# Effects of alumina phases on CO<sub>2</sub> sorption and regeneration properties of potassium-based alumina sorbents

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Received: 16 May 2013/Accepted: 26 November 2013/Published online: 4 December 2013 © Springer Science+Business Media New York 2013

**Abstract** A range of potassium-based alumina sorbents were fabricated by impregnation of alumina with K<sub>2</sub>CO<sub>3</sub> to examine the effects of the structural and textural properties of alumina on the CO<sub>2</sub> sorption and regeneration properties. Alumina materials, which were used as supports, were prepared by calcining alumina at various temperatures (300, 600, 950, and 1,200 °C). The CO<sub>2</sub> sorption and regeneration properties of these sorbents were examined during multiple tests in a fixed-bed reactor in the presence of 1 vol% CO<sub>2</sub> and 9 vol% H<sub>2</sub>O. The regeneration capacities of the potassium-based alumina sorbents increased with increasing calcination temperature of alumina. The formation of KHCO<sub>3</sub> increased with increasing calcination temperature during CO<sub>2</sub> sorption, whereas the formation of KAl(CO<sub>3</sub>)(OH)<sub>2</sub>, which is an inactive material, decreased. These results is due to the fact that the structure of alumina by the calcination temperature is related directly to the formation of the by-product [KAl (CO<sub>3</sub>)(OH)<sub>2</sub>]. The structure of alumina plays an important role in enhancing the regeneration capacity of the potassium-based alumina sorbent. Based on these results, a new potassium-based sorbent using  $\delta$ -Al<sub>2</sub>O<sub>3</sub> as a support was developed for post-combustion CO<sub>2</sub> capture. This sorbent maintained a high CO<sub>2</sub> capture capacity of 88 mg CO<sub>2</sub>/g

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sorbent after two cycles. In particular, it showed a faster sorption rate than the other potassium-based alumina sorbents examined.

**Keywords** Sorbent · Carbon dioxide · Alumina · Regeneration · Potassium carbonate

#### 1 Introduction

Carbon dioxide (CO<sub>2</sub>) is a major greenhouse gas that is released into the atmosphere by the combustion of fossil fuels (oil, natural gas, and coal) (IPCC 2005). CO<sub>2</sub> causes global warming, which may be disastrous to the environment. CO<sub>2</sub> can be removed from flue gases and waste gas streams using variety of methods, such as membrane separation, absorption with a solvent, and adsorption using molecular sieves (Hagewiesche et al. 1995; Mavroudi et al. 2003; Siriwardane et al. 2001; Takamura et al. 2001; Wilson et al. 2004).

The chemical sorption of  $CO_2$  with regenerable solid sorbents containing alkali metal and alkali earth metal is one of the more efficient techniques for removing  $CO_2$  (Abanades 2002; Arias et al. 2012; Chen et al. 2012; Gupta and Fan 2002; Hayashi et al. 1998; Hirano et al. 1995; Kwon et al. 2011; Lee et al. 2006; Li et al. 2010; Salvador et al. 2003; Zhang et al. 2011). The use of dry sorbents can be a cost-effective and energy efficient way of removing  $CO_2$ . In particular, alkali metal-based sorbents can be used for  $CO_2$  capture at low temperatures (50–70 °C) with thermal regeneration occurring easily at temperatures <150 °C. Alkali metal carbonates, such as  $Na_2CO_3$  and  $K_2CO_3$ , react with  $CO_2$  and  $CO_3$  and transform to alkali metal hydrogen carbonates after  $CO_2$  sorption according to the reaction,  $CO_3$  and  $CO_3$  could be  $CO_3$  (M = Na, K) (Liang et al. 2004; Seo



et al. 2007; Yi et al. 2007, 2008, Zhao et al. 2009a, 2012). Water vapor is always necessary for the formation of potassium hydrogen carbonate in all reactions as shown in the absorption mechanism. Several studies have examined the efficiency of the chemical sorption of CO<sub>2</sub> over K<sub>2</sub>CO<sub>3</sub> supported on porous materials, such as activated carbon, TiO<sub>2</sub>, ZrO<sub>2</sub>, silica gel, and Al<sub>2</sub>O<sub>3</sub>, using cyclic fixed-bed or fluidized-bed operations under moist conditions (Lee et al. 2008a, b, 2009, 2011; Shigemoto et al. 2006; Zhao et al. 2009b, c).

