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The effect of water on the activation and the CO_2 capture capacities of alkali metal-based sorbents

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Abstract−Alkali metal-based sorbents were prepared by the impregnation either of potassium carbonate (K_2CO_3) or of sodium carbonate (Na_2CO_3) on the supports (activated carbon (AC) and Al_2O_3). The CO_2 absorption and regeneration properties were measured in a fixed bed reactor at the low temperature conditions (CO_2 absorption at 60 °C and regeneration at 150 °C). The potassium carbonate which was supported on the activated carbon (K_2CO_3/AC) was clarified as a leading sorbent, of which the total CO_2 capture capacity was higher than those of other sorbents. This sorbent was completely regenerated and transformed to its original phase by heating the used sorbent. The activation process before CO_2 absorption needed moisture nitrogen containing 1.3-52 vol% H_2O for 2 hours either at 60 °C or at 90 °C. The activation process played an important role in CO_2 absorption, in order to form new active species defined as $K_2CO_3\cdot 1.5H_2O$, by X-ray diffraction. It was suggested that the new active species ($K_2CO_3\cdot 1.5H_2O$) could be formed by drying the $K_4H_2(CO_3)_3\cdot 1.5H_2O$ phase formed after pre-treatment with excess water.

Key words: Carbon Dioxide, Absorption, Potassium Carbonate, Potassium Hydrogen Carbonate, Activation

INTRODUCTION

Carbon dioxide (CO_2) is a major greenhouse gas that is released into the air due to the use of fossil fuels and in consequence it causes global climate warming. CO_2 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 [Hagewiesche et al., 1995; Mavroudi et al., 2003; Park et al., 2002, 2004; Siriwardane et al., 2001; Takamura et al., 2001; Wilson et al., 2004]. These methods, however, are costly and consume a lot of energy.

One of the improved techniques for the removal of CO_2 is the chemical absorption of CO_2 with solid regenerable sorbents. The use of solid sorbents containing alkali and alkali earth metals for CO_2 absorption has been reported in many literatures [Gupta and Fan, 2002; Hayashi et al., 1998; Hirano et al., 1995; Nalette et al., 1992; Lee et al., 2004; Liang et al., 2004; Okunev et al., 2000, 2003; Salvador et al., 2003; Sharonov et al., 2001, 2004]. In their papers, alkali metal carbonate was employed in CO_2 absorption at low temperatures (50-60 °C) with thermal regeneration easily occurring at a low temperature, while calcium oxide was employed in CO_2 absorption at higher temperatures (less than 860 °C). Several studies of an efficient chemical absorption over K_2CO_3 supported either on carbon [Hayashi et al., 1998; Hirano et al., 1995] or on other porous matrices such as silica gel, Al_2O_3 and vermiculite [Okunev et al., 2000] were also reported using cyclic fixed-bed operations under the moist conditions for the recovery of carbon dioxide from flue gases. The sorption of CO_2 on the K_2CO_3-Al_2O_3 composite sorbent in the presence of water vapor was studied by in-situ IR spectroscopy and X-ray diffraction analysis [Okunev et al., 2003]. Water content was essential to form potassium hydrogencarbonate in all of these absorption reactions, while moisture contained in the flue gases as high as 8-17 vol% negatively affected the adsorption capacity of molecular sieves [Hayashi et al., 1998]. Even though it is well known that water plays an important role not only in the CO_2 capture over alkali metal based sorbents but also in the pretreatment process, the role of water has not been clearly defined in the previous studies. In particular, there have been very few reports regarding the effect of water on the alkali metal promoted sorbents in the pretreatment and in the CO_2 absorption process.

In this work, the CO_2 capture capacity of sorbents was compared by using CO_2 breakthrough curves. The effect of H_2O on their capacities during the activation process was tested in a fixed bed reactor. In order to understand the mechanism of the cyclic operations, the new active potassium species formed during the activation process with H_2O were proposed and identified by the X-ray diffraction method.

