Formulation of CO_2 Sorption/Release Behaviors Using Alkali Carbonate-on-Activated Carbon

Tetsu Yanagihara and Naoya Shigemoto

Department of Chemical and Biological Technologies, Shikoku Research Institute, Inc., 2109 Yashima-Nishimachi, Takamatsu-shi, Kagawa 761-0192, Japan

Keywords: Alkali Carbonate, Alkali Hydrogencarbonate, CO_2 Recovery, Activated Carbon, Gas Solid Equilibrium

Alkali carbonates supported on activated carbon (AC) for CO_2 sorption from moist flue gases by a temperature-swing operation have been proposed. The temperature dependence of CO_2 uptake by the sorbent was investigated to understand the CO_2 sorption/release behavior. The CO_2 sorption behaviors of alkali carbonates-on-AC at various temperatures were well explained based on CO_2 gas-sorbent equilibria. However, the reverse reaction of thermal decomposition of alkali hydrogencarbonates, which were the reaction products after CO_2 sorption, did not explain the sorption behaviors. The CO_2 gas-sorbent equilibrium constants were used to determine the effect of CO_2 partial pressure in the feed gas on the CO_2 sorption capacities. The results showed that the pressure-swing operation was appropriate for sorption using alkali carbonates-on-AC. At low CO_2 partial pressures in the feed gas, the CO_2 sorption capacities achieved using alkali carbonates-on-AC were higher than that achieved using K_2CO_3 solution (i.e., the Benfield process).

Introduction

CO_2 is a major cause of global warming via the greenhouse effect; therefore, CO_2 removal from combustion flue gases helps mitigate global warming. CO_2 removal from moist flue gases using K_2CO_3 supported on porous materials such as activated carbon (AC) has been proposed (Hayashi *et al.*, 1995, 1998; Hirano *et al.*, 1995). K_2CO_3 solutions have also been employed as a CO_2 absorbent (Benson and Field, 1959; Bartoo, 1984). The use of anhydrous particles of Na_2CO_3 (Liang *et al.*, 2004) and K_2CO_3 (Park *et al.*, 2006; Duan *et al.*, 2012) as solid sorbents for CO_2 recovery from flue gases has also been examined, but these materials are highly deliquescent and dissolve in condensed moisture from the flue gases. Then, the use of alkali carbonate particles dispersed on a support such as Al_2O_3 (Liang *et al.*, 2004) has also been proposed. AC with the pores filled with hydrated K_2CO_3 particles has been used for particle dispersion. The CO_2 in the flue gas reacts with the hydration water in $K_2CO_3 \cdot 1.5H_2O$ particles, but not gaseous moisture, to form $KHCO_3$ particles; therefore, the moisture in the flue gas does not affect the CO_2 uptake performance (Hayashi *et al.*, 1995, 1998; Hirano *et al.*, 1995; Duan *et al.*, 2012).

$$K_2CO_3 \cdot 1.5H_2O + CO_2 \rightarrow 2KHCO_3 + 0.5H_2O \quad (1)$$

When the formed $KHCO_3$ particles are heated with hot steam, the entrapped CO_2 is discharged and the $K_2CO_3 \cdot 1.5H_2O$ particles are simultaneously regenerated in the AC pores for the next CO_2 recovery process. CO_2 sorption/release processes have not been sufficiently investigated, although CO_2 release reaction by thermal decomposition of $KHCO_3$ has been proposed (Hayashi *et al.*, 1998). The substantial CO_2 uptake in this process corresponds to the difference between the CO_2 uptakes at low (CO_2 sorption) and high (CO_2 release) temperatures. Formulation of the temperature dependence of CO_2 sorption/release behaviors is, therefore, important for understanding the CO_2 recovery performances of K_2CO_3-on-AC process.

AC impregnated with other alkali carbonates (M_2CO_3) such as Na_2CO_3, Rb_2CO_3, and Cs_2CO_3 instead of K_2CO_3 can be used as sorbents for CO_2 recovery from flue gases at temperature in the range 313–433 K (Shigemoto *et al.*, 2005). Selection of the optimum temperatures for the CO_2 sorption/release process enables the energy consumption for CO_2 recovery by a specific alkali carbonate-on-AC to be minimized (Shigemoto *et al.*, 2004, 2005, 2006).

In the present study, the CO_2 recovery behaviors, especially the temperature dependences of the CO_2 sorption capacities of various alkali carbonates-on-AC, were investigated by proposing the reverse reaction of alkali hydrogencarbonates thermal decomposition. Attempts were also made to formulate the temperature dependence of CO_2 sorption based on the CO_2 gas-sorbent equilibrium. The formulated temperature dependences were used to compare the CO_2 sorption performances of K_2CO_3-on-AC and K_2CO_3 solution (Benson and Field, 1959; Bartoo, 1984) to demonstrate the advantages of the former process. The effect of CO_2 partial pressure on the CO_2 capture performance of K_2CO_3-on-AC was also examined to evaluate the adaptability of the pressure-swing operation for CO_2 recovery.

