# The effect of relative humidity on CO<sub>2</sub> capture capacity of potassium-based sorbents

**Soo Chool Lee**\***, Ho Jin Chae**\***, Bo Yun Choi**\***, Suk Yong Jung**\***, Chun Yong Ryu**\***, Jung Je Park**\***, Jeom-In Baek**\*\***, Chong Kul Ryu**\*\***, and Jae Chang Kim**\***,†**

\*Department of Chemical Engineering, Kyungpook National University, Daegu 702-701, Korea \*\*Korea Electric Power Research Institute, Daejeon 305-380, Korea (*Received 4 March 2010 • accepted 30 July 2010*)

**Abstract**−Potassium-based sorbent was prepared by impregnation with potassium carbonate on activated carbon. The role of water and its effects on pretreatment and CO<sub>2</sub> absorption was investigated in a fixed bed reactor. K<sub>2</sub>CO<sub>3</sub> could be easily converted into  $K_2CO_3$  1.5H<sub>2</sub>O working as an active species by the absorption of water vapor as the following reaction: K<sub>2</sub>CO<sub>3</sub>+3/2 H<sub>2</sub>O→K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O. One mole of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O absorbed one mole of CO<sub>2</sub> as the following reaction: K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O+CO<sub>2</sub>  $\rightleftharpoons$  2KHCO<sub>3</sub>+0.5 H<sub>2</sub>O. The K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O phase, however, was easily transformed to the  $K_2CO_3$  phase by thermal desorption even at low temperature under low relative humidity. To enhance CO<sub>2</sub> capture capacity and CO<sub>2</sub> absorption rate, it is very important to maintain the K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O phase worked as an active species, as well as to convert the entire  $K_2CO_3$  to the  $K_2CO_3 \cdot 1.5H_2O$  phase during  $CO_2$  absorption at a temperature range between 50 °C and 70 °C. As a result, the relative humidity plays a very important role in preventing the transformation from K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O to the original phase (K<sub>2</sub>CO<sub>3</sub>) as well as in producing the K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O from  $K_2CO_3$ , during  $CO_2$  absorption between 50 °C and 70 °C.

Key words:  $CO_2$ , Absorption, Pretreatment,  $K_2CO_3$ ,  $K_2CO_3$  $\cdot 1.5H_2O$ 

## **INTRODUCTION**

Carbon dioxide  $(CO<sub>2</sub>)$  is a major greenhouse gas that is released into the air due to the use of fossil fuels. As a consequence,  $CO<sub>2</sub>$ causes global climate warming. 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 [1-5]. These methods, however, are costly and consume a great deal of energy.

One of the improved techniques for the removal of  $CO<sub>2</sub>$  is the chemical absorption of  $CO<sub>2</sub>$  with solid regenerable sorbents. The use of solid sorbents for CO<sub>2</sub> absorption has been reported previously [6-27]. Alkali metal carbonate was utilized in CO<sub>2</sub> absorption at low temperatures (50-60  $\degree$ C) with thermal regeneration easily occurring at low temperatures. Calcium oxide was utilized in  $CO<sub>2</sub>$ absorption at higher temperatures (less than 860 °C) [15]. Several studies regarding the efficient chemical absorption over  $K_2CO_3$ , which was supported either on carbon<sup>4</sup> or on other porous matrices such as silica gel,  $Al_2O_3$  and vermiculite [17], were also reported using cyclic fixed-bed operations under moist conditions. Water content was essential in forming potassium hydrogencarbonate in all absorption reactions, while moisture contained in the flue gases, as high as 8-17 vol%, negatively affected the adsorption capacity of molecular sieves [8]. It has been reported that  $K_2CO_3$  1.5H<sub>2</sub>O is directly related to the  $CO<sub>2</sub>$  capture capacity [8,10]. Active species, however, were easily transformed to  $K_2CO_3$  by thermal desorption even at low temperature under low concentration of water vapor due to the heat released from the exothermic reaction of the sorbent during  $CO<sub>2</sub>$  absorption [10]. The new active species  $(K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O)$  could also be formed by drying of the  $K_4H_2(CO_3)$ , 1.5H<sub>2</sub>O phase which was formed after pre-treatment with excess water [11]. The  $K_2CO_3$ based sorbent, which was prepared by impregnation of activated carbon with  $K_2CO_3$ , showed very low  $CO_2$  capture capacity of about 40 mg  $CO<sub>2</sub>/g$  sorbent in the case of 1.3 vol% H<sub>2</sub>O and 1 vol%  $CO<sub>2</sub>$ , although the ratio of  $CO<sub>2</sub>$  to water was 1 : 1.3. This result could not be explained by the fact that one mole of  $K_2CO_3$  could absorb a stoichiometric amount of one mole of  $CO<sub>2</sub>$  and one mole of  $H<sub>2</sub>O$  according to the following reaction: K<sub>2</sub>CO<sub>3</sub>+H<sub>2</sub>O+CO<sub>2</sub>  $\rightleftharpoons$  2KHCO<sub>3</sub> [8-14,17,18]. Even though it is well known that water vapor plays an important role in CO<sub>2</sub> absorption over alkali metal-based sorbents, the role of water vapor in CO<sub>2</sub> absorption has not been clearly defined. In particular, there have been very few reports regarding the effects and roles of water vapor on CO<sub>2</sub> absorption over the alkali metal-based sorbents.