EXPERIMENTAL

1. Preparation of Sorbents

Alkali metal-based sorbents used in this study were prepared by impregnation method. A typical preparation procedure for the sorbents supported on the activated carbon and alumina oxide was as follows. Five (5.0) g of the support were added to an aqueous solution containing 2.5-5 g of anhydrous alkali metal carbonate (Na_2CO_3 and K_2CO_3, Aldrich) in 15 ml of de-ionized water. Then, it was mixed with a magnetic stirrer at room temperature for 24 hours [Hirano et al., 1995]. After stirring, the mixture was dried in a rotary evapora-

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Table 1. Experimental conditions of alkali metal based sorbents

	Pretreatment	CO_2 absorption	Regeneration
Temperature (°C)	60, 90	60	150
Pressure (atm)	1	1	1
Flow rate (ml/min)	40	40	40
Gas composition (vol%)	H_2O: 1.3, 5, 9, 35, 52 N_2: Balance	CO_2: 1, H_2O: 1.3 N_2: Balance	H_2O: 1.3 N_2: Balance

tor at 60 °C. The dried samples were calcined in a furnace with N_2 flow (100 ml/min) for 4 hours at 300 °C. The ramping rate of the temperature was maintained at 3 °C/min. The amount of the impregnated alkali metal was determined by using a Varian spectra AA 800 atomic absorption spectrophotometer. Power X-ray diffraction (XRD; Philips, X'PERT) was also measured in order to confirm the structure using Cu Kα radiation.

2. Absorption Apparatus and Procedure

Carbon dioxide (CO_2) absorption and regeneration processes were performed in a fixed bed quartz reactor with a diameter of 1 cm, which was placed in an electric furnace under atmospheric pressure. One-half (0.5) g of sorbent was packed into the reactor, and space velocity (SV) was maintained at 3,000 h^{-1} to minimize severe pressure drops and channeling phenomena. 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 in order to prevent the condensation of water vapor injected to the reactor. The column used in the analysis was a 1/8 inch stainless tube packed with Porapak Q. The conditions of CO_2 absorption and regeneration and the composition of mixed gases are shown in Table 1. Before CO_2 absorption, moist nitrogen gas with 1.3-52 vol% H_2O (6.5-75% relative humidity) at 60-90 °C was supplied to sorbents for 120 minutes by using either a saturator (1.3-9 vol% H_2O) or a syringe pump (35-52 vol% H_2O). When the CO_2 concentration of the outlet gases reached the same level as the inlet gas (1 vol%) during the CO_2 absorption process, the moisture nitrogen containing 1.3 vol% H_2O only was introduced to regenerate the sorbents. The regeneration process was terminated when the CO_2 concentration reached 200 ppm. The outlet gases from the reactor were automatically analyzed every 4 minutes by a thermal conductivity detector (TCD; Donam Systems Inc.) equipped with an auto sampler (Valco Instruments CO. Inc.).

RESULTS AND DISCUSSION

1. Comparison of CO_2 Capture Capacities of Various Sorbents

Table 2 shows total CO_2 capture capacities at 60 °C and the loading amount of alkali metals of various sorbents prepared by the impregnation of alkali metal carbonates after pre-treatment under 1.3 vol% H_2O for 2 hours at 60 °C. The phrase "total CO_2 capture capacity" describes the amount of CO_2 absorbed until the output concentration of CO_2 reached 1 vol%, which is the same value as that of inlet. The total CO_2 capture capacities of the potassium carbonate supported on the alumina oxide and activatied carbon (K_2CO_3/Al_2O_3 and K_2CO_3/AC) were 38 mg CO_2/g sorbent and 34 mg CO_2/g sorbent, respectively. The total CO_2 capture capacities of sodium-based sorbents were less than that of the potassium-based sorbents as shown in Table 2. In particular, the Na_2CO_3/Al_2O_3 sorbent showed a very low CO_2 capture capacity (7 mg CO_2/g sorbent). When the regeneration of the used sorbents was carried out by heating in moisture conditions at 150 °C, the K_2CO_3/AC sorbent was completely regenerated and transformed to its original phase without deactivation. The K_2CO_3/Al_2O_3 sorbent, however, was deactivated during a multiple cycle of the CO_2 absorption and regeneration in the same

