

## Development of new alumina-modified sorbents for CO<sub>2</sub> sorption and regeneration at temperatures below 200 °C

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### ABSTRACT

A new regenerable alumina-modified sorbent was developed for CO<sub>2</sub> capture at temperatures below 200 °C. The CO<sub>2</sub> capture capacity of a potassium-based sorbent containing Al<sub>2</sub>O<sub>3</sub> (KAlI) decreased during multiple CO<sub>2</sub> sorption (60 °C) and regeneration (200 °C) tests due to the formation of the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase, which could be converted into the original K<sub>2</sub>CO<sub>3</sub> phase above 300 °C. However, the new regenerable potassium-based sorbent (Re-KAl(I)) maintained its CO<sub>2</sub> capture capacity during multiple tests even at a regeneration temperature of 130 °C. In particular, the CO<sub>2</sub> capture capacity of the Re-KAl(I)60 sorbent which was prepared by the impregnation of Al<sub>2</sub>O<sub>3</sub> with 60 wt.% K<sub>2</sub>CO<sub>3</sub> was about 128 mg CO<sub>2</sub>/g sorbent. This excellent CO<sub>2</sub> capture capacity and regeneration property were due to the characteristics of the Re-KAl(I) sorbent producing only a KHCO<sub>3</sub> phase during CO<sub>2</sub> sorption, unlike the KAlI30 sorbent which formed the KHCO<sub>3</sub> and KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phases even at 60 °C. This result was explained through the structural effect of the support containing the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase which was prepared by impregnation of Al<sub>2</sub>O<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub>.

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### 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is a major greenhouse gas that is released into the atmosphere due to the use of fossil fuels (oil, natural gas, and coal). As a consequence, CO<sub>2</sub> causes global warming, which may in time have a disastrous effect on the environment. It can be removed from flue gas and waste gas streams by various methods such as membrane separation, absorption with a solvent, and adsorption using molecular sieves [1–13]. However, these methods are costly and consume a lot of energy. One of the more efficient techniques for the removal of CO<sub>2</sub> is the chemical absorption of CO<sub>2</sub> with regenerable solid sorbents. This CO<sub>2</sub> separation technique is a cost-effective and energy-efficient way to capture CO<sub>2</sub> from flue gas [14–19]. Solid sorbents containing alkali metal for CO<sub>2</sub> capture have been recorded in different studies [19–23] as the following reaction: M<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub> = 2MHCO<sub>3</sub> (M = Na, K) [17,24–36]. Several studies, which have regarded the efficient chemical absorption of CO<sub>2</sub> over K<sub>2</sub>CO<sub>3</sub>, supported on carbon [16–18,20,24,25], and also reported using cyclic fixed-bed operations under moist conditions, for the capture of CO<sub>2</sub> from flue

gases. The sorption of CO<sub>2</sub> by the K<sub>2</sub>CO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> composite sorbent was studied with in situ IR spectroscopy and X-ray diffraction analysis [32]. Thus, several additives or supports which included activated carbon, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were used in alkali metal-based sorbents to absorb CO<sub>2</sub>. Nonetheless, these sorbents using SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were at a disadvantage in that there was a decrease of reactivity during multiple sorptions/regenerations at temperature range between 40 and 200 °C [24,30,31]. In particular, potassium-based alumina sorbents formed new structures which included KAl(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> [24,30] or KAl(CO<sub>3</sub>)<sub>2</sub>•1.5H<sub>2</sub>O [21,32] during CO<sub>2</sub> sorption even at temperatures below 60 °C. Due to these new structures, these sorbents could not be completely regenerated below 200 °C. To overcome this problem, the formation of a KHCO<sub>3</sub> crystal structures without by products during CO<sub>2</sub> sorption was a key factor [24,30–32]. In this study, to design an excellent regenerable dry sorbent for CO<sub>2</sub> capture at temperatures below 200 °C, a new alumina-modified support was used for preparation of the new sorbent.

The major objectives of this work are to identify the CO<sub>2</sub> capture capacity and regeneration property of a new regenerable K<sub>2</sub>CO<sub>3</sub>-based alumina sorbent developed in this study for use in CO<sub>2</sub> sorption at temperatures below 200 °C. In addition, changes in the physical properties of the new alumina-modified supports and the sorbents before and after CO<sub>2</sub> sorption were investigated with

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the aid of Power X-ray diffraction (XRD; Philips, X'PERT), TGA/DTA and Temperature Programmed Desorption (TPD).