One of the main objectives of this work was to investigate the role of water vapor and its effects on  $CO<sub>2</sub>$  absorption. For this purpose, the  $CO<sub>2</sub>$  capture capacity of the potassium-based sorbent was studied in the presence of various concentrations of water vapor. In addition, changes in the physical properties of the sorbent before and after the reaction, the identification of a new active species, and a mechanism were investigated by X-ray diffraction and temperature programmed desorption (TPD).

### **EXPERIMENTAL**

#### **1. Preparation of Sorbents**

The alkali metal-based sorbent used in this study was prepared by an impregnation method. A typical preparation procedure for the sorbent supported on the activated carbon (KACI30) was as fol-

E-mail: kjchang@knu.ac.kr

<sup>†</sup> To whom correspondence should be addressed.

lows: Five (5.0) g of activated carbon (AC) was added to an aqueous solution containing 2.5 g of anhydrous alkali metal carbonate  $(K_2CO_3)$ , Aldrich) in 25 ml of de-ionized water. Then, the content was mixed with a magnetic stirrer for 24 h at room temperature [8,11-13]. After stirring, the mixture was dried in a rotary evaporator at 60 °C. The dried samples were calcined in a furnace with  $N_2$  flow (100 ml/min) for 4 h at 300 °C. The ramping rate of the temperature was maintained at 3 °C/min. The surface area of the sorbent was measured at 77 K using BET (Quantachrome, AUTOSORB-1). The surface area of activated carbon (AC, 1,987 m<sup>2</sup>/g) was reduced to 471.6 m<sup>2</sup>/ g after calcination at 300 °C. Power X-ray diffraction (XRD; Philips, X'PERT) was also measured in order to confirm the structure using Cu  $K\alpha$  radiation.

## **2. Absorption Apparatus and Procedures**

CO<sub>2</sub> 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 the sorbent was packed into the reactor, and space velocity (SV) was maintained at 3,000 h<sup>-1</sup> to minimize severe pressure drops and channeling phenomena. All volumetric gas flows were measured under standard temperature and pressure (STP) conditions. The column used in the analysis was a 1/8 inch stainless tube packed with Porapak Q. The conditions for pre-treatment,  $CO<sub>2</sub>$  absorption, regeneration, and water desorption are shown in Table 1. Before  $CO<sub>2</sub>$  absorption, moist nitrogen gas with 1.3-11 vol $\%$  H<sub>2</sub>O (6.5-56 $\%$  relative humidity) at 60 °C was supplied to sorbents for 120 min using a saturator. When the  $CO<sub>2</sub>$  concentration of the outlet gases reached the same level as the inlet gas  $(1 \text{ vol}\%)$  during the  $CO<sub>2</sub>$  absorption process, nitrogen was introduced to regenerate the spent sorbent. The regeneration process was terminated when the  $CO<sub>2</sub>$  concentration reached 200 ppm. Water desorption tests during the  $CO<sub>2</sub>$  absorption were carried out under the respective water concentration  $(0, 1.3, 5.0, 9.0 \text{ vol}\% \text{ H}_2\text{O})$  after pre-treatment with 9 vol $\%$  H<sub>2</sub>O for 2 h. TPD tests of the sorbent were performed under conditions with/without 9 vol%  $H_2O$  after pre-treatment with 9 vol%  $H_2O$ , when the temperature ramping rate was  $1^{\circ}$ C/min. The outlet CO<sub>2</sub> and H<sub>2</sub>O 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.). Hydrogen gas was used as a carrier gas.