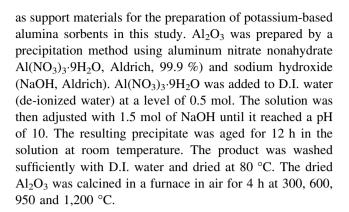
To manufacture alkali metal-based sorbents with high physical strength, inorganic materials, such as gamma-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), are commonly used as solid sorbents. On the other hand, potassium-based sorbents using alumina as an additive or support has a disadvantage in that there is a decrease in the CO<sub>2</sub> capture capacity during multiple sorption and regeneration tests at temperatures between 60 and 200 °C (Lee et al. 2006, 2011, 2013; Lee and Kim 2007; Okunev et al. 2000, 2003). This has been attributed to the formation of new by-products, such as KAl(CO<sub>3</sub>)<sub>2</sub>·1.5H<sub>2</sub>O or KAl (CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>, during CO<sub>2</sub> sorption of a potassium-based sorbent using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> even at temperatures below 60 °C. An ideal dry sorbent must have a high CO<sub>2</sub> capture capacity, high sorption rate, excellent regeneration property, and high attrition resistance to remove CO<sub>2</sub> from flue gases in a fluidized/ transport-bed reactor (Lee et al. 2008a). A previous paper reported that α-Al<sub>2</sub>O<sub>3</sub> is one of the most useful materials for designing ideal potassium-based sorbent for post-combustion CO<sub>2</sub> capture (Lee et al. 2013). This potassium-based sorbent using commercial α-Al<sub>2</sub>O<sub>3</sub> as a support exhibited high CO<sub>2</sub> capture capacity as well as excellent regeneration properties. On the other hand, this sorbent exhibited a slow sorption rate despite the excellent regeneration properties when a potassium-based sorbent was prepared using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a support material. Moreover, the effects of the structure and textural properties of alumina on the CO<sub>2</sub> capture and regeneration properties and the sorption rate are unclear.

One of the main aims of this study was to develop a new potassium alumina sorbent with a high  $CO_2$  capture capacity, excellent regeneration properties, and rapid sorption rate for post-combustion  $CO_2$  capture. In addition, the physical properties and mechanism of the potassium-based sorbents using a range of alumina materials before/after  $CO_2$  absorption were examined by X-ray diffraction (XRD), temperature programmed desorption (TPD), inductive coupled plasma (ICP), and BET.

## 2 Experimental

#### 2.1 Preparation of alumina used as a support

Commercial alumina ( $Al_2O_3$ , Aldrich, 99.9 %) and alumina ( $Al_2O_3$ ) prepared by a precipitation method were used



