Cyclic Fixed-Bed Operations over K_2CO_3-on-Carbon for the Recovery of Carbon Dioxide under Moist Conditions

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A modified chemical-absorption method capable of cyclic fixed-bed operations under moist conditions for the recovery of carbon dioxide from flue gases has been proposed employing K_2CO_3-on-carbon. Deliquescent potassium carbonate was favorably supported on activated carbon as well as on bound carbon dioxide in the presence of water vapor by the following reaction:

$$K_2CO_3 + CO_2 + H_2O \rightleftarrows 2KHCO_3.$$

After breakthrough, the entrapped carbon dioxide was released by the decomposition of hydrogencarbonate at a higher temperature above 150 °C to shift the reaction in reverse by steam, which could be condensed by cooling to afford high-purity carbon dioxide. An effective use of the pore space as microtanks for aqueous potassium carbonate was verified with XRD evidence under a very humid condition of 7.3% H_2O, as anticipated. The amount of CO_2 uptake was very small under a dry condition, but increased abruptly in the presence of moisture. Potassium carbonate on carbon was crystalline $2K_2CO_3 \cdot 3H_2O$, even when in contact with moisture of 1.7% H_2O; this revealed that it is not necessary for K_2CO_3 to be in the aqueous phase. Illustrative cyclic fixed-bed operations for the recovery of carbon dioxide under a condition close to the actual flue gas of 13.8% CO_2 with 10% H_2O at 100 °C under atmospheric pressure were demonstrated up to 10 cycles.

It is an urgent problem for global environmental preservation to minimize the amount of carbon dioxide released from power plants into the atmosphere. Excellent adsorbents, such as zeolites$^{1)}$ and carbon molecular sieves,$^{2)}$ have been proposed for the pressure-swing adsorption (PSA) of carbon dioxide in a dry gas stream. However, moisture is usually 8—17% in flue gases, badly affecting the adsorption capacity, and the PSA for carbon dioxide is shackled with the necessary pre-cut column for moisture in practical applications. In another established method for chemical absorption by aqueous potassium carbonate (Eq. 1), the Benfield process$^{3,4)}$ has no problem with moisture

$$K_2CO_3 + CO_2 + H_2O \rightleftarrows 2KHCO_3, \tag{1}$$

but is usually carried out in a battery of large tanks as an energy-consuming operation. The absorption of carbon dioxide in a high-pressure tank at a lower temperature is followed by transferring the absorbed liquid to another tank in order to recover the carbon dioxide by a pressure-swing at a higher temperature.

Attempts were made in the present work to combine the advantages of the above-mentioned two methods of pressure-swing fixed-bed adsorption and chemical absorption. Thus, carbon dioxide was chemically absorbed by cyclic fixed-bed operations over potassium carbonate supported on activated carbon to form potassium hydrogencarbonate under an appropriate moisture concentration. After a breakthrough of carbon dioxide the entrapped carbon dioxide was released by the decomposition of hydrogencarbonate to shift the reaction in Eq. 1 in reverse by steam, which could be condensed by cooling to afford carbon dioxide in high purity.

Experimental

Apparatus and Procedure. A schematic flow diagram of the apparatus is given in Fig. 1. Three lines for dry helium, moist helium, and moist carbon dioxide in helium were connected to a bed of K_2CO_3-on-carbon by turns. Potassium carbonate is highly deliquecent, and a sample of K_2CO_3-on-carbon packed in a short stainless-steel column (3 mm-i.d.) was dried overnight at 150 °C in a helium stream prior to adsorption experiments. The dry helium was abruptly replaced by moist helium (0.75—7.3 vol% H_2O) at a flow rate of 40 ml min^{-1} at 60 °C under atmospheric pressure; the breakthrough of water was monitored by a thermal-conductivity cell detector (TCD) of a Shimadzu GC-8APT gas chromatograph. Then, carbon dioxide was added at a

