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Calcium Looping for CO_2 Capture at a Constant High Temperature

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ⓈSupporting Information

ABSTRACT: A calcium looping process using calcium-oxide-based sorbent for CO_2 capture was demonstrated to operate at a constant high temperature in this work. First the operating temperature window of the process was determined by investigating the quasi-equilibrium and kinetics of carbonation/calcination of synthetic CaO-based sorbents. The results indicate that the process would be suitable to operate within 750−840 °C when the CO_2 concentration is higher than 15%. Subsequently, the process was demonstrated in a lab-scale fixed-bed reactor in 20% CO_2 (N_2 balance) by examining the temperature variations in the synthetic CaO-based sorbent particles. The effects of operating variables (such as operating temperature, switching time, and sample type) on the cyclic temperature variation were investigated. It was observed that the process operated in a highly stable manner over 100 cycles at 770 °C with the switching time of 1 min in both carbonation and calcination modes. The cost of calcium looping could be reduced significantly by operating at a constant high temperature.

1. INTRODUCTION

Calcium looping is a promising technology for CO_2 capture, with potentially lower cost than other technologies.[1] It uses the reaction between CaO and CO_2 (or carbonation reaction) for CO_2 capture and the reversible reaction (or calcination reaction) for CO_2 release and sorbent regeneration, as shown in Figure 1a.[2] Under atmospheric pressure, the operating temperature is determined to be about 650 °C for carbonation and above 900 °C for calcination, according to the chemical equilibrium of the reversible reaction.[3] However, it has been found that CaO is significantly sintered at the calcination

temperature of higher than 900 °C, leading to a lower CO_2 capture capacity after cycles.[4−7] As a result, a considerable makeup flow of fresh CaO sorbent is needed to maintain CO_2 capture efficiency in calcium looping, which, in turn, reduces the economic competitiveness and increases the complexity of the operation of calcium looping.[8] In addition, oxy-fuel combustion is required to maintain the high-temperature operation of the calciner and to provide external heat for CaO sorbent regeneration. An air separation unit is therefore needed, which, however, brings significant capital cost and operation and maintenance costs to calcium looping.[9] The cost of calcium looping could be further reduced if the loss-in-capacity problem of CaO sorbents and the oxy-fuel combustion process for sorbent regeneration can be avoided.

With this in mind, a modified calcium looping process was recently proposed by the authors.[10] The key idea is to operate the carbonation/calcination reactions near the equilibrium curve within the same temperature range but at different partial pressures of CO_2, just like a pressure swing adsorption process (referred to as "HotPSA"). As shown in Figure 1b, the operating temperature window is controlled to be lower than 900 °C to alleviate the loss-in-capacity problem but higher than 650 °C to achieve satisfactory reaction rates for carbonation and, more importantly, calcination. Also, a synthetic CaO-based sorbent is used in the process to control the conversion level of CaO to avoid excessive temperature rise in the carbonation mode under adiabatic conditions. The calcination mode is performed under a lower CO_2 concentration achieved by either
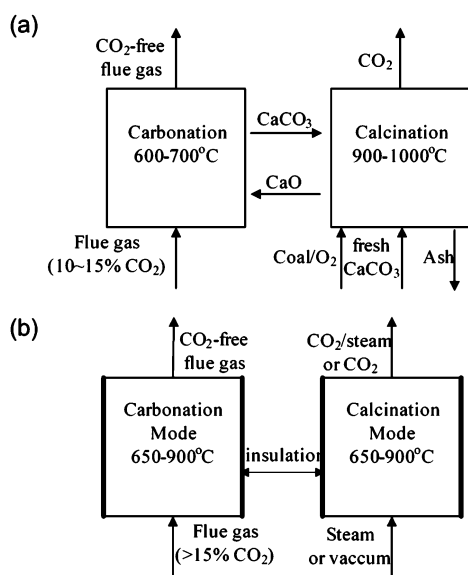

Figure 1. Schematic diagram of (a) typical calcium looping process and (b) HotPSA process.