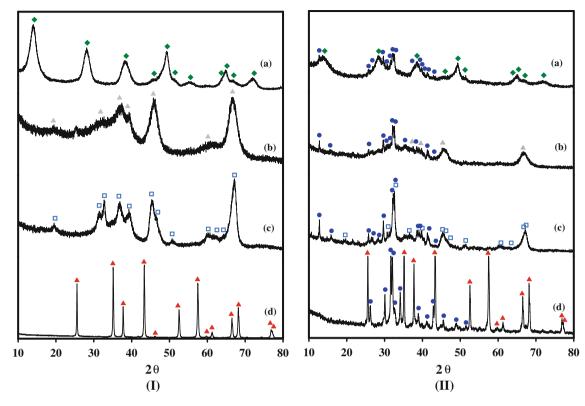
#### 2.2 Preparation of sorbent

The potassium-based sorbents used in this study were prepared by the impregnation of alumina (Al<sub>2</sub>O<sub>3</sub>) with K<sub>2</sub>CO<sub>3</sub>. A typical preparation procedure for the sorbent supported on Al<sub>2</sub>O<sub>3</sub> was as follows (Lee et al. 2006, 2008b, 2009): 5.0 g of the support was added to an aqueous solution containing 2.15 g of anhydrous alkali metal carbonate (K<sub>2</sub>CO<sub>3</sub>, Aldrich) in 25 ml of de-ionized water. The content was mixed with a magnetic stirrer for 24 h at room temperature. After stirring, the mixture was dried in a rotary evaporator at 60 °C. The dried samples were calcined in a furnace with a N2 flow (100 ml/min) for 4 h at 500 °C, except when boehmite (AlOOH) was used as a support for the sorbent material, which was calcined at 300 °C. The temperature ramping rate was 3 °C/min. The sorbents are denoted as follows: KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I40, KAl(A)I30 and KAl(A-A)I30 sorbents, where K represents  $K_2CO_3$ , Al(B), Al(G), Al(D), Al(A), Al(G-A) and Al(A-A) represent  $\gamma$ -AlOOH,  $\gamma$ - $Al_2O_3$ ,  $\delta$ - $Al_2O_3$ , and  $\alpha$ - $Al_2O_3$ ,  $\gamma$ - $Al_2O_3$  (Aldrich) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(Aldrich), respectively, I denotes the impregnation method, and 30 or 40 represents the K<sub>2</sub>CO<sub>3</sub> loading.

# 2.3 Apparatus and procedure

 ${\rm CO_2}$  absorption and regeneration processes were performed in a fixed-bed quartz reactor, with a diameter of 1 cm. The reactor 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 temperatures of the inlet and outlet lines of the reactor were maintained above 100 °C to prevent the condensation of water vapor before being injected into the reactor and G.C. column. A 1/8 in. stainless tube packed with Porapak Q was used as the column. When the  ${\rm CO_2}$  concentration of outlet gases reached the same level as that of the inlet gas (1 vol%) in the  ${\rm CO_2}$  absorption process, nitrogen was introduced for a sufficient time in multiple tests, to





**Fig. 1** XRD patterns of the **I** alumina materials calcined at 300, 600, 950 and 1,200 °C and the **II** fresh a KAl(B)I30, b KAl(G)I30, c KAl(D)I30, and d KAl(A)I30 sorbents before CO<sub>2</sub> sorption; *filled* 

diamond  $\gamma\text{-AlOOH};$  grey triangle  $\gamma\text{-Al}_2O_3;$  square  $\delta\text{-Al}_2O_3,$  filled triangle  $\alpha\text{-Al}_2O_3;$  filled dot  $K_2CO_3$ 

regenerate the spent sorbents. The outlet gases from the reactor were analyzed automatically every 4 min using a thermal conductivity detector (TCD; Donam Systems Inc.) equipped with an auto sampler (Valco Instruments CO. Inc.).

X-ray diffraction (XRD; Philips, X'PERT) using Cu K $\alpha$  radiation was performed to identify the crystalline phases in the materials. The textural properties of the materials were measured from nitrogen adsorption—desorption at  $-196~^{\circ}\text{C}$  by using a Micromeritics ASAP 2010 instrument. The amount of alkali metal impregnated was measured using an inductive coupled plasma-atomic emission spectroscopy (ICP-AES; Thermo, Thermo Jarrell Ash IRIS-AP). After dissolving  $K_2\text{CO}_3$  dispersed on alumina with deionized water under stirring, the resulting solution was analyzed by ICP-AES.

#### 3 Results and discussion

### 3.1 Structure identification of aluminas and sorbents

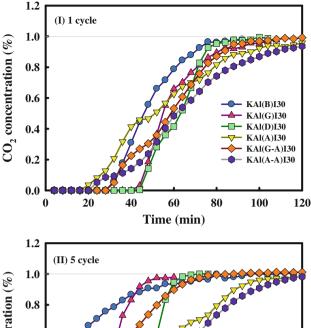
The structural changes in the alumina materials after calcination at various temperatures such as 300, 600, 950, and  $1,200\,^{\circ}\text{C}$ , which were selected through a separate TG/DTA