## 2. Experiment

### 2.1. Preparation of sorbents

The potassium-based sorbents used in this study were prepared by the impregnation of alumina-modified support with  $K_2CO_3$ . The preparation process of the alumina-modified support consisted of three steps as follows: (1) drying the product, which was prepared by the impregnation of  $Al_2O_3$  (Aldrich) with  $K_2CO_3$  in the presence of  $CO_2$ , at 100 °C (sample I), (2) washing sample I with de-ionized water (sample II), (3) calcining sample II at 200 °C (sample III). The preparation procedure for Sample I was as follows: 5.0 g of  $Al_2O_3$  were added to aqueous solution containing 2.14 g of anhydrous potassium carbonate ( $K_2CO_3$ , Aldrich) in 25 ml of de-ionized water. Then, it was stirred with a magnetic stirrer for 24 h at a room temperature in the presence of 95%  $CO_2$  with a flow rate of 15 ml/min. The mixture was dried in a rotary vacuum evaporator at 60 °C. This sample was then dried again in a furnace under a  $N_2$  flow of 100 ml/min for 5 h at 100 °C. Sorbents were prepared with an impregnation method using alumina-modified support and an aqueous solution of anhydrous potassium carbonate ( $K_2CO_3$ , Aldrich) [16,17,24,31,33]. The procedure was similar to the one employed for the preparation of alumina-modified support in the previous section except for the injection of  $CO_2$ . The dried samples were calcined in a furnace under a  $N_2$  flow (100 ml/min) for 5 h at 200 °C. The ramping rate of the temperature was maintained at 3 °C/min. We denoted the sorbent as Re-KAl(I)30, respectively, where Re represents the sorbent prepared by the alumina-modified support, K represents  $K_2CO_3$ , I represents the impregnation method, and 30 represents the loading amount of  $K_2CO_3$ . To compare its  $CO_2$  capture capacity and regeneration ability, the KAlI30 sorbent was prepared using conventional impregnation method of  $\gamma$ -alumina (Aldrich) with  $K_2CO_3$  without  $CO_2$ .

### 2.2. Apparatus and procedures

$CO_2$  sorption and regeneration processes were performed in a fixed-bed quartz reactor, with a diameter of 1 cm. It was placed in an electric furnace under atmospheric pressure. Half of the sorbent, 0.5 g, was packed into the reactor. All volumetric gas flows were measured under standard temperature and pressure (STP) conditions. The temperature of the inlet and outlet lines of the reactor was maintained above 100 °C to prevent the condensation of water vapor being injected into the reactor and G.C. column. The column used in the analysis was a 1/8 inch stainless tube packed with Porapak Q. When the  $CO_2$  concentration of the outlet gases reached the same level as that of the inlet gas (1 vol.%) in  $CO_2$  sorption process, nitrogen was introduced for a sufficient time in multiple tests, to regenerate the spent sorbents. The outlet gases from the reactor were automatically analyzed every 4 min by a Thermal Conductivity Detector (TCD; Donam Systems Inc.), which was equipped with an auto sampler (Valco Instruments CO. Inc.).

In addition, X-ray diffraction (XRD; Philips, X'PERT) was performed to identify crystalline phases in the materials at the Korean Basic Science Institute (Daegu). A Philips X'PERT instrument which used Cu K $\alpha$  radiation was utilized to do so. Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA) were also carried out using a Seiko TG/DTA 320 analyser. Nitrogen was used as the carrier gas and the heating rate was 5 °C/min.

## 3. Results and discussion

### 3.1. $CO_2$ capture capacities of KAlI30 and Re-KAl(I)30 sorbents

The  $CO_2$  capture capacity of a sorbent was evaluated by the breakthrough curve for  $CO_2$  sorption. Fig. 1 shows the breakthrough curves of KAlI30 (a) and Re-KAl(I)30 (b) sorbents at 1 and 5 cycles in the presence of 9 vol.%  $H_2O$  and 1 vol.%  $CO_2$  at 60 °C. In the case of the KAlI30 sorbent prepared by the impregnation of  $Al_2O_3$  with  $K_2CO_3$ , it was observed that the breakthrough time rapidly decreased with increasing cycle number. In the case of the Re-KAl(I)30 sorbent developed in this study, a breakthrough pattern at 1 cycle was similar to that at 5 cycles, unlike the KAlI30.

Fig. 2 shows  $CO_2$  capture capacities of the KAlI30 and Re-KAl(I)30 sorbents during multiple cycles at a regeneration temperature of 200 °C. In this study, the  $CO_2$  capture capacity of the sorbent was calculated from its breakthrough curve during  $CO_2$  sorption in the presence of water vapor and  $CO_2$ . The X-axis indicates the cycle number and the Y-axis indicates the amount of  $CO_2$  sorbed per 1 g of sorbent until the output concentration of  $CO_2$  reached 1 vol.%, which is the same as that of the inlet. As shown in Fig. 2, the  $CO_2$  capture capacity of the KAlI30 sorbent was about 86.3 mg  $CO_2$ /g sorbent at the first cyclic number. However, at the regeneration temperature of 200 °C, its  $CO_2$  capture capacity gradually decreased with increasing cycle number. On the other hand, the  $CO_2$  capture capacity of the Re-KAl(I)30 sorbent developed in this work was maintained during multiple cycles even at the same regeneration temperature of 200 °C. In previous papers [21,24,30,32], the XRD patterns of the potassium-based  $Al_2O_3$  sorbent after  $CO_2$  sorption showed two phases, which were