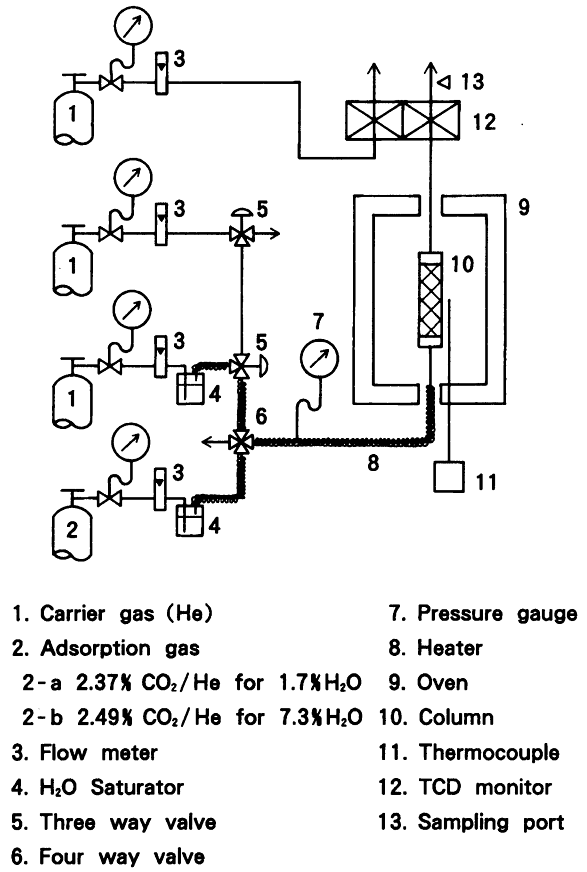

Fig. 1. A schematic flow diagram of apparatus.

concentration of 2.3 vol% without any changes in the moisture concentration and total flow rate. The effluent of the bed was taken intermittently (usually 10 µl in 30 s intervals) by a microsyringe to analyze the carbon dioxide and water by a GC-MS (type JMS-AX505X, JEOL, Tokyo). After saturation with carbon dioxide, the stream was switched back to moist helium while heating the bed up to 150 °C in order to decompose hydrogencarbonate so as to release carbon dioxide, which was again scrubbed with aqueous sodium hydroxide for analysis by a total organic carbon analyzer (TOC-5000; Shimadzu, Kyoto). The apparatus could be operated at pressures of up to 8.1×10^5 Pa (8 atm).

Cyclic operations were carried out under two conditions of 60 °C for 2.3% CO_2 with 1.7% H_2O and 100 °C for 13.8% CO_2 with 10% H_2O. Flashing of the entrapped CO_2 in moist helium was carried out at 150 °C under atmospheric pressure in both cycles.

Materials. Activated carbon (KINTAL® GA-2 (10—20 mesh; BET surface area 1576 $m^2\,g^{-1}$)) and anhydrous potassium carbonate were purchased from Cataler Industries, Shizuoka, and Wako Pure Chemicals, Osaka, respectively. Carbon dioxide and helium were supplied from a commercial cylinder without further purifications. The protocol for the preparation of K_2CO_3-on-carbon is given in the text.

Characterization. Powder X-ray diffraction patterns were measured using Cu $K\alpha$ radiation by an MXP system (MAC Science Co., Tokyo). The surface area (BET) was determined by nitrogen adsorption using a BELSORP 28SA (BEL Japan, Inc., Osaka). Scanning electron-microscopic (SEM) observations and electron-probe microanalysis (EPMA) with an energy-dispersive (EDS) mode were made by a JXA-840A electron probe microanalyzer (JEOL, Tokyo). The amount of potassium carbonate supported on an activated carbon was determined as follows. After an aliquot of the adsorbent sample was burned in a porcelain crucible, the residual ash was dissolved in water so as to be analyzed for potassium by an inductively coupled plasma atomic-emission spectrometer (ICP; SPS-1500VR, Seiko Instruments, Tokyo). The pore volume was calculated based on the skeletal and apparent densities, which were measured by a liquid-immersion method with ethanol.