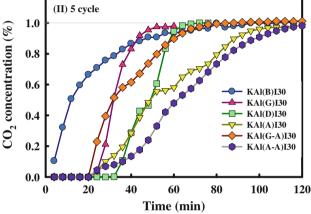
test of boehmite, were examined by XRD (Fig. 1I). As expected, the XRD patterns of the alumina materials calcined at 300, 600, 950 and 1,200 °C showed a  $\gamma$ -AlOOH phase (JCPDS No. 49-0133),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (JCPDS No. 10-0425),  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase (JCPDS No. 46-1131), and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase (JCPDS No. 88-0826), respectively. The structural properties of the fresh KAl(B)I30, KAl(G)I30, KAl(D)I30, and KAl(A)I30 sorbents before CO<sub>2</sub> sorption were examined by XRD (Fig. 1II). The XRD pattern of the fresh potassium-based alumina sorbents showed only a separate K<sub>2</sub>CO<sub>3</sub> phase (JCPDS No. 71-1466) in addition to each alumina phase without K–Al alloy products.

# 3.2 CO<sub>2</sub> capture and regeneration capacities of the potassium-based alumina sorbents

Figure 2 shows the breakthrough curves of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A)I30, and KAl(A-A)I30 sorbents at 1 and 5 cycles. The KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A)I30, and KAl(A-A)I30 sorbents were prepared by the impregnation of  $\gamma$ -AlOOH,  $\gamma$ -Al $_2$ O $_3$ ,  $\gamma$ -Al $_2$ O $_3$  (Aldrich),  $\delta$ -Al $_2$ O $_3$ ,  $\alpha$ -Al $_2$ O $_3$ , and  $\alpha$ -Al $_2$ O $_3$  (Aldrich), respectively, with 30 wt% K $_2$ CO $_3$ . In the cases of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30 and KAl(D)I30 sorbents, the breakthrough times were



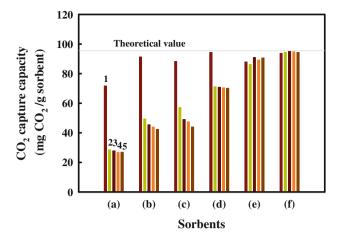




**Fig. 2** Breakthrough curves of the potassium-based alumina sorbents such as KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A)I30 and KAl(A-A)I30 at **I** 1 and **II** 5 cycles

approximately 28, 40, 32, and 44 min, respectively. On the other hand, the breakthrough times of the KAl(A)I30 sorbents were approximately 16 min despite the excellent regeneration properties and were similar to the KAl(A-A)I30 sorbent using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich) as reported elsewhere (Lee et al. 2013). After 5 cycles, the breakthrough times of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A)I30, and KAl(A-A)I30 sorbents were 0, 20, 20, 32, 20, and 16 min, respectively.

Figure 3 shows the CO<sub>2</sub> capture capacities of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A) I30, and KAl(A-A)I30 sorbents during the multiple tests for sorption (60 °C) and regeneration (200 °C). The CO<sub>2</sub> capture capacities of the sorbent were calculated from the breakthrough curve during multiple tests. The theoretical value of the sorbent was calculated from moles of K<sub>2</sub>CO<sub>3</sub> involved in the sorbent, when one mole of K<sub>2</sub>CO<sub>3</sub> absorbed a stoichiometric amount of one mole of CO<sub>2</sub>. The CO<sub>2</sub> capture capacities of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30, and KAl(D)I30 sorbents decreased at 2 cycles. On the other hand,



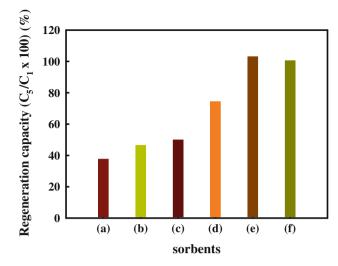
**Fig. 3** CO<sub>2</sub> capture capacities of the potassium-based alumina sorbents during multiple tests for sorption (60 °C) and regeneration (200 °C) in the presence of 1 vol% CO<sub>2</sub> and 9 vol%  $H_2O$ ; a KAl(B)I30; b KAl(G)I30; c KAl(G-A)I30; d KAl(D)I30; e KAl(A)I30; f KAl(A-A)I30

