Carbon Dioxide Photoreduction with Water Vapor By Titanium-containing Magnesium-Aluminum Layered Double Hydroxides

Jinye Xu
University of Wisconsin-Milwaukee

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CARBON DIOXIDE PHOTOREDUCTION WITH WATER VAPOR BY TITANIUM-CONTAINING MAGNESIUM-ALUMINUM LAYERED DOUBLE HYDROXIDES

by

Jinye Xu

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Engineering at The University of Wisconsin-Milwaukee

December 2014
ABSTRACT

CARBON DIOXIDE PHOTOREDUCTION WITH WATER VAPOR BY TITANIUM-CONTAINING MAGNESIUM-ALUMINUM LAYERED DOUBLE HYDROXIDES

by

Jinye Xu

The University of Wisconsin-Milwaukee, 2014
Under the Supervision of Professor Ying Li

Photocatalytic conversion of CO₂ into value-added solar fuels is a promising approach to simultaneously address the greenhouse gas pollution and energy shortage issues. TiO₂, the most widely studied photocatalyst, suffers from drawbacks like fast electron-hole recombination and limited CO₂ adsorption. In this study, Ti-containing MgAl layered double hydroxides (MgAl/Ti-LDHs) were designed to provide high activity of CO₂ photoreduction by dispersing Ti species over MgAl-LDHs which have been extensively investigated as CO₂ adsorbent. This study was the first attempt to apply MgAl/Ti-LDHs for photoreduction of CO₂ with water vapor.

MgAl/Ti-LDHs were prepared through coprecipitation (CP) method, the most common technique for LDH synthesis. However, as-prepared MgAl/Ti(CP) sample only contained amorphous Ti species, which was usually considered to be less active than crystalline TiO₂ for photoreactions. To crystallize the Ti species, the MgAl/Ti(CP) sample was treated with two different approaches: a). hydrothermal treatment of water dispersions of MgAl/Ti(CP) at 100, 150, or 200 °C. b). calcination of MgAl/Ti(CP) at 400, 500, or 600 °C and then rehydration in water, which was called the reconstruction method.
Hydrothermal treatment at 150-200 °C and reconstruction from 600 °C calcination temperature resulted in formation of anatase TiO$_2$ in MgAl/Ti samples.

The MgAl/Ti(CP) sample with amorphous TiO$_2$ resulted in more than three times of CO yield than the commercial P25-TiO$_2$, possibly due to high dispersion of Ti species and the excellent ability to adsorb CO$_2$. The hydrothermal treatment at 150°C lead to the highest CO production as a result of competing effects of TiO$_2$ crystallinity and surface area of the material. However, the sample reconstructed from 600°C calcination did not show improvement in the CO production, although it showed the highest crystallinity of anatase TiO$_2$. The reasons might be greatly decreased surface area of the overall material and anatase particles. The phase transformation of amorphous Ti in LDHs to anatase crystals using hydrothermal treatment technique was for the first time reported and was demonstrated to be effective in improving photocatalysis of Ti-containing LDHs.
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<table>
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<tr>
<th>Abbreviation (Abbrev.)</th>
<th>Full Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>LDH</td>
<td>Layered double hydroxide</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed metal oxide</td>
</tr>
<tr>
<td>CP</td>
<td>Coprecipitation</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrette-Joynere-Halenda</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
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<td>GC</td>
<td>Gas chromatograph</td>
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<td>TCD</td>
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<tr>
<td>MS</td>
<td>Mass spectra</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
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</table>
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Chapter 1  Introduction

1.1 Background

As the primary greenhouse gas (Figure 1 [1]), CO\textsubscript{2} is the major cause of global warming. The largest source of CO\textsubscript{2} emissions comes from the combustion of fossil fuels for electricity, industry, transportation and other human activities. Fossil fuels including coal, natural gas, and oil are considered as non-renewable energy because they take thousands of years to form. Considering the tremendous increase in the global demand for energy in recent years because of industrial development and population growth, it is critical to shift our energy dependence into renewable sources such as solar energy. Comparing with simply capture and storage of CO\textsubscript{2}, conversion of CO\textsubscript{2} into value added products or renewable fuels using solar light is a more exciting and promising strategy to simultaneously tackle the environmental and energy problems.

Figure 1. Global Greenhouse Gas Emissions by Gas, data from IPCC (2007).
Solar conversion of CO$_2$ is investigated in several different approaches: a). photovoltaic cells are firstly used to convert solar energy into electrical energy which later is used to electrochemically convert CO$_2$; b). solar energy utilization and electrochemical conversion of CO$_2$ occur in the same unit called photoelectrochemical cells; c). H$_2$ is firstly produced from photocatalytic water splitting and then is used to catalytically hydrogenate CO$_2$; d). direct photocatalytic reduction (also known as photoreduction) of CO$_2$ on molecular or semiconductor photocatalysts [2]. This study focuses on the photoreduction of CO$_2$ over semiconductor photocatalysts.

1.2 Basics of photocatalysis

Photoreduction of CO$_2$ is a photocatalysis process which is defined as acceleration of a photo-initiated chemical reaction in the presence of a catalyst. The discovery of photocatalysis dates back to 1921 when Renz observed the partial reduction of TiO$_2$ in the presence of organic compound under sun light illumination [3]. Since the pioneering work of Fujishimna and Honda [4] on photocatalytic water splitting in 1972, photocatalysis has gained growing attention.

In a general semiconductor based photocatalysis process, the semiconductor adsorbs incident light with higher energy than its band gap (Eg) and is excited to generate electron-hole pairs which are free charge carriers. The following possible pathways [5] of these carriers then occur (illustrated in Figure 2 [5]): 1). Reduction of surface adsorbed molecules by electrons; 2). Oxidation of surface adsorbed molecules by holes; 3). Surface recombination of electron-holes. 4). Volume recombination of electron-holes. The first two pathways are how photochemical reactions occur, such as solar water splitting [6], photocatalytic degradation of organic pollutants [7] and photoreduction of CO$_2$ [8].
1.3 Fundamentals of CO$_2$ photoreduction

Although CO$_2$ photoreduction is promising for the environmental and energy issues, it is challenging to achieve since CO$_2$ is a relatively inert and stable compound. The first report of CO$_2$ photoreduction went back to 1979 when Inoue et al. [9] discovered formation of organic compounds including formaldehyde (HCHO), formic acid (HCOOH), methyl alcohol (CH$_3$OH), and trace amounts of methane (CH$_4$) in aqueous solution under UV light illumination using a variety of semiconductors like tungsten trioxide (WO$_3$), titanium dioxide (TiO$_2$), zinc oxide (ZnO), cadmium sulfide (CdS), gallium phosphide (GaP), and silicon carbide (SiC).