Results and Discussion

Preparation and SEM Texture of K_2CO_3-on-Carbon. Potassium carbonate is highly deliquescent and was supported on activated carbon to adapt for fixed-bed operations. The K_2CO_3 load in the preparation was tentatively taken so that 40% of the pore space (1.37 cm^3/g-carbon) was occupied by 50 wt% aqueous K_2CO_3. Thus, the protocol was as follows. To a flask containing an aqueous solution of 4.04 g of K_2CO_3 in 13.3 cm^3 of water was added 10 g of activated carbon; the resultant slurry was dried in a rotary evaporator under suction at 80 °C to give a preparation of K_2CO_3-on-carbon, of which an aliquot was analyzed as 0.394 g (2.85 mmol) K_2CO_3/g-carbon by ICP analysis after burning off the carbon in a porcelain crucible. Although the surface area of 1576 m^2/g for carbon was apparently reduced to 1036 m^2/g for the present K_2CO_3-on-carbon, the calculated area of 1523 m^2/g-carbon, corrected for the impregnated K_2CO_3, was similar to the initial value of 1576 m^2/g-carbon.

Figure 2 illustrates SEM textures of carbon (a) and K_2CO_3-on-carbon (c). The white aggregates in holes scattered over the support are crystalline K_2CO_3, as shown in Fig. 2-b_2 by EPMA for potassium atom. It appears strange in reference to the high surface area of 1576 m^2/g for carbon that K_2CO_3 is supported as such large aggregates detectable by ×250 magnifications (Fig. 2-c). However, the results are rather reasonable, as anticipated. The less hydrophilic nature of carbon may cause droplets of aqueous K_2CO_3 to move toward wide pores[5] during the preparation, especially during the drying stage.

Steaming of K_2CO_3-on-Carbon. Figure 3 compares the breakthrough curves of water at 60 °C with moisture contents of 1.7 and 7.3% H_2O in helium over activated carbon (dotted lines) and K_2CO_3-on-carbon (solid lines), showing a remarkable increase in the water uptake in the presence of deliquescent K_2CO_3.

The capillary condensation behavior was observed on carbon (black circles) in the adsorption isotherm given in Fig. 4, at high humidity above $p/p_0=0.6$ (11.8% H_2O at 60°C), while at a rather low humidity around $p/p_0=0.3$ (5.9% H_2O) on K_2CO_3-on-carbon (white circles).

Drying at 150 °C in helium, potassium carbonate supported on carbon was crystalline $2K_2CO_3{\cdot}3H_2O$, as