the KAl(A)I30 sorbent showed CO2 capture capacities of approximately 90-95 mg CO<sub>2</sub>/g sorbent and no deactivation during multiple cycles even at a regeneration temperature of 200 °C, similar to the result of the KAl(A-A)I30 sorbent reported in a previous paper (Lee et al. 2013). In addition to the CO<sub>2</sub> sorption and regeneration properties of the potassium-based sorbent, the sorption rate is an important factor. The CO<sub>2</sub> sorption rate of the KAl(A)I30 sorbent cannot be enhanced using α-Al<sub>2</sub>O<sub>3</sub> as a support, which was prepared by precipitation, even though it can be regenerated completely at 200 °C. Nevertheless, the KAl(D)I30 sorbent had the longest breakthrough time and a high slope after the breakthrough point, but it decreased slightly during multiple tests. Considering that the sorption rate and regeneration properties are important factors in CO<sub>2</sub> capture, the KAl(D)I30 sorbent has potential for CO<sub>2</sub> capture in the low temperature range.

# 3.3 Effects of the structure and textural properties on the regeneration properties of potassium-based alumina sorbents

The  $C_5/C_1$  ratio was calculated from Fig. 4 to identify the regeneration properties of the sorbents in detail.  $C_1$  and  $C_5$  represent the  $CO_2$  capture capacity at 1 and 5 cycles, respectively. This value indicates the regeneration capacity of the sorbent. As shown in Fig. 4, the regeneration capacities of the KAl(B)I30, KAl(G)I30, KAl(D)I30 and KAl(A)I30 sorbents were 37.6, 46.5, 74.3 and 103.1 %, respectively, suggesting that the regeneration capacity increased with increasing calcination temperature of alumina used as a support. The deactivation problem of the alkali-based alumina sorbent using alumina could be solved using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a support. The KAl(A)I30 sorbent





**Fig. 4** Regeneration capacities  $(C_5/C_1 \times 100)$  of the potassium-based alumina sorbents such as a KAl(B)I30, b KAl(G)I30, c KAl(G-A) I30, d KAl(D)I30, e KAl(A)I30 and f KAl(A-A)I30

using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a support showed a similar result to that of the KAl(A-A)I30 sorbent, which was prepared using commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich), as reported in a previous paper (Lee et al. 2013). In particular, Fig. 4 shows that the regeneration capacity of the alkali-based alumina sorbent can be improved using  $\delta$ -Al<sub>2</sub>O<sub>3</sub> as a support. From these results, it was thought that the improved regeneration properties of the alkali-based alumina sorbent were attributed to the structural properties of the alumina support.

Table 1 lists the crystallite sizes of the alumina and the textural properties of alumina and the potassium-based alumina sorbents. The surface area of alumina decreased with increasing calcination temperature, whereas the average pore size increased, due to an increase in crystallite size, as shown in Table 1. It is well known that the surface area and average pore diameter are directly correlated with the crystallite size as reported by other researchers (Kim et al. 2007; Stichert and Schuth 1998). The regeneration capacity increased with decreasing surface area of alumina, suggesting that the enhanced regeneration capacity of the

sorbent was affected by the textural properties of alumina. On the other hand, although the surface areas of  $\gamma\text{-}Al_2O_3$  and  $\alpha\text{-}Al_2O_3$  were higher than those of the commercial  $\gamma\text{-}Al_2O_3$  and  $\alpha\text{-}Al_2O_3$  (Aldrich), respectively, the regeneration capacity of the KAl(G)I30 and KAl(A)I30 sorbents were similar to those of the KAl(G-A)I30 and KAl(A-A) I30 sorbents. In addition, although the surface area of  $\delta\text{-}Al_2O_3$  was similar to  $\gamma\text{-}Al_2O_3$  (Aldrich), the regeneration capacity of the KAl(D)I30 sorbent was much higher than that of the KAl(G-A)I30 sorbent. Therefore, the improved regeneration properties of the potassium-based alumina sorbent can be explained by the structural properties of alumina rather than by the effect of the textural properties of alumina.