Table 2. Total CO_2 capture capacity at 60 °C and the loading amount of alkali metal of the various sorbents prepared by the impregnation after the pre-treatment under 1.3 vol% H_2O for 2 hours

Sorbent	The loading amount of alkali metal (wt%)	The total CO_2 capture capacity (mg CO_2/g sorbent)
K_2CO_3/AC	30	34
Na_2CO_3/AC	30	15
K_2CO_3/Al_2O_3	28	38
Na_2CO_3/Al_2O_3	30	7

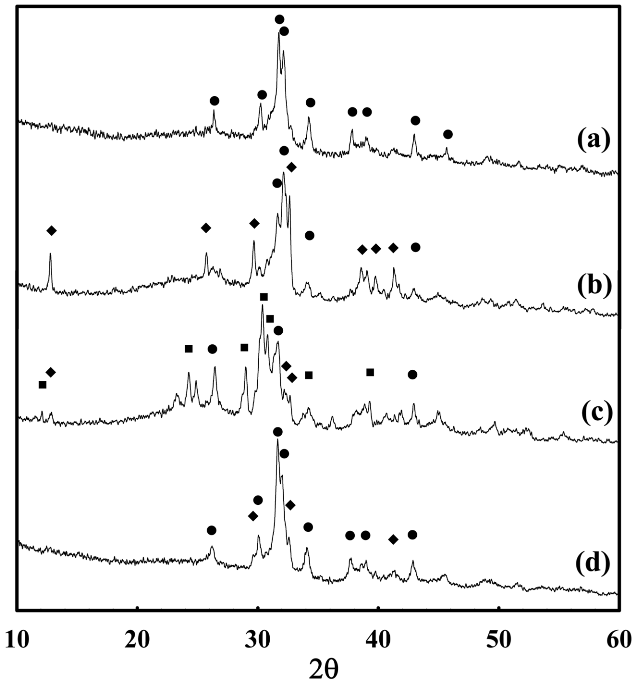

Fig. 1. XRD patterns of K_2CO_3/AC sorbents before/after CO_2 absorption at 60 °C: (a) fresh; (b) after pretreatment with 1.3 vol% H_2O; (c) after reaction with 1.3 vol% H_2O and 1 vol% CO_2 at 60 °C; (d) after regeneration with 1.3 vol% H_2O at 150 °C; (●) K_2CO_3; (◆) $K_2CO_3\cdot1.5H_2O$; (■) $KHCO_3$.