#### **RESULTS AND DISCUSSION**

#### 1. A Comparison of CO<sub>2</sub> Capture Capacity of a Sorbent at **Various Concentrations of Water Vapor**

The  $CO<sub>2</sub>$  capture capacity of a sorbent was evaluated by the break-



Fig. 1. The breakthrough curves (a) and the CO<sub>2</sub> capture capacity **(b) of KACI30 in the presence of various concentrations of water vapor and 1 vol** $\%$  $CO_2$  **at 60 °C.** 

through curve for  $CO_2$  absorption. In this study, the net  $CO_2$  capture capacity and the total  $CO<sub>2</sub>$  capture capacity were used to evaluate  $CO<sub>2</sub>$  capture capacity. Total  $CO<sub>2</sub>$  capture capacity describes the amount of  $CO_2$  absorbed until the output concentration of  $CO_2$  reaches 1 vol%, which is the same value as that of the inlet. The net CO<sub>2</sub> capture capacity is defined as the amount of  $CO<sub>2</sub>$  absorbed per 1 g of sorbent until the  $CO$ , concentration is less than 200 ppm. Fig.  $1(a)$  shows the breakthrough curves of a KACI30 sorbent at various concentrations of water vapor in the presence of  $1 \text{ vol} \%$  CO<sub>2</sub> at 60 °C. It was observed that the slope of the breakthrough curve gradually decreased with an increase in the concentration of water vapor. Fig.  $1(b)$  shows the  $CO<sub>2</sub>$  capture capacity, which was calculated from breakthrough curves, as a function of concentration of water vapor.







Fig. 2. The XRD patterns of the KACI30 sorbent after CO<sub>2</sub> absorp**tion in the presence of various water vapors such as 1.3 vol% H2O (a), 5.0 vol% H2O (b), and 9.0 vol% H2O (c) and 1 vol%**  $CO_2$ ; ( $\bullet$ ) K<sub>2</sub>CO<sub>3</sub>; ( $\bullet$ ) KHCO<sub>3</sub>.

In the case of  $1.3 \text{ vol} \% \text{ H}_2\text{O}$ , its total CO<sub>2</sub> capture capacity was about  $40 \,\mathrm{mg}$  CO<sub>2</sub>/g sorbent. This value was equivalent to about 42 percent of the theoretical value of the sorbent, when one mole of  $K_2CO_3$ absorbed a stoichiometric amount of one mole of CO<sub>2</sub> and one mole of H<sub>2</sub>O (K<sub>2</sub>CO<sub>3</sub>+H<sub>2</sub>O+CO<sub>2</sub>  $\rightleftharpoons$  2KHCO<sub>3</sub>) to form potassium hydrogencarbonate  $(KHCO<sub>3</sub>)$  [8-14,17,18]. This low capture capacity in the presence of excess water vapor could not be explained by the above reaction mechanism. As the inlet water concentration increased, the total  $CO$ , capture capacity increased to  $86.3$  mg  $CO$ /g sorbent, which was about 90.4 percent of the theoretical value. Although high  $CO<sub>2</sub>$  capture capacity was obtained, the point to note here is that the slope of the breakthrough curve is very low as shown in Fig. 1(a), indicating slow absorption of  $CO<sub>2</sub>$ .

Fig. 2 shows the XRD patterns of the KACI30 sorbent after  $CO<sub>2</sub>$ absorption in the presence of various water vapors such as 1.3 vol<sup>%</sup> H<sub>2</sub>O(a), 5.0 vol% H<sub>2</sub>O (b), and 9.0 vol% H<sub>2</sub>O (c) and 1 vol% CO<sub>2</sub>. In the case of 1.3 vol% H<sub>2</sub>O and 5 vol% H<sub>2</sub>O, the peaks of K<sub>2</sub>CO<sub>3</sub> were observed as shown in Fig. 2(a) and (b), while in the case of 9 vol $\%$  H<sub>2</sub>O, it disappeared in the XRD patterns of Fig. 2(c). This indicates that  $K_2CO_3$  was not completely converted into  $KHCO_3$ under the concentration of 1.3 vol $\%$  H<sub>2</sub>O and 5.0 vol $\%$  H<sub>2</sub>O in spite of the excess water vapor as compared to  $1.0$  vol $\%$  CO<sub>2</sub>.

#### **2. The Water Absorption of the Sorbent without CO**<sub>2</sub>

To identify this fact, the water absorption of the sorbent itself was carried out in the presence of various concentrations of water vapor.