Table 1. Characteristics of CaO Sorbents after 3 h of Calcination at 900 °C

sample	form	raw material	mass ratio	surface area (m^2/g)	pore volume (cm^3/g)	pore diameter (nm)
CaO	powder			21.42	0.11	11.21
CA5-WM		$Ca(OH)_2/Al_2O_3$	1:19	24.32	0.15	15.31
CHC15-SG		$Ca(OH)_2$/high aluminate cement	1:17	5.67	0.032	20.73
CHC15-PM			1:17	5.86	0.017	19.12
CA43	cylindrical particle	$Ca(OH)_2/Al_2O_3$	1:1	38.63	0.12	9.34
CA64			7:3	27.36	0.10	10.59
CHC50		$Ca(OH)_2$/high aluminate cement[a]	1:1	3.38	0.01	19.52
CHC90			9:1	5.63	0.014	13.04

[a]Refers to the CaO/high aluminate cement mass ratio.

steam dilution or depressurization. The time interval between the two modes is called switching time, largely depending upon the reaction rates of carbonation/calcination. The difference in the kinetics of carbonation and calcination would result in different switching times for each mode. Therefore, in practical operation, a set of fixed-bed reactors is required to operate in parallel to achieve continuous CO_2 capture. The number of required fixed-bed reactors is determined by the switching time of carbonation and calcination modes, while the CO_2 uptake of the CaO sorbent affects the reactor size.

This process is envisaged to have the following advantages: (1) alleviated sintering problem of the sorbent because of the low operating temperature and CO_2 concentration in calcination,[6,11] as confirmed in our previous work,[10] (2) no attrition and fragmentation of particles because of the employment of fixed-bed reactors, and (3) elimination of oxy-fuel combustion because of the reuse of part of the reaction heat from carbonation for subsequent calcination. However, the concept needs to be demonstrated experimentally, which is not available in the literature. Here, this work was carried out to demonstrate the process by accomplishing the following two tasks: (1) determination of a suitable operating temperature window of the process, under which the kinetics of carbonation matches with that of calcination, and (2) demonstration of the process in a lab-scale fixed-bed reactor with self-sustained operation achieved under adiabatic conditions by examining the temperature variations in the CaO sorbent particles.

The operating temperature window is determined by the chemical equilibrium and kinetics of carbonation/calcination reactions of the synthetic CaO sorbent with CO_2. However, the chemical equilibrium of the synthetic CaO sorbent reaction with CO_2 has never been studied thus far, although the equilibrium for the decomposition of pure $CaCO_3$ has been studied by several researchers decades ago using either a gas saturation method[12−14] or static method.[15,16] It is well-accepted that the equilibrium partial pressure of CO_2 of pure $CaCO_3$ can be expressed in eq 1[3]

$$\log P_{CO_2}^{eq} \ (kPa) = 9.079 - 8307.83/T \qquad (1)$$

where $P_{CO_2}^{eq}$ is the partial pressure of CO_2 at equilibrium corresponding to temperature T or, in other words, at $P_{CO_2}^{eq}$ and T, the rates of carbonation and calcination equal each other. The literature results indicate that the presence of inert materials in the synthetic sorbent or alternation of the gas atmosphere would affect the equilibrium behavior. To be specific, some researchers found earlier decomposition of the synthetic CaO-based sorbents doped with SiO_2[17] or MgO[18] than pure $CaCO_3$ under the same calcination conditions. Similarly, MacIntire and Stansel[19] reported earlier decom-

position of $CaCO_3$ in steam than in air, which was attributed to the catalytic effect of steam in calcination. Apparently, the equilibrium of the synthetic CaO sorbent reaction with CO_2 requires a better understanding to determine the operating temperature for the HotPSA. In addition, the operating temperature window for the HotPSA is affected by the kinetics of the carbonation/calcination reactions, which can be expressed by the Arrhenius equation. The activation energies for the fast regime of carbonation of pure CaO and calcination of pure $CaCO_3$ have been extensively reported to be 29−72.7 kJ/mol[20−22] and 99−210 kJ/mol,[23−25] respectively. As a comparison, the kinetics of the carbonation/calcination reactions of the synthetic sorbent has received less attention. It has been reported that dolomite that contains MgO presented a slightly lower activation energy than limestone, while the presence of $Ca_9Al_6O_{18}$ in the synthetic CaO sorbent did not affect the kinetics of carbonation.[21,26] Also, it appears that the presence of inert materials and/or impurities may affect the calcination rate of $CaCO_3$. For instance, it has been reported that P_2O_5, V_2O_5, and fly ash inhibit the calcination reaction and Al_2O_3, $BaCO_3$, and CaO have no effect, while SiO_2 and alkali carbonates accelerate the process, among which Li_2CO_3 is the best catalyst.[27−30] Therefore, it is interesting to investigate how the impurities would affect the kinetics of carbonation/calcination reactions and, thus, the operating temperature for the HotPSA.

