

Hydrotalcites for adsorption of CO₂ at high temperature

Jung-Il Yang and Jong-Nam Kim[†]

Separation Process Research Center, Korea Institute of Energy Research,
71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, Korea
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Abstract—Adsorption of carbon dioxide by hydrotalcites was investigated by using a gravimetric method at 450 °C. Hydrotalcites possessed higher adsorption capacity of CO₂ than other basic materials such as MgO and Al₂O₃. Two different preparation methods of hydrotalcite with varying Mg/Al ratio were employed to determine their effects on the adsorption capacity of CO₂. In addition, varying amounts of K₂CO₃ were impregnated on the hydrotalcite to further increase its adsorption capacity of CO₂. The hydrotalcite prepared by the high supersaturation method with Mg/Al=2 showed the most favorable adsorption-desorption pattern with high adsorption capacity of CO₂. K₂CO₃ impregnation on the hydrotalcite increased the adsorption capacity of CO₂ because it changed both the chemical and the physical properties of the hydrotalcite. The optimum amount of K₂CO₃ impregnation was 20 wt%. The hydrotalcite prepared by the high supersaturation method with Mg/Al=2 and 20 wt% K₂CO₃ impregnation has the highest adsorption capacity of CO₂ with 0.77 mmol CO₂/g at 450 °C and 800 mmHg.

Key words: Hydrotalcite, Adsorbents for CO₂, High Supersaturation Method, Mg/Al Ratio, K₂CO₃ Impregnation

INTRODUCTION

Hydrogen is produced mostly by the steam methane reforming (SMR) reaction using Ni/Al₂O₃ catalyst at a temperature of 750-900 °C and a pressure of 50-600 psig. Hydrogen production can be improved by the sorption-enhanced reaction process (SERP) that uses a mixture of SMR catalyst and adsorbent for CO₂ [Hufton et al., 1999]. The key requirement for commercial application of the SERP is the development of an adsorbent that has high CO₂ working capacity at moderately high temperature of 300-500 °C. Although zeolite A, zeolite X and activated carbon are frequently used as adsorbents for CO₂ at room temperature, they have poor CO₂ adsorbing behaviors at high temperatures (>500 °C). Thus, these adsorbents are not adequate for the applications.

The adsorbent for CO₂ adsorption at high temperatures should have several distinct features [Yong et al., 2001]. The adsorbent needs to adsorb significant amounts of CO₂ at high temperatures with desirable adsorption/desorption kinetics. Moreover, the adsorption capacity of CO₂ must be maintained in repeated adsorption/desorption cycles. Most adsorbents for CO₂ at high temperatures are composed of alkali metal oxides that utilize their basic properties for adsorbing acidic CO₂. Alkali metal oxides, such as CaO, MgO and Al₂O₃ are basic and are suitable for adsorbing CO₂ at high temperatures. Recently, hydrotalcite-like compounds were reported to have good features of adsorbents for CO₂ adsorption at high temperatures [Yong et al., 2001; Hufton et al., 1998]. Especially, magnesium-aluminum containing layered double hydroxides (LDH) are the class of solid super bases, which are efficient catalysts for aldol condensations, epoxidations, and alkene isomerisations [Santhanalakshmi and Raja, 1996; Reichle, 1980; Coma et al., 1994; Cativiela et al., 1995; Schaper et al., 1989]. Moreover, the surface basicity of the

calcined hydrotalcites varies with the ratio of Mg/Al and the number of basic sites increases with the increase in Mg/Al ratio [Parida and Das, 2000].

Hydrotalcite is double layered material which is composed of positively charged brucite-like layer and negatively charged interlayer. Positive charge is generated with trivalent cations substituting divalent cations in the brucite structure, and this charge is compensated by anion existing in the interlayer. It is represented by the general molecular formula, [M(II)_{1-x}M(III)_x(OH)₂]^{x+}A_{x/n}⁻·yH₂O wherein, M(II)=Mg, Cu, Ni, Co, Mn, Zn; M(III)=Al, Fe, Cr, V; A⁻ is any interlayer anion such as CO₃²⁻, Cl⁻, NO₃⁻, SO₄²⁻ and x=0.1-0.33 [Velu and Swamy, 1996].