**Fig. 3. The amount of water (a) absorbed on KACI30 (I) and 0.7 g** of AC (II) at various concentrations of water vapor at 60 °C **and the difference (b) between the absorption amounts of water for KACI30 (I) and that for AC (II) support.**

Fig. 3(a) shows the amounts of water absorbed on the KACI30 sorbent (I) and 0.7 g AC (II) support, which are calculated from their breakthrough curves at various concentrations of water vapor. As shown in Fig. 3(a-I), the amount of water absorbed on the sorbent depends on the concentration of water vapor. When concentration of water vapor increased from 1.3 to  $9.0$  vol $\%$  H<sub>2</sub>O, the absorption amount of water per 1 gram of the KACI30 sorbent increased linearly from  $28.8$  mg  $H<sub>2</sub>O/g$  sorbent to  $207.4$  mg  $H<sub>2</sub>O/g$  sorbent. Considering the following reaction to form the active species  $(K_2CO_3+3/2)$  $H_2O \rightarrow K_2CO_3 \cdot 1.5H_2O$  [8,10,11] the theoretical value for water absorption per 1 g KACI30 was 58.6 mg  $H_2O/g$  sorbent (58.6 mg  $H_2O/$  $0.3 \text{ g K}_2\text{CO}_3$ ). However, the amount of water absorbed in the case of 9 vol% H2O is more than 3.5 times of the theoretical value of the sorbent. This result suggests that activated carbon (AC), used as a support of KACI30, should adsorb a large amount of water. To check this fact, the absorption amounts of water on the activated carbon at various concentrations of water vapor are measured as shown in Fig. 3(a-II). With an increase in concentration of water vapor from 1.3 vol $\%$  H<sub>2</sub>O to 9.0 vol $\%$  H<sub>2</sub>O, the amount of the water absorption increased linearly from 9.9 to 32.6 mg H<sub>2</sub>O. The difference between the water absorption amounts for KACI30 (Fig. 3(a-I)) and those for AC (Fig. 3(a-II)) should represent the amount of water used to convert the sorbent from  $K_2CO_3$  into the active species,  $K_2CO_3$ .

1.5H2O. The results are shown in Fig. 3(b). When the absorption of water of the sorbent was performed with 5 vol% and 9 vol% H<sub>2</sub>O at 60 °C (25% and 46% relative humidity, respectively), the absorption amounts of water were 97.9 and 174.8 mg  $H_2O/0.3$  g  $K_2CO_3$ , respectively. It must be noted that these values are higher than the theoretical value for water absorption per 1 g of KACI30  $(0.3 \text{ g K,CO}_3)$ . It was thought that a new structure or new water consumption reaction, with the exception of the formation of  $K_2CO_3$  1.5H<sub>2</sub>O, might be needed to explain the large absorption amounts of water.

## **3. Structure Identification**

Fig. 4 shows the XRD patterns of the sorbent before (a) and after the absorption of water with various concentrations of water vapor such as  $1.3$  (b),  $5.0$  (c), and  $9.0$  (d) vol $\%$  H<sub>2</sub>O. The important point



**Fig. 4. XRD patterns of KACI30 before (a)/after pre-treatment with various concentrations of water vapor such as 1.3 (b), 5.0 (c), and 9.0 (d) vol**%  $H_2O$  at 60 °C; ( $\bullet$ )  $K_2CO_3$ ; ( $\bullet$ )  $K_2CO_3$ ·  $1.5H_2O$ ; ( $\clubsuit\bullet$ )  $K_4H_2(CO_3)_3.1.5H_2O.$ 

to note is that in the case of 1.3 vol%  $H<sub>2</sub>O$  (b),  $K<sub>2</sub>CO<sub>3</sub>$  did not completely convert into  $K_2CO_3 \cdot 1.5H_2O$ . This fact agreed with the previous result that the absorption amount of water did not reach 58.6 mg  $H<sub>2</sub>O/g$  sorbent. It was thought that this result was caused by the equilibrium of absorption and desorption of water at low relative humidity. When the absorption of water of the sorbent was performed under 5.0 (c) and 9.0 (d) vol%  $H_2O$ ,  $K_2CO_3$  could be completely converted into  $K_2CO_3$ . 1.5H<sub>2</sub>O. It was also found that a new structure assigned to a  $K_4H_2(CO_3)$ <sup>1</sup>.5H<sub>2</sub>O phase (JCPDS No. 20-0886), with the exception of  $K_2CO_3$ : 1.5H<sub>2</sub>O, was formed by absorption of water vapor. These facts indicate that  $K_4H_2(CO_3)$ , 1.5H<sub>2</sub>O, as well as  $K_2CO_3$ ·1.5H<sub>2</sub>O, could be formed by the absorption of water under the concentration range from  $5.0$  to  $9.0$  vol $\%$  H<sub>2</sub>O.