Semiconductor-based CO$_2$ photoreduction generally involves light absorption, photogenerated charge separation and transportation, and catalytic reaction on active sites.
Following the photoexcitation of the semiconductor photocatalyst, photoreduction and photooxidation occur in the conduction band (CB) and valence band (VB) respectively. Ideally, the CB potential should be more negative than the CO\textsubscript{2} reduction potential and the VB potential should be more positive than the water oxidation potential. Figure 3 [2] shows the conduction and valence band potentials and band gap energies of various semiconductors and redox potentials of CO\textsubscript{2} reduction reactions with different products. Some researchers proposed single electron transfer to CO\textsubscript{2} to form negatively charged CO\textsubscript{2}⁻ anion which had an electrochemical potential of -1.90 V, much more negative than the CB potentials of most of the semiconductors. Therefore more researchers agreed on multi-electron transfer of the CO\textsubscript{2} photoreduction reaction pathways with lower electrochemical potential values such as HCOOH/CO\textsubscript{2}, HCHO/CO\textsubscript{2} and CH\textsubscript{3}OH/CO\textsubscript{2}, CH\textsubscript{4}/CO\textsubscript{2} shown in Figure 3.

![Figure 3. Conduction band, valence band potentials, and band gap energies of various semiconductor photocatalysts relative to the redox potentials at pH 7 of compounds involved in CO\textsubscript{2} reduction.](image)

Since water is cheap and available everywhere, CO\textsubscript{2} photoreduction with water has gained lots of attention comparing with other reductants like H\textsubscript{2} which itself requires technology advances to be readily available for wide use. CO\textsubscript{2} photoreduction with water
can be either in aqueous solution or using water vapor in a gas-solid interface. Most of the work on CO$_2$ photoreduction has been done by dispersing the photocatalyst in the CO$_2$-saturated aqueous solution and the solid-liquid interface reaction produces both liquid-(formic acid, formaldehyde, and methanol) and gas-phase (methane) products. Comparing with CO$_2$ photoreduction in aqueous solution, the use of water vapor instead of liquid water makes it much easier for product separation from the reactants and photocatalysts [10], avoids the low solubility problem of CO$_2$ in water, and provides the possibility to tune the ratio of H$_2$O to CO$_2$ as well as the reaction temperature [11].

1.4 TiO$_2$-based photoreduction of CO$_2$

1.4.1 Properties of TiO$_2$

Among various photocatalysts, TiO$_2$ has been most extensively studied in photocatalytic CO$_2$ conversion [12] as well as other applications such as photocatalytic water-splitting for hydrogen production [13]. This is because of the superior advantages of TiO$_2$ such as low cost, chemical stability, low toxicity, and good photocorrosion resistance.

TiO$_2$ exists in amorphous phase or three main crystal phases: rutile, anatase and brookite. The first two crystalline forms are commonly used for photocatalysis. Both the rutile and anatase are tetragonal in structure and can be characterized as chains of TiO$_6$ octahedral with each Ti$^{4+}$ ion surrounded by six O$^{2-}$ ions, as shown in Figure 4 [14]. Two edges are shared in rutile while four edges are shared in anatase [14]. The differences in crystal structures result in different band gaps of 3.2 eV for anatase and 3.0 eV for rutile[2].
1.4.2 Challenges and approaches

The photoreduction of CO$_2$ over TiO$_2$ involves three general processes: charge separation and transfer from TiO$_2$ to CO$_2$ and H$_2$O; the adsorption, activation of CO$_2$ and dissociation of C–O bond; formation of surface intermediates and conversion of intermediates to products; desorption of products from catalyst surface [15]. The following sections discuss influential factors for CO$_2$ photoreduction over TiO$_2$-based photocatalysts.

1.4.2.1 Effect of crystal structures of TiO$_2$

Crystal structures of TiO$_2$ influence the charge separation and transfer process and therefore affect the efficiency of CO$_2$ photoreduction over TiO$_2$. Among the three main TiO$_2$ crystal phases, anatase has been shown to give higher photocatalytic activity than rutile [16, 17]. Liu et al. [8] discovered that the efficiency of CO$_2$ photoreduction over defective-free (unpretreated) TiO$_2$ followed the order anatase > brookite > rutile, while over oxygen-deficient (pretreated with He) TiO$_2$ the order was brookite > anatase > rutile (Figure 5 [8]).
Figure 5. Production of CO and CH\textsubscript{4} on the three unpretreated and He pretreated TiO\textsubscript{2} polymorphs for a period of 6 h photoillumination.

The anatase-rutile mixed-phase TiO\textsubscript{2} is reported to be more active than the corresponding pure phases for photocatalytic oxidation [18] and reduction reactions [19]. By using a hydrothermal method, Li et al. [19] synthesized anatase-rutile mixed-phase nanocomposite and found higher activity than the commercial Degussa P25-TiO\textsubscript{2} (75% anatase and 25% rutile) in CO\textsubscript{2} photoreduction. The authors attributed the reasons to be effective charge separation between anatase and rutile at the interface based on results from EPR and other experimental characterization techniques. In a recent study by Zhao et al. [20], the anatase-brookite mixed-phase TiO\textsubscript{2} nanomaterials were prepared using hydrothermal method with different ratios of the two phases by tuning urea concentrations. They found the mixed-phase TiO\textsubscript{2} gave rise in higher CO\textsubscript{2} photoreduction activities (major product was CO) than pure anatase or brookite phases. With the optimal ratio of 75% anatase and 25% brookite, the CO production was even higher than that for P25. Photoinduced charge transfer and electron–hole separation might be enhanced due to the presence of anatase-brookite interfaces (Figure 6 [20]).
1.4.2.2 Effect of dispersion of TiO₂

Dispersion of TiO₂ plays an important role in photocatalytic CO₂ reduction. Anpo et al. [21] prepared highly dispersed TiO₂ species on Y-zeolite by an ion-exchange method and demonstrated a high selectivity for gas phase methanol formation on this catalyst. They also found the tetrahedral coordination of TiO₂ by applying characterization techniques such as X-ray absorption near-edge structure analysis. Further study showed that charge transfer excited state of the anchored tetrahedral TiO₂ species favored the formation of methanol while the aggregated octahedral TiO₂ species favored the production of methane. Possible reasons might be higher lifetime of the excited Ti³⁺-O⁻ as revealed by in situ photoluminescence spectra.

