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RAPID COMMUNICATION

Simplified synthesis of K_2CO_3-promoted hydrotalcite based on hydroxide-form precursors: Effect of Mg/Al/K_2CO_3 ratio on high-temperature CO_2 sorption capacity

Hee Jin Jang[‡], **Suji Kim**[‡], **and Ki Bong Lee**[†]

Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Korea

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Abstract−Hydrotalcite was synthesized from hydroxide-form precursors to prepare a novel high-temperature CO_2 sorbent, and the effect of Mg/Al ratio on CO_2 sorption was studied. To enhance the CO_2 sorption capacity of the sorbent, K_2CO_3 was coprecipitated during the synthetic reaction. X-ray diffraction analysis indicated that the prepared samples had a well-defined crystalline hydrotalcite structure, and confirmed that K_2CO_3 was successfully coprecipitated in the samples. The morphology of the hydrotalcite was confirmed by scanning electron microscopy, and N_2 adsorption analysis was used to estimate its surface area and pore volume. In addition, thermogravimetric analysis was used to measure its CO_2 sorption capacity, and the results revealed that the Mg : Al : K_2CO_3 ratio used in the preparation has an optimum value for maximum CO_2 sorption capacity.

Keywords: Hydrotalcite, Sorption, CO_2 Sorbent, K_2CO_3 Promotion, Hydrothermal Synthesis

INTRODUCTION

The threat of global warming necessitates the development of technologies for the reduction of greenhouse gases. CO_2 is the main anthropogenic greenhouse gas, and its concentration in the atmosphere continues to increase because fossil fuels, which emit CO_2 through combustion, are still used in many industries [1]. Therefore, the capture of CO_2 from power plant flue gases is an important strategy to reduce industrial CO_2 emissions. Technologies for the direct capture of CO_2 at high temperature are required to efficiently and economically capture CO_2 from high-temperature flue gases. Calcium oxide, lithium zirconate, and hydrotalcite have been widely considered as sorbents for high-temperature CO_2 capture. Both calcium oxide and lithium zirconate have high CO_2 sorption capacities at high temperature, but the sorption capacity of calcium oxide continuously deteriorates over repeated sorption and desorption cycles, and lithium zirconate exhibits relatively slow CO_2 sorption kinetics. Moreover, both materials require very high temperatures of more than 800 °C for regeneration [2,3]. However, hydrotalcite has relatively fast CO_2 sorption kinetics, good thermal stability, and a moderate regeneration temperature.

Hydrotalcite, also known as layered double hydroxide (LDH), is composed of positively charged brucite-like layers in which some of the divalent cations are substituted with trivalent cations. The excess positive charge in the hydrotalcite layers is compensated by interlayer anions and H_2O molecules [4]. Hydrotalcite has the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}]\cdot mH_2O$, where M^{2+} is a divalent cation such as Mg^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, or Ni^{2+}, M^{3+} is a trivalent cation such as Al^{3+}, Cr^{3+}, Ga^{3+}, or Mn^{3+}, A^{n-} is an interlayer anion such as CO_3^{2-}, NO_3^-, or SO_4^{2-}, m is the amount of H_2O present in the interlayer, and x is the substitution degree of the trivalent cations [5,6]. Hydrotalcite materials have received considerable attention as catalysts, anion-exchangers, pharmaceuticals, and sorbents [7-9]. Recently, to develop and improve hydrotalcites as high-temperature CO_2-capturing sorbents, many studies have focused on the effects of different divalent and trivalent cations, synthetic pH, and promotion with alkali metals [10-13]. Of these strategies, alkali metal-promoted hydrotalcite has shown particularly improved CO_2 sorption capacity, but its current synthesis method is time-consuming and inconvenient, because the hydrotalcite synthesis and alkali metal impregnation steps are performed separately [14].