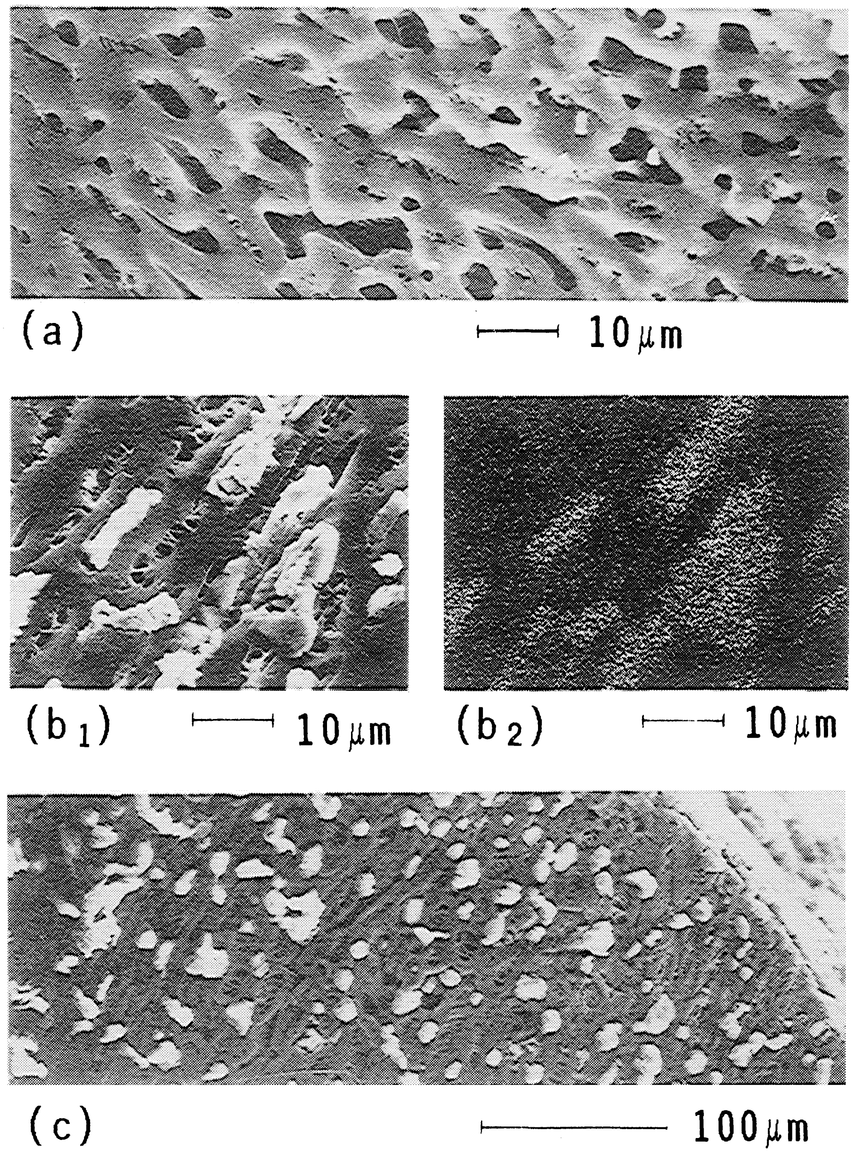

Fig. 2. SEM textures of activated carbon (a) and K_2CO_3-on-carbon (b_1,c), and intraparticle distribution of K of K_2CO_3-on-carbon (b_2) by EPMA.

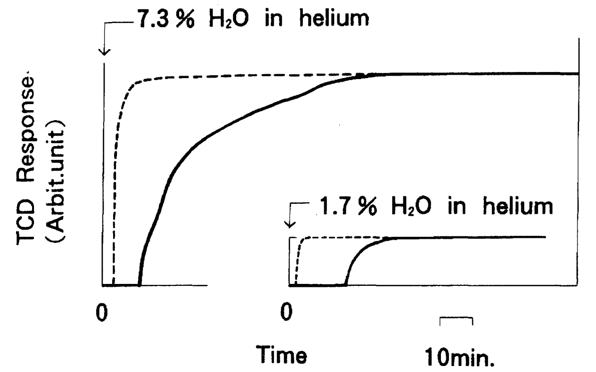

Fig. 3. Breakthrough curves of H_2O at 60 °C for K_2CO_3-on-carbon and activated carbon.

evidenced by the powder XRD in Fig. 5-a. In contact with moisture of 1.7% H_2O in helium at 60 °C, potassium carbonate was still crystalline (Fig. 5-b_1), but amorphous (i.e. aqueous solution) under highly humid condition of 7.3% H_2O (Fig. 5-c_1).

Carbon Dioxide over Steamed K_2CO_3-on-Carbon. Figure 6 illustrates the removal of carbon dioxide by fixed-bed operation over K_2CO_3-on-carbon under a moist condition. After steaming at 60 °C with 7.3% H_2O in helium, 2.3% CO_2 without any change in the moisture concentration was added. The breakthrough curve monitored as the TCD response given in Fig. 6-a agreed well with that for the moisture contents (black circles in Fig. 6-b) analyzed intermittently by GC-MS for the initial 160 min of single-component operation. The shaded area for H_2O corresponds to the amount of H_2O-uptake at 60 °C with 7.3% H_2O. Carbon dioxide was entrapped on the moist K_2CO_3-on-carbon, as shown in Fig. 6-b (white circles), where a strange