The basicity of the hydrotalcite depends on chemical compositions (type of cation, ratio of M²⁺/M³⁺, type of anion existing in the interlayer) and activation conditions. For example, calcination of the hydrotalcite above 450 °C results in mixed metal oxides with strong basicity and high surface area. Thus, it can be used as base catalyst or catalyst support [Mckenzie et al., 1992]. In this research we prepared several different Mg/Al based hydrotalcites with different preparation methods, Mg/Al ratios and different amounts of K₂CO₃ to use them as adsorbents for CO₂ adsorption at high temperatures. Therefore, the objective of this work is to investigate the relation between the preparation methods and the adsorption capacity of CO₂ at high temperatures, and finally to develop the best hydrotalcite taking high adsorption capacity of CO₂ enough for the adsorbent in the sorption enhanced reaction process.

EXPERIMENTAL

1. Preparation of Hydrotalcite

Hydrotalcites were prepared by two different methods, the low supersaturation method and the high supersaturation method, following the procedures described in the literature [Narayanan and Krishna, 1998].

[†]To whom correspondence should be addressed.
E-mail: jnkim@kier.re.kr

1-1. Low Supersaturation Method

Solution A was prepared by dissolving appropriate amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in 70 ml of distilled water depending on the ratio of Mg/Al. Solution B was prepared by dissolving 28 g of NaOH and 10 g of Na_2CO_3 in 100 ml distilled water. Solutions A and B were added to a beaker containing distilled water simultaneously with pH being controlled between 9 and 10. The resulting solution was stirred at 65 °C for 18 h and then filtered and washed with distilled water until the pH of the solution reached 7.0. The precipitate was dried at 100 °C for 24 h in an oven and finally the sample was calcined at 450 °C in air for 18 h.

1-2. High Supersaturation Method

Solutions A and B were prepared by the same procedure described above. Solution A was added to solution B dropwise in 20 min and the resultant slurry was crystallized at 65 °C with stirring for 18 h. The crystallized precipitates were filtered, washed and dried at 100 °C for 24 h. The dried sample was also calcined at 450 °C in air for 18 h.

1-3. K_2CO_3 /Hydrotalcite

With the intention to increase the basicity of the hydrotalcite for CO_2 adsorption, K_2CO_3 was impregnated on the hydrotalcite. Using incipient wetness method, the appropriate amount of K_2CO_3 was impregnated on the hydrotalcite. The impregnated sample was dried in an oven at 100 °C for 8 h. Finally dried K_2CO_3 /Hydrotalcite was calcined at 450 °C for 8 h. The amount of impregnated K_2CO_3 varied between 0 and 50 wt%.

2. Evaluation of Adsorption Capacity of CO_2

A gravimetric method was used to determine the adsorption capacity of CO_2 by the prepared hydrotalcites. The amount of sample loaded into the TGA unit (Cahn 1000, Cahn Instruments Inc.) was 65 mg. The sample was pretreated in flowing He at 500 °C for 3 h. After the temperature was lowered to 450 °C, CO_2 was introduced to the balance and the weight change was measured. The range of

adsorption pressure was between 0 to 1,000 mmHg.

RESULTS AND DISCUSSION

1. Comparison of Hydrotalcite with other Adsorbents for CO_2 at High Temperatures

Adsorption capacities of CO_2 by MgO, Al_2O_3 and the hydrotalcite (Mg/Al=2, prepared by the high supersaturation method) were measured at 450 °C, and their adsorptive isotherms are shown in Fig. 1. MgO and Al_2O_3 , individual components of the hydrotalcite, showed appreciable adsorption capacity of CO_2 , even at high temperatures due to their basicity. However, the hydrotalcite adsorbed CO_2 about 3 to 6 times more than Al_2O_3 or MgO, respectively. The highest adsorption capacity of CO_2 by the hydrotalcite was ascribed to not only its high surface area, but also its high basicity [Mckenzie et al., 1992].

2. Effect of Aluminum Contents

Fig. 2 shows adsorption capacities of CO_2 by hydrotalcites prepared by the low supersaturation method with different Mg/Al ratios. The hydrotalcite with Mg/Al ratio of 2 adsorbed the largest amount of CO_2 among hydrotalcites with Mg/Al ratios higher than 2. As the ratio of Mg/Al increased to 5, adsorption capacity of CO_2 decreased. However, as the Mg/Al ratio increased further, hydrotalcites adsorbed more CO_2 and the amount of CO_2 adsorption by the hydrotalcite with Mg/Al ratio of 10 became almost equal to that of the hydrotalcite with Mg/Al ratio of 2. Yong et al. [2001] also observed the similar valley-shaped results with the effect of aluminum contents on adsorption capacity of CO_2 by Mg/Al hydrotalcites. When the ratio of Mg/Al equaled two, the higher layer charge density of the hydrotalcite due to the larger Al content enabled higher adsorption capacity of CO_2 . However, as the content of Al decreased with the increasing Mg content, the adsorption capacity of CO_2 decreased due to the loss of the layer charge density. In other words, as Mg^{2+} ion is substituted by a trivalent cation having a similar radius like

