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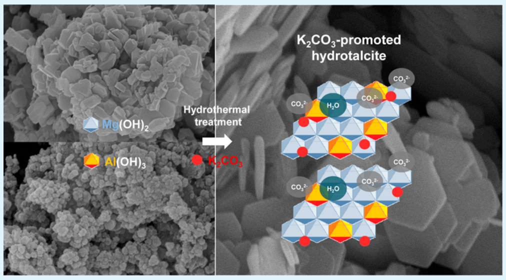
Hydrothermal Synthesis of K_2CO_3-Promoted Hydrotalcite from Hydroxide-Form Precursors for Novel High-Temperature CO_2 Sorbent

Hee Jin Jang,† Chan Hyun Lee,† Suji Kim, Sung Hyun Kim, and Ki Bong Lee*

Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Republic of Korea

Supporting Information



ABSTRACT: In many materials for CO_2 sorption, hydrotalcite is attracting substantial attention as a high temperature (200−500 °C) CO_2 sorbent because of its fast sorption/desorption kinetics and easy regenerability. However, the CO_2-sorption capacity of conventional hydrotalcite is relatively low for large-scale commercial use. To enhance CO_2-sorption capacity, hydrotalcite is conventionally impregnated with alkali metals such as K_2CO_3. Although K_2CO_3-impregnated hydrotalcite has high CO_2-sorption capacity, the preparation method takes long time and is inconvenient because hydrotalcite synthesis step and alkali metal impregnation step are separated. In this study, K_2CO_3-promoted hydrotalcite was newly synthesized from hydroxide-form percursors by a simple and eco-friendly method without a solvent-consuming washing step. Analysis based on X-ray diffraction indicated that the prepared samples had structures of well-defined hydrotalcite crystalline and un-reacted $Mg(OH)_2$ precursor. Moreover, K_2CO_3 was successfully incorporated in hydrotalcite during the synthesis step. The prepared K_2CO_3-promoted hydrotalcite showed high CO_2-sorption capacity and had potential for use as a high-temperature CO_2 sorbent.

KEYWORDS: *sorbent, K_2CO_3-promoted hydrotalcite, CO_2 sorption, hydroxide-form precursor, hydrothermal synthesis, high temperature*

INTRODUCTION

Hydrotalcite, also known as layered double hydroxide (LDH), belongs to the class of anionic clay minerals. Its structure is composed of positively charged metal-hydroxide layers and negatively charged interlayers containing anions and H_2O molecules. The net positive charge in the metal-ion layer is balanced by the net negative charge of the anion layer.[1,2] The general formula for hydrotalcites is $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}{}_{x/n}]^{x-}\cdot mH_2O$. Where M^{2+}, M^{3+}, and A^{n-} commonly represent Mg^{2+}, Al^{3+}, and $CO_3{}^{2-}$, respectively; x has values in the range 0.17−0.33; and m is the amount of H_2O present in the interlayer.[3] Hydrotalcite has received great attention because of its CO_2-sorption ability at high temperatures.[4,5] It also has good thermal stability and relatively fast CO_2-sorption kinetics; moreover, it requires only a moderate regeneration temperature. However, the CO_2-sorption capacities of conventional hydrotalcites are relatively low for large-scale commercial use.[6−8] Therefore, to enhance the CO_2-sorption capacity, hydrotalcite is impregnated with K_2CO_3 and/or Na_2CO_3.[1,9,10] However, although K_2CO_3/Na_2CO_3-promoted hydrotalcite has a high CO_2-sorption capacity, its current synthesis is time-consuming and inconvenient, because the hydrotalcite synthesis and alkali metal impregnation steps are separate.[8]

Hydrotalcite is conventionally synthesized from water-soluble nitrate precursors by a co-precipitation method.[11−13] Although hydrotalcite structure is easily developed by such co-precipitation methods, the product crystallinity is relatively low.[14] Moreover, the product must be repeatedly washed because large amounts of basic solution, including NaOH or KOH, are added during the synthesis step to control the solution pH. Furthermore, repeated washing steps generate wastewater that consequently causes environmental problems.

In this study, we directly synthesized K_2CO_3-promoted hydrotalcite from hydroxide-form precursors to produce a novel high-temperature CO_2 sorbent, and we measured its CO_2-sorption capacity at high temperature. To the best of our knowledge, this type of K_2CO_3-promoted hydrotalcite derived from hydroxide-form precursors has not been applied before as a high-temperature CO_2 sorbent.

Xu et al. reported a method for the synthesis of hydrotalcite from hydroxide precursors.[15] They used $(NH_4)_2CO_3$ as a precursor to avoid the production of sodium or potassium salt. In this study, we used K_2CO_3 instead of $(NH_4)_2CO_3$ to supply the interlayer anion, $CO_3{}^{2-}$, and to enhance the basicity of hydrotalcite as follows

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

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Table 1. Synthesis Condition and Physical Properties of K_2CO_3-promoted Hydrotalcite