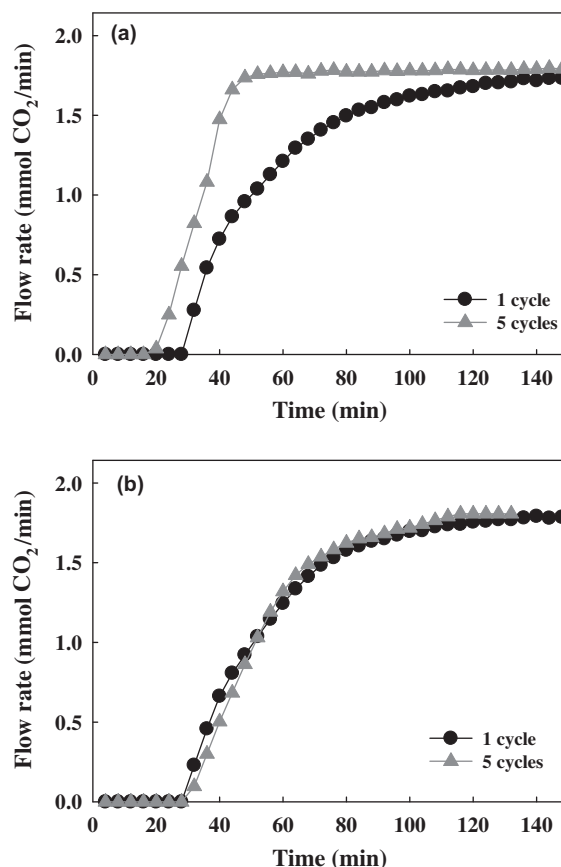
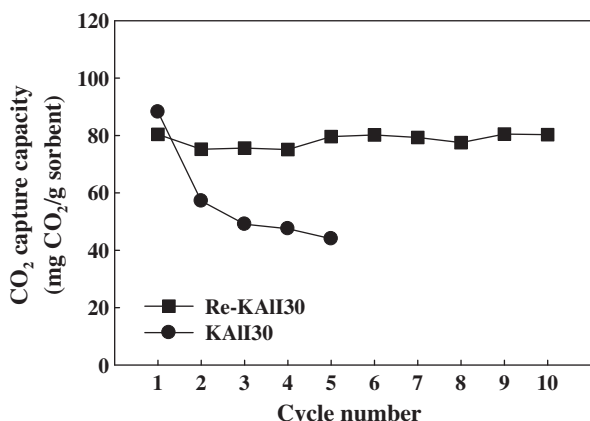


Fig. 1. Breakthrough curves of the KAlI30 (a) and Re-KAl(I)30 (b) sorbents in the presence of 9 vol.%  $H_2O$  and 1 vol.%  $CO_2$  at 60 °C at 1 and 5 cycles.

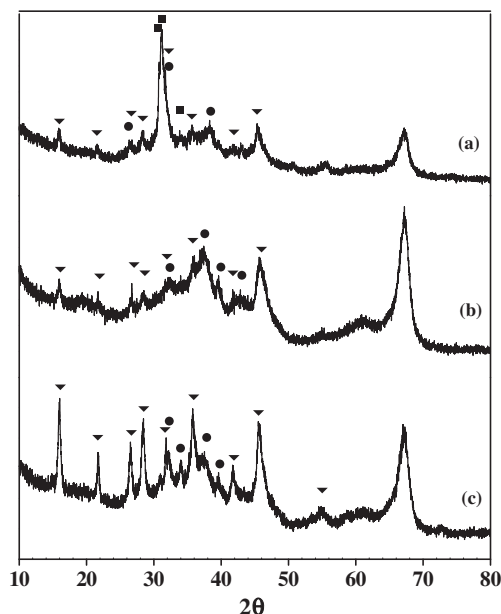


**Fig. 2.** CO<sub>2</sub> capture capacities of KAlI30 and Re-KAl(I)30 sorbents in the presence of 9 vol.% H<sub>2</sub>O and 1 vol.% CO<sub>2</sub> at 60 °C during the multiple cycles at a regeneration temperature of 200 °C.

assigned to a KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase (JCPDS No. 22-0791) [37,38] and a KHCO<sub>3</sub> phase (JCPDS No. 70-0095). Besides, it was shown that the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase formed during CO<sub>2</sub> sorption could not be completely converted into the initial phase of K<sub>2</sub>CO<sub>3</sub> even at 200 °C and that the spent KAlI30 sorbent could be completely regenerated above 300 °C [24,30].

### 3.2. The fabrication of a new alumina-modified support

Even though a potassium-based alumina sorbent has the excellent CO<sub>2</sub> capture capacity, a disadvantage of the sorbent is that it requires a regeneration temperature above 300 °C. To overcome this problem, the alumina-modified support containing the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase was used for the preparation of the new sorbent (Re-KAl(I)). Fig. 3 shows the XRD patterns of sample I, II, and III prepared in the course of support preparation. Sample I was prepared by drying the product, which was prepared by impregnation of Al<sub>2</sub>O<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub>, at 100 °C. To fabricate the support containing the alloy product like KAl(CO<sub>3</sub>)(OH)<sub>2</sub>, CO<sub>2</sub>



