

# K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> for Capturing CO<sub>2</sub> in Flue Gas from Power Plants. Part 3: CO<sub>2</sub> Capture Behaviors of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> in a Bubbling Fluidized-Bed Reactor

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**ABSTRACT:** K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> used for capturing CO<sub>2</sub> in flue gas is thoroughly investigated. The present paper focuses on the CO<sub>2</sub> capture behaviors of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> in a bubbling fluidized-bed reactor. It is found that K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> shows a higher CO<sub>2</sub> capture capacity than other potassium-based sorbents. The carbonation reaction capacities are in the range of 290–319 mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub> for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with loading amounts of 12.8–36.8%. It is abruptly decreased to 148.98 mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub> when the loading amount of K<sub>2</sub>CO<sub>3</sub> increases to 45.1%. The reason is attributed to the change of the active component distribution behavior. The total CO<sub>2</sub> sorption capacity maintains a high level when the carbonation temperature is in the range of 60–80 °C. The CO<sub>2</sub> capture behavior is significantly affected by the changing H<sub>2</sub>O concentration and the process of water pretreatment for the sorbent. The effect of the CO<sub>2</sub> concentration is not significant on the carbonation conversion when it is in the range of 10–30%. The sorbent is completely regenerated when the final temperature is higher than 300 °C in a slow heating process, and the temperature for 100% regeneration of the sorbent is 350 °C in a rapid heating process. The carbonation conversion of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> decreases from 91 to 79.6% after 80 cycles. The surface area and pore volume of the sorbent keep a stable value, and the pore size distribution behavior is not changed after 80 cycles.

## 1. INTRODUCTION

In the previous parts of this series of papers (10.1021/ef200725z and 10.1021/ef200866y),<sup>1,2</sup> the carbonation and regeneration behaviors of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> were systematically studied by thermogravimetric analysis (TGA), respectively. However, the relatively large concentration of CO<sub>2</sub> in utility flue gas suggests a fluidized-bed reactor as an appropriate contacting scheme for sorbent capture. The important issue concerned with K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> application in the fluidized-bed reactors is to choose appropriate operation conditions and then to investigate the behavior of the multiple cycles of this sorbent for CO<sub>2</sub> capture. Choosing a proper loading amount for the sorbent is another important issue. In previous papers,<sup>3–11</sup> the CO<sub>2</sub> absorption and regeneration behaviors of several alkali-metal-based sorbents were studied in a fixed-bed reactor or a bubbling fluidized-bed reactor using multiple tests. In this paper, the CO<sub>2</sub> capture capacity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> will be compared to other alkali-metal-based sorbents in detail.

## 2. EXPERIMENTAL SECTION

**2.1. Samples.** K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> used in this study was prepared by impregnating K<sub>2</sub>CO<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. K<sub>2</sub>CO<sub>3</sub> was provided as an analytical reagent, and a special  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was supplied by the Research Institute of Nanjing Chemical Industry Group. The preparation process of the sorbent consisted of three steps: mixing and impregnation, drying at 105 °C for dehydration, and calcination at 300 °C. The range of the particle size for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was chosen as 180–315  $\mu$ m, with a mean particle size of 250  $\mu$ m. The minimum fluidization velocity is 0.05 m/s. Actual loading amounts of these sorbents are 12.8, 19.9, 28.1, 36.8, and 45.1%, respectively. More information about the sorbent preparation method and its microscopic structure was reported in a previous paper.<sup>12</sup>

**2.2. Apparatus and Procedure.** A fluidized-bed reactor with an inner diameter of 0.05 m and a height of 1.0 m was used. More

information about this experimental system was reported in a previous paper.<sup>13</sup> When the test was carried out, about 300 g of the sorbent was placed into the reactor, and the height of the material was 0.15 m. The gas flow rate was chosen as 750 L/h, which corresponded to the fluidization number of 2 for the carbonation and regeneration processes. A simulated flue gas composition of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O was used for the carbonation reactions. The carbonation temperature and gas composition were kept constant. A gas analyzer was used for analyzing the CO<sub>2</sub> concentration of the outlet gas every 5 s. After the carbonation reaction was completed, the gas composition changed to 100% N<sub>2</sub>. When the CO<sub>2</sub> concentration decreased to zero, the temperature was increased to a final temperature for regeneration. Carbonation and regeneration processes were finished when the CO<sub>2</sub> concentration of the outlet gas reached the same level as that of the inlet gas. After regeneration was completed, the temperature was decreased again to the carbonation temperature. In this way, the cycling test of carbonation and regeneration cycles for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was carried out.

The carbonation test for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was carried out with two different methods (the direct carbonation and the carbonation after water pretreatment). For the case of the direct carbonation, the process was carried out under a wide range of reaction conditions by varying the temperature between 50 and 100 °C, the CO<sub>2</sub> concentration between 5 and 30%, and the H<sub>2</sub>O concentration between 0 and 20%. For the case of the carbonation after water pretreatment, the sorbent was first treated in the gas mixture of 85% N<sub>2</sub> and 15% H<sub>2</sub>O at a flow rate of 800 L/h for 30 min. The total amount of H<sub>2</sub>O passing through the sorbent was 2.68 mol. After this process, the carbonation was carried out following the same procedure as that of the direct carbonation.