$Mg(OH)_2$:$Al(OH)_3$:K_2CO_3 mole ratio in feed	Mg:Al:K mole ratio in feed	synthesis temperature (°C)	initial pH	final pH	S_{BET} (m^2 g^{-1})	Mg:Al:K mole ratio in product
3:1:0.5	3:1:1	160	10.9	13.2	113	3.7:1:0.22
3:1:1	3:1:2	160	11.1	13.3	63.2	3.3:1:1.18
3:1:3	3:1:6	130	11.3	13.1	29.0	3.6:1:1.11
3:1:3	3:1:6	160	11.3	13.3	29.8	3.4:1:1.28
3:1:3	3:1:6	200	11.3	12.8	26.6	3.7:1:1.45
3:1:5	3:1:10	160	11.5	13.8	22.7	3.5:1:1.64

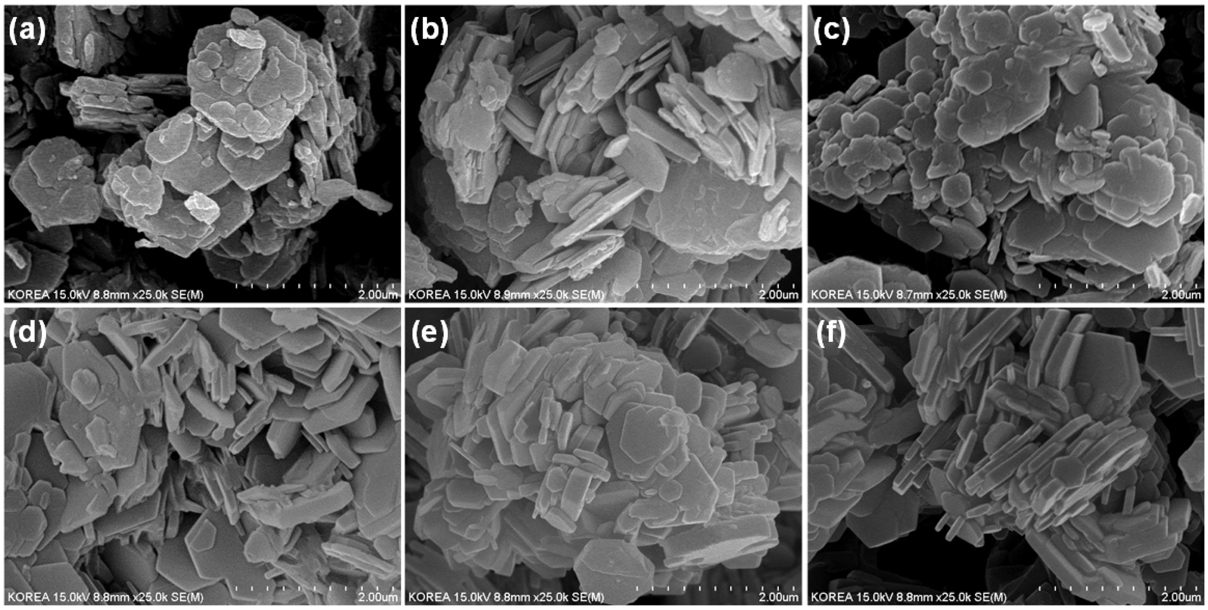

Figure 1. SEM images of K_2CO_3-promoted hydrotalcite (a) Mg:Al:K 3:1:1 [160 °C], (b) Mg:Al:K 3:1:2 [160 °C], (c) Mg:Al:K 3:1:6 [130 °C], (d) Mg:Al:K 3:1:6 [160 °C], (e) Mg:Al:K 3:1:6 [200 °C], (f) Mg:Al:K 3:1:10 [160 °C]. The value in parentheses denotes the synthesis temperature.

In this reaction, the hydroxide-form precursors and K_2CO_3 provide the cations and interlayer anions, respectively, and these collectively form the hydrotalcite structure. However, when an excessive amount of K_2CO_3 is used, the remaining K_2CO_3 is simultaneously co-precipitated during the hydrotalcite synthesis step, resulting in the production of K_2CO_3-promoted hydrotalcite.

■ RESULTS AND DISCUSSION

As can be seen in Table 1, the pH values of all the samples increased after reaction because KOH was generated as a by-product of the reaction. By using an excess amount of K_2CO_3 in the reaction, an excess of K_2CO_3 was co-precipitated during the hydrotalcite synthesis step. The stoichiometric K_2CO_3/Al ratio required to supply CO_3^{2-} ions is 0.5, and we added 1, 2, 6, and 10 times the stoichiometric amount of K_2CO_3 for comparison. As the amount of K_2CO_3 in the reactant increased, the initial pH value also increased. As the reaction temperature was increased from 130 to 160 °C, the final pH value also increased. This means that increased amounts of $Mg(OH)_2$ and $Al(OH)_3$ participated in the reaction with increasing temperature, resulting in the production of more KOH. The BET surface area (S_{BET}) of K_2CO_3-promoted hydrotalcite decreased with increasing K_2CO_3/Al ratio. Furthermore, the BET surface areas of the promoted hydrotalcites were significantly lower than that of unpromoted hydrotalcite (~230 m^2 g^{-1}) because incorporated K_2CO_3 filled and blocked hydrotalcite pores.

The inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis shows that the Mg/Al ratio in the K_2CO_3-promoted hydrotalcite was slightly higher than that in the starting solution because unreacted $Mg(OH)_2$ remained in the sample. In contrast, the K/Al ratio in the K_2CO_3-promoted hydrotalcite was considerably smaller than that in the feed. This indicates that a large portion of K_2CO_3 was washed away in the filtering step. Consequently, there was a limit to the amounts of K_2CO_3 that were incorporated.