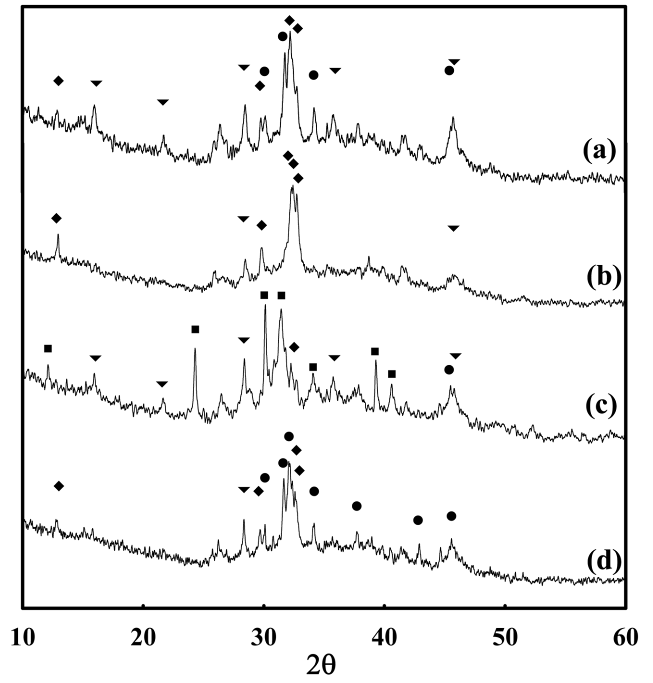

Fig. 2. XRD patterns of K_2CO_3/Al_2O_3 sorbents before/after CO_2 absorption at 60 °C: (a) fresh; (b) after pretreatment with 1.3 vol% H_2O; (c) after reaction with 1.3 vol% H_2O and 1 vol% CO_2 at 60 °C; (d) after regeneration with 1.3 vol% H_2O at 150 °C; (●) K_2CO_3; (◆) $K_2CO_3 \cdot 1.5H_2O$; (■) $KHCO_3$; (▼) $KAl(CO_3)_2(OH)_2$.

condition.

Fig. 1 and 2 shows the XRD patterns of the K_2CO_3/AC and K_2CO_3/Al_2O_3 sorbents before/after CO_2 absorption at 60 °C. The phase of the K_2CO_3/AC sorbents before reaction is shown in Fig. 1(a) and is assigned to the K_2CO_3 (JCPDS No. 71-1466). As shown in Fig. 1(b), the XRD pattern after pre-treatment with 1.3 vol% H_2O showed two crystal structures which were assigned as K_2CO_3 and $K_2CO_3 \cdot 1.5H_2O$ (JCPDS No. 73-0470). It is indicated that the K_2CO_3 phase of fresh sorbent was not completely converted into $K_2CO_3 \cdot 1.5H_2O$ after pre-treatment. The XRD pattern of this sorbent after CO_2 absorption at 60 °C showed three phases including $KHCO_3$ (JCPDS No. 70-0095), K_2CO_3, and $K_2CO_3 \cdot 1.5H_2O$. It was reported that carbon dioxide was chemically absorbed through the reaction, $K_2CO_3 + H_2O + CO_2 \rightleftarrows 2KHCO_3$, in order to form potassium hydrogencarbonate ($KHCO_3$) over potassium-based sorbents in the presence of moisture [Gidaspow and Onischak, 1975; Hirano et al., 1995; Okunev et al., 2003]. However, the K_2CO_3 phase and $K_2CO_3 \cdot 1.5H_2O$ phase were not completely converted into the $KHCO_3$ phase even after CO_2 absorption as shown in Fig. 1(c). It was reported that the maximum amount of dynamic activity corresponded to the formation of $K_2CO_3 \cdot 1.5H_2O$ rather than K_2CO_3 itself in the alumina pores [Okunev et al., 2000; Sharonov et al., 2001]. It has been considered that a low CO_2 capture capacity was due to a very little formation of an active species like $K_2CO_3 \cdot 1.5H_2O$ after the pre-treatment with 1.3 vol% H_2O as shown in Fig. 1(b) and (c).

In the case of the K_2CO_3/Al_2O_3 sorbent, the XRD results of the fresh sorbent calcined at 300 °C with nitrogen showed K_2CO_3, $K_2CO_3 \cdot 1.5H_2O$, and $KAl(CO_3)_2(OH)_2$ phase as shown in Fig. 2(a). In comparison with the K_2CO_3/AC sorbent, new diffraction lines appeared at 2θ of 15.9, 21.6, 26.7, 28.4, 31.7, 35.8, 41.9, and 45.7, which were assigned to the $KAl(CO_3)_2(OH)_2$ phase (JCPDS No. 21-0979). It is obvious that $KAl(CO_3)_2(OH)_2$ was formed by the reaction of the alumina support with K_2CO_3 during calcination. The XRD patterns of K_2CO_3/Al_2O_3 sorbent after the pre-treatment with 1.3 vol% H_2O showed $K_2CO_3 \cdot 1.5H_2O$ as a major peak along with a minor peak like $KAl(CO_3)_2(OH)_2$. After CO_2 absorption at 60 °C, the XRD patterns of this sorbent showed three phases such as K_2CO_3, $KHCO_3$, and $KAl(CO_3)_2(OH)_2$ phases. In particular, the intensity of the $KAl(CO_3)_2(OH)_2$ peak after CO_2 absorption in Fig. 2(c) increased as compared with Fig. 2(b). After the regeneration at 150 °C in the presence of 1.3 vol% H_2O, this sorbent showed three phases (K_2CO_3, $K_2CO_3 \cdot 1.5H_2O$, and $KAl(CO_3)_2(OH)_2$). The $KAl(CO_3)_2(OH)_2$ phase is not completely converted into the original K_2CO_3 phase during regeneration at 150 °C. The decrease in the total CO_2 capture capacity of K_2CO_3/Al_2O_3 sorbent after regeneration was thought to be due to the formation of the inactive phase of potassium aluminium carbonate as reported in previous papers [Okunev et al., 2003; Sharonov et al., 2001]. The total CO_2 capture capacity of the K_2CO_3/Al_2O_3 sorbent decreased continuously during multiple cycles of CO_2 absorption/regeneration as the amount of the inactive species increased.