Conventional hydrotalcite is easily synthesized by a co-precipitation method from water-soluble nitrate precursors, but the product crystallinity is relatively low. Moreover, the product must be repeatedly washed to remove remaining nitrate ions that originate from the metal nitrate precursors, and the large amounts of KOH or NaOH that are used to control the solution pH. Repeated washing steps generate wastewater and cause environmental problems.

In this study, we synthesized hydrotalcites with different Mg/Al molar ratios from hydroxide-form precursors to investigate the effect of the Mg/Al ratio on the CO_2 sorption capacity of the hydrotalcite. The purpose of this study is the development of a high-performance CO_2 sorbent using a simple and eco-friendly synthesis method. Hydroxide precursors such as $Mg(OH)_2$ and $Al(OH)_2$, and K_2CO_3 were used to supply divalent and trivalent cations, and interlayer anions, respectively, as follows [15]:

$$(1-x)Mg(OH)_2+xAl(OH)_3+(x/2)K_2CO_3+mH_2O \\ \rightarrow[Mg_{1-x}Al_x(OH)_2][CO_3]_{x/2}\cdot mH_2O+xKOH$$

The Mg/Al molar ratio was varied to 1, 2, 3, and 5 to assess the effect of Mg/Al ratio on CO_2 sorption, and the K_2CO_3/Al ratio was

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[†] To whom correspondence should be addressed.
E-mail: kibonglee@korea.ac.kr

[‡] These authors contributed equally to this work.

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Table 1. Synthetic conditions and physical properties of hydrotalcites

$Mg(OH)_2 : Al(OH)_3 : K_2CO_3$ molar ratio in feed	Initial pH	Final pH	BET surface area (m^2/g)	Pore volume (cm^3/g)
1 : 1 : 0.5	11.1	11.2	179	0.239
2 : 1 : 0.5		12.5	166	0.208
3 : 1 : 0.5		13.2	148	0.205
5 : 1 : 0.5		13.0	137	0.192
1 : 1 : 3	11.3	11.6	47.9	0.121
2 : 1 : 3		13.4	34.3	0.0813
3 : 1 : 3		13.5	29.8	0.0896
5 : 1 : 3		13.5	46.0	0.124

also varied for the K_2CO_3-promoted hydrotalcites. The stoichiometric K_2CO_3/Al molar ratio required to supply sufficient CO_3^{2-} anions is 0.5, but we added 1-6 times the stoichiometric amount of K_2CO_3 for comparison. With excess K_2CO_3 in the preparation, the remaining K_2CO_3 is co-precipitated during the hydrotalcite synthesis. In this preparation method, a washing step is not needed because the only remaining byproduct is KOH, which can be easily separated during the filtering step. Using this simple and novel method, we have synthesized K_2CO_3-promoted hydrotalcites with different Mg/Al ratios for use as high-temperature CO_2 sorbents.

EXPERIMENTAL SECTION

1. Materials

All precursors, including magnesium hydroxide ($Mg(OH)_2$, ≥95%), aluminum hydroxide ($Al(OH)_3$, reagent grade), and potassium carbonate (K_2CO_3, ≥99%), were purchased from Sigma-Aldrich (USA). All reagents were used without further purification. Distilled water was used as a solvent in the synthesis procedure.

2. Preparation of Samples

The hydrotalcites were prepared by the hydrothermal method because $Mg(OH)_2$ and $Al(OH)_3$ have very small solubility product constants (K_{sp}) at room temperature. First, predetermined amounts of $Mg(OH)_2$, $Al(OH)_3$, and K_2CO_3 were mixed with 30 mL of distilled water, and the initial pH of the mixture was measured. The mixture was then transferred to 40 mL Teflon-lined stainless steel autoclave and hydrothermally reacted at 160 °C for 24 h. The solution was then quickly cooled, and the final pH of the mother liquor was measured. The aged suspension was filtered, and the filter cake was dried at 110 °C. Finally, the resulting white powder was calcined at 500 °C for 3 h under a N_2 atmosphere.