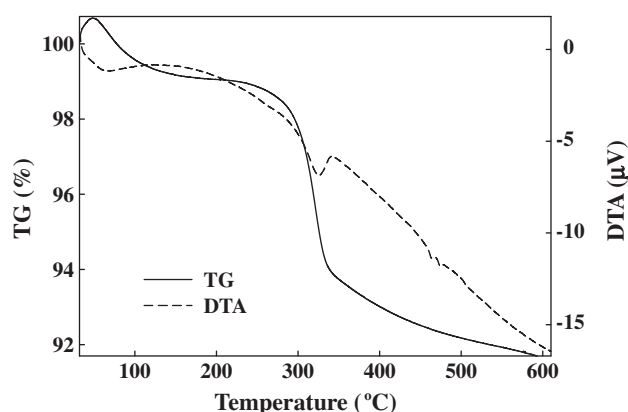
**Fig. 3.** XRD patterns of sample I (a), II (b), and III (c) in the course of the preparation of the alumina-modified support: (●) K<sub>2</sub>CO<sub>3</sub>; (■) KHCO<sub>3</sub>; (▼) KAl(CO<sub>3</sub>)(OH)<sub>2</sub>.

was injected in the course of impregnation. Sample II was prepared by washing sample I with de-ionized water. Sample III was fabricated by calcining sample II at 200 °C. As shown in Fig. 3 (a), sample I showed three phases, which were the K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub>, and KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phases. The three phases resulted from the production of KHCO<sub>3</sub> and KAl(CO<sub>3</sub>)(OH)<sub>2</sub>, which occurred during CO<sub>2</sub> sorption in the impregnation process of Al<sub>2</sub>O<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub>. Sample II showed the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase as the major peak and the K<sub>2</sub>CO<sub>3</sub> phase. This indicated that most of the K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> phases disappeared in the course of washing the sample I. Sample III calcined at 200 °C showed two phases like those of sample II, even though the intensity changed. It must be noted that this alumina-modified sorbent containing the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase was used as the support for the Re-KAl(I)30 sorbent. Fig. 4 shows the TGA/DTA results of sample III. When the ramping rate was 5 °C/min under N<sub>2</sub>, weight losses of about 1 and 5 wt.% occurred between 60 and 100 °C and between 260 and 350 °C, respectively. The initial weight loss was due to the desorption of H<sub>2</sub>O and the second weight loss was due to the desorption of CO<sub>2</sub> which in turn occurred as a result of the conversion of the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase into the separated K<sub>2</sub>CO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> phases. It was concluded that the support (sample III) could be maintaining the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase after repeated regenerations at a temperature lower than 200 °C.

### 3.3. New regenerable alumina-modified sorbents

Fig. 5 shows the XRD patterns of the Re-KAl(I)30 sorbent before and after CO<sub>2</sub> sorption at 60 °C. The XRD pattern of the fresh Re-KAl(I)30 sorbent showed the K<sub>2</sub>CO<sub>3</sub> phase, which was a monoclinic structure, and the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase. It must be noted that KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase was observed in the XRD patterns of the fresh Re-KAl(I)30 sorbent. However, the fresh KAlI30 sorbent's XRD pattern had only a K<sub>2</sub>CO<sub>3</sub> phase as reported in a previous paper [24,30]. The existence of the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase of the fresh Re-KAl(I)30 sorbent was due to the new alumina-modified support. After CO<sub>2</sub> sorption, the two phases could be identified such as the KHCO<sub>3</sub> phase and the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase. From these results, it was clear that the K<sub>2</sub>CO<sub>3</sub> phase was converted into the KHCO<sub>3</sub> phase during CO<sub>2</sub> sorption. However, it was impossible to distinguish the differences between the intensities of the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phases of XRD analysis before and after CO<sub>2</sub> sorption. Unfortunately, it was impossible to determine whether the most of K<sub>2</sub>CO<sub>3</sub> phase was converted into a single KHCO<sub>3</sub> phase or a part of the K<sub>2</sub>CO<sub>3</sub> was converted into a KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase.

To identify these results, TPD tests of the spent Re-KAl(I)30 sorbents after CO<sub>2</sub> sorption at 1 and 10 cycles were carried out at



**Fig. 4.** TGA/DTA results of the sample III.

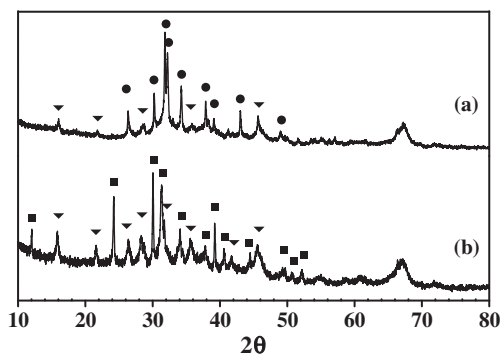


Fig. 5. XRD patterns of the Re-KAl(I)30 sorbent before (a) and after (b)  $\text{CO}_2$  sorption at 60 °C; (●)  $\text{K}_2\text{CO}_3$ ; (■)  $\text{KHCO}_3$ ; (▼)  $\text{KAl}(\text{CO}_3)(\text{OH})_2$ .

a temperature range between 60 and 400 °C with a ramping rate of 2 °C/min and these results were shown in Fig. 6 (a). It was observed in both results that there were two  $\text{CO}_2$  desorption peaks around 130 and 300 °C. It was known that these  $\text{CO}_2$  peaks were due to  $\text{CO}_2$  desorption of  $\text{KHCO}_3$  and  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  as reported in a previous paper [24,30]. Fig. 6 (b) shows the TPD results of the KAlI30 sorbent after  $\text{CO}_2$  sorption at 1 cycle and 5 cycles. From TPD results in Fig. 6 (b), it was evident that the peak area around 130 °C at 5 cycles decreased in comparison to that of the sorbent at 1 cycle. However, at a temperature range between 240 and 360 °C, the peak area at 5 cycles increased rather than decreasing, unlike the TPD results of the Re-KAl(I)30 sorbent in Fig. 6 (a). These results indicated that the formation of the  $\text{KHCO}_3$  phase decreased with an increase in cycle number during  $\text{CO}_2$  sorption, while the  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  phase increased. In the case of the Re-KAl(I)30 sorbent, the peak areas around 130 and 300 °C were almost