The regeneration test of the sorbent after carbonation was also carried out with two different methods (the slow heating process and

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the rapid heating process). In the case of the slow heating process, the sorbent was heated to the final regeneration temperature at a mean heating rate of 10 °C/min. The final regeneration temperature was in the range of 150–350 °C. Because the carbonation product could not be completely decomposed when the final temperature was in the range of 150–250 °C, the temperature increased to 350 °C after 50 min to ensure that the carbonation product was completely decomposed. In the case of the rapid heating process, the reactor was first heated to the final regeneration temperature and then the sorbent was placed into the reactor for regeneration.

The amount of alkali metal impregnated was determined by an AdvantXP X-ray fluorescence (XRF). An ASAP 2020 system with N<sub>2</sub> adsorption–desorption was used for surface area and pore structure determinations. The shape of sorbents from the view of a microscope was observed with field-emission scanning electron microscopy (SEM). The change of the particle size was determined by a sieving method.

### 3. THEORETICAL ANALYSIS

Three amounts are used for expressing the CO<sub>2</sub> capture capacity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, including the total CO<sub>2</sub> sorption capacity [ $A_C$  (mg of CO<sub>2</sub>/g of sorbent)], the carbonation reaction capacity [ $R_C$  (mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub>)], and the regeneration conversion ( $\eta_R$ ). Because the amounts of CO<sub>2</sub> captured can be calculated by the change of the CO<sub>2</sub> concentration for the outlet gases from that of the inlet gas,  $A_C$ ,  $R_C$ , and  $\eta_R$  are calculated from eqs 1, 2, and 3, respectively

$$A_C = \frac{1000n_A M_{CO_2}}{w} \quad (1)$$

$$R_C = \frac{A_C}{a} \quad (2)$$

$$\eta_R = \frac{n_R}{n_A} \times 100\% \quad (3)$$

where  $n_A$  and  $n_R$  are the total amounts of CO<sub>2</sub> absorbed in carbonation and CO<sub>2</sub> released in regeneration, respectively,  $M_{CO_2}$  is the molecular weight of CO<sub>2</sub>, and  $w$  and  $a$  are the weight of the sorbent and the loaded amount of K<sub>2</sub>CO<sub>3</sub> in the sample, respectively.

### 4. RESULTS AND DISCUSSION

**4.1. Physical Properties of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.** *4.1.1. Microscopic Structure of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with Different Loading Amounts.* The total surface area, pore volume, and mean pore size of the sorbents with different loading amounts are shown in Table 1.

The total surface area and pore volume for the sorbents decrease, while the mean pore size increases, when the loading

amount of the sorbent increases. The total surface area and pore volume are in the range of 52.1–114.6 m<sup>2</sup>/g and 0.18–0.37 cm<sup>3</sup>/g for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with different loading amounts, respectively. The Korea Institute of Energy Research (KIER) reported that the potassium-based sorbents of sorbKX35<sup>8</sup> and sorbKX35T5<sup>9</sup> and the sodium-based sorbent of sorbNX35<sup>14</sup> showed excellent CO<sub>2</sub> capture capacity in a bubbling fluidized-bed reactor; therefore, their surface areas were listed here to be compared to K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. Their surface areas are in the range of 34.9–62 m<sup>2</sup>/g, which are lower than that of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with the same loading amount. The carbonation reactivity will be affected by the surface area of the sorbent. As a result, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> may be more suitable than these sorbents.

**4.1.2. Particle Morphology of Those Potassium-Based Sorbents.** Particle morphologies of those sorbents were examined with SEM. They are shown in Figure 1.

As shown in Figure 1, active components are distributed on the surface of Al<sub>2</sub>O<sub>3</sub> as the fibers and many small white aggregates. The amount of fibers and white aggregates increases as the loading amount of K<sub>2</sub>CO<sub>3</sub> increases. White aggregates are the smallest, and the distribution of active components is quite uniform for the sorbent with the loading amount of 36.8%. When the loading amount of K<sub>2</sub>CO<sub>3</sub> increases to 45.1%, the fibers disappear and some massive crystals appear on the surface of Al<sub>2</sub>O<sub>3</sub>.

**4.2. CO<sub>2</sub> Breakthrough Curve of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> during a Single Carbonation–Regeneration Cycle.** A typical test during a carbonation–regeneration cycle was carried out for K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with a loading amount of 28.1%. As mentioned in section 2.2, the carbonation process was carried out with two different methods under the reaction condition of 60 °C, 10% CO<sub>2</sub>, 76% N<sub>2</sub>, and 14% H<sub>2</sub>O, while the regeneration process was carried out under a N<sub>2</sub> atmosphere in a final temperature of 300 °C with the heating rate of 10 °C/min. The changes of the CO<sub>2</sub> concentration of the outlet gas and temperature with time are shown in Figure 2.

