

## High-temperature CO<sub>2</sub> sorption on Na<sub>2</sub>CO<sub>3</sub>-impregnated layered double hydroxides

Yoon Jae Min<sup>\*,‡</sup>, Seok-Min Hong<sup>\*,‡</sup>, Sung Hyun Kim<sup>\*</sup>, Ki Bong Lee<sup>\*,†</sup>, and Sang Goo Jeon<sup>\*\*</sup>

<sup>\*</sup>Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-713, Korea

<sup>\*\*</sup>High Efficiency and Clean Energy Research Division, Korea Institute of Energy Research,  
152, Gajeong-ro, Yuseong-gu, Daejeon 305-343, Korea

(Received 18 March 2014 • accepted 16 April 2014)

**Abstract**—Layered double hydroxide (LDH), one of representative high-temperature CO<sub>2</sub> sorbents, has many advantages, including stable CO<sub>2</sub> sorption, fast sorption kinetics, and low regeneration temperature. However, CO<sub>2</sub> sorption uptake on LDH is not high enough for practical use; thus it is usually enhanced by impregnation with alkali metals such as K<sub>2</sub>CO<sub>3</sub>. In this study, LDH was impregnated with Na<sub>2</sub>CO<sub>3</sub>, and analyses based on scanning electron microscopy, N<sub>2</sub> 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<sub>2</sub> sorption. Although the surface area of LDH decreased after Na<sub>2</sub>CO<sub>3</sub> impregnation, CO<sub>2</sub> sorption uptake was greatly enhanced by the additional basicity of Na<sub>2</sub>CO<sub>3</sub>. The crystal structure of Na<sub>2</sub>CO<sub>3</sub> in the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH changed from monoclinic to hexagonal with increasing temperature, and the sorbed-CO<sub>2</sub> was stored in the form of carbonate. Thermogravimetric analysis was used to measure CO<sub>2</sub> sorption uptake at 200–600 °C. The sample of Na<sub>2</sub>CO<sub>3</sub>: LDH=0.35: 1 weight ratio had the largest CO<sub>2</sub> sorption uptake among the tested sorbents, and the CO<sub>2</sub> sorption uptake tended to increase even after 400 °C.

Keywords: Layered Double Hydroxide, Na<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub> 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<sub>2</sub>) emissions is the main issue in this regard, because CO<sub>2</sub> is the primary greenhouse gas. CO<sub>2</sub> 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<sub>2</sub> capture and sequestration (CCS) technologies and for paving the way for their commercialization [3,4]. In terms of the cost of CCS, CO<sub>2</sub> capture occupies the main portion; therefore, the success of CCS projects depends on the development of efficient CO<sub>2</sub> capture methods [5].

Among various CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> sorbents have been developed based on calcium oxide or lithium zirconate. They have a high CO<sub>2</sub> 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<sup>2+</sup>, M<sup>3+</sup> cations, hydroxide groups, and anions such as CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> between the layers [17]. Above 400 °C, the basic sites of LDH become active for CO<sub>2</sub> sorption as the M<sup>2+</sup> and M<sup>3+</sup> 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<sub>2</sub> capture from hot flue gases or as a CO<sub>2</sub> sorbent for sorption-enhanced reactions to produce high-purity hydrogen [22,23]. However, LDH does not exhibit sufficient CO<sub>2</sub> sorption uptake for practical use, and therefore, there have been many efforts to increase the CO<sub>2</sub> sorption uptake of LDHs. Wang et al. compared the CO<sub>2</sub> sorption performance of LDHs containing different cations at high temperatures and found that Mg-Al-CO<sub>3</sub> LDH had the greatest CO<sub>2</sub> sorption uptake [24]. For the enhancement of CO<sub>2</sub> sorption uptake on LDH, impregnation with alkali metals has been employed. Yang et al. compared the CO<sub>2</sub> sorption uptake on Mg-Al LDHs impregnated with different amounts of K<sub>2</sub>CO<sub>3</sub> and found that the CO<sub>2</sub> sorption uptake on LDH could be increased with K<sub>2</sub>CO<sub>3</sub> loading and there was an optimal

<sup>†</sup>To whom correspondence should be addressed.