3. Characterization

The pH of the reaction solution was measured before and after the reaction using a pH meter (Thermo scientific, Orion 4 star). The Brunauer-Emmett-Teller (BET) surface area and Barret-Joyner-Halenda (BJH) desorption pore volume were calculated from the N_2 adsorption isotherm at 77 K, as obtained by using an ASAP2020 analyzer (Micromeritics). The morphology of the samples was observed by field emission scanning electron microscopy (FESEM, Hitachi S-4300). Before the measurement, samples were coated with Pt using ion sputtering because visualization of structural details in FESEM requires optimal conductivity. The X-ray diffraction (XRD) patterns of the samples were measured with a Rigaku D/Max-2500V X-ray diffractometer with Cu Kα radiation (λ=0.15418 nm) and a power of 40 kV×40 mA. The 2θ scan range was from 5° to 70° at a scanning rate of 4°/min. The crystalline phases were identified by comparison of the XRD patterns with the JCPDS database.

4. CO_2 Sorption Measurement

The CO_2 sorption capacities of the hydrotalcites were measured through thermogravimetric analysis (TGA, TA Instruments Q50). Before CO_2 sorption measurement, samples were pretreated at 500 °C for 3 h under an N_2 atmosphere to remove any moisture and CO_2. After pretreatment, the temperature was decreased to the sorption temperature of 240 °C, and the sample weight was stabilized before the N_2 gas was switched to pure CO_2 gas. The sorption capacity was determined from the weight change during the CO_2 sorption at 240 °C and 1 atm CO_2 over 5 h.

RESULTS AND DISCUSSION

After the synthetic reaction, the pH value of all solutions was increased, as shown in Table 1, because KOH was generated as a byproduct. Moreover, when the K_2CO_3/Al ratio was increased from 0.5 to 3, pH values of both the initial and final solution increased. Table 1 also shows the BET surface areas and BJH desorption pore volumes. When only the stoichiometric amount of K_2CO_3 was used, the BET surface area and pore volume were higher than when an excess of K_2CO_3 ($K_2CO_3/Al=3$) was used. This implies that the remaining K_2CO_3 that did not participate in the synthetic reaction was successfully co-precipitated during the reaction, and filled and blocked the hydrotalcite pores.

The FESEM images of hydrotalcites with different Mg/Al molar ratios are shown in Fig. 1. For Mg/Al ratios of 1 or 2, there are irregular small particles on the plate-like structures. When the Mg/Al ratio increases to 3, no irregular small particles are observed. It is notable that hydrotalcite adopts its typical hexagonal plate-like morphology when the Mg/Al ratio is 3 or 5. In addition, when only stoichiometric K_2CO_3 is used, hexagonal plates do not fully develop because the amount of CO_3^{2-} is insufficient to facilitate the formation of the hexagonal plate-like morphology of hydrotalcite. The morphology does not change during calcination at 500 °C for 3 h under an N_2 atmosphere.

Fig. 2 shows the XRD patterns of the synthesized hydrotalcites with different Mg/Al and K_2CO_3/Al ratios. All the samples present characteristic hydrotalcite peaks and well-defined layered structures, although some samples present peaks for unreacted $Mg(OH)_2$. For