By using a one-pot sol–gel method, Li et al. [22] was able to disperse TiO₂ nanocrystals on a mesoporous silica substrate with high surface area (>300m²/g) and the amount of CO (primary product) evolved from CO₂ photoreduction was greatly enhanced due to high dispersion of TiO₂.
1.4.2.3 Effect of CO₂ adsorption

Basic metal oxide has been reported to adsorb CO₂. Xie et al. [23] added MgO to Pt-loaded TiO₂ for CO₂ photoreduction and found a great improvement in the production of the major product CH₄. By loading Pt-TiO₂ photocatalysts with various basic metal oxides, the authors also discovered a linear correlation between the amount of chemisorbed CO₂ on the photocatalysts and the amount of CH₄ produced (Figure 7 [23]). Although CO was also formed, no correlation between CO and the chemisorbed CO₂ was developed, which might be due to much smaller amount of CO comparing with CH₄. Among the various metal oxides loaded, MgO which resulted in the highest amount of chemisorbed CO₂ produced the greatest amount of CH₄, suggesting the effective improvement of CO₂ photoreduction activity by enhancing CO₂ adsorption of the photocatalysts. Although the amount of chemisorbed CO₂ increased with the loading amount of MgO, there existed an optimal loading of MgO for the highest production of CH₄. The authors attributed the reason to decreased contact between Pt nanoparticles and chemisorbed CO₂ when the loading amount of MgO was too high.
Figure 7. Correlation between the amount of CH$_4$ formed and the amount of CO$_2$ chemisorbed on the Pt–
TiO$_2$ photocatalysts modified with various basic metal oxides.

Even without Pt loading, MgO can significantly improve CO$_2$ photoreduction activity over TiO$_2$ with CO as the main product. Liu et al. [11] fabricated MgO-patched TiO$_2$ microspheres and demonstrated much better activity and stability than bare TiO$_2$. In addition, the temperature at which the photoreduction reaction occurred was shown to influence the production rate of CO with 150°C as the optimal temperature in the tested range of 50-170°C. The combined results from thermogravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR) suggested that the presence of MgO enhanced the CO$_2$ adsorption while moderately higher temperature enhanced the desorption of intermediates.
In a follow-up study, Liu et al. [24] discovered that dispersion of MgO over the MgO/TiO$_2$ microspheres strongly affected the production of CO at the optimum temperature 150°C. The authors prepared two types of MgO-TiO$_2$ microspheres: Mg/Ti-SP and Mg/Ti-WI. Mg/Ti-SP was fabricated through one-step spray pyrolysis and had rougher surfaces due to strong aggregation of MgO nanoparticles. Mg/Ti-WI was prepared by spray pyrolysis synthesis of pure TiO$_2$ microspheres followed by wet-impregnation with MgO and had smoother surfaces. In situ diffuse reflectance infrared Fourier transform spectroscopy showed more abundant bicarbonates and easier desorption/transformation of intermediates on the Mg/Ti-SP catalyst than Mg/Ti-WI, which might be caused by easier transfer of photogenerated electrons to the surface of Mg/Ti-SP than to Mg/Ti-WI.

1.4.2.4 Other factors and approaches

CO$_2$ photoreduction over TiO$_2$-based catalysts can also be promoted by doping of nonmetal elements, incorporation of noble metals or carbon materials as external electron trappers or carriers, and sensitization by another semiconductor [15].

Zhang et al. [12] modified TiO$_2$ nanoparticles with both copper and iodine by a combined hydrothermal and wet-impregnation method. Iodine ions were doped in the TiO$_2$ lattice leading to formation of Ti$^{3+}$ while copper was deposited on the TiO$_2$ surface. The Cu-I-TiO$_2$ catalyst was active both under UV-vis and visible light irradiation. For the case of UV-vis irradiation, the co-modified Cu-I-TiO$_2$ catalyst showed higher activity than either Cu-TiO$_2$ or I-TiO$_2$.

Zhao et al. [25] doped TiO$_2$ nanoparticles with cerium using a sol-gel method. With optimal concentration of Ce, the doped TiO$_2$ improved the formation of CO by four times
comparing with pristine TiO₂. This improvement was likely caused by increased surface area of the catalyst and stabilization of anatase phase induced by Ce doping.

1.5 Layered double hydroxides for CO₂ photoreduction

1.5.1 Structural aspects of layered double hydroxides

Layered double hydroxides (LDHs) are a class of clay materials consisting of positive charged cation layers (generally expressed as [M²⁺₁₋ₓM³⁺ₓ(OH)₂]ₓ⁺, M²⁺ and M³⁺ stand for divalent and trivalent metal ions, x=0.17~0.33), negative charged interlayer anions like CO₃²⁻, SO₄²⁻, NO₃⁻, Cl⁻, or OH⁻ and interlayer water molecules [26]. The structure of an LDH can be considered as a derivation from the brucite (Mg(OH)₂) layer where a fraction of the divalent cations are substituted by trivalent cations leading to positive charge of the brucite-like layers (Figure 8 [27]). Naturally occurring LDH is hydrotalcite with the formula of Mg₆Al₂(OH)₁₆(CO₃)·₄(H₂O) [28]. Synthetic LDHs with various combinations of M²⁺ (Mg²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ca²⁺, Mn²⁺) and M³⁺ (Al³⁺, Fe³⁺, Co³⁺, Ni³⁺, Cr³⁺, Mn³⁺, Ga³⁺, In³⁺) have been reported [26]. Even Li⁺ [29] and Ti⁴⁺ [30] can be incorporated in LDHs.
1.5.2 Synthesis of layered double hydroxides

1.5.2.1 Coprecipitation

Coprecipitation is the most commonly applied method for one-pot direct synthesis of LDHs. It involves simultaneous precipitation of two or more cations at appropriate pH values [31]. See Table 1 [32] as guidance for selection of pH for coprecipitation of some common LDHs. An aging process is usually adopted after coprecipitation in order to improve the crystallinity of LDHs or enhance the yields.

Table 1 pH values of precipitation of some M(III) and M(II) hydroxides.

<table>
<thead>
<tr>
<th>Cation</th>
<th>pH at 10^{-2} M</th>
<th>pH at 10^{-4} M</th>
<th>pH at which hydroxide re-dissolves</th>
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<tr>
<td>Al^{3+}</td>
<td>3.9</td>
<td>8.0</td>
<td>9.0–12.0</td>
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<td>Cr^{3+}</td>
<td>5.0</td>
<td>9.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>5.0</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>6.5</td>
<td>8.0</td>
<td>14</td>
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<tr>
<td>Ni^{2+}</td>
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<tr>
<td>Co^{2+}</td>
<td>7.5</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>Mn^{2+}</td>
<td>8.5</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>
1.5.2.2 Anion exchange

Layered double hydroxides have a capability of exchanging their anions with ions in a solution (Figure 9 [31]. The ion-exchange or anion-exchange method can be used when direct coprecipitation method is not applicable. The extent of anion-exchange depends on electrostatic interactions between the positively-charged host sheets and the exchanging anions and is influenced by the following factors [31]: affinity for incoming anion, exchange medium, pH value and chemical composition of the layers. Generally the affinity for divalent anions decreases in the order of $\text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{SO}_4^{2-}$ [31] and that for monovalent anions decreases in the order of $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ [33].