Once the operating temperature is determined, it is interesting to demonstrate its operation at that temperature, which has never been reported before in the literature. The goal is to achieve self-sustained operation under simulated adiabatic conditions, under which a stable temperature variation in the CaO particles over long-term operation is achieved. The stability of operation in a fixed-bed reactor is affected by several factors, such as the kinetics of the chemical reaction, the switching time between the two modes, the convective heat transfer between solid and gas, etc.[31−33] Therefore, the HotPSA process was demonstrated by examining the temperature variations in the CaO-based sorbents for multiple cycles, and the effect of the factors was investigated.

2. EXPERIMENTAL SECTION

2.1. Sorbent Preparation. The synthetic CaO-based sorbent was produced from commercial calcium hydroxide and inert material of alumina or high aluminate cement. The mass ratios of CaO/inert material in the final sorbent after 3 h of calcination at 900 °C were tabulated in Table 1. The sorbents had two forms, powder and cylindrical particle, to be used in the thermogravimetric analyzer (TGA) and bench-scale fixed-bed reactor, respectively. The synthetic sorbent in powder form was produced by various methods. For instance, CA5-WM that consists of 5% CaO and 95% alumina was made by wet mixing. CHC15-PM and CHC15-SG that contain 15%

CaO and 85% aluminate cement were made by physical mixing and sol−gel, respectively. The cylindrical CaO sorbent particle was extruded from a Prism EUROLAB 16 twin-screw extruder (Thermo Electron Corporation). Because of the fast setting nature of cement, the particles were produced with relatively lower cement to maintain continuous operation of the extruder. The cylindrical particles were cut to 3 mm long with a diameter of 1.5 mm. The chemical compositions of cement used to make the sorbents can be found elsewhere.[10] Pure CaO in powder form was employed in the TGA tests as a reference. The surface area and pore volume of those sorbents were measured using N_2 adsorption at −196 °C.

2.2. Determination of the Quasi-equilibrium Temperature in the TGA. In this work, the "quasi-equilibrium temperature" rather than the "equilibrium temperature" was obtained because no real equilibrium was achieved in the tests. The quasi-equilibrium data were determined in a Cahn-131 TGA coupled with a mass-flow control system. Before the test, the thermocouple of the TGA and the balance were carefully calibrated using five reference standard material counterpoises.

A small amount of sorbent (∼20 mg) was dispersed in a quartz sample holder to form a thin layer to eliminate the gas diffusion effect, which was confirmed by studying the reactivity of CHC15-PM with different particle sizes (see Figure S1 of the Supporting Information). Then, the sample was heated to 1000 °C at 5 °C/min in a gas mixture of CO_2 and N_2 with a predetermined CO_2 concentration in the range of 0.01−1 atm. The total flow was controlled to be 100 mL/min. Once the temperature reached 1000 °C, the furnace was programmed to cool to ambient temperature at −5 °C/min. Initially, the sample mass kept increasing because the reaction rate of carbonation was faster than that of calcination when the temperature was lower than its equilibrium temperature. Once the temperature reached or exceeded the equilibrium temperature, a sudden mass loss was observed because the reaction rate of calcination exceeded that of carbonation. The temperature corresponding to the sudden mass loss was defined as the quasi-equilibrium temperature because of the calcination of carbonated CaO, which was denoted as T_{cal} (see Figure 2). As the temperature
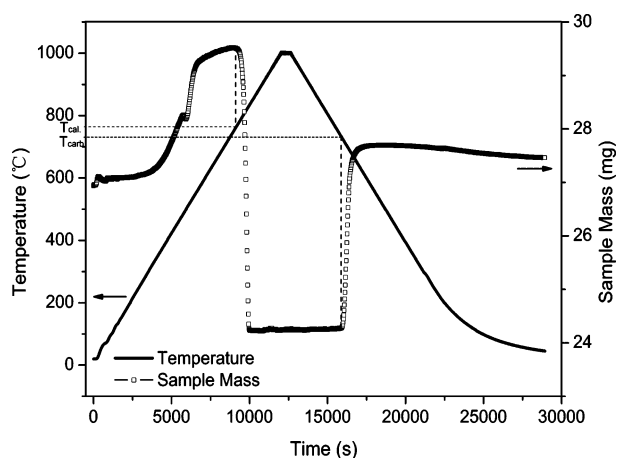
two quasi-equilibrium temperatures corresponding to the calcination of carbonated CaO and recarbonation of the calcined sorbent. All of the tests were conducted 3 times to obtain reproducible results. The real equilibrium temperature should be between the two quasi-equilibrium temperatures. However, in practical operation, the quasi-equilibrium temperatures will be more useful.