Received on February 3, 2016; accepted on May 13, 2016
DOI: 10.1252/jcej.16we031
Correspondence concerning this article should be addressed to N. Shigemoto (E-mail address: nshigemoto@ssken.co.jp).

Copyright © 2016 The Society of Chemical Engineers, Japan

1. Experimental

1.1 Preparation of alkali carbonates-on-AC

Various alkali carbonates supported on extruded AC (WH2X, 4–8 mesh, Takeda Chemical Industries Ltd.) were prepared using a previously reported method (Shigemoto *et al.*, 2005). The AC pores were filled with a saturated solution of an alkali carbonate, each of which has a different solubility in water, and then, the water in the solution was evaporated, leaving a hydrated alkali carbonate in the pores. The amount of each alkali carbonate impregnated in the AC was as follows: Na_2CO_3 17.0 wt%, K_2CO_3 26.4 wt%, Rb_2CO_3 44.0 wt%, and Cs_2CO_3 42.5 wt%. The pore size distributions were determined using a mercury porosimeter 2000 (Amco Inc.).

1.2 CO_2 sorption and its estimation

The sorbents were packed in a bench-scale column (ϕ54.5 mm×800 mm length; volume 1.87 L; Shigemoto *et al.*, 2006). Moisture was added to a dry 13% CO_2/N_2 gas with a constant flow rate (4.8 L·min^{-1}), controlled by a mass-flow meter, and the mixture (11.8% CO_2+10% H_2O+N_2 balance) was supplied to the sorbent column. The gas at the column outlet was cooled using a heat-exchanger to condense and separate the moisture, and the CO_2 concentration after CO_2 sorption was measured using an infrared CO_2 analyzer (PG-200, Horiba Seisakusho Co.). No CO_2 was initially detected at the outlet, but after a period, CO_2 broke through the column, and the outlet CO_2 concentration eventually reached the inlet CO_2 concentration; this shows that the CO_2 sorption reaction reached equilibrium (Shigemoto *et al.*, 2004, 2005, 2006). The amount of sorbed CO_2 was determined based on the area between the constant inlet CO_2 concentration line and the CO_2 breakthrough curve at the outlet.

The equilibrium conversion rate of M_2CO_3 to $2MHCO_3$, which corresponds to the equilibrium CO_2 sorption rate, was tentatively defined as the molar ratio of sorbed CO_2 to that of impregnated alkali carbonate in the sorbent, assuming stoichiometric conversion, i.e., $M_2CO_3+CO_2+H_2O=2MHCO_3$. The CO_2 conversion was estimated using a CO_2 gas-sorbent equilibrium relationship, and compared with the observed CO_2 conversion. The reproducibility of the CO_2 conversion estimation was verified by error analysis based on the calculated average absolute deviation (AAD [%]) between the observed and estimated conversions for each alkali carbonate-on-AC at various temperatures.

$$\mathrm{AAD} = (1/n)\sum(|x_{o,i}-x_{e,i}|\times 100\%/x_{e,i}) \tag{2}$$

Here, $x_{o,i}$ and $x_{e,i}$ are the observed and estimated i-th CO_2 conversions, respectively, and n is the total number of data points. The CO_2 recovery efficiency was tentatively defined as the number of moles of recovered CO_2 per mole of M_2CO_3 in the sorbent.

2. Results and Discussion

2.1 Alkali carbonate impregnation state and CO_2 sorption/release process

Figure 1 shows the pore size distributions for AC, K_2CO_3-on-AC and Rb_2CO_3-on-AC; macro-pores (>25 nm in radius) and *meso*-pores (1–25 nm in radius) were detected in all these samples. In the macro-pore region, two peaks, with central radiuses of approximately 0.7 and 5 μm, were observed; these correspond to the spaces between the primary AC particles before extrusion. Both the macro-pore peaks in the AC were higher than those in the impregnated ACs, indicating that most of the macro-pores in the AC were packed with alkali carbonate. The *meso*-pores, the volume of which increased greatly with decreasing radius in all the samples, were not extensively blocked in the impregnated ACs. Because alkali carbonate aqueous solutions are hydrophilic and the AC surface is hydrophobic, the alkali carbonate solution moves toward the wider pore spaces, as a result of surface tension (Hayashi *et al.*, 1998). Evaporation of the solvent water results in alkali carbonate hydrate crystallization in the large macropores (1–10 μm; Hirano *et al.*, 1995; Hayashi *et al.*, 1998) in the AC, forming microparticles. The smaller pores are not blocked and act as gas pathways; this facilitates CO_2 diffusion through the inner microparticles of the alkali carbonatehydrates.