Figure 1 shows the scanning electron microscopy (SEM) images of the synthesized K_2CO_3-promoted hydrotalcite. A hexagonal plate-like structure developed in all the samples, and this morphology remained after calcination at 500 °C in a N_2 atmosphere. When the K/Al ratio in the feed was small, hexagonal plates were not fully developed because the amount of CO_3^{2-} anion was insufficient to facilitate the hexagonal plate morphology of hydrotalcite (Figure 1a). From the results, it can be concluded that the reaction temperature was an important factor that affected the development of hexagonal platelike morphology (Figure 1c–e). The sample synthesized at 130 °C did not show a well-developed structure, but those synthesized at 160 and 200 °C featured complete hexagonal plates. Wang et al. extensively studied morphology and crystallinity of hydrotalcites synthesized by the conventional co-precipitation method using nitrate-form precursors.[5] The hydrotalcites synthesized by the co-precipitation method showed nanoparticle aggregates or flowerlike morphology and the size of nanoparticle crystallite was around 30 nm. In the hydrotalcite

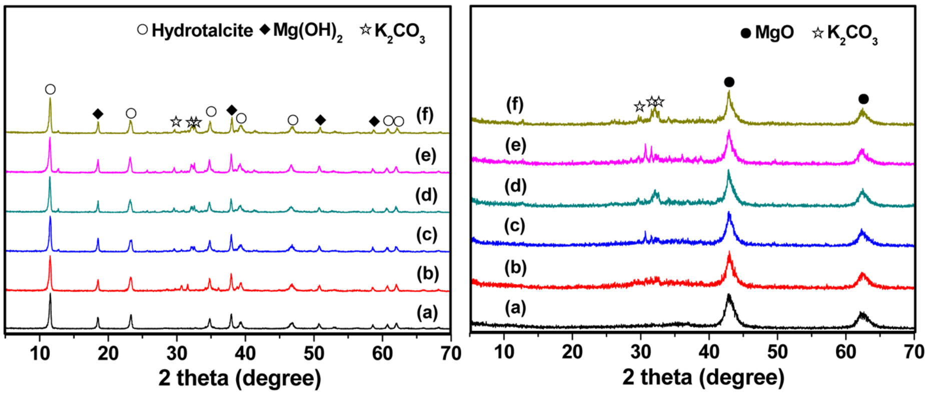

Figure 2. XRD patterns of K_2CO_3-promoted hydrotalcite (a) Mg:Al:K 3:1:1 [160 °C], (b) Mg:Al:K 3:1:2 [160 °C], (c) Mg:Al:K 3:1:6 [130 °C], (d) Mg:Al:K 3:1:6 [160 °C], (e) Mg:Al:K 3:1:6 [200 °C], (f) Mg:Al:K 3:1:10 [160 °C]. Left: before calcination; right: after calcination.

synthesized in this study, hexagonal platelike structure was well-developed and the crystallite size increased to several micrometers.

Figure 2 shows the X-ray powder diffraction (XRD) patterns of the synthesized K_2CO_3-promoted hydrotalcite. All samples had well-defined hydrotalcite crystalline and unreacted $Mg(OH)_2$ structures. This result indicates that only a limited amount of $Mg(OH)_2$ could participate in the reaction and development of hydrotalcite structure. When the Mg/Al ratio was 1 or 2 in the feed, the $Mg(OH)_2$ and $Al(OH)_3$ reactants were almost completely converted to hydrotalcite structure. In contrast, when the Mg/Al ratio increased to 3 or 5, all samples contained unreacted $Mg(OH)_2$ (Figure S1 in the Supporting Information). As the K/Al ratio increased from 1 to 10, the peak intensity of the K_2CO_3 phase became more distinct with increasing amount of co-precipitated K_2CO_3. The characteristic K_2CO_3 peaks in XRD patterns indicating the presence of separate K_2CO_3 from hydrotalcite also have been reported in other papers about K_2CO_3-promoted hydrotalcite.[1,8]

The degree of transformation (D_{trans}) was calculated using the deviations of the $Mg(OH)_2$ and hydrotalcite peak intensity ratios in the XRD spectra at their characteristic peak angles $2\theta = 38.0$ and 11.5°, respectively.[16] In Table 2, the evaluated relative contents of $Mg(OH)_2$ are presented. When the K/Al reactant ratio increased, large amounts of $Mg(OH)_2$ participated in the reaction. Interestingly, the hydrotalcite structure was better developed at 160 °C compared with its structure at either 130 or 200 °C; this XRD result agrees well with the highest pH change at 160 °C (Table 1). After calcination at 500 °C, all hydrotalcite and hydroxide phases were transformed into mixed oxide phases, and all the samples featured K_2CO_3 that did not decompose at 500 °C.

Table 2. Evaluation of Relative Contents of $Mg(OH)_2$ in K_2CO_3-Promoted Hydrotalcite Based on XRD Spectra

Mg:Al:K mole ratio in feed [synthesis temperature]	D_{trans}[a] (%)
3:1:1 [160 °C]	49.5
3:1:2 [160 °C]	50.4
3:1:6 [130 °C]	49.5
3:1:6 [160 °C]	37.6
3:1:6 [200 °C]	53.6
3:1:10 [160 °C]	36.4

[a] The degree of transformation of $Mg(OH)_2$ to hydrotalcite, $D_{trans} = I_{Mg(OH)_2}/I_{hydrotalcite}$.