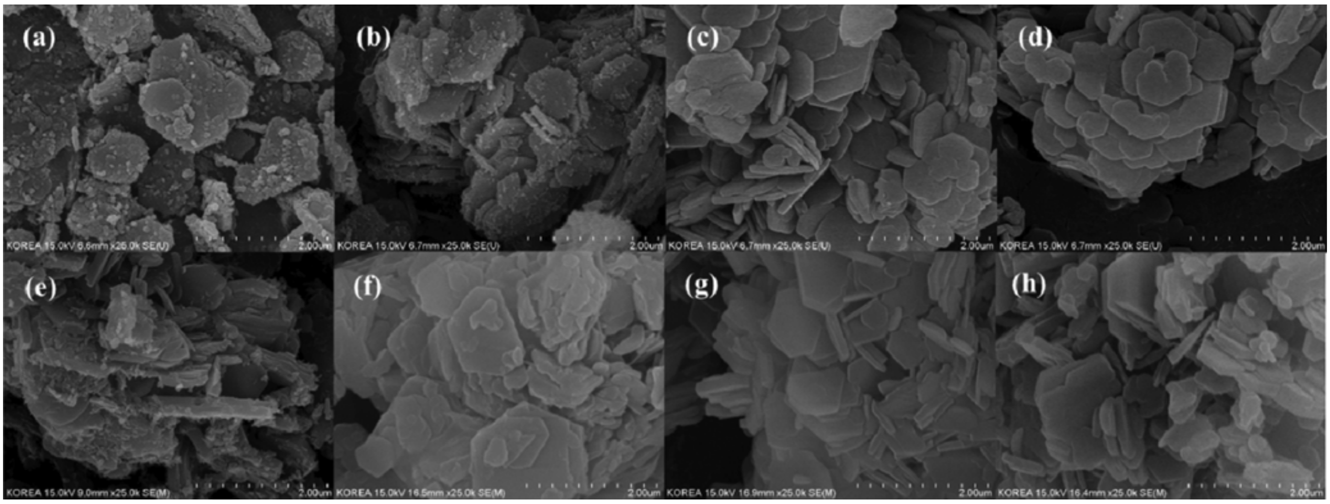

Fig. 1. SEM images of hydrotalcites synthesized with different Mg : Al : K_2CO_3 ratios: (a) 1 : 1 : 0.5, (b) 2 : 1 : 0.5, (c) 3 : 1 : 0.5, (d) 5 : 1 : 0.5, (e) 1 : 1 : 3, (f) 2 : 1 : 3, (g) 3 : 1 : 3, and (h) 5 : 1 : 3.

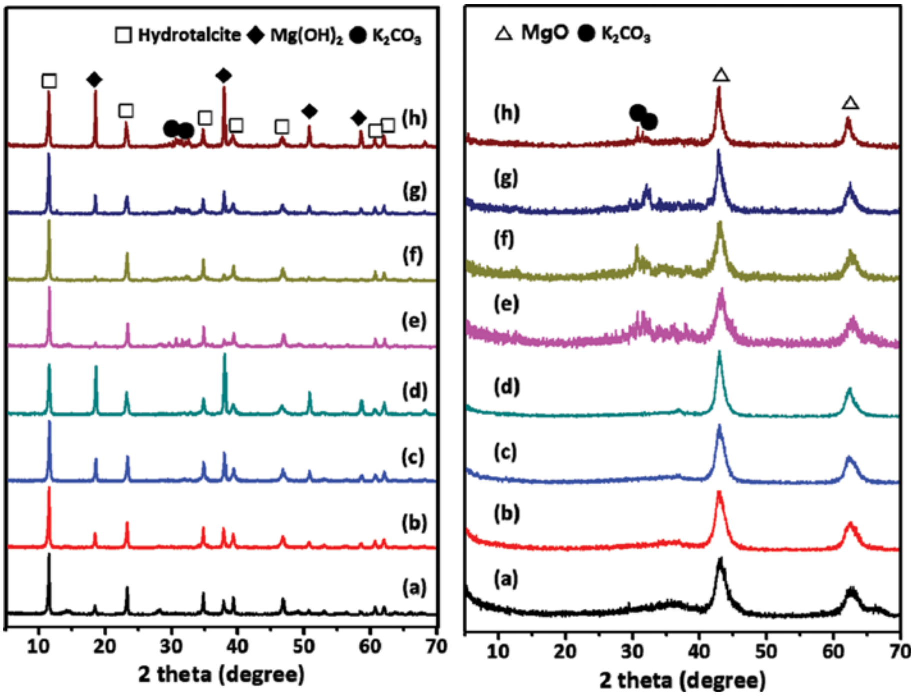

Fig. 2. XRD patterns of hydrotalcites synthesized with different Mg : Al : K_2CO_3 ratios: (a) 1 : 1 : 0.5, (b) 2 : 1 : 0.5, (c) 3 : 1 : 0.5, (d) 5 : 1 : 0.5, (e) 1 : 1 : 3, (f) 2 : 1 : 3, (g) 3 : 1 : 3, and (h) 5 : 1 : 3. Left: before calcination; right: after calcination.