2.3. Determination of Kinetic Parameters in the TGA. The reaction rate of the carbonation/calcination reactions of various sorbents required to calculate activation energy was measured in the TGA under isothermal conditions at five different temperatures (550−800 °C). The carbonation was conducted under 50 vol % CO_2 (N_2 balance) for 30 min, while the calcination was conducted under 100% N_2 at the same temperature and atmospheric pressure. The apparent activation energies for the carbonation and calcination of the CaO sorbents were subsequently obtained by linearly fitting eq 5 with experimental reaction rate data, as discussed later.

2.4. Determination of the Operating Temperature in the TGA. The operating temperature of the HotPSA was preliminarily selected on the basis of the equilibrium results and subsequently refined on the basis of the reaction rates of carbonation/calcination reactions under the selected experimental conditions, as discussed later. The carbonation was conducted within the selected temperature range at the designated CO_2 concentration, while the calcination was performed at the same temperature range in a gas mixture of N_2 and 15 vol % H_2O. To simulate the temperature increase in the carbonation mode and the temperature decrease in the calcination mode, the carbonation temperature was programmed to increase within the selected temperature range with a ramping temperature of 5 °C/min, while the calcination temperature was programmed inversely. The steam required in the calcination mode was generated by heating a section of copper tube in an oil bath at 150 °C. The volumetric flow rate of the liquid water was controlled by a liquid metering pump (SSI). The generated steam was then carried to the TGA by the N_2 stream.

2.5. Operation of the HotPSA in a Bench-Scale Fixed-Bed Reactor. The prototype of the HotPSA process was set up based on a lab-scale fixed-bed reactor, as seen in Figure 3. The system consists of a gas feeding system, a fixed-bed reactor with temperature control, and a gas analyzer. The gas feeding system has two gas channels that regulate the volumetric flow rates of CO_2 and N_2 from the gas bottles using two mass-flow controllers. The reactor system consists of a three-stage furnace and an Inconel 600 reactor that has an internal
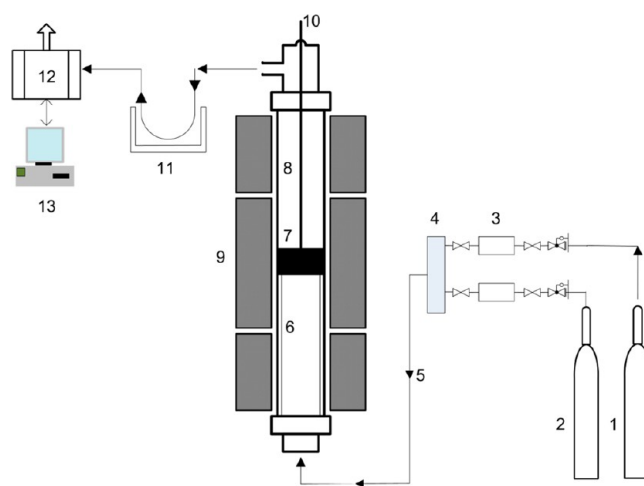
Figure 2. Variation of the temperature and sample mass of conventional CaO at 10 vol % CO_2 partial pressure (N_2 balance) and the definition of quasi-equilibrium temperatures for carbonation/calcination.

continued to rise, $CaCO_3$ was fully dissociated to CaO and CO_2. Normally, before the temperature reaches 1000 °C, the decomposition would have been completed. Subsequently, the furnace was cooled to ambient temperature, and the sample mass remained constant until a certain temperature at which a sudden increase in the sample mass was observed because the reaction rate of carbonation started to exceed that of calcination. Then, the temperature corresponding to the sudden mass increase was defined as the quasi-equilibrium temperature because of the recarbonation of the calcined sorbent, which was denoted as T_{carb}, as shown in Figure 2. Therefore, every run produced