E-mail: kibonglee@korea.ac.kr

<sup>‡</sup>These authors contributed equally to this work.

<sup>‡</sup>This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National University.

Copyright by The Korean Institute of Chemical Engineers.

K<sub>2</sub>CO<sub>3</sub> loading amount for the maximum CO<sub>2</sub> sorption uptake [25]. Lee et al. also investigated the mechanism of CO<sub>2</sub> sorption enhancement on K<sub>2</sub>CO<sub>3</sub>-impregnated LDH based on various analyses [26]. However, most attempts to enhance CO<sub>2</sub> sorption uptake on LDH have focused on the use of K<sub>2</sub>CO<sub>3</sub>. As the physical and chemical characteristics of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) are similar to those of K<sub>2</sub>CO<sub>3</sub>, and because Na<sub>2</sub>CO<sub>3</sub> is inexpensive, it has the potential to be used for LDH to increase the CO<sub>2</sub> sorption uptake.

In this study, Mg-Al LDH, which has been widely studied as a high-temperature CO<sub>2</sub> sorbent among various LDHs, was impregnated with Na<sub>2</sub>CO<sub>3</sub> and its CO<sub>2</sub> sorption performance and characteristics were analyzed. CO<sub>2</sub> sorption uptake was measured via thermogravimetric analysis. The morphology, surface characteristics, and structure of the sorbents were analyzed by scanning electron microscopy (SEM), N<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>,

≥99%, Sigma-Aldrich). In the procedure of impregnation, pristine LDH was soaked with a Na<sub>2</sub>CO<sub>3</sub> solution and then dried at 110 °C under vacuum. The soaking and drying procedure was repeated several times to facilitate the distribution of Na<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub> gas physisorption at -196 °C using a BELSORP-max system (Bel Japan, Inc.). Each sample was degassed under vacuum (<10<sup>-1</sup> Pa) at 200 °C for 3 h prior to N<sub>2</sub> 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) spectroscopy 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<sup>-1</sup> at a spectral resolution of 4.0 cm<sup>-1</sup> 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 K $\alpha$  radiation oper-