## **4. The Effects of Water on Pre-treatment and CO<sub>2</sub> Absorption**

It has been reported that the formation of  $K_2CO_3 \cdot 1.5H_2O$  plays an important role in CO<sub>2</sub> capture capacity [8], and that the  $K_2CO_3$ . 1.5H<sub>2</sub>O phase formed from the  $K_4H_2(CO_3)$ <sub>3</sub>·1.5H<sub>2</sub>O phase during pre-treatment with excess water vapor before  $CO<sub>2</sub>$  absorption, was directly related to  $CO<sub>2</sub>$  capture capacity [11]. Pre-treatment was defined as the absorption process of water vapor before  $CO<sub>2</sub>$  absorption. In this section, to investigate the effects of water vapor on pretreatment and  $CO<sub>2</sub>$  absorption,  $CO<sub>2</sub>$  breakthrough curves at 60 °C after pre-treatment in the presence of various concentrations of water vapor were compared and their net and total CO<sub>2</sub> capture capacities are shown in Table 2. When  $CO<sub>2</sub>$  was absorbed in the presence of 9 vol%  $H_2O$  without pre-treatment, the net and total  $CO_2$  capture capacities of the sorbent were  $37.7$  and  $82.0$  mg  $CO<sub>2</sub>/g$  sorbent, respectively. After pre-treatment with 9 vol $\%$  H<sub>2</sub>O, the net CO<sub>2</sub> capture capacity increased to  $62.8 \text{ mg } CO<sub>2</sub>/g$  sorbent, while the total  $CO<sub>2</sub>$  capture capacity was slightly increased to the value of 86.4 mg  $CO<sub>2</sub>/g$  sorbent (equivalent to about 91 percent of the theoretical value). This result indicates that the pre-treatment process plays an impor $t$ ant role in the net  $CO$ , capture capacity, because the active species,  $K_2CO_3 \cdot 1.5H_2O$ , is already formed by the pre-treatment with water vapor, as mentioned in the XRD results of a previous section. When CO<sub>2</sub> absorption of the sorbent was performed in the absence of water, even after pre-treatment with 9 vol% H<sub>2</sub>O, the net and total  $CO<sub>2</sub>$  capture capacities were only 50.2 and 67.4 mg  $CO<sub>2</sub>/g$  sorbent, respectively. As the water concentration increased from 1.3 vol%  $H<sub>2</sub>O$  to 9 vol%  $H<sub>2</sub>O$ , the net and total  $CO<sub>2</sub>$  capture capacities increased from 50.2 mg  $CO_2/g$  sorbent to 62.8 mg  $CO_2/g$  sorbent, and from 67.4 mg  $CO_{2}/g$  sorbent to 86.4 mg  $CO_{2}/g$  sorbent, respectively. It is clear that the concentration of water vapor in the  $CO<sub>2</sub>$  absorp-

Table 2. The net CO<sub>2</sub> capture capacity and total CO<sub>2</sub> capture capacity of KACI30 in the presence of various concentrations of **water vapor and 1 vol** $\%$  $\mathbb{C}\mathbf{O}_{2}$  **at 60**  $^{\circ}\mathbb{C}$ 

Concentration of water vapor (vol%)		$CO2$ capture capacity (mg $CO2/g$ sorbent)		Total $CO2$ capture capacity/
Pretreatment	$CO$ , absorption	Net CO <sub>2</sub> capture capacity	Total CO <sub>2</sub> capture capacity	theoretical value $\times$ 100 (%)
$\bf{0}$	9.0	37.7	82.0	85.9
1.3	9.0	37.7	83.0	86.9
5.0	9.0	44.0	84.0	87.9
9.0	9.0	62.8	86.4	90.5
9.0	5.0	56.5	75.4	78.9
9.0	1.3	50.2	74.8	78.3
9.0	0	50.2	67.4	70.6



Fig. 5. The desorption amounts of water during CO<sub>2</sub> absorption **in the presence of various concentrations of water vapor at 60 <sup>o</sup> C after pretreatment with 9 vol% H2O.**

tion process, as well as in pre-treatment process, is an important factor in obtaining the enhanced  $CO<sub>2</sub>$  capture capacity of the sorbent. In particular, the total CO<sub>2</sub> capture capacity of the sorbent depends on the concentration of water vapor, despite the complete formation of  $K_2CO_3$  1.5H<sub>2</sub>O through its pre-treatment with water vapor.