Figure 9. Schematic diagram showing ion exchange of layered double hydroxides.

The carbonates in the interlayer space of layered double hydroxides can also be exchanged with those derived from atmospheric CO$_2$ under ambient conditions (Figure 10 [34]), as revealed in a recent study by Ishihara et al. [34]. In their study combining $^{13}$C labeling and FTIR spectra techniques, initially intercalated $^{13}$CO$_3^{2-}$ was found to be replaced by atmospheric CO$_3^{2-}$ at a rate depending on humidity. The most rapid rate was under dry air condition with very low humidity giving rise to a half-life exchange of ~24h. CO$_2$ and N$_2$ adsorption experiments showed that LDH had a CO$_2$ adsorption capacity of ~4cc/g (equivalent to 0.178mmol/g) and nanospace in H-bonding network functioned as initial CO$_2$ uptake points. Although the exact pathway from CO$_2$ to interlayer carbonates
was not explained, this work demonstrated dynamic exchange between the interlayer carbonates and the CO₂ in the atmosphere.

Figure 10. Dynamic exchange of carbonate anions of LDH with atmospheric CO₂.

1.5.2.3 Reconstruction

The LDH structure can be decomposed upon thermal treatment. As revealed in Figure 11 [35], the evolution of LDH structures go through three steps [35]: loss of physisorbed water at lower temperature (<100°C); loss of structural interlayer water (100-250°C); dehydroxylation and decomposition of carbonates in the interlayer space (250-600°C) leading to mixed metal oxide (MMO) composing of MgO and Al₂O₃.
Figure 11. TGA and MS profiles of LDH structures under thermal evolution.

Upon rehydration in ambient air or water, the mixed metal oxide (MMO) can be reconstructed into the original composition and structure of LDH, which is the so-called memory effect. Phases of LDH [35] under structural transformation have been identified and illustrated in Figure 12 [35]. This reconstruction process takes place in gas phase with water vapor [35, 36] and liquid phase with or without target anions [35-37]. A simple dissolution-reprecipitation mechanism for the reconstruction process was suggested by Rajamathi et al. [38], who fabricated the LDH structure by soaking the physical mixture of MgO and Al₂O₃ in a Na₂CO₃ solution.
1.5.3 Photocatalytic applications of layered double hydroxides

Because of advantages like highly tunable chemical composition, anion exchange and reconstruction properties, layered double hydroxides have attracted increasing attention in photocatalytic applications such as water oxidation and hydrogen generation.

By preparing LDHs with proper metal ions, LDHs with visible light absorption abilities have been designed for photocatalytic water oxidation. Photocatalytic properties of Zn/Ti, Zn/Cr, and Zn/Ce-LDHs have been explored by Silva et al. [39] for visible light water oxidation with AgNO$_3$ as the sacrificial electron acceptor agent. Due to intense visible light absorption peaks originated from Cr, the Zn/Cr-LDH proved to produce much higher O$_2$ evolution volume than the other two LDHs. The fresh Zn/Cr-LDH also presented better O$_2$ generation efficiency than the corresponding MMO calcined at 450°C. The layered structural features which collapsed upon thermal treatment at temperatures above 400°C were believed to favor O$_2$ generation because its water sorption property made it

---

**Figure 12.** Structural transformation of Layered double hydroxides.
easier for water to access to both external and internal material surfaces. In another study for photocatalytic water oxidation performed by Lee et al. [40], Ni/Ti and Cu/Ti-LDHs were observed to show two absorption bands under visible light irradiation. Both of the two LDHs presented higher O\textsubscript{2} generation rate than TiO\textsubscript{2} nanoparticles. Large surface area and visible range light absorption band were considered as crucial factors for the excellent photocatalytic properties of the LDHs in the water oxidation process.

Hydrogen generation by visible light water reduction was reported using MgAlFe-LDH as the photocatalyst [41]. Incorporation of Fe\textsuperscript{3+} gave rise in the visible light absorption ability and thus the efficient H\textsubscript{2} generation property of the original MgAl LDH by lowering the band gap, the value of which was quantitatively dependent on the dosage of Fe\textsuperscript{3+}.

1.5.4 CO\textsubscript{2} photoreduction over layered double hydroxides

Although photocatalytic properties of LDHs have been explored for many applications, very few reports are available in the literature for CO\textsubscript{2} photoreduction. In a pioneer study by Teramura et al. [42], LDHs consisting of Mg, Zn or Ni as divalent metals and Al, Ga, or In as trivalent metals were examined for photocatalytic reduction of CO\textsubscript{2} dissolved in liquid water (Figure 13 [42]). For all of these compositional combinations, CO was observed as the major reduction product from CO\textsubscript{2} and O\textsubscript{2} was the oxidation product from water.
Using H$_2$ as the reducing agent, Ahmed et al. [43] studied the conversion of gas phase CO$_2$ into methanol over LDH compounds formulated as [Zn$_{3-x}$Cu$_x$M$_{III}$OH]$_8$$^{2+}$ (CO$_3$)$_2$$^-$·mH$_2$O (x=0-1.5, M=Al$_{III}$ or Ga$_{III}$). The highest conversion of 0.16% occurred on [Zn$_3$Al(OH)$_8$]$^{2+}$ (CO$_3$)$_2$$^-$·mH$_2$O with the major product of CO (94 mol% selectivity). The most selectivity of 68 mol% for methanol was observed for [Zn$_{1.5}$Cu$_{1.5}$Ga (OH)$_8$]$^{2+}$ (CO$_3$)$_2$$^-$·mH$_2$O. The incorporation of Cu was responsible for the improvement in the selectivity of methanol over CO due to the binding of CO$_2$ at the Cu sites as hydrogen carbonate species. The authors further found that replacing interlayer carbonate anions with [Cu(OH)$_4$]$^{2-}$ improved the rate of methanol formation and the interlayer Cu species was 5.9 times more active than the octahedral Cu located in the positively-charged layers [44]. Although the selectivity of methanol is attractive, the use of H$_2$ as the reducing agent limits the application of this reaction because H$_2$ is not readily available.