2. The Effect of Pre-treatment with H_2O on the CO_2 Absorption

In order to investigate the effect of H_2O concentration during the pre-treatment on the CO_2 capture capacity of the sorbent, the total CO_2 capture capacity and the net CO_2 capture capacity of the K_2CO_3/AC sorbent in the presence of 1.3 vol% H_2O and 1 vol% CO_2 were compared at various H_2O concentrations with or without pre-treatment of sorbents and those results were shown in Table 3. The amount of H_2O in the pre-treatment was controlled in the range of 1.3-52

Table 3. Total CO_2 capture capacity and net CO_2 capture capacity of 30 wt% K_2CO_3/AC sorbent in the presence of 1.3 vol% H_2O and 1 vol% CO_2 after the pre-treatment at various concentrations of H_2O for 2 hours either at 60 °C or at 90 °C

Pretreatment conditions		Net CO_2 capture capacities (mg CO_2/g sorbent)	Total CO_2 capture capacities (mg CO_2/g sorbent)
Concentration of water (%)	Temperature (°C)		
-	-	12.6	25.2
1.3	60	25.1	33.2
5.0	60	37.7	56.2
9.0	60	37.7	62.0
30.0	90	25.1	102.2
52.0	90	25.1	105.0

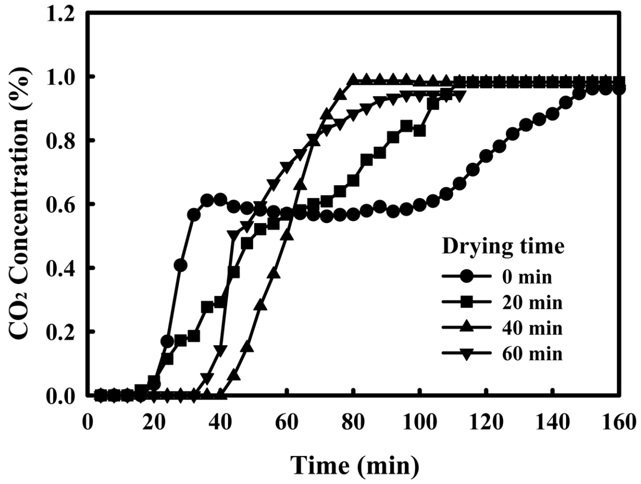

Fig. 3. The breakthrough curves of K_2CO_3/AC sorbents as a function of drying time after the pre-treatment with 52 vol% H_2O at 90 °C and dried for different time durations.

vol%. The net CO_2 capture capacity is defined as the amount of CO_2 absorbed per 1 g of sorbent until the CO_2 concentration, which was emitted from the reactor, remained less than 200 ppm. The total CO_2 capture capacity and the net CO_2 capture capacity of the sorbent without the pre-treatment process was 25.2 mg CO_2/g sorbent and 12.6 mg CO_2/g sorbent, respectively. Depending upon the pre-treatment conditions at various H_2O concentrations, the total CO_2 capture capacity of the K_2CO_3/AC sorbent was varied between 25.2 mg CO_2/g sorbent and 105 mg CO_2/g sorbent. In particular, when the pre-treatment of sorbent was performed with 30 vol% and 52 vol% H_2O at 90 °C (50% and 75% relative humidity, respectively), the rapid increase in the total CO_2 capture capacity was observed under the same absorption experimental condition. This amount was almost completely consistent with the theoretical value of the sorbent, when one mole of K_2CO_3 absorbed a stoichiometric amount of one mole of CO_2.

