High-temperature CO_2 sorption on Na_2CO_3-impregnated layered double hydroxides

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Abstract−Layered double hydroxide (LDH), one of representative high-temperature CO_2 sorbents, has many advantages, including stable CO_2 sorption, fast sorption kinetics, and low regeneration temperature. However, CO_2 sorption uptake on LDH is not high enough for practical use; thus it is usually enhanced by impregnation with alkali metals such as K_2CO_3. In this study, LDH was impregnated with Na_2CO_3, and analyses based on scanning electron microscopy, N_2 gas physisorption, *in situ* X-ray diffraction, and Fourier transform infrared spectroscopy were carried out to elucidate the characteristics of sorbents and the mechanism of CO_2 sorption. Although the surface area of LDH decreased after Na_2CO_3 impregnation, CO_2 sorption uptake was greatly enhanced by the additional basicity of Na_2CO_3. The crystal structure of Na_2CO_3 in the Na_2CO_3-impregnated LDH changed from monoclinic to hexagonal with increasing temperature, and the sorbed-CO_2 was stored in the form of carbonate. Thermogravimetric analysis was used to measure CO_2 sorption uptake at 200-600 °C. The sample of Na_2CO_3 : LDH=0.35 : 1 weight ratio had the largest CO_2 sorption uptake among the tested sorbents, and the CO_2 sorption uptake tended to increase even after 400 °C.

Keywords: Layered Double Hydroxide, Na_2CO_3, CO_2 Sorption, High Temperature

INTRODUCTION

Global warming is accelerating, and abnormal weather patterns are occurring more frequently due to the increase of atmospheric greenhouse gases, which are mainly caused by the use of fossil fuels. With the increased awareness of the problem, global leaders are holding regular United Nations Framework Convention on Climate Change conferences and exerting much effort in various areas such as politics, economics, and technology to reduce greenhouse gas emissions [1,2]. Reduction of carbon dioxide (CO_2) emissions is the main issue in this regard, because CO_2 is the primary greenhouse gas. CO_2 emissions account for more than 70% of the total amount of greenhouse gases emitted to the atmosphere. Related studies are aimed at developing efficient CO_2 capture and sequestration (CCS) technologies and for paving the way for their commercialization [3,4]. In terms of the cost of CCS, CO_2 capture occupies the main portion; therefore, the success of CCS projects depends on the development of efficient CO_2 capture methods [5].

Among various CO_2 capture methods, adsorption is drawing attention as a promising technology. Adsorption utilizes environmentally benign reusable sorbents, requires relatively low energy, and can easily be scaled up to large processes [6]. Various materials such as zeolite, activated carbon, and alumina, which are inexpensive and have high adsorption capabilities, have been developed for use in CO_2 adsorption [7-9]. As these materials lose all or part of their ad-

sorption capacity at high temperatures, other sorbents must be developed for high-temperature use. A few high-temperature CO_2 sorbents have been developed based on calcium oxide or lithium zirconate. They have a high CO_2 sorption uptake up to 10 mol/kg at temperatures above 600 °C, but their disadvantages include thermal and cyclic instability, slow sorption kinetics, and requirement of high thermal energy for regeneration at 700-900 °C [10-15]. As an alternative high-temperature sorbent to overcome these disadvantages, layered double hydroxide (LDH or hydrotalcite) is receiving more and more interest [16].