# 3.4 Structure identification of the sorbents after CO<sub>2</sub> sorption and regeneration

The structure changes in the KAl(B)I30, KAl(G)I30, KAl(D)I30 and KAl(A)I30, sorbents after CO<sub>2</sub> sorption and regeneration at 60 and 200 °C, respectively, were examined by XRD (Fig. 5). After CO<sub>2</sub> sorption, the XRD patterns of the KAl(B)I30, KAl(G)I30 and KAl(D)I30 sorbents showed KAl(CO<sub>3</sub>)(OH)<sub>2</sub> phases (JCPDS No. 22-0791) and KHCO<sub>3</sub> phases (JCPDS No. 70-0995) (Lee et al. 2006, 2011, 2013; Lee and Kim 2007) as shown in Fig. 5I). In the case of the KAl(D)I30 sorbent, the intensity of the XRD preaks associated with the KHCO<sub>3</sub> phase was higher than those of the other sorbents. On the other hand, the XRD patterns of the KAl(A)I30 sorbents after CO<sub>2</sub> sorption showed a KHCO<sub>3</sub> phase in addition to an α-Al<sub>2</sub>O<sub>3</sub> phase as shown in Fig. 5 (Id), indicating that the XRD patterns are similar to that of the KAl(A-A)I30 sorbent as reported elsewhere (Lee et al. 2013). After regeneration under nitrogen at 200 °C, the XRD patterns of the KAl(B)I30, KAl(G)I30 and KAl(D)I30 sorbents revealed K<sub>2</sub>CO<sub>3</sub> and KAl(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> phases. This means that KAl(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> is not converted to the original active material, such as K<sub>2</sub>CO<sub>3</sub>. These results suggest that the new by-product like KAl(CO<sub>3</sub>)(OH)<sub>2</sub> is affected by the structure of alumina and that the regeneration capacity of the

Table 1 Crystallite sizes and textural properties of the alumina and potassium-based alumina sorbents

Sample name	Crystallite size (nm)	Surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Sample name	Surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)
γ-AlOOH	4.7	230.0	0.28	4.9	KAl(B)I30	8.4	0.04	18.2
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.4	183.5	0.35	7.6	KAl(G)I30	57.7	0.17	11.6
γ-Al <sub>2</sub> O <sub>3</sub> (Aldrich)	8.9	156.9	0.23	5.9	KAl(G-A)I30	27.7	0.07	9.7
$\delta$ -Al <sub>2</sub> O <sub>3</sub>	6.2	158.5	0.52	13.3	KAl(D)I30	31.7	0.13	15.8
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	45.3	15.5	0.24	62.9	KAl(A)I30	6.8	0.04	24.3
$\alpha\text{-Al}_2O_3 \; (Aldrich)$	103.4	0.1	0.0003	78.5	KAl(A-A)I30	0.1	0.0026	60.4



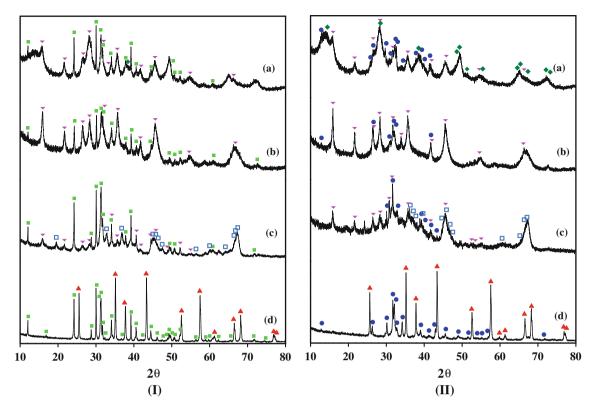


Fig. 5 XRD patterns of the a KAl(B)I30, b KAl(G)I30, c KAl(D)I30 and d KAl(A)I30 sorbents after I CO<sub>2</sub> sorption and II regeneration; (filled square) KHCO<sub>3</sub>; (inverted triangle) KAl(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>; (filled diamond)  $\gamma$ -AlOOH; (square)  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, (filled triangle)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; (filled dot) K<sub>2</sub>CO<sub>3</sub>

potassium-based alumina sorbent is related directly to the new by-product.