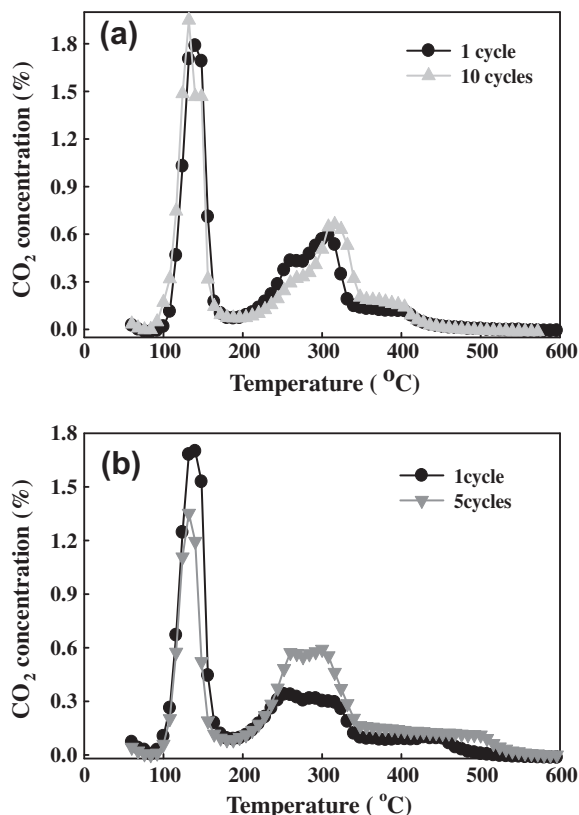


Fig. 6. TPD results of the Re-KAl(I)30 (a) and KAl(I)30 (b) sorbents after  $\text{CO}_2$  sorption.

maintained in spite of an increase in cycle number, unlike the TPD results of the KAlI30 sorbent. In addition, the amounts of  $\text{CO}_2$  desorption calculated from the initial peaks around 130 °C at 1 and 10 cycles were about 82 mg  $\text{CO}_2$ /g sorbent. This value was similar to the  $\text{CO}_2$  capture capacity. From these results, it is clear that the  $\text{K}_2\text{CO}_3$  phase in the Re-KAl(I)30 sorbent forms  $\text{KHCO}_3$  and do not form  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  during  $\text{CO}_2$  sorption. These results demonstrate the reason why the  $\text{CO}_2$  capture capacity of the Re-KAl(I)30 sorbent is maintained during multiple cycles in Fig. 2. It was concluded that the excellent regeneration property of the Re-KAl(I)30 sorbent was attributed to the structural effect of the support which contained the  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  phase.

### 3.4. The regeneration property of the Re-KAl(I)30 sorbent

Fig. 7 shows the  $\text{CO}_2$  capture capacity of the Re-KAl(I)30 sorbent in the presence of 1 vol.%  $\text{CO}_2$  and 9 vol.%  $\text{H}_2\text{O}$  at 60 °C during multiple cycles at regeneration temperatures of 130 and 150 °C. The  $\text{CO}_2$  capture capacity of the sorbent was maintained during multiple cycles even below 150 °C, unlike the KAlI30 sorbent. To identify the regeneration ability of the Re-KAl(I)30 sorbent, the  $\text{CO}_2$  concentrations desorbed were measured during regeneration at various temperatures (130, 150, and 200 °C) and these results were shown in Fig. 8. It was observed that the amount of  $\text{CO}_2$  desorbed at each regeneration temperature was nearly constant (80–81 mg  $\text{CO}_2$ /g sorbent). However, it was known that the regeneration rate decreased with decreasing regeneration temperature. These results indicated that most of the  $\text{CO}_2$  sorbed during  $\text{CO}_2$  sorption was desorbed during the regeneration. They also indicated that the  $\text{K}_2\text{CO}_3$  from the Re-KAl(I)30 sorbent developed in this work was not converted into the  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  phase during  $\text{CO}_2$  sorption. It was only converted into a  $\text{KHCO}_3$  phase.