LDH is a solid-state inorganic material composed of brucite layers, which are formed through the combination of M^{2+}, M^{3+} cations, hydroxide groups, and anions such as CO_3^{2-}, HCO_3^-, Cl^-, and NO_3^{2-} between the layers [17]. Above 400 °C, the basic sites of LDH become active for CO_2 sorption as the M^{2+} and M^{3+} cations are converted to metal oxides through calcination and the anions in the interlayer are decomposed [18]. Some of the advantages of LDH are fast sorption kinetics, low regeneration temperature, and good stability for continuous sorption processes [19-21]. Thus, the use of LDH has been examined in the process of direct CO_2 capture from hot flue gases or as a CO_2 sorbent for sorption-enhanced reactions to produce high-purity hydrogen [22,23]. However, LDH does not exhibit sufficient CO_2 sorption uptake for practical use, and therefore, there have been many efforts to increase the CO_2 sorption uptake of LDHs. Wang et al. compared the CO_2 sorption performance of LDHs containing different cations at high temperatures and found that Mg-Al-CO_3 LDH had the greatest CO_2 sorption uptake [24]. For the enhancement of CO_2 sorption uptake on LDH, impregnation with alkali metals has been employed. Yang et al. compared the CO_2 sorption uptake on Mg-Al LDHs impregnated with different amounts of K_2CO_3 and found that the CO_2 sorption uptake on LDH could be increased with K_2CO_3 loading and there was an optimal

K_2CO_3 loading amount for the maximum CO_2 sorption uptake [25]. Lee et al. also investigated the mechanism of CO_2 sorption enhancement on K_2CO_3-impregnated LDH based on various analyses [26]. However, most attempts to enhance CO_2 sorption uptake on LDH have focused on the use of K_2CO_3. As the physical and chemical characteristics of sodium carbonate (Na_2CO_3) are similar to those of K_2CO_3, and because Na_2CO_3 is inexpensive, it has the potential to be used for LDH to increase the CO_2 sorption uptake.

In this study, Mg-Al LDH, which has been widely studied as a high-temperature CO_2 sorbent among various LDHs, was impregnated with Na_2CO_3 and its CO_2 sorption performance and characteristics were analyzed. CO_2 sorption uptake was measured via thermogravimetric analysis. The morphology, surface characteristics, and structure of the sorbents were analyzed by scanning electron microscopy (SEM), N_2 gas physisorption, *in situ* X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR).

EXPERIMENTAL SECTION

1. Samples and Reagents

Three kinds of LDHs (MG30, MG50, and MG70; the number represents the ratio of MgO) were provided by Sasol Germany, GmbH. The LDHs were tested without any other modification (represented as pristine LDH) or further impregnated with sodium carbonate (Na_2CO_3,

≥99%, Sigma-Aldrich). In the procedure of impregnation, pristine LDH was soaked with a Na_2CO_3 solution and then dried at 110 °C under vacuum. The soaking and drying procedure was repeated several times to facilitate the distribution of Na_2CO_3 in the LDH. Finally, the samples were calcined in static air at 550 °C for 6 h. Pristine LDHs were also used after calcination in static air at 550 °C for 6 h (represented as calcined LDH).