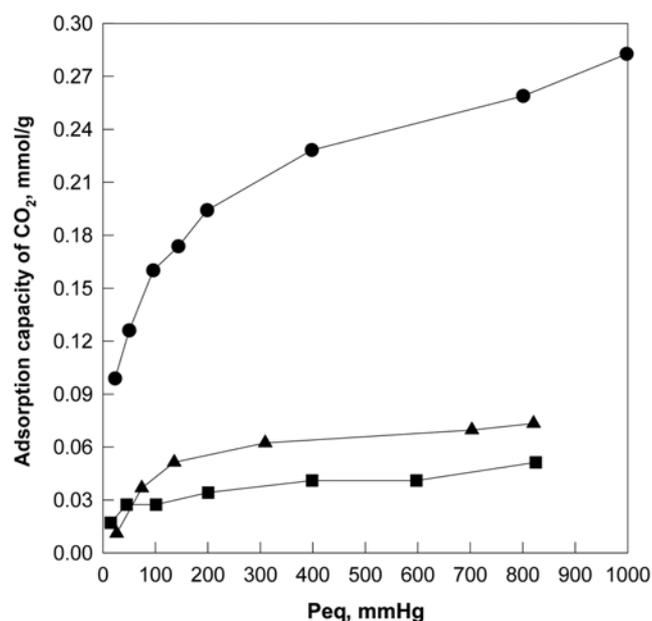


Fig. 1. CO_2 adsorption isotherms of various adsorbents ($T=450$ °C, ●—Hydrotalcite (Mg/Al=2, high), ■—MgO, ▲— Al_2O_3).

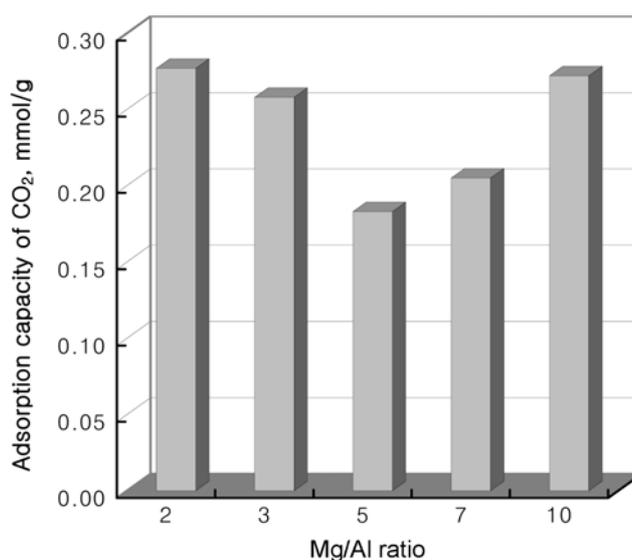


Fig. 2. Adsorption capacity of CO_2 on hydrotalcites with varying ratios of Mg/Al ($T=450$ °C, prepared by low supersaturation method).

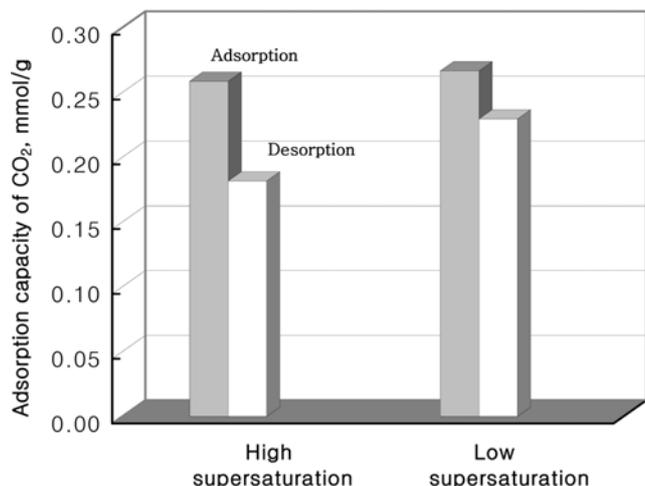


Fig. 3. Adsorption-desorption behavior of the hydrotalcites prepared by two different preparation methods ($T=450\text{ }^{\circ}\text{C}$, adsorptive pressure=800 mmHg, desorptive pressure=50 mmHg).