### 3.5. The enhancement of the $\text{CO}_2$ capture capacity of Re-KAl(I) sorbents

The effect of the amount of  $\text{K}_2\text{CO}_3$  loaded on the  $\text{CO}_2$  capture capacity of Re-KAl(I) sorbents in the presence of 9.0 vol.%  $\text{H}_2\text{O}$  and 1 vol.%  $\text{CO}_2$  at 60 °C was investigated. Fig. 9 shows the  $\text{CO}_2$  capture capacities (a) and the amount of  $\text{CO}_2$  sorption per 1 g of  $\text{K}_2\text{CO}_3$  (b) of the Re-KAl(I) sorbents as a function of the amount of  $\text{K}_2\text{CO}_3$  loaded in the presence of 1 vol.%  $\text{CO}_2$  and 9 vol.%  $\text{H}_2\text{O}$  at 60 °C. The Re-KAl(I)30, Re-KAl(I)40, Re-KAl(I)50, and Re-KAl(I)60 sorbents were prepared by impregnation of the alumina-modified support containing  $\text{KAl}(\text{CO}_3)(\text{OH})_2$  with 30, 40, 50, and 60 wt.%  $\text{K}_2\text{CO}_3$ . In

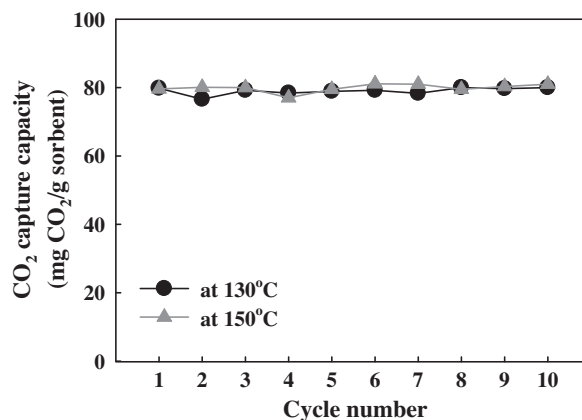


Fig. 7. The  $\text{CO}_2$  capture capacity of the Re-KAl(I)30 sorbent in the presence of 1 vol.%  $\text{CO}_2$  and 9 vol.%  $\text{H}_2\text{O}$  at 60 °C during the multiple cycles at regeneration temperatures of 130 and 150 °C.



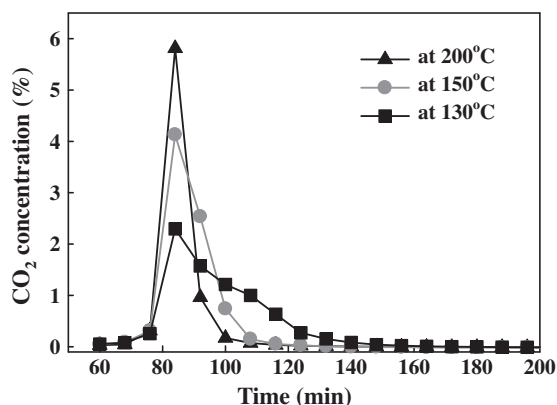


Fig. 8. The CO<sub>2</sub> desorption curves of the Re-KAl(I)30 sorbent at various regeneration temperatures such as 130, 150, and 200 °C.

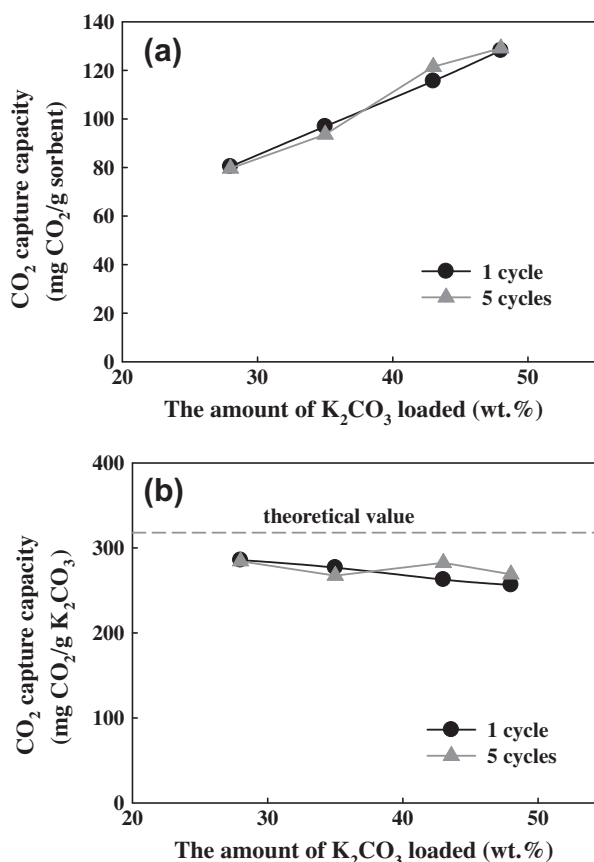


Fig. 9. The CO<sub>2</sub> capture capacities (a) and the amount of CO<sub>2</sub> sorption per 1 g of K<sub>2</sub>CO<sub>3</sub> (b) of the Re-KAl(I) sorbents as a function of the amount of K<sub>2</sub>CO<sub>3</sub> loaded in the presence of 1 vol.% CO<sub>2</sub> and 9 vol.% H<sub>2</sub>O at 60 °C.

a separated ICP-AES experiment, it was known that the amounts of K<sub>2</sub>CO<sub>3</sub> loaded were actually 28, 35, 43 and 48 wt.%, respectively. The CO<sub>2</sub> capture capacity of the sorbent increased proportionately with the amount of K<sub>2</sub>CO<sub>3</sub> loaded. In particular, the CO<sub>2</sub> capture capacity of the Re-KAl(I)60 sorbent was about 128 mg CO<sub>2</sub>/g sorbent. In addition, it was confirmed that the CO<sub>2</sub> capture capacities of the Re-KAl(I) sorbents at 5 cycles, as well as at 1 cycle, were equivalent to about 80–90 percent of their theoretical values (318.3 mg CO<sub>2</sub>/g K<sub>2</sub>CO<sub>3</sub>) which were calculated from the mol of K<sub>2</sub>CO<sub>3</sub> loaded in the sorbent.