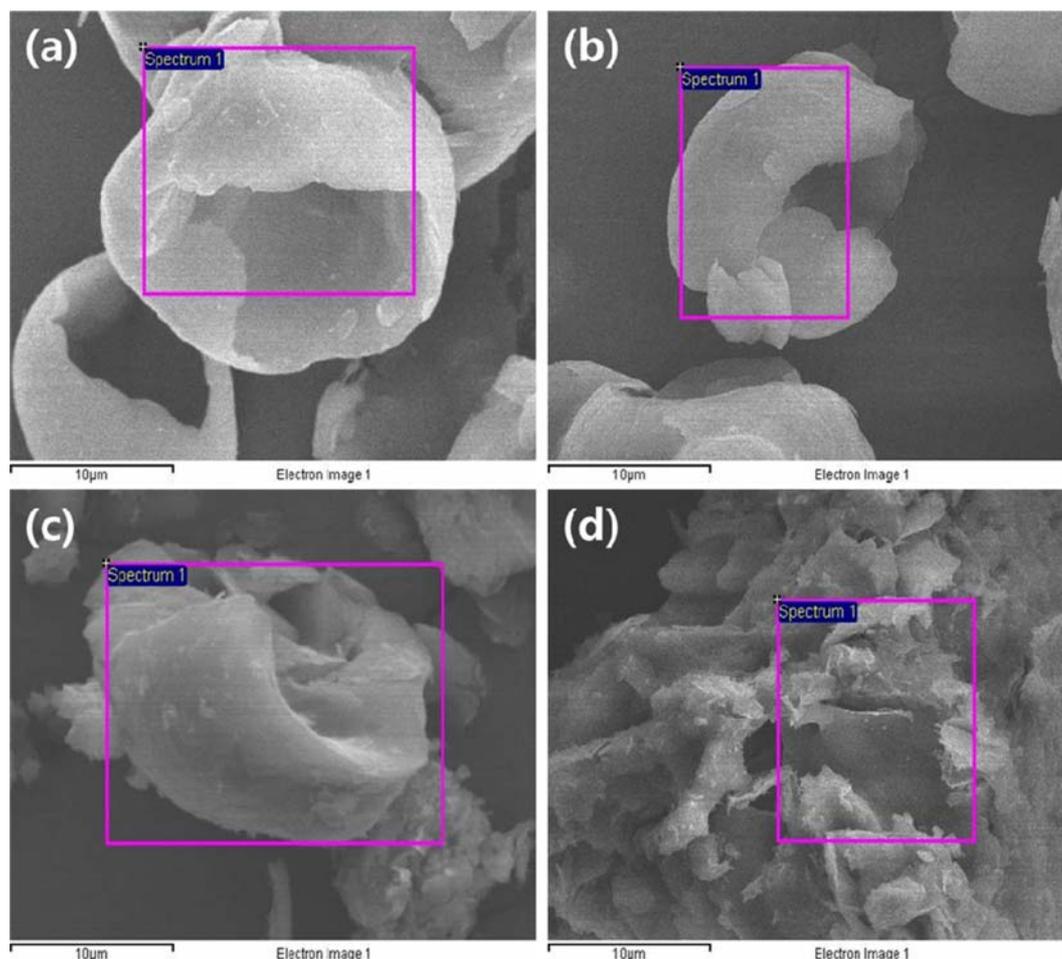


Fig. 1. SEM images of (a) pristine LDH MG70, (b) calcined LDH MG70, and (c) and (d) Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70.

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

### 3. CO<sub>2</sub> Sorption

Equilibrium CO<sub>2</sub> sorption uptakes on LDHs were measured with a thermogravimetric analyzer (TGA, Q50, TA Instruments). Before the CO<sub>2</sub> sorption experiments began, moisture and CO<sub>2</sub> on the samples were removed by means of an N<sub>2</sub> 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<sub>2</sub> balanced by N<sub>2</sub> at a pressure of ~1 atm and a temperature of 200-600 °C.

## RESULTS AND DISCUSSION

### 1. Characterization of Na<sub>2</sub>CO<sub>3</sub>-impregnated Mg-Al LDH

Fig. 1 shows the SEM images of pristine and calcined LDH MG70 and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70. Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70 contains 0.35 g of Na<sub>2</sub>CO<sub>3</sub> per 1 g of LDH MG70. If not mentioned otherwise, the ratio of Na<sub>2</sub>CO<sub>3</sub> and LDH was kept at 0.35 : 1 for the Na<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub>, 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<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub>. The Na element in Na<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub> at various weight ratios. Pristine LDH MG70 had a relatively low surface area of 63.9 m<sup>2</sup>/g, but after calcination, its surface area increased to 215.2 m<sup>2</sup>/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<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub> that was impregnated.

TGA analyses were performed to determine the thermal stability of Na<sub>2</sub>CO<sub>3</sub>, pristine LDH MG70, and Na<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub> maintained its weight up to a temperature of 900 °C, and then it slowly lost its weight as Na<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70 from EDX analysis**

Elements	Pristine LDH		Calcined LDH		Na <sub>2</sub> CO <sub>3</sub> -impregnated LDH			
	(a)		(b)		(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<sub>2</sub>CO<sub>3</sub>-impregnated LDHs**

	Pristine LDH		Calcined LDH		Na <sub>2</sub> CO <sub>3</sub> -impregnated LDH MG70		
	MG70		MG70		0.1 : 1	0.35 : 1	1 : 1*
BET surface area (m <sup>2</sup> /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 <sup>3</sup> /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<sub>2</sub>CO<sub>3</sub> : LDH