2. Characterization

The Brunauer-Emmett-Teller (BET) surface area, pore size, and pore volume of the samples were determined from the data of N_2 gas physisorption at −196 °C using a BELSORP-max system (Bel Japan, Inc.). Each sample was degassed under vacuum (<10^{-1} Pa) at 200 °C for 3 h prior to N_2 physisorption. Particle morphology and textural description of the samples were observed by scanning electron microscope (SEM) images, which were taken by a Hitachi S-4300 (Hitachi, Japan) coupled with an energy-dispersive X-ray (EDX) spectroscope Horiba EX-200 (Horiba, Japan). EDX analysis was used to identify the elemental composition of samples. Fourier transform infrared (FT-IR) spectra of samples were recorded from 4,000 to 400 cm^{-1} at a spectral resolution of 4.0 cm^{-1} using the KBr technique on a Varian 660-IR spectrophotometer. A total of 128 scans were taken at room temperature. The *in situ* X-ray diffraction (*in situ* XRD) patterns of samples were recorded on a Rigaku X-ray diffractometer (Rigaku D/MAX-III C) with Cu Kα radiation oper-
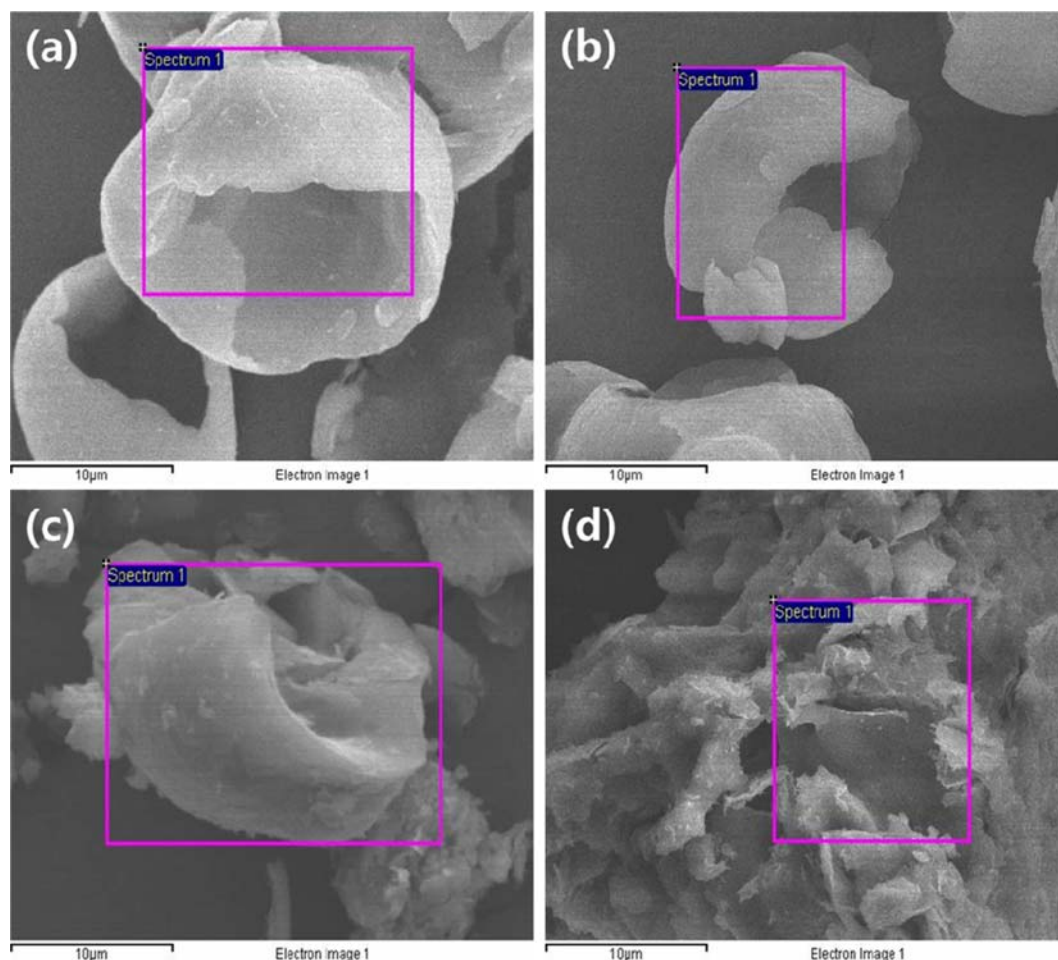

Fig. 1. SEM images of (a) pristine LDH MG70, (b) calcined LDH MG70, and (c) and (d) Na₂CO₃-impregnated LDH MG70.

ated at 40 kV and 100 mA. The scan range was from 10° to 80° (2θ). XRD analysis can identify crystal structures.

3. CO_2 Sorption

Equilibrium CO_2 sorption uptakes on LDHs were measured with a thermogravimetric analyzer (TGA, Q50, TA Instruments). Before the CO_2 sorption experiments began, moisture and CO_2 on the samples were removed by means of an N_2 gas flow at 600 °C for 8 h. After pre-treatment, the change in the sample weight was recorded under the flow of ~50% CO_2 balanced by N_2 at a pressure of ~1 atm and a temperature of 200-600 °C.