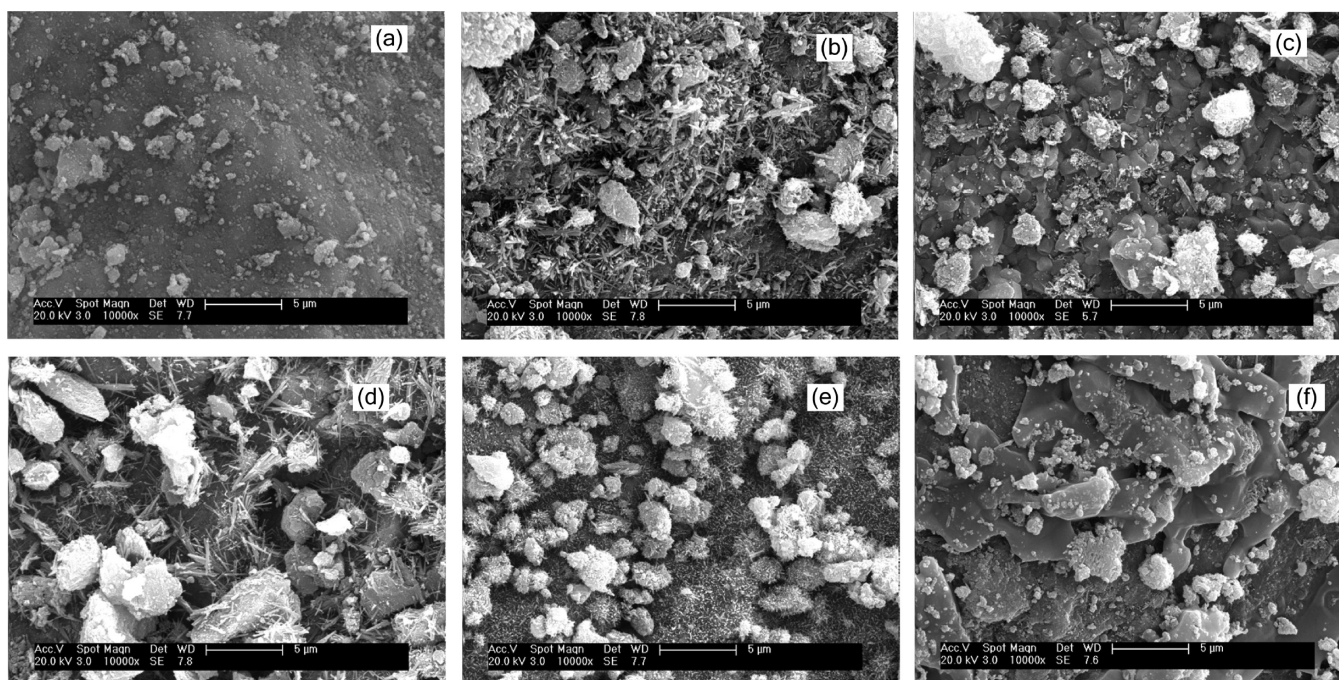
Figure 2 shows that, for the test of direct carbonation, the CO<sub>2</sub> concentration is nearly zero for the first 3 min, indicating that CO<sub>2</sub> removal is 100%, then rapidly increases to 8% in 6.88 min, and remains constant for 30 min. The CO<sub>2</sub> concentration increases to 10% at the time of 31.63 min, indicating the finish of the carbonation process. For the test of carbonation after water pretreatment, the CO<sub>2</sub> concentration stays at nearly zero for 6 min and then increases to 10% at the time of 14.33 min. The time for 100% CO<sub>2</sub> removal increases. The regeneration processes for the sorbents with those two different carbonation processes are similar. The release of CO<sub>2</sub> starts at 95 °C and reaches the maximum amount at 175 °C. The regeneration process finishes before the temperature reaches 300 °C.

It was reported<sup>15</sup> that the carbonation reaction rate of K<sub>2</sub>CO<sub>3</sub> was very high in the first 5 min, and then it decreased to a low value. In this way, the carbonation of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is deduced to include a fast and a slow reaction stage. For the test of direct carbonation, K<sub>2</sub>CO<sub>3</sub> is quickly reacted with CO<sub>2</sub> and H<sub>2</sub>O to give near complete CO<sub>2</sub> removal in the fast reaction stage. The reaction rate and CO<sub>2</sub> removal decrease in the slow reaction stage; therefore, the CO<sub>2</sub> concentration increases to 8% and remains for 30 min. As reported previously,<sup>8,14</sup> CO<sub>2</sub> removal decreased abruptly from the beginning of the carbonation process for sorbKX35 and sorbNX35. In comparison to those sorbents, the CO<sub>2</sub> capture capacity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is improved by controlling the surface area and pore volume to enhance the capability of water sorption. After water pretreat-

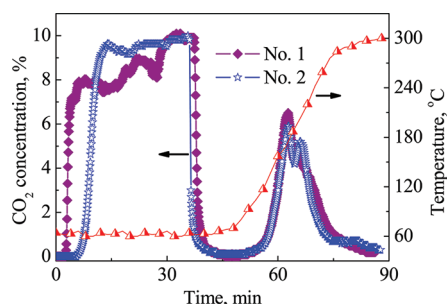
**Table 1. Microscopic Structure of Those Sorbents**

sorbent	loading amount (%)	surface area (m <sup>2</sup> /g)	pore volume (cm <sup>3</sup> /g)	mean pore size (nm)
K <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0	196.4	0.43	9.48
	12.8	114.6	0.37	11.8
	19.9	104.9	0.33	13.8
	28.1	95.1	0.28	15.1
	36.8	81.1	0.23	15.5
	45.1	52.1	0.18	16.4
SorbKX35 <sup>8</sup>	35	34.9	0.18	
SorbKX35T5 <sup>9</sup>	35	38.5	0.31	21.5
SorbNX35 <sup>14</sup>	35	62	0.29	19





**Figure 1.** SEM images taken at the magnification of 10000 $\times$  for  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  with different loading amounts of (a) 0%, (b) 12.8%, (c) 19.9%, (d) 28.1%, (e) 36.8%, and (f) 45.1%.