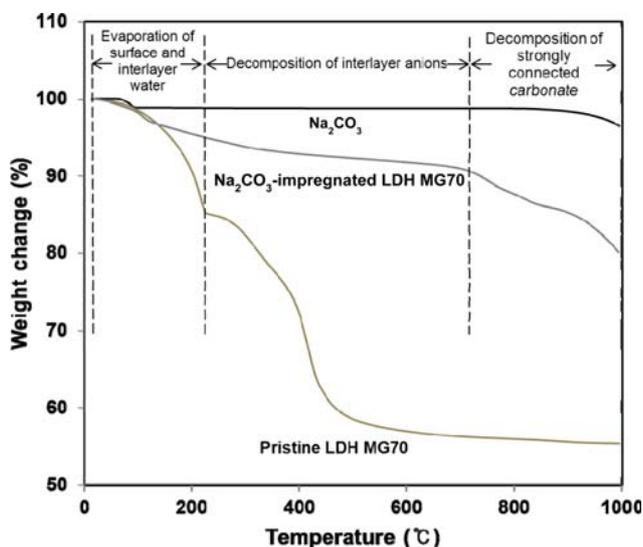


Fig. 2. TGA analyses of Na<sub>2</sub>CO<sub>3</sub>, pristine LDH, and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH.

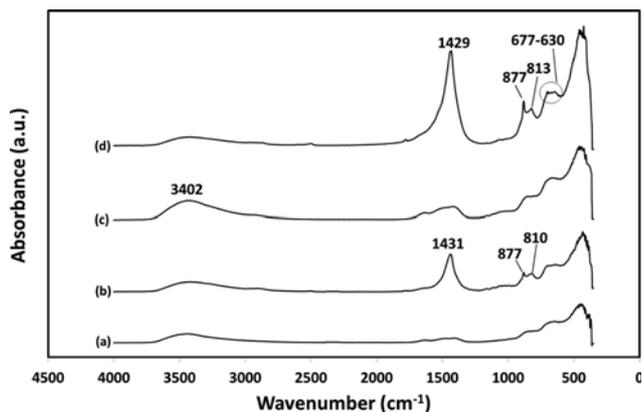


Fig. 3. FT-IR spectra of (a) cleaned LDH MG70, (b) CO<sub>2</sub>-sorbed LDH MG70, (c) cleaned Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70, and (d) CO<sub>2</sub>-sorbed Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70.

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 Na<sub>2</sub>CO<sub>3</sub> and that strongly combined in the LDH decomposed together, and the second step is considered to correspond to the melting of Na<sub>2</sub>CO<sub>3</sub>.

Fig. 3 shows the FT-IR spectra of the cleaned or CO<sub>2</sub>-sorbed LDH MG70 and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70. The cleaned samples were prepared by purging with N<sub>2</sub> gas at a temperature of 600 °C for 8 h to remove impurities such as water and CO<sub>2</sub>. The samples were then cooled to room temperature while the N<sub>2</sub> gas purge was maintained. The CO<sub>2</sub>-sorbed samples were obtained after being cleaned at 600 °C for 8 h with N<sub>2</sub> flow, cooled to 400 °C, exposed to a pure CO<sub>2</sub> stream at 400 °C for 9 h, and then cooled to room temperature while the CO<sub>2</sub> gas stream was maintained. The broad peak around 3,400 cm<sup>-1</sup>, 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<sup>-1</sup> area was the characteristic vibration of metal oxides, Mg-O and Al-O [30]. The broad band between

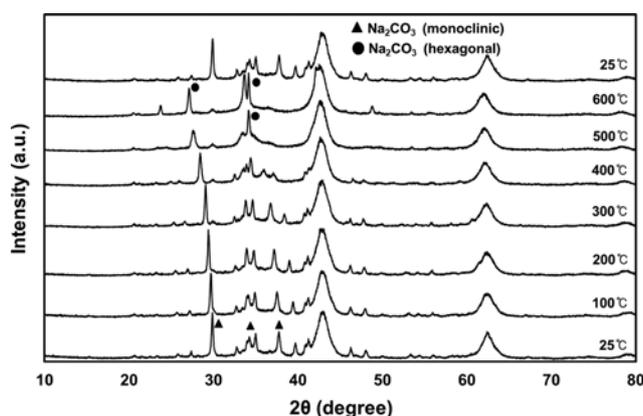


Fig. 4. *In situ* XRD spectra at different temperatures for Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70 in the flow of N<sub>2</sub>.