The CO_2-sorption capacities of the K_2CO_3-promoted hydrotalcites were measured using thermogravimetric analysis (TGA) at 240 °C and ~1 bar CO_2 (Figure 3). The temperature of 240 °C was thought to be an appropriate condition for the sorption enhanced water gas shift reaction in which high-temperature CO_2 sorbents can be used.[17] For samples synthesized at 160 °C, when the K/Al ratio was increased from 1 to 6, the CO_2-sorption capacity increased from 0.85 to 1.31 mol kg^{-1}. However, when the K/Al ratio was further increased to 10, the sorption capacity decreased. This is probably caused by two conflicting effects: K_2CO_3 enhances the basicity of the samples, which helps to sorb acidic CO_2, but it can also fill and block pores to reduce the number of sorption sites. Consequently, the amount of incorporated K_2CO_3 has an optimum value for maximum CO_2 sorption. In our study, the Mg:Al:K optimum ratio in the reactants was 3:1:6, which corresponds to the ratio 3.4:1:1.28 obtained after the reaction at 160 °C. In the prepared K_2CO_3-promoted hydrotalcite having the maximum CO_2-sorption capacity, the fraction of K_2CO_3 is estimated at about 24 wt % and this value corresponds with the optimum K_2CO_3 ratio (22−35 wt %) reported in the literature.[1,8,18]

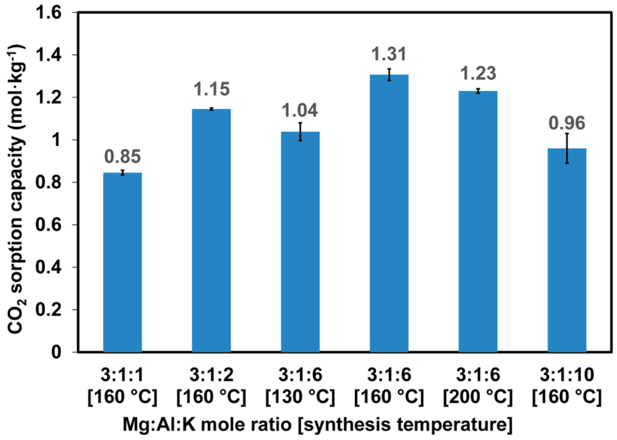

Figure 3. CO_2-sorption capacity of K_2CO_3-promoted hydrotalcite at ~1 bar CO_2 and 240 °C.

Figure 4 represents the CO_2-sorption capacity of K_2CO_3-promoted hydrotalcite at different temperatures between 240 and 500 °C. The tested K_2CO_3-promoted hydrotalcite was synthesized with the Mg:Al:K molar ratio of 3:1:6 and at the

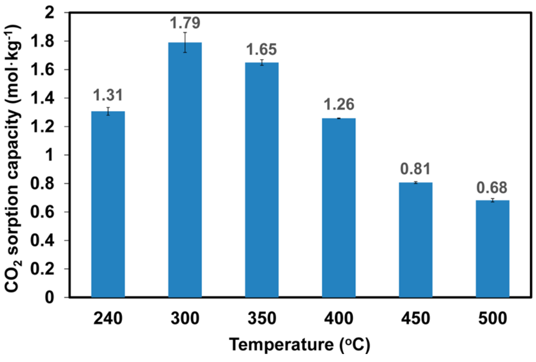

Figure 4. CO_2-sorption capacity of K_2CO_3-promoted hydrotalcite (Mg:Al:K 3:1:6, synthesized at 160 °C) at different temperatures and ~1 bar CO_2.

temperature of 160 °C. It is noticeable that the CO_2-sorption capacity of K_2CO_3-promoted hydrotalcite is maximum at the temperature of 300 °C, implying the occurrence of chemisorption and its value (1.79 mol kg^{-1}) is remarkably high. Table 3 compares the CO_2-sorption capacity of Mg–Al hydrotalcites at temperatures between 200 and 400 °C found in literature.[1,5,8,12,19−26] The CO_2-sorption capacity of the newly prepared K_2CO_3-promoted hydrotalcite is comparable with or higher than that of conventional hydrotalcites and previously reported K_2CO_3-promoted hydrotalcites under similar conditions.

Table 3. Comparison of CO_2-Sorption Capacities of Mg–Al Hydrotalcites at Temperatures between 200 and 400 °C Found in Literature

ref	sorption temperature (°C)	feeding composition and pressure	CO_2-sorption capacity (mol kg^{-1})	comments
5	200	pure CO_2, 1 atm	0.83	unpromoted
12	200 300	pure CO_2, 100 kPa	0.486 0.249	unpromoted
19	200 300	pure CO_2, 1 atm	0.41 0.212	unpromoted
20	200 300	pure CO_2, 1 bar	0.1 0.52	unpromoted
21	200 300 400	pure CO_2, 1 atm	1.2 1.25 1.15	unpromoted, intercalated with stearic acid
this work	240 300	pure CO_2, 1 bar	1.31 1.79	K_2CO_3-promoted
22	200	70% CO_2, 1 bar	1.4	K_2CO_3-promoted, Al partially substituted by Ga
23	300	30% CO_2, 1.34 bar	1.109	K_2CO_3/Na_2CO_3-promoted
24	300	1 bar CO_2	1.5	K_2CO_3-promoted
25	300 400	30% CO_2, 1.34 bar	1.25 1.08	K_2CO_3/Na_2CO_3-promoted
8	400	5.8% CO_2 and 10.7% H_2O, 1 bar	0.37 (reversible capacity)	K_2CO_3-promoted
1	400	pure CO_2, 1 bar	0.94	K_2CO_3-promoted
26	383	50% CO_2, 50% H_2O, 1 bar	1.13	KNO_3-promoted