The hydration water of the alkali carbonate microparticles, which are held in the AC porous cavities, directly reacts with gaseous CO_2 which promotes the formation of the hydrogencarbonates. When the $MHCO_3$ microparticles are heated, CO_2 is directly released into the vacant pore spaces, promoting CO_2 discharge to outside the sorbent particles.

2.2 Formulation of CO_2 sorption using reverse reaction of alkali hydrogencarbonate thermal decomposition

Alkali hydrogencarbonates, which are the products of CO_2 sorption by alkali carbonates, decomposes at high temperatures to afford CO_2, H_2O and the alkali carbonate:

$$2MHCO_3 \rightarrow H_2O + CO_2 + M_2CO_3 \tag{3}$$

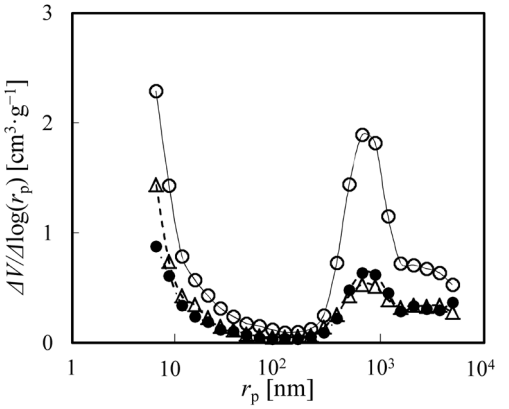


Fig. 1 Pore size distributions for AC (○), K_2CO_3-on-AC (△) and Rb_2CO_3-on-AC (●)

The thermal decomposition pressure P [kPa] is expressed as a function of the temperature T [K] by the following equation (Mellor, 1937).

$$\ln P = A - B/T \tag{4}$$

Here, (A, B) are (25.2, 7.69×10^3) for $NaHCO_3$, (22.9, 7.87×10^3) for $KHCO_3$, (27.3, 9.90×10^3) for $RbHCO_3$, and (37.0, 1.45×10^4) for $CsHCO_3$, respectively (Mellor, 1937). The partial pressure of water (P_{H_2O}) is the same as that of CO_2 (P_{CO_2}); therefore, $P_{H_2O}=P_{CO_2}=P/2$ because CO_2 and H_2O are formed in equimolar amounts. The equilibrium constant for the decomposition reaction, K_1 is therefore as follows.

$$K_1=[M_2CO_3][CO_2][H_2O]/[MHCO_3]^2 = P_{H_2O}P_{CO_2}=(P/2)^2 \tag{5}$$

Here, the square brackets indicate molar concentration; the terms for the solid components, i.e. $[M_2CO_3]$ and $[MHCO_3]$, can be neglected. The temperature dependence of K_1 can be obtained by substituting Eq. (4) into Eq. (5).

$$K_1=(1/4)e^{(2A-2B/T)} \tag{6}$$

The CO_2 sorption reactions for alkali carbonates supported on AC are expressed as follows (Shigemoto *et al.*, 2005).

$$Na_2CO_3+H_2O+CO_2\rightarrow 2NaHCO_3 \tag{7}$$

$$M_2CO_3\cdot xH_2O+CO_2\rightarrow 2MHCO_3+(x-1)H_2O \tag{8}$$

Here, (M, x)=(K, 1.5), (Rb, 1), and (Cs, 2). Anhydrous Na_2CO_3 reacts with CO_2 and H_2O, but the hydrates of the other carbonates, i.e. M=K, Rb and Cs, combine with CO_2. If the reverse reactions of the thermal decomposition (Eq. (3)), which are not exactly the same as the CO_2 sorption reactions (Eqs. (7) and (8)), are tentatively adopted as the CO_2 sorption reactions, the equilibrium constant of the reverse reaction, K_{-1} ($=1/K_1$) is expressed as follows.

$$K_{-1}=[MHCO_3]^2/[M_2CO_3][CO_2][H_2O] = 1/(P_{H_2O}P_{CO_2}) \tag{9}$$

$$K_{-1}=4e^{(-2A+2B/T)} \tag{10}$$

Figure 2 shows the temperature dependence of K_{-1}, based on ln K_{-1} vs. $1/T$. The ln K_{-1} value for each alkali carbonate increased in proportion to $1/T$ and the K_{-1} values increased in the order of $Na_2CO_3<K_2CO_3<Rb_2CO_3<Cs_2CO_3$, showing that CO_2 sorption by alkali carbonates was favored at lower temperatures (larger $1/T$). We postulate that 1 mol of the initial feed gas simulating the flue gas contains CO_2 ($N^0_{CO_2}$ [mol]), H_2O ($N^0_{H_2O}$ [mol]), and inert gas ($1-N^0_{CO_2}-N^0_{H_2O}$ [mol]), where $N^0_{CO_2}+N^0_{H_2O}<1$. Once CO_2 sorption reaches equilibrium with the CO_2 conversion x (molar ratio), the molar amount of each component (N_{CO_2} [mol] and N_{H_2O} [mol]) in the gas and the total gas amount (N_{total} [mol]) become as follows.