Al^{3+} , the positive charge density of the layer increases. In order to maintain the electrical neutrality, more anions occupy the interlayer positions where water crystallization also takes place. Thus, the space of the interlayer increases with the Al contents, due to the water evaporation during the calcinations procedure. Therefore, the hydrotalcite with $\text{Mg}/\text{Al}=2$ is most effective in CO_2 adsorption. On the other hand, the number of basic sites increased with the increase in Mg content [Parida and Das, 2000], resulting in increased CO_2 adsorption on the hydrotalcite with $\text{Mg}/\text{Al}=10$.

3. Effect of Preparation Methods

Hydrotalcites were prepared by two different methods of the varying precipitation rate during the preparation of hydrotalcite precursor. Fig. 3 shows adsorption/desorption behaviors of hydrotalcites prepared by the low supersaturation method and the high supersaturation method. Although both hydrotalcites showed almost same adsorption capacity of CO_2 , the hydrotalcite prepared by the high supersaturation method had the higher effective adsorption capacity. The hydrotalcite prepared by the high supersaturation method is known to have a low crystallinity, many crystalline nuclei and the high surface area due to its smaller particle size [Narayanan and Krishna, 1998]. The surface area of the hydrotalcites prepared by the high supersaturation method was 2.46 times larger than that of the hydrotalcite prepared by the low supersaturation method (Table 1). Even with the higher surface area, the average pore radius of the hydrotalcite by the high supersaturation was larger. The higher surface area and the larger pore seem to be attributed to the better de-

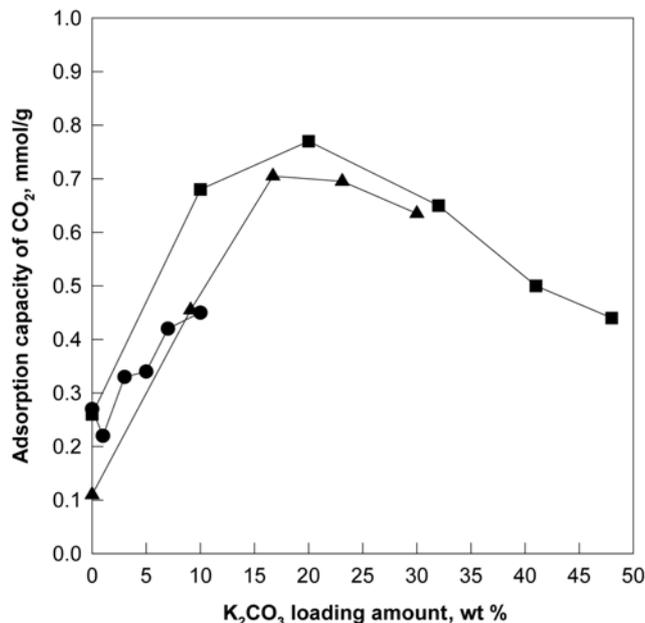


Fig. 4. Effect of the K_2CO_3 loading on CO_2 adsorption ($T=450\text{ }^{\circ}\text{C}$, $P=800\text{ mmHg}$, \bullet — $\text{Mg}/\text{Al}=2$ (low supersaturation), \blacksquare — $\text{Mg}/\text{Al}=2$ (high supersaturation), \blacktriangle — $\text{Mg}/\text{Al}=10$ (high supersaturation)).

sorption behavior of the hydrotalcite prepared by the high supersaturation method.

4. Effect of K_2CO_3 Content

Hoffman et al. [Hoffman and Pennline, 2000], reported that the adsorption capacity of CO_2 by the hydrotalcite could be increased by K_2CO_3 impregnation in the presence of steam according to the reaction below.



The reaction can be reversed by supplying heat to the reaction. Thus, the adsorbent that already adsorbed CO_2 can be thermally regenerated in a moving bed or in a fluidized bed. The increased basicity due to the impregnated alkali metal carbonate may provide the positive effect of adsorbing more CO_2 by the hydrotalcite even without steam. Based on that assumption, different amounts of K_2CO_3 were impregnated on three different hydrotalcites, and their adsorption capacities of CO_2 are shown in Fig. 4. It should be pointed out that CO_2 adsorption experiments were carried out without steam in this research. First, K_2CO_3 was impregnated up to 10 wt% on the hydrotalcite prepared by the low supersaturation method. As shown in Fig. 4, the adsorption capacity of CO_2 was increased almost linearly with the amount of K_2CO_3 impregnation, indicating

Table 1. Chemical and physical properties of the hydrotalcites by two different preparation methods