**Figure 2.** Changes of the  $\text{CO}_2$  concentration of the outlet gas and temperature with time during a typical carbonation–regeneration test: (No. 1) direct carbonation and (No. 2) carbonation after water pretreatment.

ment, sufficient  $\text{H}_2\text{O}$  is physically adsorbed in the sorbent and the reaction rate is improved.  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  shows its full performance for  $\text{CO}_2$  capture. This observation is consistent with the results for sorbKX35 and sorbNX35.<sup>8,14</sup>

**4.3.  $\text{CO}_2$  Capture Capacity of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  with Different Loading Amounts.** The tests during a carbonation–regeneration cycle were carried out for  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  with different loading amounts. The carbonation process was carried out with the method of direct carbonation, and the regeneration process was carried out with the slow heating process. The reaction condition was the same as mentioned in section 2.2.

Calculated from eqs 1, 2, and 3,  $A_C$ ,  $R_C$ , and  $\eta_R$  for  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  with different loading amounts are listed in Table 2.

$A_C$  is only 1.21 mg of  $\text{CO}_2/\text{g}$  of sorbent for  $\text{Al}_2\text{O}_3$ , which means that the physical adsorption capacity is weak for this sorbent.  $A_C$  increases from 41 to 107 mg of  $\text{CO}_2/\text{g}$  of sorbent, while  $R_C$  is slightly decreased from 319 to 290 mg of  $\text{CO}_2/\text{g}$  of  $\text{K}_2\text{CO}_3$ , when the loading amount of  $\text{K}_2\text{CO}_3$  increases from 12.8 to 36.8%.  $A_C$  decreases to 67 mg of  $\text{CO}_2/\text{g}$  of sorbent, and  $R_C$  is abruptly decreased to 149 mg of  $\text{CO}_2/\text{g}$  of  $\text{K}_2\text{CO}_3$ , when

**Table 2.**  $\text{CO}_2$  Capture Capacity of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  with Different Loading Amounts

loading amount (%)	$A_C$ (mg of $\text{CO}_2/\text{g}$ of sorbent)	$R_C$ (mg of $\text{CO}_2/\text{g}$ of $\text{K}_2\text{CO}_3$ )	$\eta_R$ (%)
0	1.2		
12.8	41	319	100
19.9	63	317	99.4
28.1	82	293	98.7
36.8	107	290	98.3
45.1	67	149	97.9

the loading amount of  $\text{K}_2\text{CO}_3$  increases to 45.1%. The reason is attributed to the change of the active component distribution behavior. Active components are distributed on the surface of  $\text{Al}_2\text{O}_3$  as fibers and many small white aggregates when the loading amount of  $\text{K}_2\text{CO}_3$  is in the range of 12.8–36.8%. However, they change to some massive crystals when the loading amount of  $\text{K}_2\text{CO}_3$  is 45.1%. It is found that  $\eta_R$  reaches nearly 100% for all sorbents in this regeneration reaction condition.  $\eta_R$  is slightly decreased from 99.99 to 97.94% when the loading amount of  $\text{K}_2\text{CO}_3$  increases from 12.8 to 45.1%.

It was reported that  $R_C$  of  $\text{K}_2\text{CO}_3/\text{SiO}_2$ ,  $\text{K}_2\text{CO}_3/\text{USY}$ ,  $\text{K}_2\text{CO}_3/\text{CsNaX}$ , and  $\text{K}_2\text{CO}_3/\text{CaO}$  were only in the range of 34–198 mg of  $\text{CO}_2/\text{g}$  of  $\text{K}_2\text{CO}_3$ . Sorbents such as  $\text{K}_2\text{CO}_3/\text{activated carbon}$ ,  $\text{K}_2\text{CO}_3/\text{TiO}_2$ ,  $\text{K}_2\text{CO}_3/\text{ZrO}_2$ , and  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  showed excellent  $\text{CO}_2$  capture capacity, and  $R_C$  values were in the range of 274–290 mg of  $\text{CO}_2/\text{g}$  of  $\text{K}_2\text{CO}_3$ .<sup>3–6</sup> Recently, a K–Fe-based sorbent using  $\text{K}_2\text{CO}_3$  and nanoporous  $\text{FeOOH}$  was developed, and  $R_C$  was 105 mg of  $\text{CO}_2/\text{g}$  of  $\text{K}_2\text{CO}_3$ .<sup>10</sup> All of the above results were obtained from the tests in a fixed-bed reactor. A powder-form sorbent was used, and the  $\text{CO}_2$  concentration was 1% in simulated flue gas. A sorbent with a special particle size was often used in real operation (dozens of micrometers for the fast fluidized-bed reactor or hundreds of micrometers for the bubbling fluidized-bed