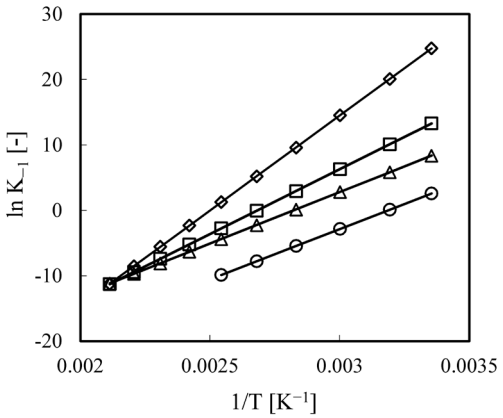


Fig. 2 Temperature dependence of equilibrium constant K_{-1}; $NaHCO_3$ (○), $KHCO_3$ (△), $RbHCO_3$ (□), $CsHCO_3$ (◇)

$$N_{CO_2}=N^0_{CO_2}(1-x) \tag{11}$$

$$N_{H_2O}=N^0_{H_2O}-N^0_{CO_2}x \tag{12}$$

$$N_{total}=1-2N^0_{CO_2}x \tag{13}$$

The partial pressures of each component, i.e. P_{H_2O} and P_{CO_2}, after the reaction at a total pressure π [kPa], are as follows.

$$P_{CO_2}=\pi(N_{CO_2}/N_{total}) = \pi N^0_{CO_2}(1-x)/(1-2N^0_{CO_2}x) \tag{14}$$

$$P_{H_2O}=\pi(N_{H_2O}/N_{total}) = \pi(N^0_{H_2O}-N^0_{CO_2}x)/(1-2N^0_{CO_2}x) \tag{15}$$

Substituting Eqs. (14) and (15) into Eq. (9) gives Eq. (16).

$$Cx^2+Dx+E=0 \tag{16}$$

Here, $C=K_{-1}\pi^2-4N^0_{CO_2}$, $D=4N^0_{CO_2}-K_{-1}\pi^2$ $(N^0_{CO_2}+N^0_{H_2O})$, and $E=K_{-1}\pi^2N^0_{H_2O}-1$. Solving Eq. (16) gives the CO_2 conversion x as Eq. (17).

$$x=\frac{-D+\sqrt{(D)^2-4CE}}{2C} \tag{17}$$

The actual CO_2 conversion was estimated by creating the same reaction conditions as those in previous experiments using various alkali carbonates supported on AC (Shigemoto *et al.*, 2004, 2005, 2006); the conditions replicated were those in Eqs. (10) and (16), i.e. T, π, $N^0_{CO_2}$, and $N^0_{H_2O}$. Although the experimental conditions were $N^0_{CO_2}=0.118$, $N^0_{H_2O}=0.10$, $\pi=101.3$ kPa, and temperatures of 333 to 473 K, $N^0_{CO_2}$ was set at the same value as $N^0_{H_2O}$, i.e. 0.10, because the H_2O concentration in the feed gas was lower than the CO_2 concentration, and H_2O became the limiting component for CO_2 sorption.

Figure 3 shows the estimated CO_2 conversions against the

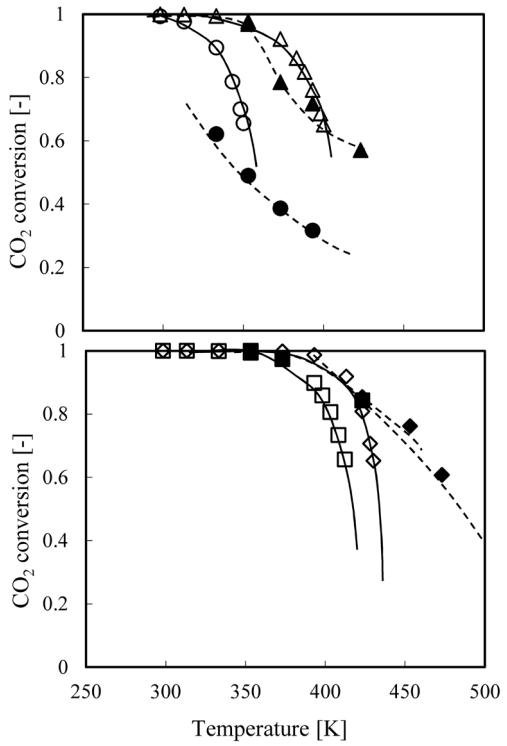


Fig. 3 Temperature dependence of conversion from M_2CO_3 to $2MHCO_3$ in bench experiment (closed symbols) and calculated value (open symbols); Na_2CO_3-on-AC (○, ●), K_2CO_3-on-AC (△, ▲), Rb_2CO_3-on-AC (□), Cs_2CO_3-on-AC (◇, ◆)