Mg/Al mole ratio	Preparation methods	K_2CO_3 loading amount [wt%]	Adsorption CO_2 adsorbed [mmol/g]	Ave. pore radius [\AA]	BET surface area [m^2/g]	Pore volume [cm^3/g]
2	Low supersaturation	0	0.270	58.28	62.65	0.18
	K_2CO_3 impregnation	41	0.460	109.23	13.32	0.07
2	High supersaturation	0	0.260	65.62	153.95	0.51
	K_2CO_3 impregnation	32	0.650	130.72	27.38	0.18

that the number of basic sites for CO₂ adsorption was increased by K₂CO₃ impregnation. To investigate the effect of K₂CO₃ loading further, the amounts of K₂CO₃ up to 48 wt% were impregnated on the more effective hydrotalcite (Mg/Al=2, prepared by the high supersaturation method). And the K₂CO₃ loading amount was increased considering the fact revealed in low supersaturation case that the adsorption capacity of CO₂ was increased with the loading amount of K₂CO₃. Different from the low supersaturation, in high supersaturation there was an optimum amount of K₂CO₃ loading for high CO₂ adsorption as shown in Fig. 4. That could be explained as follows. Although high loading of K₂CO₃ could be favorable to CO₂ adsorption due to its increased basic sites, the pores for CO₂ adsorption were blocked with the loading of K₂CO₃. Therefore, about 20 wt% K₂CO₃ loading was desirable for CO₂ adsorption. To confirm the results, the impregnation of K₂CO₃ to the other hydrotalcite was also carried out. In the present case, Mg/Al=10 prepared by high supersaturation was tested because the hydrotalcite also adsorbed large amounts of CO₂. The result was also shown in Fig. 4. Similar to the results given by Mg/Al=2, 20 wt% K₂CO₃/hydrotalcite gave the highest adsorption capacity of CO₂, but the amount was smaller than that given by Mg/Al=2. Therefore, it was certain that the K₂CO₃ impregnation on hydrotalcite increased the CO₂ adsorption amount by affecting the structure and chemical properties of the hydrotalcite. In Table 1, physical properties of the specific hydrotalcites are presented. As shown, the adsorption capacity of CO₂ and average pore radius were sharply increased in the case of the K₂CO₃ impregnated hydrotalcites. On the other hand, BET surface area and pore volume were decreased. These data indicate that the increased basicity by impregnation of K₂CO₃ gave the increased adsorption capacity of CO₂, but the impregnation of K₂CO₃ on the hydrotalcite blocked the pore from the smallest one. Therefore, the average pore radius was increased, and BET surface area and pore volume were decreased. Based on the results given by the Table 1, the data shown in the Fig. 4 can be interpreted like this. As the impregnated amount of K₂CO₃ increased to the critical value, which was enough to block the pores of the hydrotalcite partially, the basicity given by K₂CO₃ increased linearly with K₂CO₃ impregnation. Therefore, adsorption capacity of CO₂ was increased with increasing the K₂CO₃ impregnation, and that was very desirable conditions for CO₂ adsorption. However, the pores for CO₂ adsorption could be blocked totally and the effective K₂CO₃ for CO₂ adsorption would be lessened as the impregnated K₂CO₃ amount increased over the critical value. Therefore, there was an optimum value of K₂CO₃ impregnation. That is, the K₂CO₃ impregnation on the hydrotalcite changed the physical and chemical properties of the hydrotalcite and there was critical value of K₂CO₃ impregnation for obtaining high adsorption capacity of CO₂.

CONCLUSIONS

The hydrotalcite with a composition of Mg/Al=2 was a suitable adsorbent for CO₂ at high temperature of 450 °C, and its adsorption

capacity of CO₂ came to 0.28 mmol/g. The hydrotalcite prepared by a high supersaturation method took on desirable desorption characteristics because of its higher surface area and larger pore size. Furthermore, K₂CO₃ impregnation on the hydrotalcite was favorable to CO₂ adsorption due to its increased basic property. Therefore, the adsorption capacity of CO₂ was increased with the amount of K₂CO₃ impregnation. However, above the critical amount of K₂CO₃ impregnation, the adsorption capacity of CO₂ was decreased because the impregnated K₂CO₃ blocked the pore of the hydrotalcite for CO₂ adsorption. Therefore, it is clear that there was an optimum amount of K₂CO₃ impregnation for taking high CO₂ adsorption. The optimum amount was 20 wt% in case of the hydrotalcite prepared by high supersaturation with Mg/Al=2. And the hydrotalcite with 20 wt% K₂CO₃ impregnation took the highest adsorption capacity of CO₂ with 0.77 mmol/g at 450 °C and 800 mmHg.

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