#### 4. Conclusions

The CO<sub>2</sub> capture capacity of a potassium-based sorbent containing Al<sub>2</sub>O<sub>3</sub> poses disadvantage in that there was a decrease of CO<sub>2</sub> capture capacity during multiple tests at temperatures below 200 °C. To overcome this problem, a new alumina-modified support containing the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase was used for preparation of the new sorbent. The new regenerable potassium-based sorbent (Re-KAl(I)) maintained its CO<sub>2</sub> capture capacity during multiple tests even at a regeneration temperature of 130 °C. This excellent regeneration property was due to the characteristics of the Re-KAl(I) sorbent producing only a KHCO<sub>3</sub> phase during CO<sub>2</sub> sorption, unlike the KAlI30 sorbent which formed the KHCO<sub>3</sub> and KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phases even at 60 °C. This result was explained through the structural effect of the support containing the KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phase which was prepared by impregnation of Al<sub>2</sub>O<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub>. In conclusion, the Re-KAl(I) sorbent could be used as the sorbent for CO<sub>2</sub> sorption at temperatures below 200 °C in that it could satisfy the high CO<sub>2</sub> capture capacity and the excellent regeneration ability even at 130 °C.

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#### References

- [1] Hagewiesche DP, Ashour SS, Al-Ghawas HA, Sandall OC. Absorption of carbon dioxide into aqueous blends of monoethanolamine and N-methyldiethanolamine. *Chem Eng Sci* 1995;50(7):1071–9.
- [2] Mavroudi M, Kaldis SP, Sakellariopoulos GP. Reduction of CO<sub>2</sub> emissions by a membrane contacting process. *Fuel* 2003;82:2153–9.
- [3] Siriwardane RV, Fisher ShenMS, EP PostonJA. Adsorption of CO<sub>2</sub> on molecular sieves and activated carbon. *Energy Fuels* 2001;15:279–84.
- [4] Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide on basic alumina at high temperatures. *J Chem Eng Data* 2000;45(6):1093–5.
- [5] Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide onto hydrotalcite-like compounds (HTLCs) at high temperatures. *Ind Eng Chem Res* 2001;40:204–9.
- [6] Takamura Y, Narita S, Aoki J, Hironaka S, Uchida S. Evaluation of dual-bed pressure swing adsorption for CO<sub>2</sub> recovery from boiler exhaust gas. *Sep Purif Technol* 2001;24:519–28.
- [7] Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide on chemically modified high surface area carbon-based adsorbents at high temperatures. *Adsorption* 2001;7(1):41–50.
- [8] Yong Z, Rodrigues AE. Hydrotalcite-like compounds as adsorbents for carbon dioxide. *Engng Convers Manage* 2002;43:1865–76.
- [9] Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, et al. Test results from a CO<sub>2</sub> extraction pilot plant at boundary dam coal-fired power station. *Energy* 2004;29:1259–67.
- [10] Yong Z, Rodrigues AE. Adsorbent materials for carbon dioxide. *Adsorpt Sci Technol* 2001;19(3):255–66.
- [11] Shena Ci, Grande CA, Li P, Yu J, Rodrigues AE. Adsorption equilibria and kinetics of CO<sub>2</sub> and N<sub>2</sub> on activated carbon. *Chem Eng J* 2010;160:398–407.
- [12] Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide at high temperature: a review. *Sep Purif Technol* 2002;26:195–205.
- [13] Dantas TLP, Amorim SM, Luna FMT, Silva Jr JJ, Azevedo DCS, Rodrigues AE, et al. Adsorption of carbon dioxide onto activated carbon and nitrogen-enriched activated carbon: surface changes, equilibrium and modeling of fixed-bed adsorption. *Sep Sci Technol* 2010;45:73–84.
- [14] Oliveira ELG, Grande CA, Rodrigues AE. CO<sub>2</sub> sorption on hydrotalcite and alkali modified (K and Cs) hydrotalcites at high temperatures. *Sep Purif Technol* 2008;62:137–47.
- [15] Gupta H, Fan LS. Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. *Ind Eng Chem Res* 2002;41:4035–42.
- [16] Hayashi H, Taniuchi J, Furuyashiki N, Sugiyama S, Hirano S, Shigemoto N, et al. Efficient recovery of carbon dioxide from flue gases of coal-fired power plants by cyclic fixed-bed operations over K<sub>2</sub>CO<sub>3</sub>-on-carbon. *Ind Eng Chem Res* 1998;37:185–91.
- [17] Hirano S, Shigemoto N, Yamashita S, Hayashi H. Cyclic fixed-bed operations over K<sub>2</sub>CO<sub>3</sub>-on-carbon for the recovery of carbon dioxide under moist conditions. *Bull Chem Soc Jpn* 1995;68:1030–5.