1,600 and 1,400 cm<sup>-1</sup> that appeared in the cleaned LDH and Na<sub>2</sub>CO<sub>3</sub>-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 CO<sub>2</sub> was sorbed on LDH (Fig. 3(b) and 3(d)) [31]. Moreover, new spectra appeared at 877 and 810 cm<sup>-1</sup> in the CO<sub>2</sub>-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 Na<sub>2</sub>CO<sub>3</sub> (Fig. 3(c)). In the CO<sub>2</sub>-sorbed Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH, the single peak for O-C-O stretching became sharper at 1,429 cm<sup>-1</sup>, and the intensity of the peaks for covalent carbonate 877–813 cm<sup>-1</sup> became stronger. These results demonstrated that more CO<sub>2</sub> was sorbed in the forms of unidentate and covalent carbonate in the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH.

Fig. 4 shows the changes in the crystal structure of the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH sample in the flow of N<sub>2</sub> in a temperature range of 25–600 °C. Similar XRD spectra were observed for the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH in the flow of CO<sub>2</sub> (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 Na<sub>2</sub>CO<sub>3</sub>. Na<sub>2</sub>CO<sub>3</sub> 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 Na<sub>2</sub>CO<sub>3</sub> in LDH can be recovered.

## 2. CO<sub>2</sub> Sorption Uptake on Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH

Fig. 5 compares the CO<sub>2</sub> sorption uptakes at 400 °C on the calcined LDH MG70 and LDH MG70 impregnated with Na<sub>2</sub>CO<sub>3</sub> at various weight ratios. Calcined LDH showed a low CO<sub>2</sub> sorption uptake of 0.14 mmol/g sorbent, but its CO<sub>2</sub> sorption uptake increased considerably to 0.48 mmol/g sorbent with the slight addition of Na<sub>2</sub>CO<sub>3</sub> (at a weight ratio of Na<sub>2</sub>CO<sub>3</sub> : LDH=0.1 : 1), and it reached a maximum of 0.68 mmol/g sorbent at a weight ratio of Na<sub>2</sub>CO<sub>3</sub> : LDH=0.35 : 1. The CO<sub>2</sub> sorption uptake, however, was reduced upon further addition of Na<sub>2</sub>CO<sub>3</sub> at a weight ratio of Na<sub>2</sub>CO<sub>3</sub> : LDH = 1 : 1, signifying that there is an optimum Na<sub>2</sub>CO<sub>3</sub> amount for im-

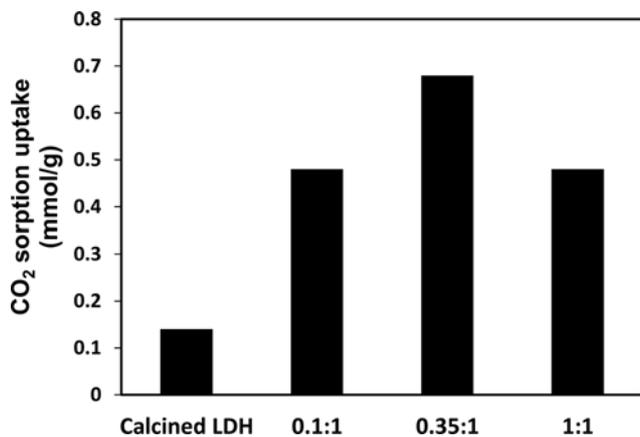


Fig. 5. CO<sub>2</sub> sorption uptake at 400 °C on calcined LDH MG70 and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70 with various weight ratios of Na<sub>2</sub>CO<sub>3</sub> : LDH.