Figure 5 shows the CO_2-sorption isotherm data for Mg:Al:K = 3:1:6 hydrotalcite synthesized at 160 °C. The isotherm data were measured at 240 and 500 °C. The experimental data in the range 0.05−1.0 bar of CO_2 partial pressure were fitted with Langmuir, Freundlich, and bi-Langmuir isotherm models. The fitting parameters of isotherm models are listed in Table S1 (see the Supporting Information). The bi-Langmuir isotherm model that is regarded to be adequate for the contribution of both physical and chemical sorption agrees well with experimental data.[26]

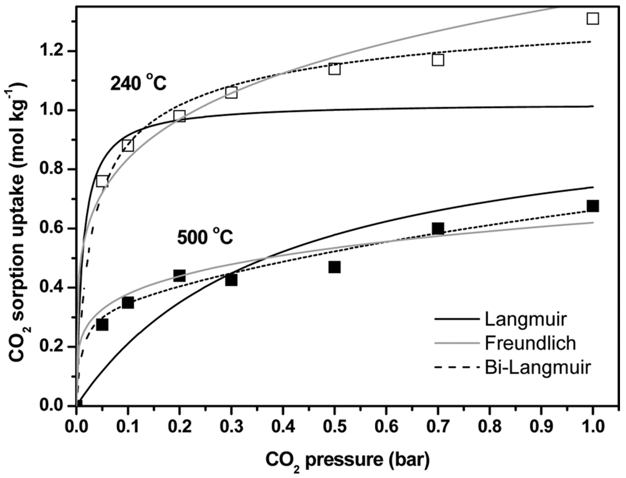

Figure 5. Sorption isotherm data of K_2CO_3-promoted hydrotalcite (Mg:Al:K 3:1:6, synthesized at 160 °C) at 240 and 500 °C.

The scheme of regeneration is also a crucial factor for practical application of sorption operation. The working capacity between 10 and 1 bar at 240 °C is very low for the K_2CO_3-promoted hydrotalcite (see Figure S2 in the Supporting Information), therefore a pressure swing adsorption scheme is not adequate for cyclic processes. From the sorption isotherm data at 240 and 500 °C (Figure 5), a temperature and pressure swing adsorption scheme is expected to be available for the sorption at 240 °C and 1 bar CO_2 pressure. In this aspect, a cyclic sorption/desorption test was carried out with sorption at 240 °C under CO_2 flow for 90 min and desorption at 500 °C under N_2 flow for 90 min (Figure 6). The CO_2-sorption capacity on the K_2CO_3-promoted hydrotalcite decreased initially and then became stabilized after three cycles. The regeneration of used K_2CO_3-promoted hydrotalcite could be achieved with a temperature and pressure swing adsorption

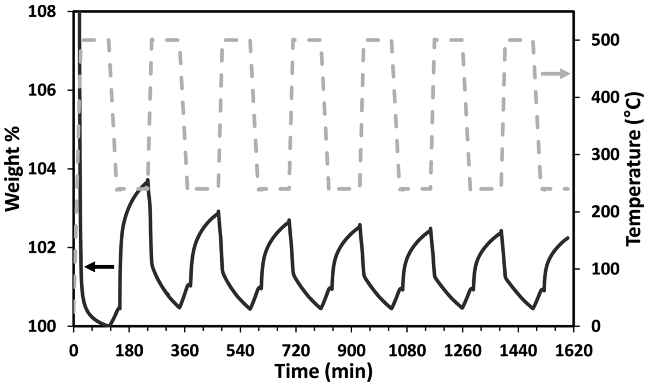

Figure 6. Cyclic sorption/desorption test for K_2CO_3-promoted hydrotalcite (Mg:Al:K 3:1:6, synthesized at 160 °C); condition: sorption at 240 °C under CO_2 flow, desorption at 500 °C under N_2 flow.

scheme but the stabilized CO_2-sorption capacity after three cycles was about 50% of that in the first cycle.

Figure 7 shows CO_2 breakthrough curves at 240 °C and three different pressures (0.5, 5, and 10 bar) from a column packed with ~1 g K_2CO_3-promoted hydrotalcite (Mg:Al:K 3:1:6, synthesized at 160 °C). The normalized concentration at the column outlet is plotted as a function of time. The inlet gas flow rate was fixed at 100 cm^3 STP min^{-1} with 50% CO_2 balanced with N_2. The CO_2-sorption kinetic was relatively fast and the outlet concentration reached inlet concentration within 10−15 min.