reaction temperatures; the experimental CO_2 conversions are also indicated. For K_2CO_3-on-AC, the calculated and experimental CO_2 conversions were in good agreement; this is in accordance with previously reported results (Hayashi *et al.*, 1998). However, for the other alkali carbonates supported on AC, the difference between the experimental and estimated values increased with increasing reaction temperature, although there was good agreement at low temperatures. This shows that the CO_2 sorption reactions cannot essentially be expressed by the reverse reactions of thermal decomposition of alkali hydrogencarbonates, especially at high temperatures, at which the CO_2 conversions are low.

2.3 Formulation of CO_2 sorption based on CO_2 gas-sorbent equilibrium

In the Benfield process, which uses a hot K_2CO_3 solution, the equilibrium reaction can be expressed by the equilibrium constant K_2, which is related to the liquid phase concentrations of K_2CO_3 and $KHCO_3$ [mol·L^{-1}], and the CO_2 partial pressure, $P^0_{CO_2}$ [kPa] in the gas phase (Kohl and Riesenfeld, 1985a).

$$K_2 = \frac{[KHCO_3]^2}{[K_2CO_3]P^0_{CO_2}} \tag{18}$$

The K_2 values for a 30% K_2CO_3 solution are 0.441, 0.228, 0.129, and 0.0836 mol·L^{-1}·kPa^{-1} at 343, 363, 383, and 403 K, respectively (Kohl and Riesenfeld, 1985b).

The $\ln K_2$ against $1/T$ plots in **Figure 4** (×) show a linear

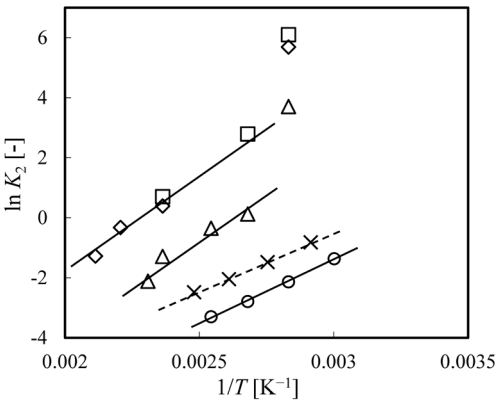


Fig. 4 Equilibrium constant for $KHCO_3$ formation from 30% K_2CO_3 solution (×) and alkali carbonate on AC in bench scale; Na_2CO_3-on-AC (○), K_2CO_3-on-AC (△), Rb_2CO_3-on-AC (□), Cs_2CO_3-on-AC (◇). CO_2 partial pressure = 13 kPa

correlation.

$$\ln(K_2) = -12.07 + 3853/T \tag{19}$$

Because the hydrated alkali carbonate particles are widely dispersed in the AC particles, the M_2CO_3-on-AC sorbents are considered to be pseudo-absorption solutions of alkali carbonates, similar to the 30% K_2CO_3 solution for the Benfield process. It is assumed that the CO_2 in the gas phase and $M_2CO_3/MHCO_3$ in the solid sorbent are in equilibrium. K_2 can be expressed as Eq. (20).

$$K_2 = \frac{4Mx^2}{(1-x)P_{CO_2}} \tag{20}$$

Here, M [mol·L^{-1}] is the alkali carbonate concentration per unit apparent volume of the sorbent, x and $1-x$ are the conversion rate of carbonate to hydrogencarbonate and the residual amount of carbonate, respectively.