RESULTS AND DISCUSSION

1. Characterization of Na_2CO_3-impregnated Mg-Al LDH

Fig. 1 shows the SEM images of pristine and calcined LDH MG70 and Na_2CO_3-impregnated LDH MG70. Na_2CO_3-impregnated LDH MG70 contains 0.35 g of Na_2CO_3 per 1 g of LDH MG70. If not mentioned otherwise, the ratio of Na_2CO_3 and LDH was kept at 0.35 : 1 for the Na_2CO_3-impregnated LDHs. Large spherical particles with thin film and empty inner space appeared in LDH (Fig. 1(a)). The surfaces became smoother after calcination, but no significant changes occurred in the morphology (Fig. 1(b)). After impregnation with Na_2CO_3, the films were indented and the surfaces became rough (Fig. 1(c)). Moreover, some of the other particles had rugged morphologies because of excess Na_2CO_3 that attached to the LDH surfaces (Fig. 1(d)). Table 1 shows the results of the EDX analysis of the inside of the red rectangles in Fig. 1. The Mg : Al atomic ratio of the samples was maintained at about 3 : 1. For the pristine LDH, the C : O atomic ratio was high at 1 : 3.9 when the carbonate base existed in the interlayer, but it decreased to 1 : 1.5 after calcination due to the decomposition of the carbonate group. In the case of the Na_2CO_3-impregnated LDH, the C : O atomic ratio was comparatively high at 1 : 2.7-2.9 even after calcination due to the carbonate

group included in Na_2CO_3. The Na element in Na_2CO_3-impregnated LDH was measured at 5.5-31.91 wt%, which was in a wide range depending on the analysis location. This result indicates that some Na_2CO_3 might exist in a bulk phase after impregnation.

Table 2 shows the surface areas, pore sizes, and pore volumes of pristine/calcined LDH MG70 and LDH MG70 impregnated with Na_2CO_3 at various weight ratios. Pristine LDH MG70 had a relatively low surface area of 63.9 m^2/g, but after calcination, its surface area increased to 215.2 m^2/g due to the decomposition of the anions in the interlayer and the activation of openings. The average pore size decreased, while the total pore volume increased as micropores were activated by the calcination. In the case of Na_2CO_3-impregnated LDHs, the surface area and total pore volume were reduced in correspondence to an increase in the amount of Na impregnated on the LDH, because Na_2CO_3 particles blocked the pores of the LDH. The pore blockage appeared more significant in micropores because the average pore diameter increased with an increase in the amount of Na_2CO_3 that was impregnated.

TGA analyses were performed to determine the thermal stability of Na_2CO_3, pristine LDH MG70, and Na_2CO_3-impregnated LDH MG70 (Fig. 2). The weight decreased during the initial heating up to 200 °C because the moisture on the surface and water of hydration in the interlayers evaporated [27]. Na_2CO_3 maintained its weight up to a temperature of 900 °C, and then, it slowly lost its weight as Na_2CO_3 started melting [28]. The weight of pristine LDH MG70 was reduced by as much as 16% when heated to 200 °C because it contained much water on the surface and in the interlayer. An additional weight reduction of 27% was observed when the LDH was heated to 500 °C due to the decomposition of the carbonate group in the interlayers. In the Na_2CO_3-impregnated LDH MG70, there was only a slight reduction of the weight when heated up to 200 °C as it contained a little water on the surface and in the interlayer due to the calcination in the previous process. The weight slowly de-

Table 1. Chemical composition of pristine LDH MG70, calcined LDH MG70, and Na_2CO_3-impregnated LDH MG70 from EDX analysis

| Elements | Pristine LDH (a) | | Calcined LDH (b) | | Na_2CO_3-impregnated LDH | | | |
| | | | | | (c) | | (d)* | |
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	15.73	21.60	26.30	36.20	16.12	23.51	15.66	22.44
O	61.31	63.20	40.41	41.77	43.92	48.10	45.37	48.81
Mg	17.43	11.82	24.27	16.50	25.57	18.43	5.22	3.70
Al	5.54	3.39	9.02	5.53	8.90	5.78	1.84	1.17
Na	0	0	0	0	5.50	4.19	31.91	23.88
Mg : Al	75.9 : 24.1	77.7 : 22.3	72.9 : 27.1	74.9 : 25.1	74.2 : 25.8	76.1 : 23.9	73.9 : 26.1	76.0 : 24.0