- [18] Shigemoto N, Yanagihara T, Sugiyama S, Hayashi H. Material balance and energy consumption for CO<sub>2</sub> recovery from moist flue gas employing K<sub>2</sub>CO<sub>3</sub>-on-activated carbon and its evaluation for practical adaptation. *Energy Fuels* 2006;20(2):721–6.
- [19] Liang Y, Harrison DP, Gupta RP, Green DA, McMichael WJ. Carbon dioxide capture using dry sodium-based sorbents. *Energy Fuels* 2004;18:569–75.
- [20] Lee SC, Choi BY, Lee SJ, Jung SY, Ryu CK, Kim JC. CO<sub>2</sub> absorption and regeneration using Na and K based sorbents. *Stud Surf Sci Catal* 2004;153:527–30.
- [21] Okunev AG, Sharonov VE, Aistov YI, Parmon VN. Sorption of carbon dioxide from wet gases by K<sub>2</sub>CO<sub>3</sub>-in-porous matrix: Influence of the matrix nature. *React Kinet Catal Lett* 2000;71(2):355–62.
- [22] Zhao CW, Chen XP, Zhao CS. Effect of crystal structure on CO<sub>2</sub> capture characteristics of dry potassium-based sorbents. *Chemosphere* 2009;75:1401–4.
- [23] Yi CK, Jo SH, Seo YW, Lee JB, Ryu CK. Continuous operation of the potassium-based dry sorbent CO<sub>2</sub> capture process with two fluidized-bed reactors. *Int J Green Gas Cont* 2007;1(1):31–6.
- [24] Lee SC, Choi BY, Lee TJ, Ryu CK, Ahn YS, Kim JC. CO<sub>2</sub> absorption and regeneration of alkali metal-based solid sorbents. *Catal Today* 2006;111:385–90.
- [25] Lee SC, Choi BY, Ryu CK, Ahn YS, Lee TJ, Kim JC. The effect of water on the activation and the CO<sub>2</sub> capture capacities of alkali metal-based sorbents. *Korean J Chem Eng* 2006;23(3):374–9.
- [26] Gidaspow D, Onischak M. Process for regenerative sorption CO<sub>2</sub>. U S Patent 3865924, 1975.
- [27] Zhao CW, Chen XP, Zhao CS. CO<sub>2</sub> absorption using dry potassium-based sorbents with different supports. *Energy Fuels* 2009;23(9):4683–7.
- [28] Yi CK, Jo SH, Seo YW. The effect of voidage on the CO<sub>2</sub> sorption capacity of K-based sorbent in a dual circulating fluidized bed process. *J Chem Eng Jan* 2008;41(7):691–4.
- [29] Seo YW, Jo SH, Ryu CK, Yi CK. Effects of water vapor pretreatment time and reaction temperature on CO<sub>2</sub> capture characteristics of a sodium-based solid sorbent in a bubbling fluidized-bed reactor. *Chemosphere* 2007;69:712–8.
- [30] Lee SC, Kim JC. Dry potassium-based sorbents for CO<sub>2</sub> capture. *Catal Surv Asia* 2007;11(4):171–85.
- [31] Lee SC, Chae HJ, Lee SJ, Park YH, Ryu CK, Yi CK, et al. Novel regenerable potassium-based dry sorbents for CO<sub>2</sub> capture at low temperatures. *J Mol Catal B: Enzym* 2009;56(2–3):179–84.
- [32] Okunev AG, Sharonov VE, Gubar AV, Danilova IG, Paukshtis EA, Moroz EM, et al. Sorption of carbon dioxide by the composite sorbent “potassium carbonate in porous matrix”. *Russ Chem Bull Int Ed* 2003;52(2):359–63.
- [33] Lee SC, Chae HJ, Lee SJ, Choi BY, Yi CK, Lee JB, et al. Development of regenerable MgO-based sorbent promoted with K<sub>2</sub>CO<sub>3</sub> for CO<sub>2</sub> capture at low temperatures. *Environ Sci Technol* 2008;42(8):2736–41.
- [34] Seo YW, Jo SH, Ryu HJ, Bae DH, Ryu CK, Yi CK. Effect of water pretreatment on CO<sub>2</sub> capture using a potassium-based solid sorbent in a bubbling fluidized bed reactor. *Korean J Chem Eng* 2007;24(3):457–60.
- [35] Lee SC, Chae HJ, Kwon YM, Nam LeeWS, HS JungSY, Lee JB, et al. Characteristics of new potassium-based sorbents prepared with nano-titanium oxide for carbon dioxide capture. *J Nanoelectron Optoelectron* 2010;5(2):212–7.
- [36] Lee SC, Chae HJ, Choi BY, Jung SY, Ryu CY, Park JJ, Baek JI, Ryu CK, Kim JC. The effect of relative humidity on CO<sub>2</sub> capture capacity of potassium-based sorbents. *Korean J Chem Eng*, 2011, in press.
- [37] Fernandez-Carrasco L, Puertas F, Blanco-Varela MT, Vazquez T, Rius J. Synthesis and crystal structure solution of potassium dawsonite: an intermediate compound in the alkaline hydrolysis of calcium aluminate cements. *Cem Concr Res* 2005;32:641–6.
- [38] Wang Y, Zhu JH, Huang WY. Synthesis and characterization of potassium-modified alumina superbases. *Phys Chem Chem Phys* 2001;3:2537–43.