This equation was used to plot the equilibrium constant K_2 for the alkali carbonates-on-AC against $1/T$, as shown in Figure 4. Previously reported bench-scale conversion ratios were used (Hayashi *et al.*, 1995, 1998; Hirano *et al.*, 1995). The $\ln K_2$ values for all alkali carbonates-on-AC increased in proportion to $1/T$ at low $1/T$ values (high temperatures); the slopes of the correlation lines were the same as each other and similar to that for a 30% K_2CO_3 solution. The experimental $\ln K_2$ data for Rb_2CO_3-on-AC and Cs_2CO_3-on-AC were arranged around one correlation line. However, at higher $1/T$ values (low temperatures) the $\ln K_2$ values for K_2CO_3-on-AC and Cs_2CO_3-on-AC abruptly increased because $x^2/(1-x)$ becomes too large as x approaches 1. The correlations in Figure 4, except those at high $1/T$ values, show that the CO_2 gas-sorbent equilibrium constants K_2 for pseudo-alkali carbonate solutions can be expressed as Eq. (21).

$$\ln K_2 = F + G/T \tag{21}$$

Here, (F, G) are (−14.12, 4240) for Na_2CO_3-on-AC,

(−11.89, 4500) for K_2CO_3-on-AC, (−14.87, 6591) for Rb_2CO_3-on-AC, and (−14.79, 6459) for Cs_2CO_3-on-AC. Rearranging Eq. (20) gives the following quadratic equation:

$$4Mx^2 + K_2P_{CO_2}x - K_2P_{CO_2} = 0 \tag{22}$$

The carbonate conversion x is given by Eq. (23).

$$x = \frac{-K_2P_{CO_2} + \sqrt{(K_2P_{CO_2})^2 + 16MK_2P_{CO_2}}}{8M} \tag{23}$$

If M and P_{CO_2} are constant, x is solely a function of T because $K_2 = e^{(F+G/T)}$ (Eq. (21)).

Figure 5 shows the reaction temperature dependence of M_2CO_3 conversion to $MHCO_3$, estimated using Eq. (23) (open symbols) and experimentally (closed symbols; Shigemoto *et al.*, 2005). The estimated conversions for the 30% K_2CO_3 solution are also indicated. **Table 1** shows the ADDs between the observed and estimated conversions for each sorbent at various temperatures: the ADDs were

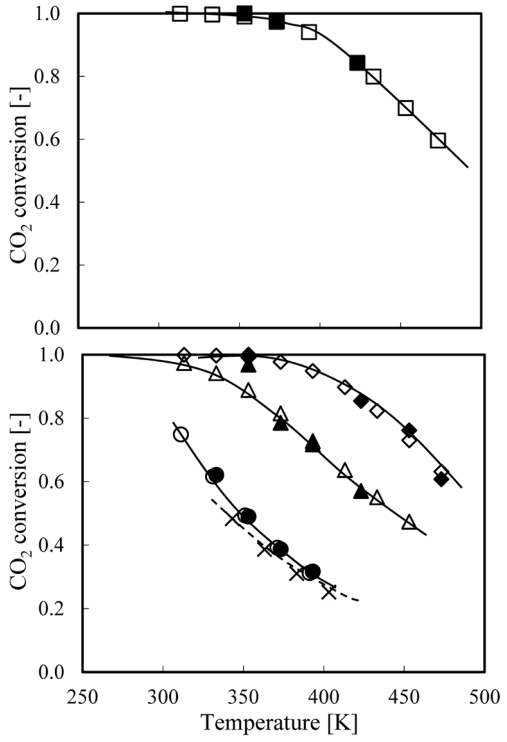


Fig. 5 $MHCO_3$ conversion from M_2CO_3 estimated (open symbols) and measured (closed symbols); Na_2CO_3-on-AC (○, ●), K_2CO_3-on-AC (△, ▲), Rb_2CO_3-on-AC (□, ■), Cs_2CO_3-on-AC (◇, ◆), 30%K_2CO_3 solution (×)

Table 1 Average of absolute deviation (AAD) between the observed and estimated CO_2 conversion

Salt	*n* (Temperature [K])	AAD [%]
Na_2CO_3	4 (313, 351, 371, 391)	1.08
K_2CO_3	4 (353, 373, 393, 423)	4.44
Rb_2CO_3	3 (353, 373, 423)	0.38
Cs_2CO_3	4 (353, 423, 453, 473)	2.50

in the range 0.4–4.4%, indicating that the CO_2 conversion estimates were good. The estimated conversions decreased with increasing temperature: a concave curve and convex curves in the upper direction successfully reproduced the experimental data for Na_2CO_3-on-AC and the other M_2CO_3-on-AC, respectively. The estimated curves shifted in the higher temperature direction in the order of Na_2CO_3-$<K_2CO_3$-$<Rb_2CO_3$-$\sim Cs_2CO_3$-on-AC. The temperature dependences of the conversions for Rb_2CO_3-on-AC and Cs_2CO_3-on-AC were almost the same. The temperature dependence of $KHCO_3$ formation for 30% K_2CO_3 solution was more similar to that for Na_2CO_3-on-AC rather than that for K_2CO_3-on-AC.