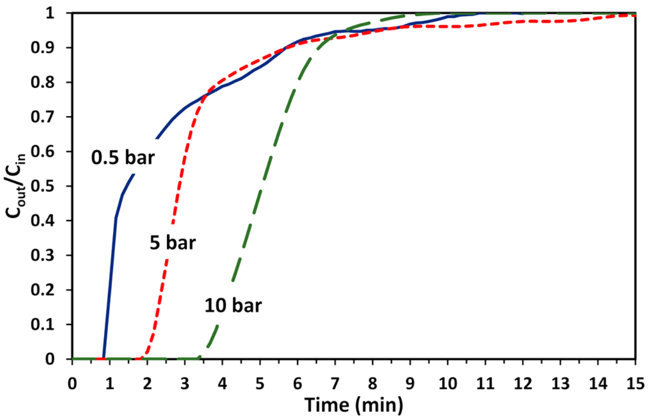

Figure 7. CO_2 breakthrough curves at 240 °C and different pressures from a column packed with K_2CO_3-promoted hydrotalcite (Mg:Al:K 3:1:6, synthesized at 160 °C).

CONCLUSIONS

We have developed a newly synthesized K_2CO_3-promoted hydrotalcite from hydroxide-form precursors for the development of a novel high-temperature CO_2 sorbent. The new synthesis method is simple and eliminates a washing step to reduce the amount of water required as solvent. The synthesized K_2CO_3-promoted hydrotalcite shows well-developed hexagonal plate-like structure and K_2CO_3 is successfully incorporated into hydrotalcite during the synthesis procedure. There is an optimal ratio of Mg:Al:K and synthesis temperature for the development of hydrotalcite structure and CO_2 sorption. The newly prepared K_2CO_3-promoted hydrotalcite of which Mg:Al:K molar ratio in reactants is 3:1:6 (3.4:1:1.28 in the synthesized product) and synthesis temperature is 160 °C shows highest CO_2-sorption capacity (1.31 mol kg^{-1}) at 240 °C among samples tested. The K_2CO_3-promoted hydrotalcite also has very high CO_2-sorption capacity (1.79 mol kg^{-1}) at 300 °C and relatively fast CO_2-sorption kinetics. However, the initial CO_2-sorption capacity decreases with cyclic sorption/desorption operation and the CO_2-sorption capacity becomes stabilized after three cycles to about 50% of the initial value.

EXPERIMENTAL SECTION

Synthesis of K_2CO_3-Promoted Hydrotalcite. Various synthetic methods have been successfully applied for the preparation of hydrotalcite. Among many synthesis methods such as co-precipitation, urea hydrolysis, reconstruction, and hydrothermal methods, hydrotalcite is commonly synthesized by a co-precipitation method.[27] In the co-precipitation method, hydrotalcite is synthesized from precipitation of two or more cations by mixing a solution containing metal ions with a basic solution for pH control and an alkali solution containing chemical species for interlayer anionic groups. The metal ion precursors are normally water-soluble nitrate forms. In the co-precipitation method, pH control is important and generally high pH between 8 and 10 is required to obtain hydrotalcite. Ionized magnesium and aluminum participate in a reaction to develop hydrotalcite structure and the reaction occurs easily at moderate temperature. Although hydrotalcite structure is easily developed, the co-precipitation method based on nitrate form precursors has some drawbacks. Basic solution such as NaOH or KOH should be carefully added to control the pH of solution. Moreover, a large quantity of water is used to wash produced precipitate because a large amount of nitrate ions and sodium or potassium salts are produced as by-products. The synthesized hydrotalcite is further impregnated with alkali metals (mostly potassium carbonate, K_2CO_3) to prepare promoted-hydrotalcite for enhanced CO_2 sorption.[8] In the procedure of impregnation, pristine hydrotalcite is soaked with K_2CO_3 solution and then dried at high temperature under vacuum. The soaking and drying procedure is repeated several times to facilitate the distribution of K_2CO_3 in the hydrotalcite. Finally, the sample is calcined at a high temperature of 400−550 °C.

In this study, to synthesize K_2CO_3-promoted hydrotalcite in a new simple method, 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). Figure S2 (see the Supporting Information) shows the SEM images of $Mg(OH)_2$ and $Al(OH)_3$ and the size distribution of particles estimated from the SEM images. $Mg(OH)_2$ has relatively large and irregular-shaped crystal structures, and its average particle size is 0.626 μm. The SEM image show that $Al(OH)_3$ agglomerates and forms small clusters and the agglomerated clusters have many cracks on their particle surface. The average particle size of $Al(OH)_3$ is 0.068 μm. All the reagents were used without further purification, and distilled water was used as the solvent for the synthesis procedure. The K_2CO_3-promoted hydrotalcite was synthesized by a hydrothermal method that is effective for $Mg(OH)_2$ and $Al(OH)_3$, because they have very small solubility product constants (K_{sp}) at room temperature.[28] Predetermined amounts of the reactants, $Mg(OH)_2$ (0.79 M), $Al(OH)_3$ (0.26 M), and K_2CO_3, were mixed with 30 mL of distilled water, and the initial pH of the mixture was measured. Then, the mixture was transferred to a 40 mL Teflon-lined stainless steel autoclave and hydrothermally reacted at 130−200 °C. The reaction was conducted for 24 h in an autoclave reactor at a stirring speed of 60 rpm, and the solution was quickly cooled after the reaction. Then, the final pH of the mother liquor was measured, after which the aged suspension was filtered through a filter paper with 1 μm pore diameter and dried at 110 °C for 24 h. Finally, the resulting white powder was calcined at 500 °C for 3 h under a N_2 atmosphere.