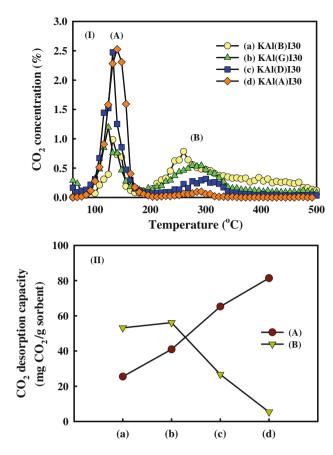
To confirm these results in detail, the TPD tests of these sorbents were carried out by measuring the concentration of CO<sub>2</sub> desorbed when the temperature ramping rate was 1 °C/ min, as shown in Fig. 6I. The TPD results for the potassiumbased alumina sorbents, such as KAl(B)I30, KAl(G)I30, KAl(D)I30 and KAl(A)I30, showed two CO<sub>2</sub> peaks. This suggests that there are two types of structures, due to the CO<sub>2</sub> desorption of KHCO3 and KAl(CO3)(OH)2, as reported elsewhere (Lee et al. 2006, 2011, 2013; Lee and Kim 2007). Figure 6b shows the CO<sub>2</sub> desorption capacity calculated from each TPD peak area. As shown in Fig. 6II, the peak area of (A) for the KHCO<sub>3</sub> increased with increasing calcination temperature, whereas the peak area of (B) for the KAl(CO<sub>3</sub>) (OH)<sub>2</sub> decreased. The structure of alumina by the calcination temperature is related directly to the formation of the by-product [KAl(CO<sub>3</sub>)(OH)<sub>2</sub>], which is an inactive material. The structure of alumina plays an important role in enhancing the regeneration capacity of the potassium-based alumina sorbent.

## Development of new potassium-based δ-alumina sorbent

As mentioned previously, the KAl(D)I30 sorbent showed an excellent sorption rate compared to the other potassium-

based alumina sorbents examined, even though the sorbent showed deactivation during multiple tests due to the formation of a by-product. Considering that the CO<sub>2</sub> capture capacity of the KAl(D)I30 sorbent was maintained after two cycles, as shown in Fig. 2, it is believed that its CO<sub>2</sub> capture capacity can be increased by increasing the K<sub>2</sub>CO<sub>3</sub> loading. The KAl(D)I40 sorbent was prepared by the impregnation of δ-Al<sub>2</sub>O<sub>3</sub>, which has a higher surface area (158.5 m<sup>2</sup>/g) and pore volume (0.52 cm<sup>3</sup>/g) than  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, with 40 wt% K<sub>2</sub>CO<sub>3</sub>. The CO<sub>2</sub> capture capacity of the KAl(D)I40 sorbent was compared with those of the KAl(G)I40 and KAl(A)I40 sorbents using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Figure 7 shows the CO<sub>2</sub> capture capacities of the KAl(G)I40, KAl(D)I40 and KAl(A)I40 sorbents during multiple tests. The KAl(G)I40 and KAl(D)I40 sorbents showed similar types of deactivation for KAl(G)I30 and KAl(D)I30 sorbents with 30 wt% K<sub>2</sub>CO<sub>3</sub> during multiple tests. The KAl(A)I40 sorbent maintained a CO<sub>2</sub> capture capacity of approximately 94 mg CO<sub>2</sub>/g sorbent during multiple cycles. When the amount of CO<sub>2</sub> sorption per 1 g of K<sub>2</sub>CO<sub>3</sub> was calculated from this value, the KAl(A)I40 sorbent showed a CO<sub>2</sub> capture capacity of approximately 235 mg CO<sub>2</sub>/g K<sub>2</sub>CO<sub>3</sub>. This was approximately 73 % of the theoretical value of the sorbent (318.3 mg CO<sub>2</sub>/g K<sub>2</sub>CO<sub>3</sub>), which was calculated from the 40 wt% K<sub>2</sub>CO<sub>3</sub> added to the sorbent. Considering that the CO<sub>2</sub> capture





**Fig. 6 I** TPD results of the *a* KAl(B)I30, *b* KAl(G)I30, *c* KAl(D)I30 and *d* KAl(A)I30 sorbents after CO<sub>2</sub> sorption and **II** CO<sub>2</sub> desorption capacities calculated from each TPD peak area: *A* peak area in the temperature range 100–200 °C; *B* peak area in the temperature range 200–400 °C