To the author’s knowledge, only one report about photoreduction of CO$_2$ over layered double hydroxides using water vapor is available in the literature. In the study by
Katsumata et al. [45], ZnCr-LDHs loaded with various amount of noble metal co-catalysts Pt, Pd and Au were tested for CO$_2$ photoreduction under UV irradiation. CO was observed to be the primary product and its amount was highest for the LDH loaded with 0.1mass% of Pt (Figure 14 [45]). Although ZnCr-LDH was reported to be active for visible light water oxidation [39], no CO was detected for the CO$_2$ photoreduction test under visible light irradiation [45], suggesting that CO$_2$ photoreduction was more challenging than water oxidation. In addition, the use of expensive noble metals should be discouraged for the economic and environmental considerations.

![Figure 14. Yields of CO for photocatalytic conversion of CO$_2$ over Pt-LDH, Pd-LDH, and Au-LDH samples after 3h of UV irradiation.](image)

1.5.5 Design of Ti-containing layered double hydroxides for CO$_2$ photoreduction

In this study, Ti-containing layered double hydroxides are designed for CO$_2$ photoreduction because layered double hydroxides can provide high dispersion of Ti species and good CO$_2$ adsorption ability.

1.5.5.1 Dispersion of Ti species over layered double hydroxides

Zhao et al. [46] dispersed TiO$_6$ units over Ni/Ti-, Zn/Ti- and MgAl/Ti-LDHs with the coprecipitation method. The dispersed TiO$_6$ units were confirmed by high-angle annular dark-field scanning transmission electron microscopy mapping and XPS.
measurements. H₂ production from photocatalytic water splitting over the Ti-containing LDHs was greatly enhanced comparing with aggregated TiO₆ in the inorganic layered material K₂Ti₄O₉. The authors explained this enhancement with decreased electron hole recombination efficiency shown from transient-absorption and photoluminescence spectra results.

1.5.5.2 CO₂ capture with layered double hydroxides

CO₂ capture relies on the adsorption of CO₂ on sorbents. The adsorption process can be classified into physi- and chemisorption according to if the chemical bonds are formed. Layered double hydroxides have been extensively studied for CO₂ capture from flue gas [47, 48].

Both chemisorption and physisorption occurs in the CO₂ adsorption of LDHs. The CO₂ adsorption capacity of LDHs depends on many parameters in the synthesis process. Sharma et al. [49] studied the CO₂ adsorption over Mg-Al-CO₃ LDH. The capacity was found to be in the range of 8-22 cm³/g at 1 bar pressure and 30 °C with varied preparation parameters including cation molar ratio, mode of addition of magnesium and aluminum precursors, addition temperature, agitation, and drying. These parameters influenced the crystallinity, disk diameter, and surface area of the LDHs and therefore affected the CO₂ adsorption capacity. Higher crystallinity and bigger disk diameter lead to increased basic sites which favor chemisorption, while surface area determines physisorption.

Thermal treatment also affected the CO₂ adsorption capacity of LDHs. By comparing the amount of CO₂ uptake at 200 °C over LDHs calcined at 200, 350, 400, 450, and 600 °C, Ram Reddy et al. [47] observed an optimum calcination temperature of 400°C
due to the tradeoff between surface area and the number of available basic sites (Figure 15 [47]).

![Figure 15. Effect of calcination temperature on CO₂ capture capacity over LDH.](image)

The calcined derivative of MgAl-LDH possessed higher CO₂ adsorption capacity than its individual components MgO and Al₂O₃. Yang et al. [50] compared CO₂ adsorption over MgO, Al₂O₃ and 450°C calcined hydrotalcite (MgAl-LDH with a molar ratio of Mg/Al=2) and found 3 to 6 times more of CO₂ adsorption capacity on hydrotalcite than Al₂O₃ or MgO due to higher surface area as well as basicity (Figure 16 [50]).
1.5.5.3 Crystallization of amorphous TiO\textsubscript{2} by hydrothermal treatment

Coprecipitation (CP) is the most commonly applied method for synthesis of Ti-containing LDHs. However, the TiO\textsubscript{2} species exist as amorphous phase and usually have a larger band gap than nanocrystal anatase (3.3-3.5 eV for amorphous [51] vs. 3.2 eV for crystalline TiO\textsubscript{2} [52]). Pure amorphous TiO\textsubscript{2} was reported to be inactive during photocatalytic reactions due to its defective states [53].

In order to crystallize amorphous TiO\textsubscript{2} in Ti-containing LDH, a direct approach is to calcine the LDH and then reconstruct it in water. The temperature for crystallization of amorphous TiO\textsubscript{2} powders by calcination in air is as high as 450°C [54]. Lu et al. [55]
calcined CuMgAlTi-LDH in air at 400°C for 5 h and reconstructed the corresponding CuMgAlTi-MMO in water for 24 h at room temperature. Anatase type TiO₂ peaks were detected in the XRD pattern of the reconstructed TiO₂/CuMgAl-RLDH sample.

Another method for crystallization of amorphous TiO₂ is hydrothermal treatment. Yanagisawa et al. [56] developed the hydrothermal technique for low temperature crystallization of anatase from amorphous titania prepared by precipitation method. They found that anatase nucleation was accelerated in the presence of water which promoted the change of localized structure of the amorphous titania to anatase structure. The authors further investigated the catalyst role of water in this crystallization process [57]. As shown in Figure 17 [57], the first step is formation of bridges between two water molecules and surface OH groups of two different TiO₆ octahedra sharing only one common vertex. The second step is dehydration of the original two water molecules and two further water molecules, leaving the two octahedral sharing a face (anatase).

![Figure 17. Reaction scheme for hydrothermal crystallization of anatase.](image)

Mesoporous framework of amorphous TiO₂ was also reported to be crystallized using water as the catalyst. In the study by Assaker et al. [58], mesoporous titania were
placed in deionized water at room temperature or refluxed at 80, 100, or 120°C under stirring (Figure 18 [58]). The hexagonal pore ordering was preserved at lower temperatures (room temperature, 80°C, 100°C) or higher temperature for a short period (120°C, less than 1 h). For immersion at all the different temperatures, nanocrystalline anatase was observed and the crystallinity increased with temperature. Photocatalytic properties of the untreated and treated samples were tested by photodegradation of methyl orange (MeO). Before water treatment, the photoactivity was nearly negligible. Upon water treatment, the photoactivity was enhanced due to the presence of anatase nanocrystals.

![Figure 18. Water-catalyzed crystallization of amorphous mesoporous TiO₂ framework.](image)

1.5.6 Objectives of the current study

The first objective of the current study is to prepare Ti-containing MgAl-LDH using coprecipitation method and to test its photoactivity for CO₂ photoreduction with water vapor. Although amorphous TiO₂ is generally believed to be inactive for photocatalytic reactions, high dispersion of Ti species and CO₂ adsorption ability might make the Ti-containing MgAl-LDH active for CO₂ photoreduction.