Table 3. Total CO<sub>2</sub> Sorption Capacity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with a Loading Amount of 28.1% in Various Reaction Conditions<sup>a</sup>

	temperature (°C)	50	60	70	80	90	100
change reaction temperature	A <sub>C</sub> for tests of direct carbonation (mg of CO <sub>2</sub> /g of sorbent)	69	90	90	81	68	24
	A <sub>C</sub> for tests of carbonation after water pretreatment (mg of CO <sub>2</sub> /g of sorbent)	63	87	81	69	62	53
	CO <sub>2</sub> concentration (%)	5	10	15	20	25	30
change CO <sub>2</sub> concentration	A <sub>C</sub> for tests of direct carbonation (mg of CO <sub>2</sub> /g of sorbent)	66	88	90	90	90	90
	A <sub>C</sub> for tests of carbonation after water pretreatment (mg of CO <sub>2</sub> /g of sorbent)	82	84	87	90	90	91
	H <sub>2</sub> O concentration (%)	10	12	14	16	18	20
change H <sub>2</sub> O concentration	A <sub>C</sub> for tests of direct carbonation (mg of CO <sub>2</sub> /g of sorbent)	50	75	84	85	88	90
	H <sub>2</sub> O concentration (%)	0	5	10	15	20	
	A <sub>C</sub> for tests of carbonation after water pretreatment (mg of CO <sub>2</sub> /g of sorbent)	70	81	81	87	89	

<sup>a</sup>The base reaction conditions are a temperature of 60 °C, gas composition of 10% CO<sub>2</sub>, 76% N<sub>2</sub>, and 14% H<sub>2</sub>O, and theoretical CO<sub>2</sub> sorption capacity of the sorbent of 90 mg of CO<sub>2</sub>/g of sorbent.

reactor), and the CO<sub>2</sub> concentration in flue gas was in the range of 10–20%. The CO<sub>2</sub> capture behavior will be changed as these conditions were changed. The carbonation reaction capacity of K<sub>2</sub>CO<sub>3</sub>/MgO is higher than the theoretical value (in the range of 365–593 mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub>).<sup>3,5,11</sup> The reason is that many other formations [such as K<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>Mg-(CO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and Mg(OH)<sub>2</sub>] are produced. The sorbent could be completely regenerated above 450 °C. For a bubbling fluidized-bed reactor used as the carbonator, it was found that the potassium-based sorbents, sorbKX35 and sorbKX35TS, showed excellent CO<sub>2</sub> capture capacity and R<sub>C</sub> values were in the range of 257–318 mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub>.<sup>7–9</sup> However, the support material was not published. In previous works,<sup>12,13</sup> R<sub>C</sub> values of K<sub>2</sub>CO<sub>3</sub>/activated carbon and K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> were in the range of 279–284 mg of CO<sub>2</sub>/g of K<sub>2</sub>CO<sub>3</sub>. In comparison to all of the sorbents above, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with loading amounts between 12.8 and 36.8% showed a higher CO<sub>2</sub> capture capacity.

**4.4. Effects of Operating Conditions on CO<sub>2</sub> Capture Behaviors of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.** To choose proper carbonation operating conditions, the carbonation processes of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with a loading amount of 28.1% were carried out with the methods mentioned in section 2.2. The base test condition was as follows: the temperature was 60 °C, and the gas composition was 10% CO<sub>2</sub>, 76% N<sub>2</sub>, and 14% H<sub>2</sub>O. Only one factor was changed, while other factors were kept under the same conditions. In this way, the effects of the temperature, CO<sub>2</sub> concentration, and H<sub>2</sub>O concentration on carbonation were studied. Calculated from eq 1, the total CO<sub>2</sub> sorption capacities of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with a loading amount of 28.1% in various reaction conditions are listed in Table 3.

A<sub>C</sub> decreases from 90 to 24 mg of CO<sub>2</sub>/g of sorbent for tests of direct carbonation and decreases from 87 to 53 mg of CO<sub>2</sub>/g of sorbent for tests of carbonation after water pretreatment when the temperature increases from 60 to 100 °C. It was reported that the carbonation reaction of alkali-metal-based sorbent occurred in a narrow temperature range of 60–70 °C in TGA.<sup>16</sup> Because the gas–solid mixing and the contact reaction intensity are higher in the fluidized-bed reactor, the temperature range for high carbonation conversion becomes wider. The decomposition of KHCO<sub>3</sub> is started at 95 °C; therefore, A<sub>C</sub> is very little when the reaction temperature is 100 °C. The temperature of 50 °C is lower than the dew point of this feed gas composition. In this condition, H<sub>2</sub>O is condensed, the sorbent is agglomerated, and the fluidization behavior is destroyed. As a result, the CO<sub>2</sub> capture capacity is not high enough. To obtain a high CO<sub>2</sub> removal and a high carbonation

conversion in a fluidized-bed reactor, the carbonation temperature must be controlled in the range of 60–80 °C.