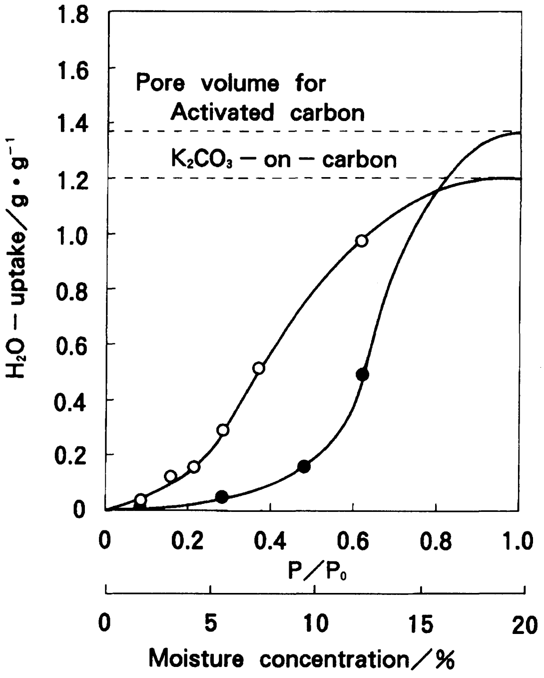

Fig. 4. Adsorption isotherms of H_2O for K_2CO_3-on-carbon (○) and for activated carbon (●) at 60 °C.

lump on the breakthrough curve of carbon dioxide was observed for the TCD response due to a displacement release of H_2O, as detected on the plateau in Fig. 6-b (peak, black circles). Moreover, the TCD-monitor was not available for the multicomponent system, but was still useful as a rough measure to detect the breakthrough of carbon dioxide.

Figure 7 shows the effect of the moisture concentration on the CO_2-uptake under fixed-bed operation over K_2CO_3-on-carbon. Carbon dioxide is entrapped as potassium bicarbonate by the reaction given in Eq. 1, and the amount of CO_2-uptake was very small under dry condition, but abruptly increased in the presence of moisture, as shown in Fig. 7-a and 7-b. The decomposition of bicarbonate was completely reversible to afford carbon dioxide, as verified in Fig. 8, where the amount of CO_2 released vs. CO_2-uptake lies on a line of 1 : 1-correlations.

Powder XRD Evidence for Chemistry of the $\mathbf{CO_2}$-Uptake. The powder XRD given in Fig. 5 provides evidence for the chemistry of the present technology. Although potassium carbonate is highly deliquescent, it was still crystalline $2K_2CO_3{\cdot}3H_2O$ even in contact with moisture of 1.7% H_2O in helium at 60 °C (Fig. 5-b_1). Potassium hydrogencarbonate (black circles in Fig. 5-b_2) was detected in the presence of 2.3% CO_2 with 1.7% H_2O, signifying that carbon dioxide was chemically entrapped, based on the reaction given in Eq. 1, rather than adsorption. The broad XRD pattern under a highly humid condition of 7.3% H_2O (Fig. 5-c_1) shows that potassium carbonate is supported on carbon as an aqueous solution. Potassium hydrogencarbonate

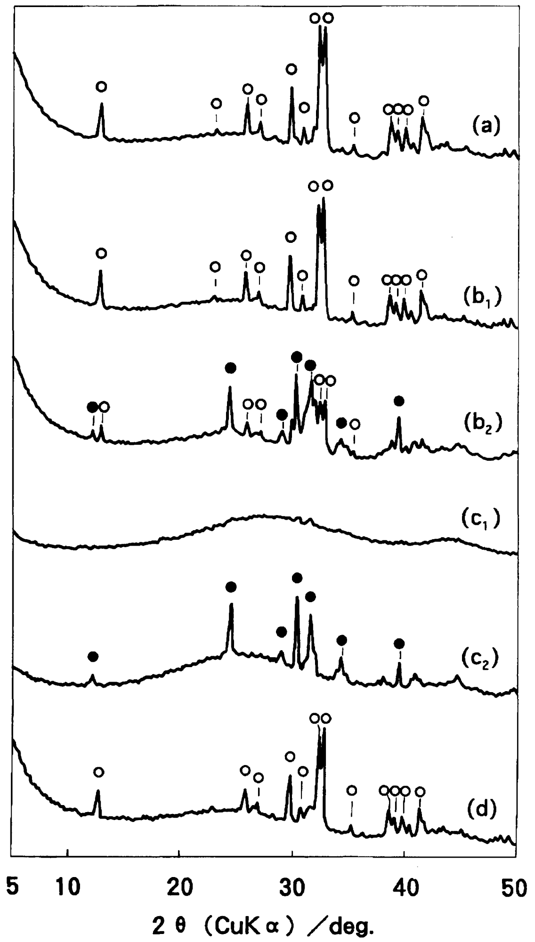

Fig. 5. Powder X-ray diffraction patterns of K_2CO_3-on-carbon. (a) dried at 150 °C in He; (b_1) 1.7% H_2O in He at 60 °C; (b_2) 2.3% CO_2 with 1.7 %H_2O in He at 60 °C; (c_1) 7.3% H_2O in He at 60 °C; (c_2) 2.3% CO_2 with 7.3%H_2O in He at 60 °C; (d) heated up to 150 °C in moist He; ○, $2K_2CO_3{\cdot}3H_2O$; ●, $KHCO_3$.