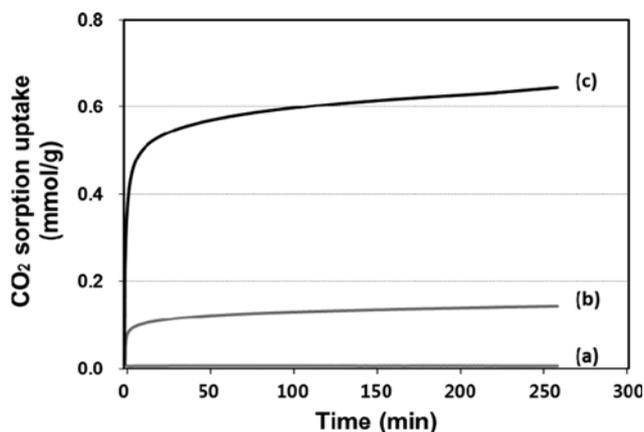


Fig. 6. CO<sub>2</sub> sorption kinetics at 400 °C on (a) Na<sub>2</sub>CO<sub>3</sub>, (b) calcined LDH MG70, and (c) Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70.

pregnation. This is thought to be caused by two conflicting effects: increasing basicity and reducing surface area with an increase in the Na<sub>2</sub>CO<sub>3</sub> content (Table 2).

In sorption processes, fast sorption kinetics is as important as high sorption capacity. The change of CO<sub>2</sub> sorption uptake with time was tested using a thermogravimetric analysis for Na<sub>2</sub>CO<sub>3</sub>, calcined LDH MG70, and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH as shown in Fig. 6. In the experiments, the change of sample weight was continuously recorded with CO<sub>2</sub> gas flow at the temperature of 400 °C and the pressure of ~1 atm. For both calcined LDH MG70 and Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70, CO<sub>2</sub> sorption uptake initially increased fast and then approached an equilibrium value. The thermogravimetric analysis showed that Na<sub>2</sub>CO<sub>3</sub> itself had practically no sorption ability for CO<sub>2</sub> gas.

Fig. 7 shows the CO<sub>2</sub> sorption isotherm of the Na<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub> partial pressure, which corresponds to the type I isotherm according to the IUPAC classification.

Fig. 8 represents the CO<sub>2</sub> sorption uptake of Na<sub>2</sub>CO<sub>3</sub>-impregnated LDHs at different temperatures between 200 and 600 °C. The Na<sub>2</sub>CO<sub>3</sub>-

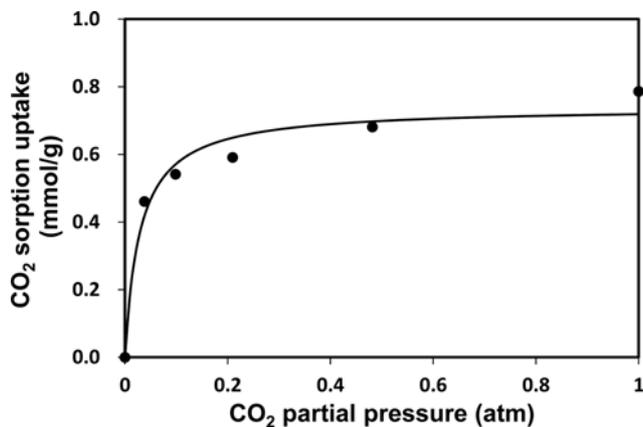


Fig. 7. CO<sub>2</sub> sorption isotherm of Na<sub>2</sub>CO<sub>3</sub>-impregnated LDH MG70 measured at 400 °C.