The second objective is to crystallize the amorphous Ti species in the coprecipitated LDH by using reconstruction and hydrothermal treatment methods. The two treating
methods will be compared in terms of crystal structures, morphologies, textual and optical properties and CO\textsubscript{2} photoreduction activities of treated samples.
Chapter 2  Experiments

2.1 Catalyst preparation

2.1.1 Synthesis of Ti-containing MgAl-LDH

Ti-containing MgAl-LDH was fabricated with the co-precipitation method reported in reference [55]. A schematic diagram displaying the preparation process was shown in Figure 19. Firstly solution A containing 1.6 M NaOH and 0.16 M Na$_2$CO$_3$ was prepared in beaker A and solution B containing 0.6 M Mg(NO$_3$)$_2$$\cdot$6H$_2$O, 0.2 M Al(NO$_3$)$_3$$\cdot$9H$_2$O, and 0.3 M TiCl$_4$ was prepared in beaker B. Then solution A was added dropwise to beaker B with rigorous stirring until reaching a pH of 10. The resultant white mixture was aged in an oil bath of 60°C for 18 h. Solids were then collected by vacuum filtration and dried overnight at 80°C. Powders were collected after grinding and sieving. The molar ratio of Mg: Al: Ti was kept as 30:10:15. The sample was denoted as MgAl/Ti(CP) or CP.
2.1.2 Hydrothermal treatment of MgAl/Ti(CP)

MgAl/Ti(CP) powders were dispersed in water (1wt%) and stirred for 30 min. Then the mixture was transferred into a hydrothermal vessel and heated at a specific temperature (100, 150, or 200°C) for 24 h. After reaction, powder samples were recovered by filtration, vacuum drying and grinding. Samples were denoted as MgAl/Ti(HT100), MgAl/Ti(HT150), and MgAl/Ti(HT200) or simply HT100, HT150 and HT200.
2.1.3 Calcination and reconstruction of MgAl/Ti(CP)

MgAl/Ti(CP) powders were firstly calcined in a furnace at 400, 500, or 600°C for 2 h and then dispersed in water and rigorously stirred at room temperature for 24 h. Powders were collected after filtering and drying at 80°C and were denoted as MgAl/Ti(R400), MgAl/Ti(R500), and MgAl/Ti(R600) or simply R400, R500 and R600.

2.2 Characterization of materials

Crystal structures of samples were characterized with X-ray diffraction (XRD, Scintag XDS 2000) using Cu Kα irradiation (λ=0.1540562 nm) at 45 kV and a diffracted beam monochromator at 40 mA in the 2θ range of 5°-70° at a scan rate of 2°/min. Bragg’s law and Scherrer equation were applied for unit parameter and crystal size calculations.

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. Iridium nanoparticles were coated to a thickness of 4 nm on the samples to minimize charging effects. A voltage of 5kV was used for imaging.

Porous textual characterization was performed with nitrogen adsorption–desorption at 77 K. The Brunauer–Emmett–Teller (BET) method was used for surface area estimation and the Barrette-Joynere-Halenda (BJH) method for cumulative pore volume analysis (Micrometrics, ASAP 2020).

Thermal stability analysis of the MgAl/Ti(CP) material was carried out on a thermogravimetric analyzer (TGA-DAT-2960 SDT) at a heating ramp of 10°C/min from
room temperature to 800°C in air flow. Temperature-programed desorption of CO$_2$ (10 °C/min) was recorded with Mass Spectrometer. To characterize surface chemistry of the sample under thermal treatment, FTIR (Fourier transform infrared) spectra 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) which was equipped with a heater and a temperature controller, as well as cooling water circulation.

In order to compare the CO$_2$ adsorption capacity of different samples, CO$_2$ adsorption isotherms were taken with the thermogravimetric analyzer. Firstly 15-20 mg of samples were loaded in an Al$_2$O$_3$ container and heated to 150°C at a ramp of 10°C/min under Argon flow (100 ml/min). After the weight was stabilized, Argon flow was replaced with moisturized CO$_2$ flow (120 ml/min). The weight versus time was recorded and analyzed for a period of 60 minutes.

2.3 Photocatalytic activity test

The experiment setup is shown in Figure 20. The tests were performed in a quartz tube photoreactor. 50-70 mg of samples were dispersed on glass fiber filter paper and loaded on the inner wall of tube reactor. CO$_2$ (99.999%, Praxair) was continuously passed through a water bubbler to allow a mixture of CO$_2$ and H$_2$O vapor (H$_2$O ≈ 2.3 v/v%) to flow through the photoreactor. A UV lamp (10 mW/cm$^2$, < 380 nm) was used as the light source. Two 250 W infrared lamps were applied to heat up the photoreactor from the sides to reach a temperature of 150°C at the catalyst. The photoreactor was operated in a continuous-flow mode (120 mL/min for air purging and 2.0 mL/min for reaction), 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).

Figure 20. Schematic diagram showing experiment setup for photoreduction activity tests.
Chapter 3 Results

3.1 Structural properties of MgAl/Ti(CP)

Crystal structure of the pristine MgAl/Ti(CP) sample was examined by XRD characterization. As shown in Figure 21, characteristic LDH reflections were clearly observed: a series of \( (00l) \) basal peaks of \((003)\) and \((006)\) at lower angles \((2\theta<25^\circ)\), a series of \((01l)\) non-basal peaks of \((012), (015)\) and \((018)\) at moderate angles \((30^\circ<2\theta<50^\circ)\), and a series of \((hk0)\) and \((hkl)\) non-basal peaks of \((110)\) and \((113)\) at higher angles \((55^\circ<2\theta<65^\circ)\) [26]. The basal spacing \(d_{(003)}\) which equals the thickness of one brucite-like layer plus one interlayer was determined to be 0.759 nm. Unit cell parameters for a 3-layer polytype were calculated to be \(c=3d_{(003)}=2.276\) nm and \(a=2d_{(110)}=0.305\) nm (average metal-metal distance within the layers). These values were similar with those reported in the literature [59]. Applying the Scherrer equation on the \((003)\) peak, the crystallite size in the stacking direction of the MgAl/Ti(CP) sample was determined as 8.3 nm.

Crystal structural change of the MgAl/Ti(CP) material upon heating was recorded in Figure 22. At lower temperature \((200^\circ C)\), characteristic reflections for LDH structure were still clear. However, all the peaks were broadened suggesting that crystallinity decreased upon thermal treatment. When the calcination temperature was raised to 400-500 \(^\circ\)C, the layered structure was completely lost, leaving mixed metal oxide (MMO) of MgO and Al\(_2\)O\(_3\). When the temperature further increased to 600\(^\circ\)C, crystal TiO\(_2\) (anatase type, JCPDS no. 21-1272) and spinel phase MgAl\(_2\)O\(_4\) appeared.

