample. For the reconstructed samples, however, only R400 showed slightly increased CO production, while the R500 and R600 showed rather decreased CO production compared with the CP sample. Nevertheless, they all had photocatalytic activities higher than P25.

Fig. 8. Amount of CO (normalized by catalyst mass) evolved by CO₂ photoreduction with water vapor during 5 h UV irradiation.

Fig. 9. Amount of CO (normalized by catalyst surface area) evolved by CO₂ photoreduction with water vapor during 5 h UV irradiation

The results of CO production by the various catalysts were also normalized by surface area and compared in **Fig. 9**, which further demonstrated the better performance of hydrothermally treated sample over those prepared by calcination-reconstruction method. The CO₂ adsorption capability normalized by surface area was also added in Table 3. HT200 had the highest CO production per unit surface area and was twice as high as those of CP and P25 samples. Even though HT200 and R600 had similar CO₂ adsorption capacity per unit surface area, the photoactivity of HT200 was greater than that of R600. Since HT200 and R600 had similar band gap energies, a possible reason is that HT200 had a smaller anatase crystallite size (12.3 nm) than R600 (30.1 nm), which resulted in more number of surface active sites. However, HT150 had the smallest anatase crystallite size (8.4 nm), but the surface area normalized photoactivity of HT150 was slightly less than that of HT 200. This maybe because the CO₂ adsorption capacity of HT150 per unit surface area was lower and its band gap was slightly larger than HT200. The above results suggest there exists an optimal anatase crystallite size for CO₂ photoreduction, due to the balance between band gap and surface active sites of TiO₂ particles.^{47,48}

By correlating Fig. 8 and Fig. 9 with the materials properties, it can be concluded that the materials properties that may affect the CO₂ photoreduction activities include TiO₂ crystallinity and crystallite size, band gap, surface area, and CO₂ adsorption ability. Among all the samples tested, the two samples HT150 and HT200 showed the highest overall CO production. HT150 was the most active catalyst when normalized by mass and HT200 was the most active one when normalized by surface area. It is likely the combination of the following properties made them superior catalysts to others: (1) their band gaps were among the smallest (3.31-3.32 eV), (2) HT150 had a relatively high surface area (117.0 m²/g), (3) both had crystallized anatase TiO₂ with small crystallite size (8.4 and 12.3 nm for HT150 and HT200, respectively), and (4) the LDH composition and structure enhanced their CO₂ adsorption capacities. Although R600 also had anatase TiO₂ nanocrystals and relatively small band gap, its relatively large crystallite size (30.1 nm) and low surface area (74 m²/g) prevented improvement in the overall photocatalytic activity. However, the general higher activity of all MgAlTi-LDH materials than P25 suggests the advantages of this type of new photocatalyst materials because of their better TiO₂ dispersion and higher CO₂ adsorption capacity.

4. Conclusions

In this study, a new series of photocatalysts, MgAlTi-LDHs, with different materials structures have been fabricated and demonstrated for CO₂ photoreduction with water vapor to produce CO. The MgAlTi(CP) sample prepared by a coprecipitation method had amorphous TiO₂ species but was fairly active and had much higher photoactivity than the commercial TiO₂-P25. Hydrothermal treatment at 150-200°C converted the amorphous Ti species in the LDHs to anatase nanocrystals while maintaining the characteristic LDH structures. The optimum hydrothermal temperature was identified to be in the range of 150 to 200 °C (corresponding to photocatalysts HT150 and HT200). HT150 was four times more active than P25 and 50% more active than the CP sample, when normalized by catalyst mass. HT150 was four times more active than P25 and 50% more active than the CP sample, when normalized by catalyst mass. The activity of HT200 was twice as high as those of CP and P25, when normalized by catalyst surface area. Alternatively, reconstructing the CP sample at a calcination temperature of 600°C resulted in crystal anatase TiO₂, but the larger anatase crystallite size and relatively low surface area of R600 made its catalytic activity inferior to the HT150 and HT200 samples. In general, distributed crystalline TiO₂ in LDHs has better photocatalytic activity than amorphous TiO₂ for CO₂ photoreduction with H₂O. Band gap, specific surface area, and TiO₂ crystallinity and crystallite size are all important factors affecting the photocatalytic activity, and the enhanced CO₂ adsorption capacity introduced by the MgAl-LDH is particularly beneficial to CO₂ photoreduction. The discovery of this new type of MgAlTi-LDH (HT) material is important in the development of efficient CO₂ reduction photocatalysts.

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6. Reference

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