**5. The Behavior of Water Vapor in CO<sub>2</sub> Absorption Process** 

Fig. 5 shows the desorption amount of water during the  $CO<sub>2</sub>$  absorption under the respective water concentration after pre-treatment with  $9 \text{ vol} \%$  H<sub>2</sub>O for 2 h. The amounts of water decreased from 224 mg  $H_2O/g$  sorbent to 108.7 mg  $H_2O/g$  sorbent, with an increase in the inlet water concentration. It was impossible to explain the desorption amount of water by the following reaction only:  $K_2CO_3$ .  $1.5H<sub>2</sub>O+CO<sub>2</sub>+H<sub>2</sub>O \rightarrow 2KHCO<sub>3</sub>+1.5H<sub>2</sub>O$ , in which the desorption amount of water was constant regardless of the concentration of water vapor due to excess water vapor during the  $CO<sub>2</sub>$  absorption. It could be deduced that the high desorption amount of water was due to the physisorbed water and the conversion process such as



**Fig. 6. TPD experimental results of sorbent activated through pretreatment with 9 vol% H<sub>2</sub>O at 60 °C under conditions with/ without 9 vol** $\%$  **H<sub>2</sub>O.** 

the conversion of  $K_4H_2(CO_3)$ <sup>3</sup>; 1.5H<sub>2</sub>O to  $K_2CO_3$ <sup>3</sup>; 1.5H<sub>2</sub>O and the transformation of  $K_2CO_3 \cdot 1.5H_2O$  to  $K_2CO_3$ , as well as the reaction. Fig. 6 shows the TPD results of the sorbent under conditions with/ without  $9 \text{ vol} \% \text{ H}_2\text{O}$  after pre-treatment with  $9 \text{ vol} \% \text{ H}_2\text{O}$ , when the temperature ramping rate was 1 °C/min. In both cases, the TPD result of the sorbent showed two types of water peaks. In the presence of 9 vol $\%$  H<sub>2</sub>O, however, the desorption temperature of water increased as compared with that in the absence of water. This result indicates that there are two kinds of species within the sorbent after pre-treatment with  $9 \text{ vol} \% \text{ H}_2\text{O}$ , and that two peaks are shifted to the higher temperatures in the presence of  $9 \text{ vol} \% \text{ H}_2\text{O}$ . The two kinds of species agreed well with the XRD result shown in Fig. 4(d)  $(K<sub>4</sub>H<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·1.5H<sub>3</sub>O$  and  $K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>3</sub>O$ . It has been reported that a K<sub>2</sub>CO<sub>3</sub> phase of the KACI30 sorbent transformed into a  $K_4H_2(CO_3)$ <sub>3</sub>· 1.5H<sub>2</sub>O phase by pre-treatment under the excess water vapor (52) vol%  $H_2O$ ) at 90 °C, and the  $K_4H_2(CO_3)_3 \cdot 1.5H_2O$  phase could be converted into the  $K_2CO_3 \cdot 1.5H_2O$  phase by drying under  $N_2$  at 60 °C [11]. As shown in Fig. 7, this suggested that  $K<sub>d</sub>H<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·1.5H<sub>3</sub>O$ could be converted into  $K_2CO_3$  1.5H<sub>2</sub>O during CO<sub>2</sub> absorption at 60 °C and that the first peak was due to conversion of  $K_4H_2(CO_3)$ .  $1.5H<sub>2</sub>O$  into  $K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O$ .

## **6. The Effect of Relative Humidity on Water Desorption and** CO<sub>2</sub> Capture Capacity

The amount of water vapor desorbed was measured at various  $CO<sub>2</sub>$  absorption temperatures under 9 vol $\%$  H<sub>2</sub>O, after pre-treatment with 9 vol $\%$  H<sub>2</sub>O. As shown in Fig. 8(a), in spite of the same



**Fig. 7. XRD patterns of the KACI30 sorbent before (a) and after (b) pretreatment with the excess water vapor**  $(52 \text{ vol\% H}_2O)$ and after (c) drying for 40 min with  $N_2$  at 60 °C; ( $\bullet$ ) K<sub>2</sub>CO<sub>3</sub>;  $(\clubsuit\spadesuit\spadesuit)$  K<sub>4</sub>H<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·1.5H<sub>2</sub>O;  $(\spadesuit)$  K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O.