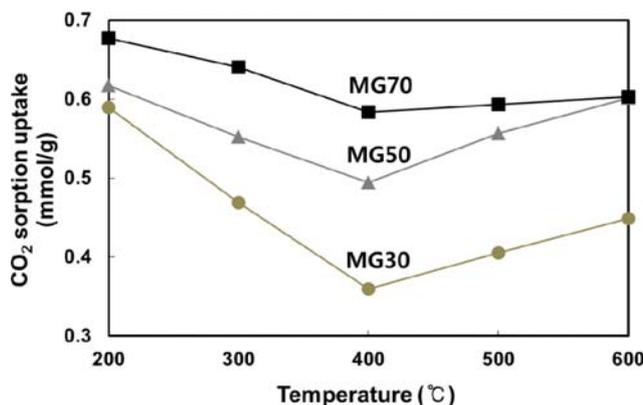


Fig. 8. Effect of temperature on the CO<sub>2</sub> sorption uptake of Na<sub>2</sub>CO<sub>3</sub>-impregnated LDHs.

impregnated LDH MG70 showed higher CO<sub>2</sub> sorption uptake than other samples over the entire temperature range, and all the samples showed maximum CO<sub>2</sub> sorption uptake at 200 °C. The CO<sub>2</sub> 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<sub>2</sub> sorption uptake increased with increasing temperature, implying the occurrence of chemisorption. This is probably caused by the change in the Na<sub>2</sub>CO<sub>3</sub> structure in the LDH with temperature. Na<sub>2</sub>CO<sub>3</sub> was mainly in the monoclinic form until 400 °C, but hexagonal Na<sub>2</sub>CO<sub>3</sub> became predominant over 400 °C (Fig. 4). The hexagonal Na<sub>2</sub>CO<sub>3</sub> is thought to have a higher affinity to CO<sub>2</sub>, resulting in the increased CO<sub>2</sub> sorption uptake even at high temperatures.

## CONCLUSIONS

The high-temperature CO<sub>2</sub> sorption uptake on LDHs could be enhanced by impregnation with Na<sub>2</sub>CO<sub>3</sub>. There was an optimal amount of Na<sub>2</sub>CO<sub>3</sub> for a maximum CO<sub>2</sub> sorption uptake, which resulted from two conflicting effects: increasing basicity and decreasing surface area with increasing amount of Na<sub>2</sub>CO<sub>3</sub>. Among three LDHs (MG30, MG50, and MG70) having different ratio of magnesium, Na<sub>2</sub>CO<sub>3</sub>-impregnated MG70 showed higher CO<sub>2</sub> sorption uptake than other samples, implying that the CO<sub>2</sub> sorption uptake increased with in-

creasing content of magnesium in the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDHs. With increasing temperature, the CO<sub>2</sub> sorption uptake on Na<sub>2</sub>CO<sub>3</sub>-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<sub>2</sub> chemisorption behavior can be related to the change of Na<sub>2</sub>CO<sub>3</sub> phase in LDHs from monoclinic to hexagonal with increasing temperature. Also, the FT-IR analysis showed that the sorbed CO<sub>2</sub> was stored in the form of carbonate in the Na<sub>2</sub>CO<sub>3</sub>-impregnated LDHs.

#### ACKNOWLEDGEMENTS

This research was supported by the Energy Efficiency and Resources R&D program (No. 2011201020004A) and the Human Resources Development Program (No. 20134010200600) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy. The authors also acknowledge the Korea CCS R&D Center (KCRC) Grant funded by the Korea government Ministry of Science, ICT & Future planning (No. 2012-0008898) and the Korea Research Council of Fundamental Science and Technology (KRCF) for the additional support received from the National Agenda Program (NAP).