Characterization of Samples. The composition of synthesized K_2CO_3-promoted hydrotalcite was identified by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY2C, HOBIN YVON). Mg, Al and K concentration was measured. The morphology of samples was observed by field emission scanning electron microscopy (FESEM, S-4300, Hitachi). Because visualization of structural details of specimens in FESEM requires optimal conductivity, samples were coated by Pt ion using an ion sputter (E-1045, Hitachi) for 150 s. The structure of samples was identified by X-ray diffraction. The X-ray diffraction (XRD) patterns of samples were measured using a Rigaku X-ray diffractometer (Rigaku D/Max-2500 V) with Cu Kα radiation ($\lambda = 0.15418$ nm) and a power of 40 kV × 40 mA. The scan range was from 5° to 70° 2θ at a scanning rate of 4° min^{-1}. The crystalline phases were identified by comparison with JCPDS files.

CO_2 Sorption Measurement. Equilibrium CO_2-sorption uptakes on fresh K_2CO_3-promoted hydrotalcites were measured using thermogravimetric analysis (TGA, Q50, TA Instruments). Before the CO_2-sorption experiments would begin, moisture and CO_2 on the samples were removed by means of an N_2 gas flow at 500 °C. After pre-treatment, the change in the sample weight was recorded under the flow of pure CO_2 gas or mixture of CO_2 and N_2 at a pressure of ~1 bar and a temperature of 240−500 °C. In the cyclic CO_2 sorption/desorption test, the CO_2 sorption was measured at 240 °C and the sample was regenerated at 500 °C under N_2 flow after each CO_2 sorption step.

■ ASSOCIATED CONTENT

S Supporting Information

Additional XRD spectra data of K_2CO_3-promoted hydrotalcite, sorption isotherm data including high-pressure region at 240 °C, SEM images and particle size distribution of metal precursors, and fitting parameters of sorption isotherm models. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kibonglee@korea.ac.kr.

Author Contributions

†H.J.J. and C.H.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lee, J. M.; Min, Y. J.; Lee, K. B.; Jeon, S. G.; Na, J. G.; Ryu, H. J. Enhancement of CO_2 Sorption Uptake on Hydrotalcite by Impregnation with K_2CO_3. *Langmuir* **2010**, *26*, 18788−18797.

(2) Pérez, M. R.; Crespo, I.; Ulibarri, M. A.; Barriga, C.; Rives, V.; Fernández, J. M. Influence of Divalent Metal on the Decomposition Products of Hydrotalcite-Like Ternary Systems M^{II}−Al−Cr (M^{II} = Zn, Cd). *Mater. Chem. Phys.* **2012**, *132*, 375−386.

(3) Yong, Z.; Rodrigues, A. E. Hydrotalcite-Like Compounds as Adsorbents for Carbon Dioxide. *Energy Convers. Manage.* **2002**, *43*, 1865−1876.

(4) Wang, Q.; Wu, Z.; Tay, H. H.; Chen, L.; Liu, Y.; Chang, J.; Zhong, Z.; Luo, J.; Borgna, A. High Temperature Adsorption of CO_2 on Mg−Al Hydrotalcite: Effect of the Charge Compensating Anions and the Synthesis pH. *Catal. Today* **2011**, *164*, 198−203.

(5) Wang, Q.; Tay, H. H.; Guo, Z.; Chen, L.; Liu, Y.; Chang, J.; Zhong, Z.; Luo, J.; Borgna, A. Morphology and Composition Controllable Synthesis of Mg−Al−CO_3 Hydrotalcites by Tuning the Synthesis pH and the CO_2 Capture Capacity. *Appl. Clay. Sci.* **2012**, *55*, 18−26.

(6) Ding, Y.; Alpay, E. Equilibria and Kinetics of CO_2 Adsorption on Hydrotalcite Adsorbent. *Chem. Eng. Sci.* **2000**, *55*, 3461−3474.

(7) Lee, K. B.; Verdooren, A.; Caram, H. S.; Sircar, S. Chemisorption of Carbon Dioxide on Potassium-Carbonate-Promoted Hydrotalcite. *J. Colloid Interface Sci.* **2007**, *308*, 30−39.

(8) Walspurger, S.; Boels, L.; Cobden, P. D.; Elzinga, G. D.; Haije, W. G.; van den Brink, R. W. The Crucial Role of the K^+−Aluminium Oxide Interaction in K^+-Promoted Alumina- and Hydrotalcite-Based Materials for CO_2 Sorption at High Temperatures. *ChemSusChem* **2008**, *1*, 643−650.

(9) Halabi, M. H.; de Croon, M. H. J. M.; van der Schaaf, J.; Cobden, P. D.; Schouten, J. C. High Capacity Potassium-Promoted Hydrotalcite for CO_2 Capture in H_2 Production. *Int. J. Hydrogen Energy* **2012**, *37*, 4516−4525.

(10) Yang, J.-I.; Kim, J.-N. Hydrotalcites for Adsorption of CO_2 at High Temperature. *Korean J. Chem. Eng.* **2006**, *23*, 77−80.