Fig. 8. The amount of water desorbed at various  $CO<sub>2</sub>$  absorption **the amount of water desorbed at various**  $\text{CO}_2$  **absorption**<br>**Fig. 9. CO<sub>2</sub> capture capacity of the sorbent in the presence of 9 vol%**<br>**H**O<sub>2</sub> and 1 vol<sup>qt</sup>, CO<sub>2</sub> as a function of absorption temperatures of a solution t

concentration of water vapor  $(9 \text{ vol}\% \text{ H},O)$ , it was observed that the desorption amount of water increased with an increase in temperature. Fig. 8(b) shows the desorption amount of water as a function of relative humidity calculated at each temperature. The amount of water desorbed was linearly increased with a decrease in relative humidity. It was found that the desorption amount of water vapor directly depended on relative humidity, indicating that relative humidity was more important than the concentration of water vapor in the reactor.

Fig. 9 shows the  $CO$ , capture capacity of the sorbent as a function of absorption temperature and relative humidity in the presence of 9 vol%  $H_2O$  after pre-treatment with 9 vol%  $H_2O$  at 60 °C. As shown in Fig. 9(a), the sorbent showed  $CO<sub>2</sub>$  capture capacity of about 87 mg  $CO<sub>2</sub>/g$  sorbent at 50 °C and 60 °C, while the value gradually decreased with an increase in temperature. To identify the effect of relative humidity on total  $CO<sub>2</sub>$  capture capacity, the  $CO<sub>2</sub>$  capture capacity was represented as a function of relative humidity. It was found that the total CO<sub>2</sub> capture capacity of the sorbent almost linearly decreased with a decrease in relative humidity. In a separate experiment, it was known that  $KHCO<sub>3</sub>$  desorbed most  $CO<sub>2</sub>$  in the temperature range between 80 °C and 160 °C [10]. This means that the KHCO<sub>3</sub> phase was starting to transform to  $K_2CO_3$  by thermal decomposition from 80 °C. These results indicated that the  $CO<sub>2</sub>$  capture capacity of the sorbent could be affected by the thermal decomposition of KHCO<sub>3</sub> between 80 °C and 100 °C. As a result, to obtain



H<sub>2</sub>O and 1 vol% CO<sub>2</sub> as a function of absorption tempera**ture and relative humidity.**

excellent  $CO<sub>2</sub>$  capture capacity, the sorbent always needs sufficient relative humidity during  $CO<sub>2</sub>$  absorption between 50 °C and 70 °C. It was concluded that the relative humidity in the reactor plays a very important role in preventing the transformation from  $K_2CO_3$ . 1.5H<sub>2</sub>O to the original phase,  $K_2CO_3$ , as well as in producing the  $K_2CO_3·1.5H_2O$  from  $K_2CO_3$ , during CO<sub>2</sub> absorption.

## **CONCLUSIONS**

KACI30 showed not only a high  $CO<sub>2</sub>$  capture capacity of 86.4 mg CO<sub>2</sub>/g sorbent, which was 91% of the theoretical value of 30 wt%  $K<sub>2</sub>CO<sub>3</sub>$ , but also excellent  $CO<sub>2</sub>$  absorption rate after pre-treatment with 9 vol $\%$  H<sub>2</sub>O. The role of water vapor in pre-treatment was to enhance the net  $CO<sub>2</sub>$  capture capacity by converting the  $K<sub>2</sub>CO<sub>3</sub>$  phase to active species,  $K_2CO_3 \cdot 1.5H_2O$ , through pre-treatment with sufficient water vapor. It, however, was found that  $K_2CO_3$ : 1.5H<sub>2</sub>O could be easily transformed again to  $K_2CO_3$  by thermal desorption even at low temperatures under very low concentration of water vapor due to the low relative humidity during CO<sub>2</sub> absorption. To enhance  $CO<sub>2</sub>$  capture capacity, it is very important to maintain the active species as well as to convert the entire  $K_2CO_3$  to the  $K_2CO_3 \cdot 1.5H_2O$  phase during  $CO<sub>2</sub>$  absorption between 50 °C and 70 °C. The sufficient relative humidity in the reactor plays a very important role in preventing the active species from transforming to the original phase,  $K_2CO_3$ ,

in  $CO<sub>2</sub>$  absorption process. In conclusion, in the  $CO<sub>2</sub>$  absorption process, the CO<sub>2</sub> capture capacity of the potassium-based sorbent depends on the relative humidity in the reactor and CO<sub>2</sub> absorption temperature.

#### **ACKNOWLEDGEMENT**

We gratefully acknowledge the financial support from Electric Power Technology Evaluation & Planning center (ETEP). This work is the outcome of a Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MKE).