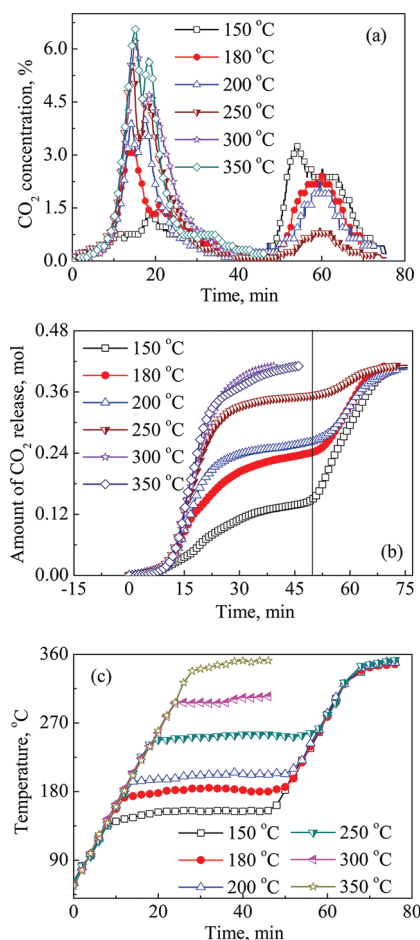
A<sub>C</sub> increases from 66 to 90 mg of CO<sub>2</sub>/g of sorbent for tests of direct carbonation and increases from 82 to 91 mg of CO<sub>2</sub>/g of sorbent for tests of carbonation after water pretreatment when the CO<sub>2</sub> concentration increases from 5 to 30%. The low value of A<sub>C</sub> for the sorbent in the reaction condition of 5% CO<sub>2</sub> is attributed to the fact that the total amount of CO<sub>2</sub> absorbed mainly depends upon the CO<sub>2</sub> capture process in the fast reaction stage. If a small quantity of CO<sub>2</sub> is supplied, the amount of CO<sub>2</sub> absorbed is little in the fast reaction stage. The total amount of CO<sub>2</sub> absorbed will be limited even though the time is long for the slow reaction stage. A<sub>C</sub> is higher than the theoretical value when the CO<sub>2</sub> concentration is higher than 20%. It is deduced that a physical adsorption process occurs for CO<sub>2</sub> on the surface of the sorbent.

A<sub>C</sub> increases from 50 to 90 mg of CO<sub>2</sub>/g of sorbent for tests of direct carbonation when the H<sub>2</sub>O concentration increases from 10 to 20%. For tests of carbonation after water pretreatment, A<sub>C</sub> increases from 70 to 89 mg of CO<sub>2</sub>/g of sorbent when the H<sub>2</sub>O concentration increases from 0 to 20%. Although the amount of H<sub>2</sub>O supplied is enough in the pretreatment stage, A<sub>C</sub> does not reach the theoretical value if no H<sub>2</sub>O is supplied unceasingly in the CO<sub>2</sub> capture process. As pointed out in ref 17, for the carbonation process of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O is adsorbed at first and then CO<sub>2</sub> quickly reacts with the adsorbed H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> to produce KHCO<sub>3</sub>. The process of H<sub>2</sub>O adsorbed is important; therefore, water pretreatment plays an important role for carbonation.

**4.5. Effect of the Temperature on Sorbent Regeneration Behaviors of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.** **4.5.1. For a Slow Heating Process.** After the CO<sub>2</sub> absorption process finished in the same reaction conditions (at 60 °C in 10% CO<sub>2</sub>, 76% N<sub>2</sub>, and 14% H<sub>2</sub>O), the regeneration of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with a loading of 28.1% was carried out at different final temperatures with a mean heating rate of 10 °C/min. Results of regeneration and the change of the temperature with time are shown in Figure 3.

As shown in Figure 3b, the total amount of CO<sub>2</sub> release increases from 0.15 to 0.35 mol as the final regeneration temperature increases from 150 to 250 °C. Calculated from eq 3, η<sub>R</sub> values of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are in the range of 35.4–85.5%. The total amount of CO<sub>2</sub> release increases to 0.41 mol, indicating that the sorbent is completely regenerated, when the temperature increases to 350 °C. The CO<sub>2</sub> release curve is similar, and the final amount of CO<sub>2</sub> release reaches the theoretical value, when the final temperature is higher than 300 °C. Viewing the CO<sub>2</sub> release curves in Figure 3a and the

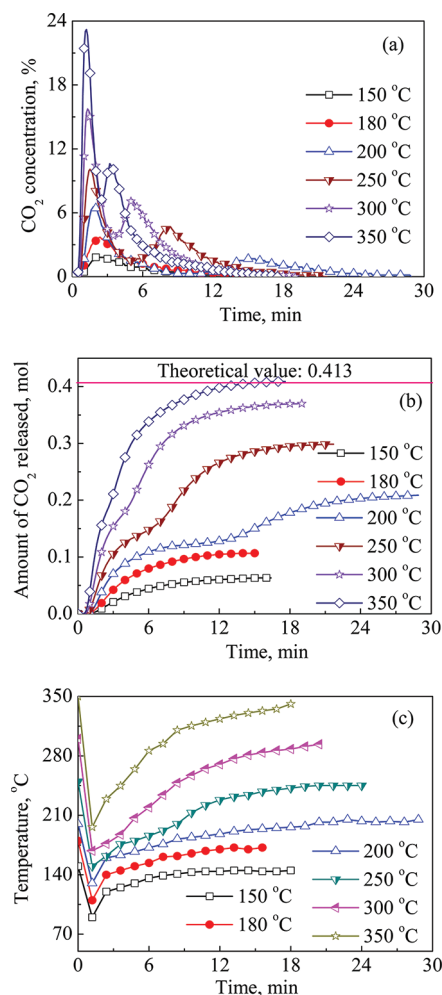




**Figure 3.** Effect of the final temperature on regeneration for a slow heating process: (a) change of the  $\text{CO}_2$  concentration, (b) amount of  $\text{CO}_2$  release, and (c) temperature change.