(11) Hutson, N. D.; Speakman, S. A.; Payzant, E. A. Structural Effects on the High Temperature Adsorption of CO_2 on a Synthetic Hydrotalcite. *Chem. Mater.* **2004**, *16*, 4135−4143.

(12) Ram Reddy, M. K.; Xu, Z. P.; Lu, G. Q.; Diniz da Costa, J. C. Layered Double Hydroxides for CO_2 Capture: Structure Evolution and Regeneration. *Ind. Eng. Chem. Res.* **2006**, *45*, 7504−7509.

(13) Zeng, S.; Xu, X.; Wang, S.; Gong, Q.; Liu, R.; Yu, Y. Sand Flower Layered Double Hydroxides Synthesized by Co-Precipitation for CO_2 Capture: Morphology Evolution Mechanism, Agitation Effect and Stability. *Mater. Chem. Phys.* **2013**, *140*, 159−167.

(14) Othman, M. R.; Helwani, Z.; Martunus; Fernando, W. J. N. Synthetic Hydrotalcites from Different Routes and Their Application as Catalysts and Gas Adsorbents: A Review. *Appl. Organometal. Chem.* **2009**, *23*, 335−346.

(15) Xu, X.; Li, D.; Song, J.; Lin, Y.; Lv, Z.; Wei, M.; Duan, X. Synthesis of Mg−Al−Carbonate Layered Double Hydroxide by an Atom-Economic Reaction. *Particuology* **2010**, *8*, 198−201.

(16) Zhang, Z.; Chen, G.; Xu, K. One-Pot Green Hydrothermal Synthesis of Stearate-Intercalated MgAl Layered Double Hydroxides. *Appl. Clay Sci.* **2013**, *72*, 206−210.

(17) Lee, K. B.; Beaver, M. G.; Caram, H. S.; Sircar, S. Reversible Chemisorbents for Carbon Dioxide and Their Potential Applications. *Ind. Eng. Chem. Res.* **2008**, *47*, 8048−8062.

(18) Meis, N. N. A. H.; Bitter, J. H.; de Jong, K. P. On the Influence and Role of Alkali Metals on Supported and Unsupported Activated Hydrotalcites for CO_2 Sorption. *Ind. Eng. Chem. Res.* **2010**, *49*, 8086−8093.

(19) Wang, Q.; Tay, H. H.; Ng, D. J. W.; Chen, L.; Liu, Y.; Chang, J.; Zhong, Z.; Luo, J.; Borgna, A. The Effect of Trivalent Cations on the Performance of Mg-M-CO_3 Layered Double Hydroxides for High-Temperature CO_2 Capture. *ChemSusChem* **2010**, *3*, 965−973.

(20) Yong, Z.; Mata, V.; Rodrigues, A. E. Adsorption of Carbon Dioxide onto Hydrotalcite-Like Compounds (HTlcs) at High Temperatures. *Ind. Eng. Chem. Res.* **2001**, *40*, 204−209.

(21) Wang, Q.; Tay, H. H.; Zhong, Z.; Luo, J.; Borgna, A. Synthesis of High-Temperature CO_2 Adsorbents from Organo-Layered Double Hydroxides with Markedly Improved CO_2 Capture Capacity. *Energy Environ. Sci.* **2012**, *5*, 7526−7530.

(22) Yavuz, C. T.; Shinall, B. D.; Iretskii, A. V.; White, M. G.; Golden, T.; Atilhan, M.; Ford, P. C.; Stucky, G. D. Markedly Improved CO_2 Capture Efficiency and Stability of Gallium Substituted Hydrotalcites at Elevated Temperatures. *Chem. Mater.* **2009**, *21*, 3473−3475.

(23) Helwani, Z.; Wiheeb, A. D.; Kim, J.; Othman, M. R. Improved Carbon Dioxide Capture Using Metal Reinforced Hydrotalcite Under Wet Conditions. *Int. J. Greenhouse Gas Control* **2012**, *7*, 127−136.

(24) Hanif, A.; Dasgupta, S.; Divekar, S.; Arya, A.; Garg, M. O.; Nanoti, A. A Study on High Temperature CO_2 Capture by Improved Hydrotalcite Sorbents. *Chem. Eng. J.* **2014**, *236*, 91−99.

(25) Othman, M. R.; Fernando, W. J. N. Elevated Temperature Carbon Dioxide Capture via Reinforced Metal Hydrotalcite. *Microporous Mesoporous Mater.* **2011**, *138*, 110−117.

(26) Wu, Y.-J.; Li, P.; Yu, J.-G.; Cunha, A. F.; Rodrigues, A. E. K-Promoted Hydrotalcites for CO_2 Capture in Sorption Enhanced Reactions. *Chem. Eng. Technol.* **2013**, *36*, 567−574.

(27) Cavani, F.; Trifirò, F.; Vaccari, A. Hydrotalcite-Type Anionic Clays: Preparation, Properties and Applications. *Catal. Today* **1991**, *11*, 173−301.

(28) Boclair, J. W.; Braterman, P. S. Layered Double Hydroxide Stability. 1. Relative Stabilities of Layered Double Hydroxides and Their Simple Counterparts. *Chem. Mater.* **1999**, *11*, 298−302.