* (a), (b), (c), and (d) correspond with the samples in Fig. 1

Table 2. Surface area and porosity of pristine/calcined LDH and Na_2CO_3-impregnated LDHs

| | Pristine LDH MG70 | Calcined LDH MG70 | Na_2CO_3-impregnated LDH MG70 | | |
			0.1 : 1	0.35 : 1	1 : 1*
BET surface area (m^2/g)	63.9	215.2	38.7	19.4	6.7
Average pore diameter (nm)	10.9	5.1	12.8	14.30	20.5
Total pore volume (cm^3/g)	0.22	0.27	0.15	0.08	0.04

* 0.1 : 1, 0.35 : 1, and 1 : 1 indicate the weight ratio of Na_2CO_3 : LDH
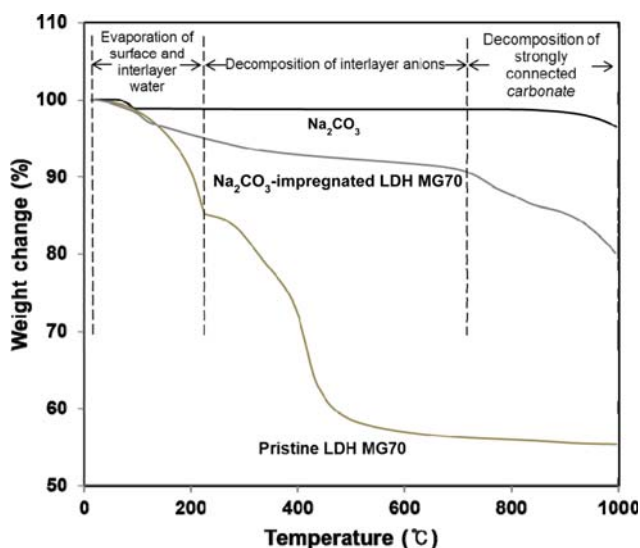
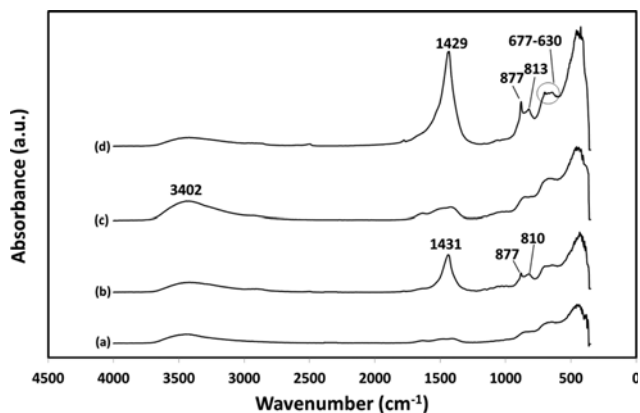Fig. 2. TGA analyses of Na₂CO₃, pristine LDH, and Na₂CO₃-impregnated LDH.

Fig. 3. FT-IR spectra of (a) cleaned LDH MG70, (b) CO₂-sorbed LDH MG70, (c) cleaned Na₂CO₃-impregnated LDH MG70, and (d) CO₂-sorbed Na₂CO₃-impregnated LDH MG70.

Fig. 4. *In situ* XRD spectra at different temperatures for Na₂CO₃-impregnated LDH MG70 in the flow of N₂.

creased when heated up to 700 °C because of the decomposition of much of the carbonate in the interlayers. After that, weight reduction was observed in two steps; the first step was deemed to happen when the carbonate in Na₂CO₃ and that strongly combined in the LDH decomposed together, and the second step is considered to correspond to the melting of Na₂CO₃.