temperature change curves in Figure 3c, it is found that, for all conditions, the first peak of  $\text{CO}_2$  release appears at the temperature of 180 °C and a second peak appears at the temperature of 210 °C. A third peak of  $\text{CO}_2$  release appears when the reaction temperature is higher than 280 °C. The temperature-programmed desorption (TPD) test result of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  after  $\text{CO}_2$  absorption in a fixed bed showed two  $\text{CO}_2$  desorption peaks.<sup>19</sup> One was in the temperature of 85–150 °C, which was due to the decomposition of  $\text{KHCO}_3$ , and the other was in the temperature of 260–320 °C, which was due to the decomposition of  $\text{KAl}(\text{CO}_3)_2(\text{OH})_2$ . The regeneration process was simple because a powder-form sorbent was used.<sup>5</sup> The regeneration process of our sorbent is more complicated because the sorbent is a particle with the size of 180–315  $\mu\text{m}$  and the sorbent preparation process and the reaction condition are different. It is deduced that  $\text{KHCO}_3$  is decomposed first when the temperature is lower than 180 °C, then an intermediate product for the carbonation of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  is decomposed, and finally,  $\text{KAl}(\text{CO}_3)_2(\text{OH})_2$  is decomposed when the temperature is higher than 250 °C.<sup>2</sup>

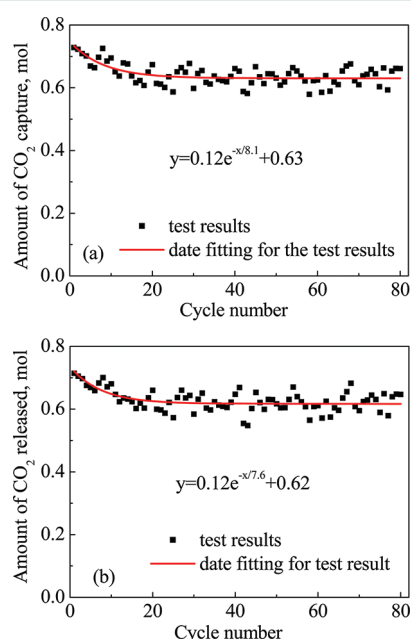
**4.5.2. For a Rapid Heating Process.** To simulate the real heating rate in a fluidized bed, a regeneration test with the rapid heating process for the sorbent being the same as section 4.5.1 was carried out at different final temperatures. Results of regeneration and the change of the temperature with time are shown in Figure 4.



**Figure 4.** Effect of the temperature on regeneration for the rapid heating process: (a) change of the  $\text{CO}_2$  concentration, (b) amount of  $\text{CO}_2$  release, and (c) temperature change.

As shown in Figure 4a, the first maximum value of  $\text{CO}_2$  release appears at 2 min for all conditions and the value increases from 1.82 to 23.2% as the regeneration temperature increases from 150 to 350 °C. A second peak appears when the regeneration temperature is higher than 200 °C. Figure 4b shows that the total amount of  $\text{CO}_2$  release increases from 0.06 to 0.41 mol as the regeneration temperature increases from 150 to 350 °C. Figure 4c shows that the temperature decreases to a minimum value at 2 min, because the cooling sorbent was used and the endothermic reaction of regeneration was carried out. The amount of  $\text{CO}_2$  release for the rapid heating process is less than that for the slow heating process at the same reaction temperature, because the regeneration processes are different for these two different methods. For the slow heating process, the decomposition of those products is carried out one by one as the temperature increases from a low value to a high value. For the rapid heating process, the decomposition of those products is carried out at the same time as the temperature quickly increases to the value that they needed. A lot of  $\text{CO}_2$  is desorbed, and the temperature decreases with the endothermic reaction during the first several minutes. The total amount of  $\text{CO}_2$  release is limited by the short reaction time. The possibility of using gases other than nitrogen for the regeneration should be investigated in future research.

**4.6. Multiple Cycle Behaviors of  $K_2CO_3/Al_2O_3$  with a Loading Amount of 36.8%. 4.6.1.  $CO_2$  Capture Capacities of  $K_2CO_3/Al_2O_3$  in 80 Cycles.** Following the methods in section 2.2, an 80 carbonation–regeneration cycle test was carried out for  $K_2CO_3/Al_2O_3$  with a loading amount of 36.8%. The amount of  $CO_2$  capture and  $CO_2$  release changes with the cycle number, as shown in Figure 5.