The breakthrough curves of the K_2CO_3/AC sorbent pre-treated with 52 vol% H_2O were shown in Fig. 3 as a function of drying time after pre-treatment. It was observed that the slope of the breakthrough for the sample without drying rapidly increased at 20 minutes. The concentration of CO_2 exiting from the reactor was maintained at about 0.6% for 100 minutes and then it slowly increased. This shape of the breakthrough curve was not found when the sorbents were pre-treated with a low concentration such as 1.3 vol% or 9 vol% of water. In order to investigate the differences in shapes depending on the pre-treatment conditions, the K_2CO_3/AC sorbents pre-treated with 52 vol% H_2O at 90 °C were dried at 60 °C and the absorption experiments were repeated as shown in Fig. 3. The CO_2 absorption rates of sorbents after drying for 40 minutes were faster than those of sorbent without drying. In particular, the highest net CO_2 capture capacity was observed when sorbent was dried for 40 minutes after the pre-treatment with H_2O. The total CO_2 capture capacities of all these sorbents, however, slightly decreased with increasing the drying time. The total CO_2 capture capacity of the sorbent after an activation process, in which the sorbent was pre-treated with excess water and then dried, was 91 mg CO_2/g sorbent at 60 °C. This indicates that the activation process was an important factor in the CO_2 absorption process. It is thought that the new active species on the sorbent are formed through an activation process and they play an important role in CO_2 absorption.

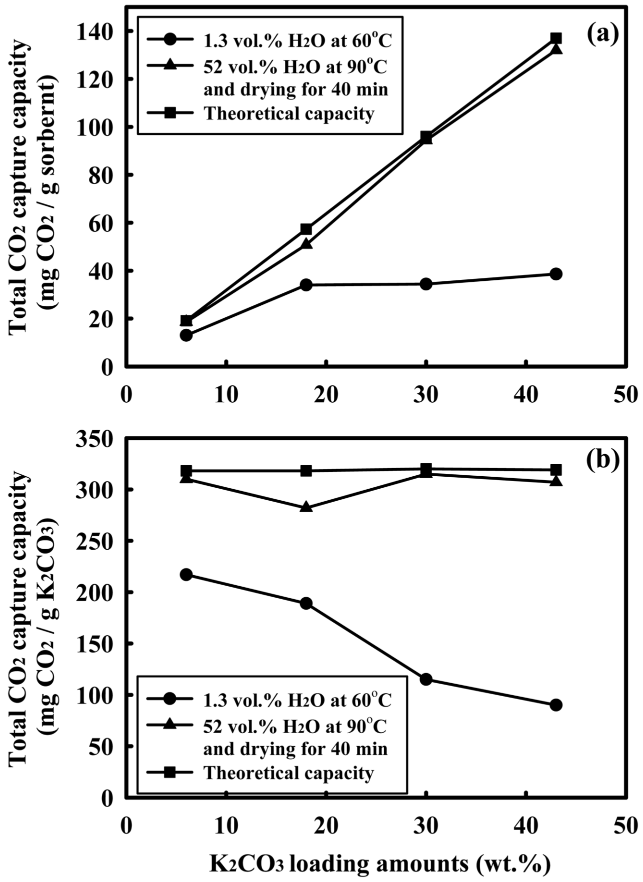

Fig. 4. Total CO_2 capture capacities of sorbents with different K_2CO_3 loading amounts represented by the unit of mg CO_2/g sorbent and mg CO_2/g K_2CO_3 after activation process.