was again detected for 2.3% CO_2 with 7.3% H_2O (black circles in Fig. 5-c_2). The entrapped carbon dioxide was released by the decomposition of hydrogencarbonate by heating up to 150 °C in moist helium to regenerate crystalline $2K_2CO_3{\cdot}3H_2O$ (Fig. 5-d).

We at first presumed an effective use of the pore space as microtanks containing concentrated aqueous solution of potassium carbonate for cyclic chemical-absorption technology capable of fixed-bed operation. Under the highly humid condition illustrated in Fig. 6, the portrayal was verified as presumed with XRD evidence (Fig. 5-c_1 and c_2) for chemical absorption by supported aqueous K_2CO_3. However, it appears worthwhile noting that the reaction in Eq. 1 could be favorably carried out in a gas–solid flow system, as observed for 2.3% CO_2 with 1.7% H_2O at 60 °C (Fig. 5-b_1 and 5-b_2). Every component of CO_2, H_2O, and K_2CO_3 should be present to forward the reaction, but it is unnecessary for K_2CO_3 to be in the aqueous phase. Figure 7-a suggests that the microtank condition (7.3% H_2O) leads to a sigmoid

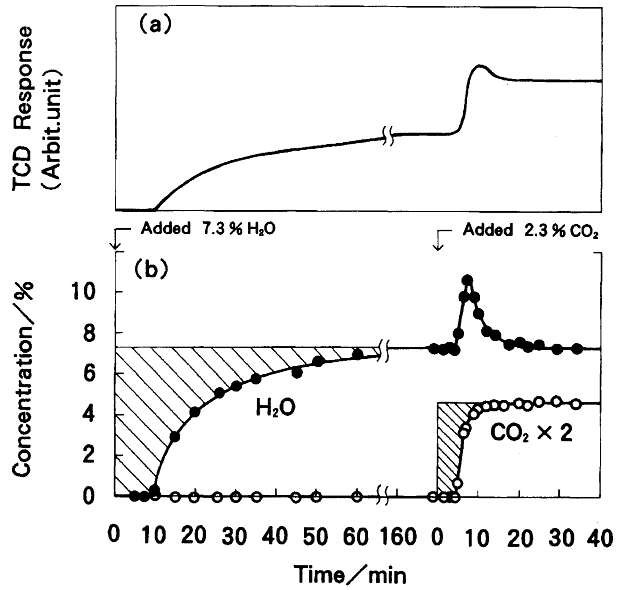

Fig. 6. Illustrative breakthrough curves of CO_2 and H_2O by fixed-bed operation over K_2CO_3-on-carbon for 2.3% CO_2 with 7.3% H_2O at 60 °C. ○, CO_2; ●, H_2O.