The CO_2 recovery behavior is better explained using Eq. (23), without a water term, than by Eq. (17), which includes the water partial pressure. This strongly suggests that CO_2 gas reacts with the hydration water of M_2CO_3-on-AC, but does not directly combine with the moisture in the gas phase. In the CO_2 release step, a large volume of steam was supplied to raise the temperature of the CO_2-entrapped sorbent. This high partial pressure of steam relatively reduces the CO_2 partial pressure and promotes CO_2 release, but does not directly affect the CO_2 conversion because the water partial pressure term is not included in Eq. (23).

CO_2 recovery efficiencies in the range 0.24–0.27 [mol-CO_2/mol-K_2CO_3] have been reported for CO_2 recoveries from gases with higher CO_2 partial pressure (0.14–0.28 MPa) using 30% K_2CO_3 solution (Benson and Field, 1960). For 30% K_2CO_3 solution, CO_2 sorption/release can be restricted by CO_2 diffusion through the gas–liquid interface and HCO_3^-/CO_3^{2-} ions transfer between the interface and bulk solution. In contrast, K_2CO_3 (26.4%)-on-AC provided a CO_2 recovery efficiency of 0.49 [mol-CO_2/mol-K_2CO_3], supplying a gas with a lower CO_2 partial pressure (0.015 MPa) (Shigemoto *et al.*, 2005), indicating a clearly higher CO_2 recovery efficiency than that achieved with the 30% K_2CO_3 solution. The K_2CO_3 microparticles directly sorb CO_2 gas, and then the formed $KHCO_3$ microparticles easily release CO_2 into the gas phase, though HCO_3^-/CO_3^{2-} ions diffuse into the inner microparticles.

2.4 Effect of CO_2 partial pressure on CO_2 sorption

Equation (23) can be used to determine the effect of CO_2 partial pressure in the feed gas on the CO_2 sorption rate for K_2CO_3-on-AC, as shown in **Figure 6**; the reaction temperature was varied, and the CO_2 partial pressure was in the range 0.5–20 kPa. In the figure, the effect of the CO_2 partial pressure for the 30% K_2CO_3 solution below the boiling point of water (373 K; otherwise water evaporates) is also shown as a reference. At a constant temperature, K_2CO_3 conversion to $KHCO_3$ decreased with decreasing CO_2 partial pressure in the feed gas; at a CO_2 partial less than 5 kPa, the conversion abruptly declined. The decrease in CO_2 conversion with respect to the CO_2 partial pressure became greater at high temperatures. In ordinary combustion flue gases, the CO_2 concentration is in the range of 10–15%, giving a CO_2 partial pressure of 10–15 kPa at a total pressure of 100 kPa.

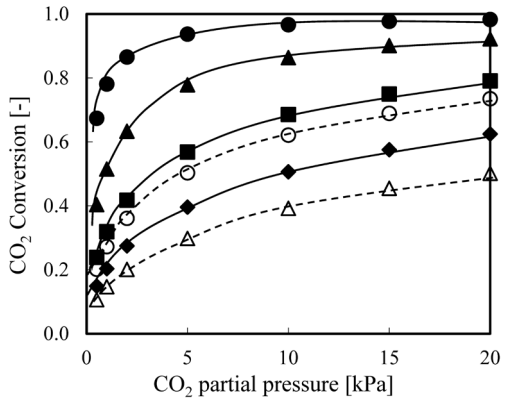


Fig. 6 Effect of CO_2 partial pressure and temperature rise on K_2CO_3 conversion for K_2CO_3-on-AC (closed symbols) and 30% K_2CO_3 solution (open symbols); temperature (K), 313 (●, ○), 353 (▲, △), 393 (■), 433 (◆)

In this CO_2 partial pressure range, the K_2CO_3 conversion was higher at low temperatures, i.e. 313 (●)–353 (▲) K, and the CO_2 partial pressure slightly affected the conversion, as shown in Figure 6. In contrast, at a higher temperature, i.e. 433 K (◆), where a lower CO_2 conversion corresponds to higher CO_2 release from $KHCO_3$, a lower CO_2 partial pressure in the released gas promotes CO_2 release and substantially increases the CO_2 recovery efficiency.

The effect of the CO_2 partial pressure on CO_2 sorption conversion for the 30% K_2CO_3 solution (○ (313 K) and △ (353 K) in Figure 6) indicates a similar trend to that for K_2CO_3-on-AC, although the absolute CO_2 conversion at the same temperature was lower than that for K_2CO_3-on-AC. This lower CO_2 conversion with the 30% K_2CO_3 solution indicates a smaller CO_2 uptake capacity. If 13% CO_2 gas at 0.1 MPa is compressed to 1.0 MPa (10 fold), the CO_2 partial pressure is 130 kPa and gives a high conversion of 0.846 for 30% K_2CO_3 solution. This higher conversion shows that K_2CO_3 absorption methods, such as the Benfield process, are suitable for CO_2 recovery from flue gases with high CO_2 partial pressures.