Fig. 3 shows the FT-IR spectra of the cleaned or CO₂-sorbed LDH MG70 and Na₂CO₃-impregnated LDH MG70. The cleaned samples were prepared by purging with N₂ gas at a temperature of 600 °C for 8 h to remove impurities such as water and CO₂. The samples were then cooled to room temperature while the N₂ gas purge was maintained. The CO₂-sorbed samples were obtained after being cleaned at 600 °C for 8 h with N₂ flow, cooled to 400 °C, exposed to a pure CO₂ stream at 400 °C for 9 h, and then cooled to room temperature while the CO₂ gas stream was maintained. The broad peak around 3,400 cm⁻¹, which appeared in all the samples, indicated a bending vibration of the H-bond in the hydroxyl groups in the brucite-like layers [29]. The 677-630 cm⁻¹ area was the characteristic vibration of metal oxides, Mg-O and Al-O [30]. The broad band between
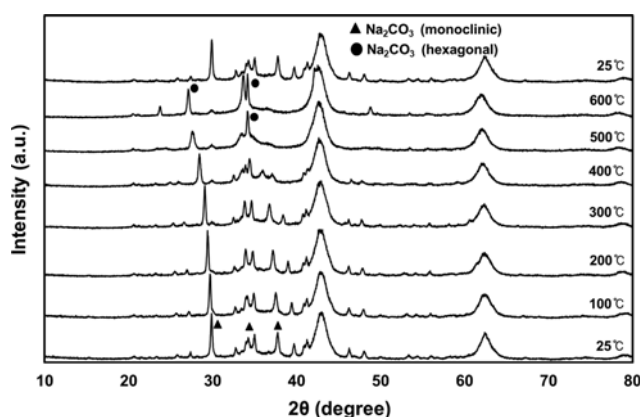
1,600 and 1,400 cm⁻¹ that appeared in the cleaned LDH and Na₂CO₃-impregnated LDH corresponded to the IR absorption spectrum for bidentate carbonate and bicarbonate. The single sharp peak in this area confirmed that an asymmetric O-C-O stretching mode occurred when CO₂ was sorbed on LDH (Fig. 3(b) and 3(d)) [31]. Moreover, new spectra appeared at 877 and 810 cm⁻¹ in the CO₂-sorbed LDH, and these confirmed the formation of the covalent carbonate [29]. No significant change was observed in the chemical bond after the impregnation with Na₂CO₃ (Fig. 3(c)). In the CO₂-sorbed Na₂CO₃-impregnated LDH, the single peak for O-C-O stretching became sharper at 1,429 cm⁻¹, and the intensity of the peaks for covalent carbonate 877-813 cm⁻¹ became stronger. These results demonstrated that more CO₂ was sorbed in the forms of unidentate and covalent carbonate in the Na₂CO₃-impregnated LDH.

Fig. 4 shows the changes in the crystal structure of the Na₂CO₃-impregnated LDH sample in the flow of N₂ in a temperature range of 25-600 °C. Similar XRD spectra were observed for the Na₂CO₃-impregnated LDH in the flow of CO₂ (data not shown). The large and broad peaks observed at 40-45° and 60-65° were the (400) and (440) reflections of amorphous MgO structure with d=0.209 and 0.148 nm, respectively, and these XRD spectra were found not to change noticeably with temperature change [32]. The spectra denoted with a triangle at temperatures of 25-400 °C were the characteristic peaks of monoclinic Na₂CO₃. Na₂CO₃ maintained a monoclinic form up to 400 °C, changed into a hexagonal form over 500 °C, and completely converted to a hexagonal structure at 600 °C [33]. When the sample was cooled to 25 °C, the XRD spectrum was observed to return to its original pattern, implying that the crystal structure of Na₂CO₃ in LDH can be recovered.