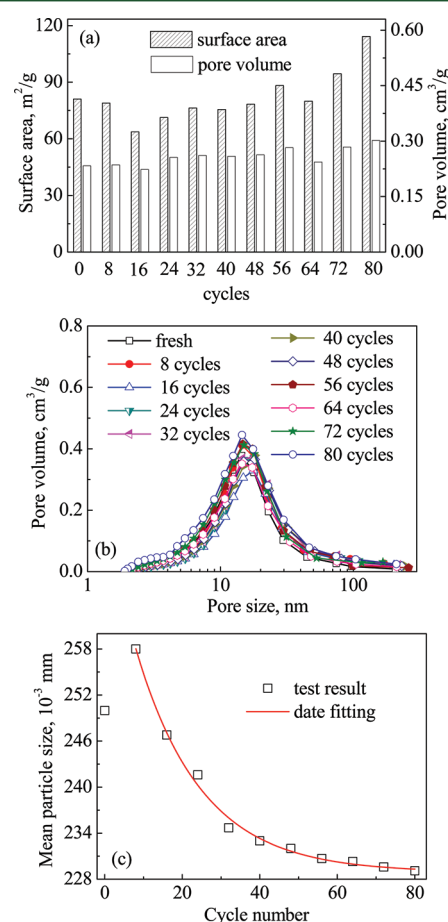


**Figure 5.**  $CO_2$  capture behavior of  $K_2CO_3/Al_2O_3$  with a loading amount of 36.8% in 80 cycles (a) for carbonation and (b) for regeneration.

As shown in Figure 5, the amount of  $CO_2$  capture and  $CO_2$  release of the sorbent decrease from 0.73 and 0.71 mol to 0.64 and 0.62 mol, respectively, in the first 20 cycles and then keep a stable value in the rest of the cycles. In comparison to the theoretical value, it is found that the carbonation conversion of the sorbent decreases from 91 to 79.6% as the cycle number increases from 1 to 80. The regeneration conversion keeps nearly 100%. It was reported that the carbonation conversion of  $K_2CO_3/Al_2O_3$  decreased from 98.1 to 94% after 10 cycles.<sup>13</sup> In comparison to that in ref 13, the carbonation conversion is a bit lower in this paper, because the surface area is much higher (196.5  $m^2/g$ ) and the loading amount is lower (24.5%) for the sorbent in ref 13. The differences in the particle size distribution of the sorbent and the gas flow rate may lead to the difference in the  $CO_2$  capture capacity. Although the carbonation conversion of  $K_2CO_3/Al_2O_3$  with a loading amount of 36.8% is a bit lower than expected, it can be improved by optimizing the reaction conditions. This study employs gas streams for absorption consisting of a  $CO_2$ ,  $N_2$ , and  $H_2O$  mixture. However, coal-derived flue gas is a complex mixture. A typical untreated flue gas can contain 5–7%  $H_2O$ , 3–4%  $O_2$ , 15–16%  $CO_2$ , 1 ppb total Hg, 20 ppm CO, 10 ppm hydrocarbons, 100 ppm HCl, 800 ppm  $SO_2$ , 10 ppm  $SO_3$ , 500 ppm  $NO_x$ , and balance  $N_2$ .<sup>18–20</sup> There can be potential impacts of the acid gases, such as  $SO_2$ ,  $SO_3$ , HCl, and NO, on the basic sorbents, and this could be a fruitful area for future study and research.

**4.6.2. Structure Change of  $K_2CO_3/Al_2O_3$  with Cycle Numbers.** The surface area, pore volume, pore size distribution,

and mean particle size of  $K_2CO_3/Al_2O_3$  with a loading amount of 36.8% changed with cycle numbers, as shown in Figure 6.



**Figure 6.** Structure change of  $K_2CO_3/Al_2O_3$  with a loading amount of 36.8% with cycle numbers: (a) surface area and pore volume, (b) pore size distribution, and (c) mean particle size.

The surface area and pore volume of the sorbent keep a stable value in 80 cycles, and the pore size distribution behavior is not changed. Figure 6c shows that the mean particle size of the sorbent increases to 258  $μm$  after 8 carbonation/regeneration cycles and then decreases to 229.1  $μm$  as the cycle number increases to 80. The change of the particle size is in accordance with the exponential decay, and the mean particle size keeps a stable value when the cycle number increases to 80. The total change of the particle size is lower than 30  $μm$ .

## 5. CONCLUSION

$CO_2$  capture and sorbent regeneration behaviors of  $K_2CO_3/Al_2O_3$  were systematically investigated in a bubbling fluidized-bed reactor. In comparison to all of the sorbents above,  $K_2CO_3/Al_2O_3$  with loading amounts between 12.8 and 36.8% showed a higher  $CO_2$  capture capacity. To obtain a high  $CO_2$  removal and a high carbonation conversion in a fluidized-bed reactor, the carbonation temperature must be controlled in the range of 60–80  $^{\circ}C$ . The effect of the  $CO_2$  concentration on carbonation is not significant, but the changing of the  $H_2O$  concentration and the process of water pretreatment for the sorbent play an important role in the  $CO_2$  capture behavior. For a slow heating process, the sorbent is completely regenerated when the final temperature is higher than 300

°C. However, to simulate the real heating rate in the fluidized bed, the regeneration test must be carried out with a rapid heating process. It needs a higher regeneration temperature. The carbonation conversion of  $K_2CO_3/Al_2O_3$  decreases from 91 to 79.6% after 80 cycles. This value is a bit lower than expected. The impacts of flue gas constituents, the cost of  $CO_2$  capture by  $K_2CO_3/Al_2O_3$ , and the sorbent attrition resistance can be investigated in future studies.

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### Notes

The authors declare no competing financial interest.

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