#### **REFERENCES**

- 1. D. P. Hagewiesche, S. S. Ashour, H. A. Al-Ghawas and O. C. Sandall, *Chem. Eng. Sci*., **50**(7), 1071 (1995).
- 2. B. D. Lee, D. M. Kim, J. H. Cho and S. W. Park, *Korean J. Chem. Eng.*, **26**(3), 818 (2009).
- 3. R. V. Siriwardane, M. S. Shen, E. P. Fisher and J. A. Poston, *Energy Fuels*, **15**, 279 (2001).
- 4. Y. Takamura, S. Narita, J. Aoki, S. Hironaka and S. Uchida, *Sep. Purif. Technol.*, **24**, 519 (2001).
- 5. M. Wilson, P. Tontiwachwuthikul, A. Chakma, R. Idem, A. Veawab, A. Aroonwilas, D. Gelowitz and J. C. Mariz, *Energy*, **29**, 1257 (2004).
- 6. D. J. Fauth, E. A. Frommell, J. S. Hoffman R. P. Reasbeck and H. W. Pennline, *Fuel Process. Technol*., **86**, 1503 (2005).
- 7. B. Ficicilar and T. Dogu, *Catal. Today*, **115**, 274 (2006).
- 8. H. Hayashi, J. Taniuchi, N. Furuyashiki, S. Sugiyama, S. Hirano, N. Shigemoto and T. Nonaka, *Ind. Eng. Chem. Res.*, **37**, 185 (1998).
- 9. S. C. Lee, B. Y. Choi, S. J. Lee, S. Y. Jung, C. K. Ryu and J. C. Kim, *Stud. Surf. Sci. Catal.*, **153**, 527 (2004).
- 10. S. C. Lee and J. C. Kim, *Catal. Surv. Asia*, **11**(4), 171 (2007).
- 11. S. C. Lee, B. Y. Choi, C. K. Ryu, Y. S. Ahn, T. J. Lee and J. C. Kim, *Korean J. Chem. Eng.*, **23**(3), 374 (2006).
- 12. S. C. Lee, B. Y. Choi, T. J. Lee, C. K. Ryu, Y. S. Ahnand J. C. Kim, *Catal. Today*, **111**, 385 (2006).
- 13. S. C. Lee, H. J. Chae, B. Y. Choi, S. J. Lee, C. K. Yi, J. B. Lee, C. K. Ryu and J. C. Kim, *Environ. Sci. Technol.*, **42**, 2736 (2008).
- 14. S. C. Lee, H. J. Chae, S. J. Lee, Y. H. Park, C. K. Ryu, C. K. Yi and J. C. Kim, *J. Mol. Catal. B: Enzym.*, **56**(2-3), 179 (2009).
- 15. Y. Liang, D. P. Harrison, R. P. Gupta, D. A. Green and W. J. McMichael, *Energy & Fuels*, **18**, 569 (2004).
- 16. H. Lu, E. P. Reddy and P. G. Smirniotis, *Ind. Eng. Chem. Res*., **45**, 3944 (2006).
- 17. T. A. Nalette, P. J. Birbara and J. R. Aylward, US Patent, 5,079,209 (1992).
- 18. A. G. Okunev, V. E. Sharonov, Y. I. Aistov and V. N. Parmon, *React. Kinet. Catal. Lett.*, **71**(2), 355 (2000).
- 19. S. W. Park, D. H. Sung, B. S. Choi, K. J. Oh and K. H. Moon, *Sep. Sci. Technol.*, **41**(12), 2665 (2006).
- 20. R. V. Siriwardane, C. Robinson, M. Shen and T. Simony, *Energy Fuels*, **21**, 2088 (2007).
- 21. J. I. Yang and J. N. Kim, *Korean J. Chem. Eng.*, **23**(1), 77 (2006).
- 22. C. W. Zhao, X. P. Chen and C. S. Zhao, *Chemosphere*, **75**, 1401 (2009).
- 23. S. C. Lee, Y. M. Kwon, Y. H. Park, W. S. Lee, J. J. Park, C. K. Ryu, C. K. Yi and J. C. Kim, *Top. Catal.*, **53**(7), 641 (2010).
- 24. C. W. Zhao, X. P. Chen and C. S. Zhao, *Energy Fuels*, **23**(9), 4683 (2009).
- 25. Y. W. Seo, S. H. Jo, C. K. Ryu and C. K. Yi, *Chemosphere*, **69**, 712 (2007).
- 26. Y. W. Seo, S. H. Jo, H. J. Ryu, D. H. Bae, C. K. Ryu and C. K. Yi, *Korean J. Chem. Eng.*, **24**(3), 457 (2007).
- 27. C. K. Yi, S. H. Jo and Y. W. Seo, *J. Chem. Eng. Jpn.*, **41**(7), 691 (2008).