The structural change of the MgAl/Ti(CP) sample upon thermal treatment can be explained with thermogravimetric analysis (TGA) result. As shown in Figure 23, three
stages with a total weight loss of 34.4% were identified: room temperature to 216 °C, 216-410 °C, and 410-800 °C. In the first stage, water molecules from the material surface and interlayer gallery was lost, but the layered structure was still preserved. In the second stage, dehydroxylation of the brucite-like layers and decarbonation occurred [60], leading to gradual loss of the layered structure. In the third stage, carbonates in the interlayer space were further eliminated [37].

Figure 21. XRD patterns of MgAl/Ti(CP), MgAl/Ti(HT100), MgAl/Ti(HT150), MgAl/Ti(HT200), MgAl/Ti(R400), MgAl/Ti(R500), and MgAl/Ti(R600) samples. (Asterisk refers to Al₂O₃ phase; S refers to spinel MgAl₂O₄; A refers to anatase TiO₂)
Figure 22. XRD patterns of MgAl/Ti(CP) calcined at 200-600°C for 2 h.

Desorption of CO$_2$ as a result of decarbonation during the heating process (room temperature to 600 °C with a ramp of 10 °C/min) was recorded as the TPD profile shown in Figure 24. The peak around 420 °C coincided well with the second and third weight losses in the TGA curve.
Figure 23. TGA curve of MgAl/Ti (CP).

Figure 24. TPD profile of MgAl/Ti (CP) for CO\textsubscript{2} desorption. (MS: mass spectra)

FTIR spectra of the sample heated to 50-500 °C (open system with air flow) were recorded in Figure 25. At 50 °C, the high frequency bands at 3550 and 3100 cm\textsuperscript{-1} were
ascribed to vibrations of H$_2$O and OH$^-$ groups [37]. 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 [37, 61]. As the temperature increased, the former two bands gradually decreased and finally disappeared at 300 °C, but new bands at 1566 and 1327 cm$^{-1}$ for bidentate carbonate (b$\text{--CO}_3^{2-}$) [61] 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$\text{--CO}_3^{2-}$) [61] were present.

Figure 25. FTIR spectra of MgAl/Ti (CP) heated at different temperatures in air (open system).
3.2 Structural properties of reconstructed and hydrothermal treated samples

Hydrothermal and reconstruction treatments did not affect a lot the lattice parameters of LDH structures (basal spacing d_{(003)}=0.751-0.767 \text{ nm} and unit cell parameter a=0.303-0.306 \text{ nm}, consistent with the literature [55]) but affected the their crystallinity significantly (crystallite size =4.8-19.9 \text{ nm}). These parameters were summarized in Table 2. Hydrothermal treatment at 100, 150, and 200 °C increased the crystallite size of 8.3 \text{ nm} for the CP sample to 11.9, 14.4 and 19.9 \text{ nm} respectively. In the literature, hydrothermal treatment was applied in the aging process to increase crystallinity of LDH structures [49]. Reconstructed samples from 400, 500, and 600 °C calcination decreased the crystallite size to 4.8, 5.5 and 6.0 \text{ nm}. For both kinds of treatment, the higher the temperature, the larger the crystallite size.

The (101) diffraction peaks for anatase type TiO_2 (JCPDS no. 21-1272) were observed at 25.3°, 25.2° and 25.7° for HT150, HT200 and R600 samples (Figure 21), respectively. The corresponding anatase crystallite size was calculated as 8.4, 12.3 and 30.1 \text{ nm} respectively. The mechanism for the formation of anatase crystals from amorphous TiO_2 by hydrothermal method in the presence of water was studied by Yanagisawa et al. [57]. They found lower crystallization temperature in hydrothermal condition than heating in air, which was attributed to the acceleration of nucleation by water. At 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 [56]. The results in the current work agreed well with the proposed mechanism.
Reflections for impurities like spinel MgAl₂O₄ and Al₂O₃ [62] were also present on the R600 sample, indicating incomplete reconstruction of the LDH structure.

Table 2 Crystal structural parameters of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
</tr>
</thead>
<tbody>
<tr>
<td>basal spacing (nm)</td>
<td>0.759</td>
<td>0.751</td>
<td>0.753</td>
<td>0.767</td>
<td>0.751</td>
<td>0.758</td>
<td>0.759</td>
</tr>
<tr>
<td>LDH crystallite size (nm)</td>
<td>8.3</td>
<td>11.9</td>
<td>14.4</td>
<td>19.9</td>
<td>4.8</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>lattice parameter a (nm)</td>
<td>0.305</td>
<td>0.304</td>
<td>0.304</td>
<td>0.305</td>
<td>0.303</td>
<td>0.304</td>
<td>0.306</td>
</tr>
<tr>
<td>Anatase crystallite size (nm)</td>
<td>/</td>
<td>/</td>
<td>8.4</td>
<td>12.3</td>
<td>/</td>
<td>/</td>
<td>30.1</td>
</tr>
</tbody>
</table>

3.3 Morphology and textual properties

Morphologies of the samples were recorded by SEM imaging (Figure 26). The pristine CP sample was composed of densely aggregated small nanoflakes (~50nm). Porous flower-like morphologies were observed for all the hydrothermal and reconstruction treated samples. Hydrothermal treatment resulted in larger flakes of ~100nm for HT100, ~500nm for HT150 and ~1000 nm for HT200, which was probably caused by the increased crystallinity after hydrothermal treatment. Reconstructed samples consisted of relatively small flakes (~100nm) and the flake size was not obviously affected by the calcination temperature.
Nitrogen adsorption/desorption isotherms were taken at 77K to analyze textual properties of the samples. As shown in Figure 27A, all of the samples display a type IV isotherm (IUPAC classification) and type H3 hysteresis loop [48, 63], indicating mesoporous structures formed by aggregates of flakes or slit pores between edged flakes.
The relative pressure (P/P₀) at the loop closing points 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.

Figure 27. N₂ adsorption-desorption isotherms (A) and Pore size distribution (B).

Pore size distribution (Figure 27B) of the samples were plotted using BJH desorption dV/dD data. Average pore size and pore volume were summarized in Table 3. 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 [48]. Hydrothermal treatment at 100°C did not change the pore size distribution a lot, 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 LDH crystallite 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 5nm. 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 increasing trend in LDH crystallinity as revealed by XRD characterization.