#### REFERENCES

1. M. L. Parry, T. R. Carter and M. Hulme, *Global Environ.*, **6**, 1 (1996).
2. M. Oppenheimer and A. Peterson, *Climatic Change*, **73**, 195 (2005).
3. R. Svensson, M. Odenberger, F. Johnsson and L. Strömberg, *Energy Convers. Manage.*, **45**, 2343 (2004).
4. R. Peltier, *Power*, **152**, 38 (2008).
5. T. F. Wall, *P. Combust. Inst.*, **31**, 31 (2007).
6. X. Xu, C. Song, J. M. Andrésen, B. G. Miller and A. W. Scaroni, *Micropor. Mesopor. Mater.*, **62**, 29 (2003).
7. R. V. Siriwardane, M.-S. Shen and E. P. Fisher, *Energy Fuels*, **19**, 1153 (2005).
8. B.-K. Na, K.-K. Koo, H.-M. Eum, H. Lee and H. K. Song, *Korean J. Chem. Eng.*, **18**, 220 (2001).
9. C.-F. Mao and M. A. Vannice, *Appl. Catal. A*, **111**, 151 (1994).
10. S. F. Wu, T. H. Beum, J. I. Yang and J. N. Kim, *Ind. Eng. Chem. Res.*, **46**, 7896 (2007).
11. K. Kuramoto, S. Fujimoto, A. Morita, S. Shibano, Y. Suzuki, H. Hatano, L. Shi-Ying, M. Harada and T. Takarada, *Ind. Eng. Chem. Res.*, **42**, 975 (2003).
12. E. P. Reddy and P. G. Smirniotis, *J. Phys. Chem. B*, **108**, 7794 (2004).
13. J.-I. Ida and Y. S. Lin, *Environ. Sci. Technol.*, **37**, 1999 (2003).
14. E. Ochoa-Fernández, H. K. Rusten, H. A. Jakobsen, M. Rønning, A. Holmen and D. Chen, *Catal. Today*, **106**, 41 (2005).
15. V. Guzmán-Velderrain, D. Delgado-Vigil, V. Collins-Martínez and A. L. Ortiz, *J. New Mater. Electron. Syst.*, **11**, 131 (2008).
16. K. B. Lee, A. Verdooren, H. S. Caram and S. Sircar, *J. Colloid Interface Sci.*, **308**, 30 (2007).
17. S. Kannan, D. Kishore, K. Hadjiivanov and H. Knözinger, *Langmuir*, **19**, 5742 (2003).
18. M. K. Ram Reddy, Z. P. Xu, G. Q. Lu and J. C. Diniz Da Costa, *Ind. Eng. Chem. Res.*, **45**, 7504 (2006).
19. Y. Ding and E. Alpay, *Chem. Eng. Sci.*, **55**, 3461 (2000).
20. Z. Yong, V. Mata and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, **40**, 204 (2001).
21. N. D. Hutson and B. C. Attwood, *Adsorption*, **14**, 781 (2008).
22. K. B. Lee, M. G. Beaver, H. S. Caram and S. Sircar, *Ind. Eng. Chem. Res.*, **47**, 8048 (2008).
23. H. M. Jang, K. B. Lee, H. S. Caram and S. Sircar, *Chem. Eng. Sci.*, **73**, 431 (2012).
24. Q. Wang, H. H. Tay, D. J. W. Ng, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo and A. Borgna, *ChemSusChem*, **3**, 965 (2010).
25. J.-I. Yang and J.-N. Kim, *Korean J. Chem. Eng.*, **23**, 77 (2006).
26. J. M. Lee, Y. J. Min, K. B. Lee, S. G. Jeon, J. G. Na and H. J. Ryu, *Langmuir*, **26**, 18788 (2010).
27. N. D. Hutson, S. A. Speakman and E. A. Payzant, *Chem. Mater.*, **16**, 4135 (2004).
28. J.-W. Kim and H.-G. Lee, *Metall. Mater. Trans. B*, **32**, 17 (2001).
29. M. R. Othman, N. M. Rasid and W. J. N. Fernando, *Chem. Eng. Sci.*, **61**, 1555 (2006).
30. T. López, P. Bosch, M. Asomoza, R. Gómez and E. Ramos, *Mater. Lett.*, **31**, 311 (1997).
31. J. I. Di Cosimo, V. K. Díez, M. Xu, E. Iglesia and C. R. Apesteguía, *J. Catal.*, **178**, 499 (1998).
32. D. Tichit, M. N. Bennani, F. Figueras and J. R. Ruiz, *Langmuir*, **14**, 2086 (1998).
33. A. Arakcheeva and G. Chapuis, *Acta Crystallogr. B*, **61**, 601 (2005).