To confirm the effect of the activation of sorbent, the total CO_2 capture capacities of sorbents with various K_2CO_3 loadings were tested after activation under two different conditions (1.3 vol% H_2O at 60 °C, 52 vol% H_2O at 90 °C). Fig. 4(a) and (b) show the total CO_2 capture capacities of sorbents with different K_2CO_3 loadings, which are represented by the unit of mg CO_2/g sorbent and mg CO_2/g K_2CO_3, respectively, after the activation process to convert to $K_2CO_3\cdot 1.5H_2O$ from K_2CO_3 by only pre-treatment of the sorbent in the presence of the low concentration of water (1.3 vol% H_2O) or by drying for 40 minutes after the pre-treatment with excess water (52 vol% H_2O). As shown in Fig. 4(a), the total CO_2 capture capacities of three sorbents, in which 18 wt%, 30 wt%, and 43 wt% of K_2CO_3 were impregnated, were almost on the same values under the condition of pre-treatment with 1.3 vol% H_2O. In the case of activation with 52 vol% H_2O and drying, the total CO_2 capture capacities of those sorbents increased linearly from 25 mg CO_2/g sorbent to 137 mg CO_2/g sorbent. The corresponding theoretical values of the total CO_2 capture capacities for the sorbents with four different K_2CO_3 loading amount were shown in Fig. 4. In order to investigate the effect of the activation of sorbents in detail, the amount of the CO_2 absorption per 1 gram of K_2CO_3 was calculated from the breakthrough curves during CO_2 absorption after activation and it was shown in Fig. 4(b). For the sorbent pre-treated with 1.3 vol% H_2O, the amount of the CO_2 absorption per 1 gram of K_2CO_3 decreased with from 220 mg CO_2/g K_2CO_3 to 90 mg CO_2/g K_2CO_3 as the K_2CO_3 loading amount increased. In the case of activation with 52 vol% H_2O and drying, these total CO_2 capture capacities were almost the same as the theoretical values of the sorbents. Considering that all theoretical values of the K_2CO_3/AC sorbents are about 320 mg CO_2/g K_2CO_3, these values are equivalent to 90-98 percent of those of the sorbents.

These results indicate that the CO_2 capture capacity of potassium-based sorbents depends on the activation of the sorbent. If the potassium-based sorbent is fully activated under the severe pre-treatment conditions, excellent CO_2 capture capacity and absorption rate can be obtained. It is also indicated that the K_2CO_3 is more easily and effectively converted to the activated form by drying process after the pre-treatment of excess water.

3. Structure Identification of the Active Sorbents by XRD

The formation of active species in sorbents is directly related to the CO_2 capture capacity. The structural change after pre-treatment with water has already been mentioned by other researchers [Hayashi et al., 1998; Hirano et al., 1995; Okunev et al., 2003]. The relationship between CO_2 capture capacities and structural changes during the activation process by moisture nitrogen, however, has not been clearly defined. Fig. 5 shows the X-ray diffraction patterns of structural changes of the K_2CO_3/AC sorbents before/after CO_2 absorption. Fig. 5(a) shows the XRD patterns of fresh sorbents (43 wt% K_2CO_3) calcined at 300 °C. When the pre-treatment with 52 vol% H_2O was carried out, new diffraction lines with 2θ of 11.6, 23.3, 30.9, 31.9, 36.1, 38.9, and 47.5 appeared on the XRD results, which were assigned to $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ referring to the JCPDS file number 20-0886. After drying this sample for 40 minutes, the $K_2CO_3 \cdot 1.5H_2O$ phase, which was assigned to the JCPDS file number 73-0470, was formed on the activated carbon support from the $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ phase as shown in Fig. 5(c). This fact indicates that the new active species, $K_2CO_3 \cdot 1.5H_2O$, could be formed by drying the $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ phase which is formed after the pre-treatment with excess H_2O. As shown in Fig. 5(d), the XRD pattern shows that the only $KHCO_3$ phase was formed after CO_2 absorption over the new active species. In the case of activation with 1.3 vol% H_2O, K_2CO_3 was not completely converted into the active species, $K_2CO_3 \cdot 1.5H_2O$ because of the low concentration of water as stated in the previous section. In the case of activation with 52 vol% H_2O, K_2CO_3 could be completely converted into $K_2CO_3 \cdot 1.5H_2O$. This indicates that the enhanced CO_2 capture capacity can be obtained by converting the entire $K_2CO_3 \cdot 1.5H_2O$ phase to the $KHCO_3$ phase and that the sorbents can be fully regenerated to the original state if the sorbents are fully activated with excess water.