2. CO₂ Sorption Uptake on Na₂CO₃-impregnated LDH

Fig. 5 compares the CO₂ sorption uptakes at 400 °C on the calcined LDH MG70 and LDH MG70 impregnated with Na₂CO₃ at various weight ratios. Calcined LDH showed a low CO₂ sorption uptake of 0.14 mmol/g sorbent, but its CO₂ sorption uptake increased considerably to 0.48 mmol/g sorbent with the slight addition of Na₂CO₃ (at a weight ratio of Na₂CO₃ : LDH=0.1 : 1), and it reached a maximum of 0.68 mmol/g sorbent at a weight ratio of Na₂CO₃ : LDH=0.35 : 1. The CO₂ sorption uptake, however, was reduced upon further addition of Na₂CO₃ at a weight ratio of Na₂CO₃ : LDH =1 : 1, signifying that there is an optimum Na₂CO₃ amount for im-
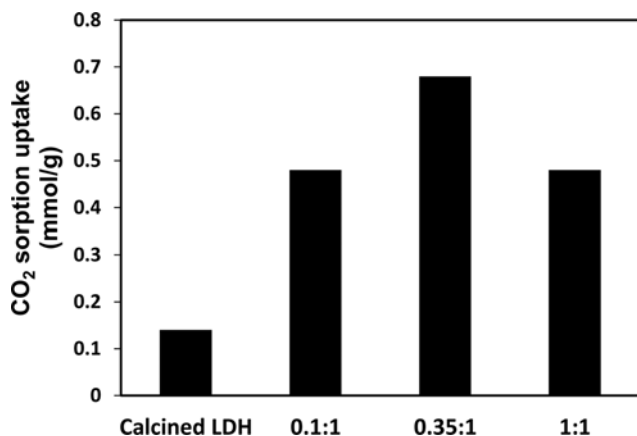
Fig. 5. CO_2 sorption uptake at 400 °C on calcined LDH MG70 and Na$_2$CO$_3$-impregnated LDH MG70 with various weight ratios of Na$_2$CO$_3$: LDH.
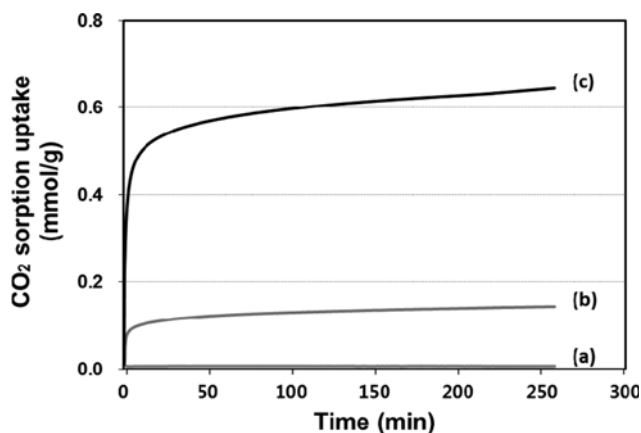

Fig. 7. CO_2 sorption isotherm of Na$_2$CO$_3$-impregnated LDH MG70 measured at 400 °C.

Fig. 6. CO_2 sorption kinetics at 400 °C on (a) Na$_2$CO$_3$, (b) calcined LDH MG70, and (c) Na$_2$CO$_3$-impregnated LDH MG70.
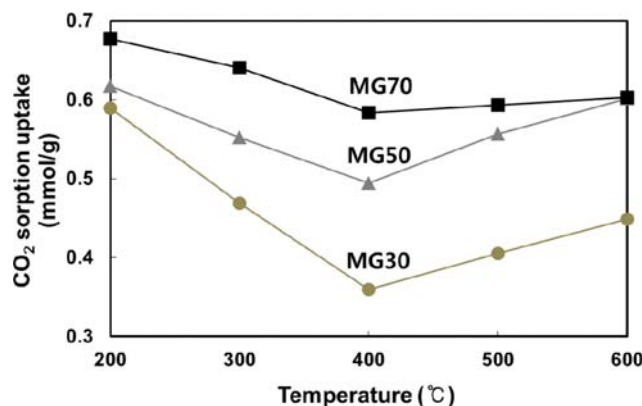
Fig. 8. Effect of temperature on the CO_2 sorption uptake of Na$_2$CO$_3$-impregnated LDHs.

pregnation. This is thought to be caused by two conflicting effects: increasing basicity and reducing surface area with an increase in the Na$_2$CO$_3$ content (Table 2).