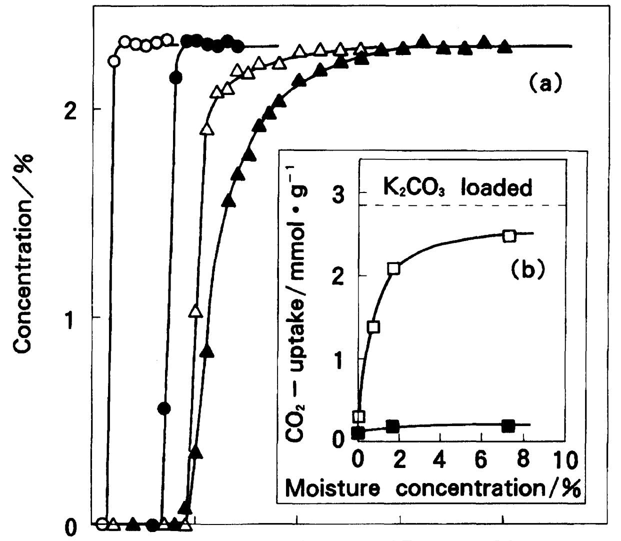

Fig. 7. Effect of moisture concentration on the CO_2-uptake at 60 °C. (a) Breakthrough curves of 2.3% CO_2 over K_2CO_3-on-carbon; ○, in the absence of H_2O; ●, 0.75% H_2O; △, 1.7% H_2O; ▲, 7.3% H_2O; (b) CO_2-uptake under moist conditions for K_2CO_3-on-carbon; □, K_2CO_3-on-carbon; ■, activated carbon.

breakthrough curve slowly approaching toward saturation without a very large increase in the CO_2-uptake, while a rather sharp step in breakthrough was observed for crystalline condition (1.7% H_2O).

Flue Gas Conditions in Practice. Figure 9 shows the effects of the temperature and total pressure on the CO_2 uptake in fixed-bed operation over K_2CO_3-on-carbon for a mixture of 2.3% CO_2 with 1.7% H_2O in helium, of which the composition was taken on purpose to adjust the partial pressure of moist CO_2, as in the actual flue gas. Thus, increasing the total pressure up to 6.1×10^5 Pa (6 atm), the partial pressure would be 1.4×10^4 Pa (0.138 atm) CO_2 and 1.0×10^4 Pa (0.102 atm) H_2O, just corresponding to the composition of 14% CO_2 with 10% H_2O under atmospheric pressure for the flue gas, in practice.

The amounts of CO_2-uptake decreased with increasing temperature due to the decomposition of potassium hydrogencarbonate, and increased with increasing total

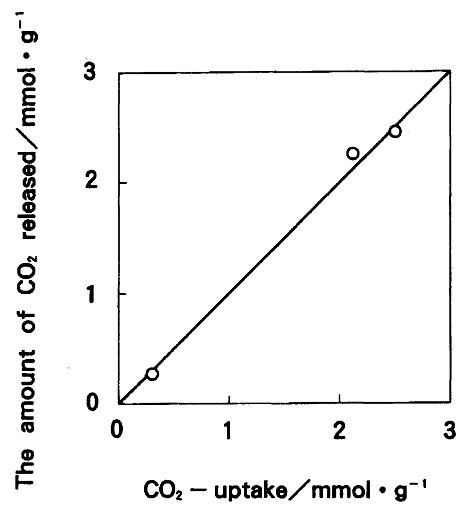

Fig. 8. Reversible desorption of carbon dioxide entrapped as hydrogencarbonate by K_2CO_3-on-carbon on steaming at 150 °C.

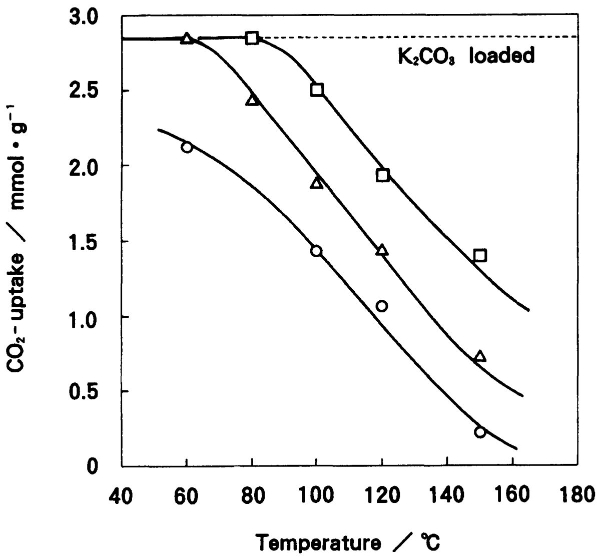

Fig. 9. Effects of temperature and pressure on the CO_2-uptake over K_2CO_3-on-carbon for crystalline condition. absorption, 60 °C for 2.3% CO_2 with 1.7% H_2O; flashing in moist helium at 150 °C; ○, atmospheric pressure; △, 3.0×10^5 Pa (3 atm); □, 6.1×10^5 Pa (6 atm).