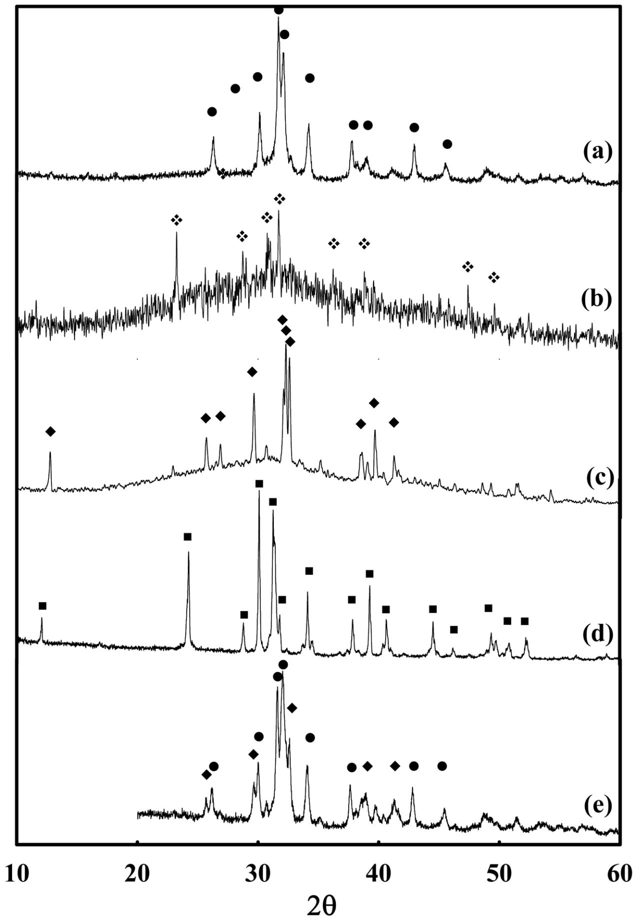

Fig. 5. XRD patterns of K_2CO_3/AC sorbents before/after CO_2 absorption at 60 °C: (a) fresh; (b) after pretreatment with 52 vol% H_2O; (c) after drying for 40 minutes with N_2 (d) after absorption of CO_2 in the presence of 1.3 vol% H_2O and 1 vol% CO_2 at 60 °C; (e) after regeneration with 1.3 vol% H_2O at 150 °C; (●) K_2CO_3; (◆) $K_2CO_3 \cdot 1.5H_2O$; (■) $KHCO_3$; (❖) $K_4H_2(CO_3)_3 \cdot 1.5H_2O$.

CONCLUSIONS

The CO_2 capture capacity was measured in a fixed bed reactor at low temperature conditions (CO_2 absorption at 60 °C and regeneration at 150 °C). The K_2CO_3/AC sorbent was clarified as the leading sorbent of which the total CO_2 capture capacity was higher than that of other sorbents. This sorbent was completely regenerated into its original phase by heating the entrapped sorbent. The CO_2 capture capacity of the K_2CO_3/Al_2O_3 sorbent, however, decreased during multiple cycles of CO_2 absorption/regeneration. This result was explained through the formation of $KAl(CO_3)_2(OH)_2$ which was not completely converted to the original K_2CO_3 phase. The activation process with excess water before CO_2 absorption must be always carried out in order to enhance not only the CO_2 capture capacity of the sorbent but also the rate of CO_2 absorption. The enhanced CO_2 capture capacity can be obtained by converting the entire $K_2CO_3 \cdot 1.5H_2O$ phase to the $KHCO_3$ phase if the sorbents are fully activated with excess water. The new active species could be formed by drying the $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ phase formed after pre-treatment with excess water.

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