the hydrotalcites prepared with Mg/Al ratios of 1 or 2, the characteristic $Mg(OH)_2$ peaks are not significant. When the Mg/Al ratio increases from 2 to 3 or 5, the $Mg(OH)_2$ peak intensity increases. This indicates that $Mg(OH)_2$ conversion decreases with increasing Mg/Al ratio. This result also implies that only a limited amount of $Mg(OH)_2$ participates in the synthetic reaction and is incorporated into the hydrotalcite structure. A plausible explanation for this is that as the Mg/Al ratio increases, a relatively large number of Mg ions cannot substitute with Al ions to develop the hydrotalcite structure because the number of Al ions is relatively small.

When only a stoichiometric amount of K_2CO_3 is used, no K_2CO_3 peaks appear because almost all the K_2CO_3 participates in the synthetic reaction and supplies the CO_3^{2-} anions to form the hydrotalcite structure. However, K_2CO_3 peaks are clearly detected when excess amounts of K_2CO_3 are used. This indicates that K_2CO_3 is co-precipitated during the synthesis step. Thus, by using excess K_2CO_3 as a precursor material, K_2CO_3-promoted hydrotalcite is successfully synthesized.

The degree of transformation was calculated from the $Mg(OH)_2$ and hydrotalcite peak intensity ratios in the XRD patterns at their characteristic peak angles of 38.0° and 11.5° (2*θ*), respectively [16]. The relative contents of $Mg(OH)_2$ and hydrotalcite are shown in

Table 2. Relative content of $Mg(OH)_2$ in the synthesized hydrotalcites based on XRD patterns

Mg : Al : K molar ratio in feed	$I_{Mg(OH)_2}/I_{hydrotalcite}$ (%)
1 : 1 : 0.5	11.3
2 : 1 : 0.5	15.3
3 : 1 : 0.5	40.9
5 : 1 : 0.5	120
1 : 1 : 3	9.2
2 : 1 : 3	11.1
3 : 1 : 3	38.4
5 : 1 : 3	108

Table 2. When the Mg/Al ratio is 1 or 2, a relatively small amount of unreacted $Mg(OH)_2$ remains, but as the Mg/Al ratio increases to 3 or 5, a relatively large amount of unreacted $Mg(OH)_2$ remains in the sample. Moreover, when only a stoichiometric amount of K_2CO_3 is used, the relative amount of unreacted $Mg(OH)_2$ in the sample is higher than that when an excess amount of K_2CO_3 is used. This is because a stoichiometric amount of K_2CO_3 is not enough to efficiently supply the interlayer anions. However, the K_2CO_3/Al ratio does not significantly influence the synthesis conversion. A relatively small increase in the reaction conversion is observed even when six-times the stoichiometric amount of K_2CO_3 is used.

In general, hydrotalcite itself is not directly applied as a CO_2 sorbent, but is thermally treated before use. During thermal treatment, the hydrotalcite loses its interlayer water and anions, and then dehydroxylation and decarbonation occur. During the thermal treatment, the hydrotalcite structure is transformed into an amorphous mixed oxide [17]. The thermally treated hydrotalcite has a higher surface area and pore volume than pristine hydrotalcite [18,19], and this enhances its CO_2 sorption capacity. Therefore, in this study, all hydrotalcites were calcined before CO_2 sorption tests. Fig. 2 also shows the XRD patterns of hydrotalcites after calcination at 500 °C for 3 h under a N_2 atmosphere. After calcination, all the hydrotalcite and $Mg(OH)_2$ phases are transformed to mixed oxides. However, the K_2CO_3 phase remains in the samples.