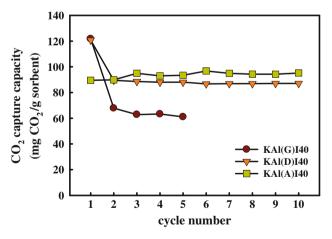


Fig. 7  $CO_2$  capture capacities of the KAl(G)I40, KAl(D)I40 and KAl(A)I40 sorbents during the multiple tests

capacity of the KAl(A)I30 sorbent is 292 mg  $CO_2/g$   $K_2CO_3$ , which is 92 % of the theoretical capacity of the sorbent with 30 wt%  $K_2CO_3$ , the amount of  $CO_2$  sorption

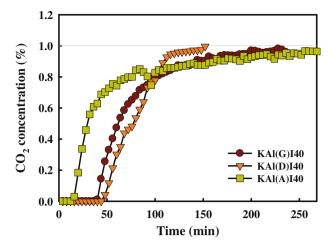


Fig. 8 Breakthrough curves of the KAl(G)I40, KAl(D)I40 and KAl(A)I40 sorbents at 1 cycle

per gram of K<sub>2</sub>CO<sub>3</sub> in the KAl(A)I40 sorbent decreased. This was attributed to the limitation in increasing the amount of K<sub>2</sub>CO<sub>3</sub> loaded in the potassium-based sorbent using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a support, because  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a very small surface area. In a separate experiment, it was confirmed that the amount of K<sub>2</sub>CO<sub>3</sub> loaded in the potassiumbased sorbent was approximately 31.2 wt% by ICP-AES. On the other hand, the CO<sub>2</sub> capture capacity of the KAl(D)I40 sorbent was approximately 88 mg CO<sub>2</sub>/g sorbent after two cycles. In particular, as shown in Fig. 8, both the breakthrough time of the the KAl(D)I40 sorbent and the slope of a breakthrough curve after the breakthrough time were higher than those of the KAl(A)I40 sorbent. From these results, it was concluded that the KAl(D)I40 sorbent, which was prepared by the impregnation of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> with 40 wt% K<sub>2</sub>CO<sub>3</sub>, can be used as a sorbent for post-combustion CO<sub>2</sub> capture owing to its high CO<sub>2</sub> capture and regeneration capacities, and excellent sorption rate.

### 4 Conclusions

This study examined the effects of the structure and textural properties of alumina on the  $CO_2$  sorption and regeneration properties of the potassium-based alumna sorbents. The regeneration capacities of the KAl(B)I30, KAl(G)I30, KAl(G-A)I30, KAl(D)I30, KAl(A)I30, and KAl(A-A)I30 sorbents were 37.6, 46.5, 49.9, 74.3, 103.1 and 100.5 %, respectively. The deactivation problem of the alkali-based alumina sorbent using alumina can be solved using  $\alpha$ -Al $_2O_3$  as a support. The regeneration capacity of the alkali-based alumina sorbent can be improved using  $\delta$ -Al $_2O_3$  as a support. The results suggest that the regeneration capacities of the potassium-based alumina sorbents increased with increasing calcination temperature of alumina, even though



their  $CO_2$  capture capacities were similar. The improved regeneration properties can be explained by the structural properties of alumina rather than by the effects of the textural properties. In particular, the KAl(D)I30 sorbent showed a high sorption rate compared to the other potassium-based alumina sorbents, even though the sorbent showed deactivation during multiple tests due to the formation of by-products. Based on these results, a new regenerable potassium-based  $\delta$ -Al<sub>2</sub>O<sub>3</sub> sorbent [KAl(D)I40], which was approximately 88 mg  $CO_2$ /g sorbent after 2 cycles, was developed for post-combustion  $CO_2$  capture.

Acknowledgments This work was supported by R&D program under Agency for Defense Development, Republic of Korea. We acknowledge the financial support by grants from Korea CCS R&D Center, funded by the Ministry of Education, Science and Technology of Korean government. This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (2010201020007A).

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