The BET surface area decreased from 169.9 m$^2$/g for the CP sample to 117.0 and 78.3 m$^2$/g at 150 and 200°C hydrothermal treatment temperatures. However the HT100 sample had slightly increased BET surface area of 181.4 m$^2$/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 m$^2$/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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>169.9</td>
<td>181.4</td>
<td>117</td>
<td>78.3</td>
<td>111.4</td>
<td>102.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>5.5</td>
<td>6.3</td>
<td>10.8</td>
<td>14.3</td>
<td>4.2</td>
<td>4.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Pore volume (cm$^3$/g)</td>
<td>0.25</td>
<td>0.3</td>
<td>0.38</td>
<td>0.33</td>
<td>0.14</td>
<td>0.16</td>
<td>0.2</td>
</tr>
</tbody>
</table>

3.4 Optical and CO$_2$ adsorption properties

Band gaps of samples, measured from absorption edges of UV-Vis spectra, were shown in Table 4. The CP sample had a band gap of 3.40 eV, in consistent with the reported value for amorphous TiO$_2$\textsuperscript{[51]}. 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 narrowed down to 3.32 and 3.31 eV, which could be attributed to the presence of anatase TiO$_2$ in the two samples. Band gaps of the reconstructed samples were determined to be 3.42, 3.35 and 3.30 eV at calcination temperatures of 400, 500 and 600°C. The smallest band gap was observed for the R600 sample which had the largest anatase crystallite size of 30.1 nm.

CO$_2$ adsorption capacities were measured from CO$_2$ isotherms obtained by the TGA instrument and shown in Table 4. The original CP sample had an adsorption capacity of 2.07\% for CO$_2$, nearly three times of that over the rest of samples tested. The decrease in CO$_2$ adsorption capacity was mainly caused by the decreased surface area after hydrothermal and reconstruction treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>3.4</td>
<td>3.4</td>
<td>3.32</td>
<td>3.31</td>
<td>3.42</td>
<td>3.35</td>
<td>3.3</td>
</tr>
<tr>
<td>CO$_2$ adsorption capacity (wt%)</td>
<td>2.07</td>
<td>/</td>
<td>0.66</td>
<td>0.62</td>
<td>0.85</td>
<td>/</td>
<td>0.59</td>
</tr>
</tbody>
</table>

3.5 Photocatalytic activity for CO$_2$ reduction

CO$_2$ photoreduction activities of samples were tested by UV light irradiation for 5 h with continuous moisturized CO$_2$ gas feeding (2 mL/min). In the dark condition, no product was observed. Under the light irradiation, CO was identified as the major product with only trace amount of CH$_4$ detected, which was consistent with our previous reports [8, 64] on TiO$_2$ based photocatalysts. To verify the carbon source of CO, control
experiment was performed on the HT150 sample (Figure 28). The total yields of CO accumulated in 5 h irradiation were 5.15 umol/g for He feeding and 9.12 umol/g for CO₂ feeding.

![CO production rate over the MgAl/Ti (HT150) sample with moisturized CO₂ or He feeding.]

The amount of CO per unit gram of TiO₂ evolved within 5 h with CO₂ feeding was compared for all the MgAl/Ti-LDH samples in Figure 29. Amorphous TiO₂ was usually considered to be in active for photoreactions. However, in this study, the CO production amount per unit gram of TiO₂ for MgAl/Ti(CP) was more than three times of that for commercial P25-TiO₂ which was a mixture of antase and rutile. As reported in ALDRICH MSDS, BET surface area of P25 was 35-65 m²/g, much smaller than that of MgAl/Ti(CP) (169.9 m²/g). The higher photoactivity of MgAl/Ti(CP) could be attributed to better dispersion of amorphous TiO₂, larger surface area and CO₂ adsorption ability.
Since crystalline phases of TiO$_2$ were generally more active than amorphous phase for photoreactions, it was interesting to test if crystallization of the amorphous TiO$_2$ in MgAl/Ti(CP) could enhance the CO$_2$ photoreduction activity. Two different methods—hydrothermal and reconstruction treatments were used to achieve the phase transformation. All the hydrothermal treated samples showed better photoactivity than the MgAl/Ti(CP) sample. As for the reconstructed samples, only R400 showed slightly increased CO production. These results are due to combined effects of TiO$_2$ crystallinity, surface area, and CO$_2$ adsorption ability. Among all the samples tested, the HT150 sample showed the best photoactivity due to decreased band gap (3.32 eV) by formation of anatase TiO$_2$ nanocrystals (8.4 nm) and relatively large surface area (117.0 m$^2$/g). As for the HT200 sample which had anatase nanocrystals of 12.3 nm, the greatly decreased specific surface area (78.3 m$^2$/g) prevented improvement in the overall photocatalytic activity.

Figure 29. Amount of CO evolved after UV irradiation for 5 h with moisturized CO$_2$ feeding (normalized for unit gram of TiO$_2$).
To understand the effect of TiO$_2$ crystallization on CO$_2$ photoreduction activity, the amount of CO produced over HT150, HT200 and R600 was normalized by unit specific surface area and compared in Figure 30. The anatase crystal sizes were 8.4 nm, 12.3 nm and 30.1 nm for HT150, HT200 and R600 respectively. The order of photoactivity was HT200 > HT150 > R600, suggesting an optimal anatase size of 12.3 nm for CO$_2$ photoreduction. Too large anatase crystallite size in R600 might compromise the CO$_2$ photoreduction activity because of the increased surface area of anatase nanoparticles. Similar size effect of TiO$_2$ nanoparticles has been observed for CO$_2$ photoreduction [65] and other photocatalytic reactions [66] where an optimum size existed for highest photocatalytic reactivity due to a balance between band gap and surface area of TiO$_2$ particles. The current results showed that hydrothermal treatment was a better method than reconstruction for crystallization of Ti in MgAl/Ti-LDHs in terms of CO$_2$ photoreduction improvement.

![Figure 30. Amount of CO production normalized by specific surface area.](image-url)
Chapter 4   Conclusions

In this study, MgAl/Ti-LDHs have been for the first time studied for CO₂ photoreduction with water vapor and have shown better photoactivity than the commercial P25-TiO₂. Hydrothermal treatment at 150-200°C converted the amorphous Ti species in the LDH samples to anatase nanocrystals (confirmed by XRD) while maintaining the characteristic LDH structures. 150°C was demonstrated to be the optimum hydrothermal treatment temperature for the highest photocatalytic activity for CO₂ reduction. Although hydrothermal treatment at a higher temperature (200°C) gave rise in better TiO₂ crystallinity, the greatly decreased surface area prevented further improvement of the CO₂ photoreduction activity. Reconstructed sample with a calcination temperature of 600°C also resulted in crystal anatase TiO₂. But the large anatase crystallite size and small surface area did not improve CO production comparing with pristine MgAl/Ti (CP) sample. Future investigations on formation of crystal TiO₂ of suitable particle size without lowering the specific surface area might help further enhance the photocatalytic activities.
Chapter 5  References