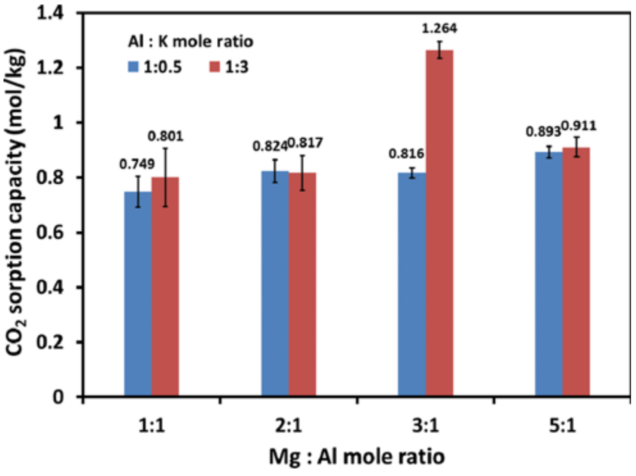

Fig. 3. CO_2 sorption capacities at 240 °C and 1 atm CO_2 for hydrotalcites prepared with different Mg/Al and K_2CO_3/Al ratios.

Fig. 3 compares the CO_2 sorption capacities at 240 °C and 1 atm CO_2 for the hydrotalcites prepared with different Mg/Al and K_2CO_3/Al ratios. In the hydrotalcites prepared with a stoichiometric amount of K_2CO_3 (Al : K=1 : 0.5), the Mg/Al ratio has no significant effect on CO_2 sorption capacity. Upon increasing the Mg/Al ratio from 1 to 5, the CO_2 sorption capacity shows a slight increase, but it is not significant. However, when excess K_2CO_3 is used (Al : K=1 : 3), the effect of the Mg/Al ratio on CO_2 sorption capacity is significant. The hydrotalcite prepared with a Mg/Al ratio of 3 shows significantly increased CO_2 sorption capacity because the co-precipitated K_2CO_3 enhances the CO_2 sorption. Its CO_2 sorption capacity is much higher than that of conventional hydrotalcites [12,20,21]. Conversely, the other hydrotalcite samples exhibit similar CO_2 sorption capacities, even those prepared with K_2CO_3 co-precipitation. It was reported that the effect of K_2CO_3 amount on the CO_2 sorption capacity of hydrotalcite can vary depending on the Mg/Al ratio [11]. Also, the K_2CO_3 is thought to have two conflicting effects on the CO_2 sorption capacity of hydrotalcite. The increasing amount of K_2CO_3 enhances the basicity of the hydrotalcite, which is beneficial for the sorption of weakly acidic CO_2. However, co-precipitated K_2CO_3 also can block and fill the pores of hydrotalcite, resulting in the decreased number of sorption sites and finally reduced physisorption of CO_2. Therefore, the amount of co-precipitated K_2CO_3 has an optimum value for maximum CO_2 sorption capacity of hydrotalcite.

CONCLUSIONS

Hydrotalcites were synthesized from hydroxide-form precursors to assess the effect of Mg/Al ratio on CO_2 sorption capacity. When only a stoichiometric amount K_2CO_3 was used in the preparation, the Mg/Al ratio did not significantly affect the CO_2 sorption capacity of the hydrotalcite. When excess K_2CO_3 was used, K_2CO_3-promoted hydrotalcite was successfully synthesized and the resultant K_2CO_3-promoted hydrotalcite exhibited improved CO_2 sorption capacity. This new method is simple and eco-friendly because the synthetic reaction and K_2CO_3 co-precipitation occur simultaneously, thus avoiding wasteful and time-consuming washing steps. The hydrotalcite prepared with a Mg/Al ratio of 3 showed significantly increased CO_2 sorption capacity, implying that an optimum K_2CO_3/Al/Mg ratio for CO_2 sorption exists. In this study, the optimum Mg : Al : K_2CO_3 ratio for CO_2 sorption was 3 : 1 : 3, and the CO_2 sorption capacity of the resultant hydrotalcite was much higher than that of conventional hydrotalcites.

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