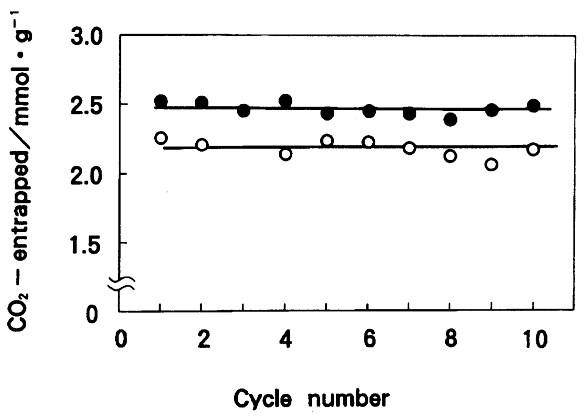

Fig. 10. Illustrative cyclic fixed-bed operations for recovery of carbon dioxide over K_2CO_3-on-carbon. ○, absorbed at 60 °C for 2.3% CO_2 with 1.7% H_2O and flashed in moist helium at 150 °C under atmospheric pressure; ●, absorbed at 100 °C for 13.8% CO_2 with 10% H_2O and flashed in moist helium at 150 °C under atmospheric pressure.

pressure to shift the reaction given in Eq. 1 in favor of trapping carbon dioxide, as shown in Fig. 9. Under atmospheric pressure, carbon dioxide was entrapped on K_2CO_3-on-carbon up to 2.2 mmol/g (79% capacity based on K_2CO_3 loaded) at 60 °C for 2.3% CO_2 with 1.7% H_2O.

At a total pressure of 6 atm, the supported carbonate was completely converted to hydrogencarbonate below 80 °C and a CO_2 uptake of 2.5 mmol/g (88% capacity based on K_2CO_3 loaded) was obtained at a flue-gas exhaust temperature of 100 °C, suggesting promising applications of the present technology to practical flue gases of 14% CO_2 with 10% H_2O at 100 °C under atmospheric condition.

Illustrative Cyclic Fixed-Bed Operations. A cyclic fixed-bed operation for the recovery of carbon dioxide over K_2CO_3-on-carbon under a moist condition of 2.3% CO_2 with 1.7% H_2O at 60 °C up to 10 cycles is illustrated in Fig. 10. The white circles indicate where the amount of carbon dioxide released in flashing with moist helium at 150 °C took place in each cycle. The reproducible CO_2 uptake of an average of 2.2 $\mathrm{mmol\,g^{-1}}$ agreed well with that given in Fig. 7(b) for the same condition. A successful cyclic operation at a condition of 13.8% CO_2 with 10% H_2O in He at 100 °C under atmospheric pressure, close to the actual flue gas, is again demonstrated in Fig. 10; the black circles show an average CO_2 uptake of 2.5 $\mathrm{mmol\,g^{-1}}$, in good agreement with that obtained for 2.3% CO_2 with 1.7% H_2O at 100 °C under 6 atm pressure (0.138 atm CO_2, 0.102 atm H_2O), as given in Fig. 9.

Flashing at 150 °C in moist helium to release carbon dioxide was taken in the present work due to experimental convenience. A temperature swing is generally unfavorable for fixed-bed operation, especially on a large scale. However, low-pressure steam (4.9×10^5 Pa ($5\ \mathrm{kg\,cm^{-2}}$) at 150 °C—1.5×10^6 Pa ($15\ \mathrm{kg\,cm^{-2}}$) at 200 °C) which could be condensed by cooling to afford carbon dioxide in high purity, is easily available at thermal power plants, and steaming without inert gas for the recovery of entrapped carbon dioxide will be effective in practical applications.

Conclusion

A modified chemical-absorption method capable of cyclic fixed-bed operations for the recovery of carbon dioxide from flue gases has been proposed which employs K_2CO_3-on-carbon. Deliquescent potassium carbonate was favorably supported on activated carbon and bound carbon dioxide as hydrogencarbonate under moist conditions. The hydrogencarbonate was reversibly decomposed to afford carbon dioxide by steaming at 150 °C.

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