In sorption processes, fast sorption kinetics is as important as high sorption capacity. The change of CO_2 sorption uptake with time was tested using a thermogravimetric analysis for Na$_2$CO$_3$, calcined LDH MG70, and Na$_2$CO$_3$-impregnated LDH as shown in Fig. 6. In the experiments, the change of sample weight was continuously recorded with CO_2 gas flow at the temperature of 400 °C and the pressure of ~1 atm. For both calcined LDH MG70 and Na$_2$CO$_3$-impregnated LDH MG70, CO_2 sorption uptake initially increased fast and then approached an equilibrium value. The thermogravimetric analysis showed that Na$_2$CO$_3$ itself had practically no sorption ability for CO_2 gas.

Fig. 7 shows the CO_2 sorption isotherm of the Na$_2$CO$_3$-impregnated LDH MG70 measured at 400 °C. The equilibrium sorption uptake sharply increased in the low pressure region and then approached a maximum value with increasing CO_2 partial pressure, which corresponds to the type I isotherm according to the IUPAC classification.

Fig. 8 represents the CO_2 sorption uptake of Na$_2$CO$_3$-impregnated LDHs at different temperatures between 200 and 600 °C. The Na$_2$CO$_3$-
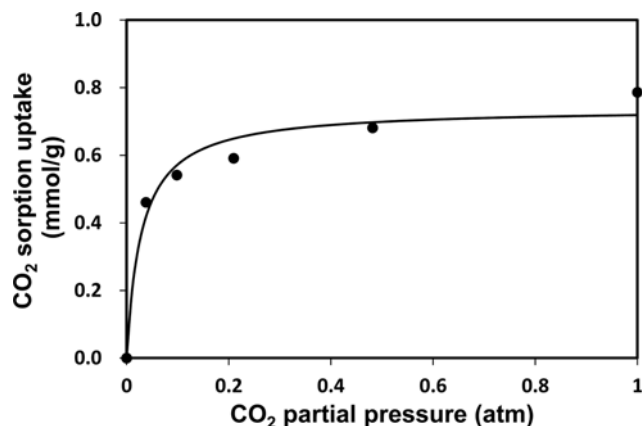
impregnated LDH MG70 showed higher CO_2 sorption uptake than other samples over the entire temperature range, and all the samples showed maximum CO_2 sorption uptake at 200 °C. The CO_2 sorption uptake decreased as temperature increased from 200 to 400 °C, which is the general pattern of exothermic sorption. However, between 400 and 600 °C, the CO_2 sorption uptake increased with increasing temperature, implying the occurrence of chemisorption. This is probably caused by the change in the Na$_2$CO$_3$ structure in the LDH with temperature. Na$_2$CO$_3$ was mainly in the monoclinic form until 400 °C, but hexagonal Na$_2$CO$_3$ became predominant over 400 °C (Fig. 4). The hexagonal Na$_2$CO$_3$ is thought to have a higher affinity to CO_2, resulting in the increased CO_2 sorption uptake even at high temperatures.

CONCLUSIONS

The high-temperature CO_2 sorption uptake on LDHs could be enhanced by impregnation with Na$_2$CO$_3$. There was an optimal amount of Na$_2$CO$_3$ for a maximum CO_2 sorption uptake, which resulted from two conflicting effects: increasing basicity and decreasing surface area with increasing amount of Na$_2$CO$_3$. Among three LDHs (MG30, MG50, and MG70) having different ratio of magnesium, Na$_2$CO$_3$-impregnated MG70 showed higher CO_2 sorption uptake than other samples, implying that the CO_2 sorption uptake increased with in-

creasing content of magnesium in the Na_2CO_3-impregnated LDHs. With increasing temperature, the CO_2 sorption uptake on Na_2CO_3-impregnated LDHs decreased in the temperature range of 200-400 °C but increased in the temperature range of 400-600 °C. This unique high-temperature CO_2 chemisorption behavior can be related to the change of Na_2CO_3 phase in LDHs from monoclinic to hexagonal with increasing temperature. Also, the FT-IR analysis showed that the sorbed CO_2 was stored in the form of carbonate in the Na_2CO_3-impregnated LDHs.

ACKNOWLEDGEMENTS

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