Conclusion

The temperature dependences of CO_2 sorption by alkali carbonates-on-AC were unfavorably estimated using the reverse reaction of thermal decomposition of alkali hydrogencarbonates. Use of the CO_2 gas-sorbent equilibrium relationship gave good estimates of these temperature dependences, which agreed well with the experimental data. In CO_2 sorption at low temperatures, the CO_2 conversion was slightly affected by a higher CO_2 concentration in the feed gas. At higher temperatures, a lower CO_2 partial pressure promoted CO_2 release, showing that pressure-swing operation can be used with alkali carbonate-on-AC sorbents. The microparticles of alkali carbonates in the AC pores facilitated CO_2 sorption/release, providing higher CO_2 recovery efficiencies than that achieved using 30% K_2CO_3 absorption.

Literature Cited

Bartoo, R. K.; "Removing Acid Gas by the Benfield Process," *Chem. Eng. Prog.*, **80**, 35–39 (1984)

Benson, H. E. and J. H. Field; "Method of Separating CO_2 and H_2S from Gas Mixtures," U.S. Patent No. 2,886,405 (1959)

Benson, H. E. and J. H. Field; "New Data for Hot Carbonate Process," *Petrol. Refiner*, **39**, 127–132 (1960)

Duan, Y., D. R. Luebke, H. W. Pennline, B. Li, M. J. Janik and J. W. Halley; "Ab Initio Thermodynamic Study of the CO_2 Capture Properties of Potassium Carbonate Sesquihydrate, $K_2CO_3 \cdot 1.5H_2O$," *J. Phys. Chem. C*, **116**, 14461–14470 (2012)

Hayashi, H., S. Hirano, N. Shigemoto and S. Yamada; "Characterization of Potassium Carbonate Supported on Porous Materials and Application for the Recovery of Carbon Dioxide from Flue Gases under Moist Conditions," *Nippon Kagaku Kaishi*, **1995**, 1006–1012 (1995)

Hayashi, H., J. Taniuchi, N. Furuyashiki, S. Sugiyama, S. Hirano, N. Shigemoto and T. Nonaka; "Efficient Recovery of Carbon Dioxide from Flue Gases of Coal-Fired Power Plants by Cyclic Fixed-Bed Operations over K_2CO_3-on-Carbon," *Ind. Eng. Chem. Res.*, **37**, 185–191 (1998)

Hirano, S., N. Shigemoto, S. Yamada and H. Hayashi; "Cyclic Fixed-Bed Operation over K_2CO_3-on-Carbon for the Recovery of Carbon Dioxide under Moist Conditions," *Bull. Chem. Soc. Jpn.*, **68**, 1030–1035 (1995)

Kohl, A. L. and F. C. Riesenfeld; Gas Purification, 4th ed., p. 217, Gulf Publishing Co., New York, U.S.A. (1985a).

Kohl, A. L. and F. C. Riesenfeld; Gas Purification, 4th ed., p. 220, Gulf Publishing Co., New York, U.S.A. (1985b)

Liang, R. P., D. P. Harrison, R. P. Gupta, D. A. Green and W. J. McMichael; "Carbon Dioxide Capture Using Sodium-Based Sorbent," *Energy Fuels*, **18**, 569–575 (2004)

Mellor, J. W.; A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume II, p. 764, Longmans Green, London, U.K. (1937)

Park, S. W., D. H. Sung, B. S. Choi, J. W. Lee and H. Kumazawa; "Carbonation Kinetics of Potassium Carbonate by Carbon Dioxide," *J. Ind. Eng. Chem.*, **12**, 522–530 (2006)

Shigemoto, N., T. Yanagihara, S. Sugiyama and H. Hayashi; "Recovery of CO_2 from Moist Gases by Fixed–Bed Operations over K_2CO_3-on-Carbon in a Bench-Scale Plant," *Kagaku Kogaku Ronbunshu*, **30**, 668–673 (2004)

Shigemoto, N., T. Yanagihara, S. Sugiyama and H. Hayashi; "Bench-Scale CO_2 Recovery from Moist Flue Gases by Various Alkali Carbonates Supported on Activated Carbon," *J. Chem. Eng. Japan*, **38**, 711–717 (2005)

Shigemoto, N., T. Yanagihara, S. Sugiyama and H. Hayashi; "Material Balance and Energy Consumption for CO_2 Recovery from Moist Flue Gas Employing K_2CO_3-on-Activated Carbon and Its Evaluation for Practical Adaptation," *Energy Fuels*, **20**, 721–726 (2006)