Figure 3. Schematic diagram of the fixed-bed reactor system: (1) N_2 cylinder, (2) CO_2 cylinder, (3) mass-flow controller, (4) gas mixer, (5) stainless-steel tubing, (6) quartz support, (7) CaO-based particles, (8) Inconel 600 reactor, (9) three-stage furnace, (10) thermocouple, (11) condenser, (12) Fourier transform infrared (FTIR) spectrometer, and (13) data acquisition system.
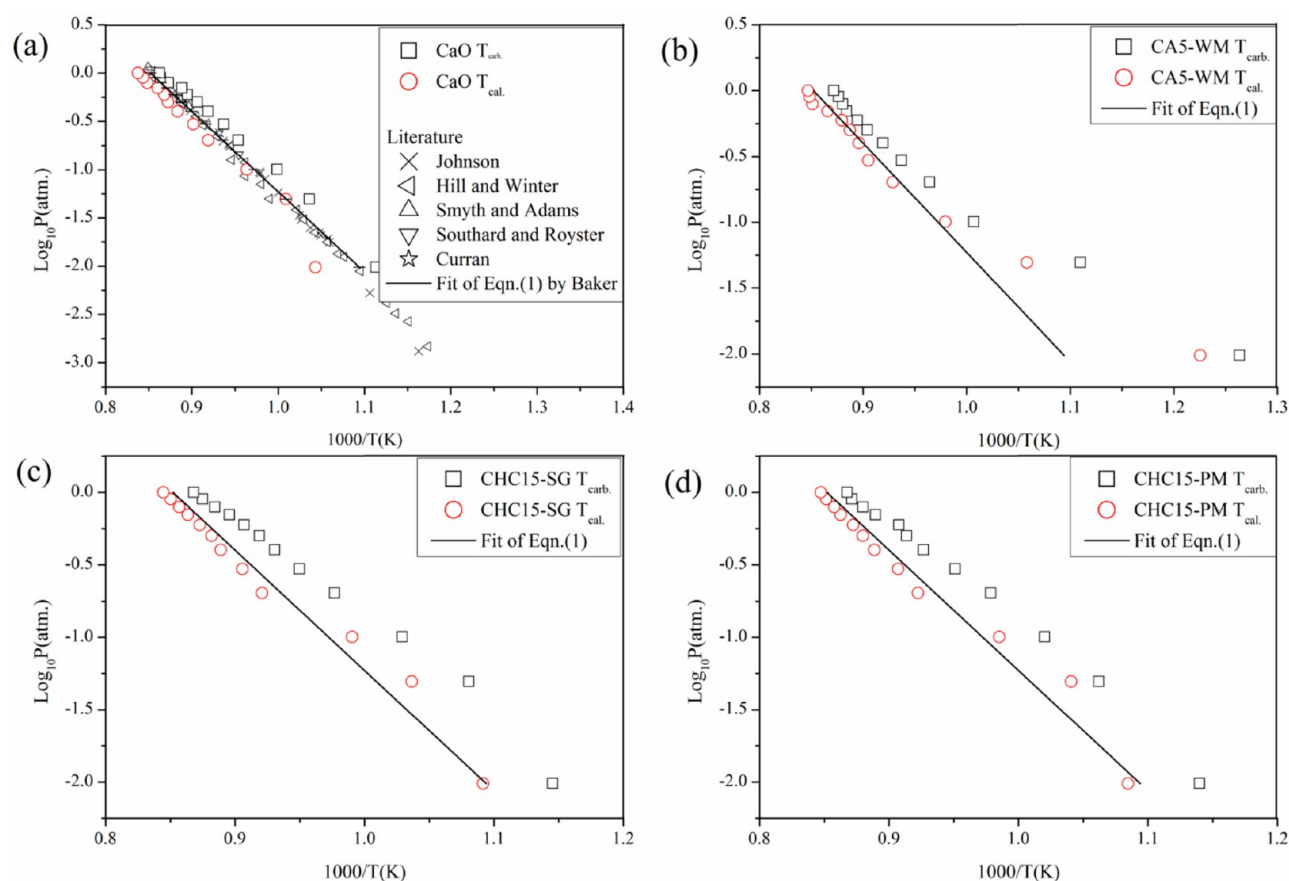
Figure 4. Quasi-equilibrium partial pressure of CO_2 resulting from the carbonation/calcination reactions of (a) CaO and literature data, (b) CA5-WM, (c) CHC15-SG, and (d) CHC15-PM under atmospheric pressure. Literature data were reproduced from refs 12−16 and the model eq 1 by Baker.[3]

diameter of 27 mm and a length of 550 mm. The furnace has a constant temperature zone with a length of 100 mm.

The operation of the HotPSA in a single fixed-bed reactor involves carbonation and calcination modes sequentially by switching the corresponding gaseous reactants. In each run, about 10 g (unless stated otherwise) of particles was centered in the reactor to form a bed with a height of 3.5 mm and a bed porosity of 0.47−0.49. Then, the furnace was heated to a desired temperature within 700−790 °C, at which the carbonation and calcination were performed. The carbonation mode was conducted under 20 vol % CO_2 (N_2 balance) at various temperatures, while the calcination mode was conducted in N_2. The furnace was kept heating at the desired temperature to simulate the adiabatic conditions. The switching time for the carbonation and calcination modes was set the same and varied between 1 and 5 min in this work. The temperature in the CaO particle was continuously measured by a thermocouple every 10 s.

3. RESULTS AND DISCUSSION

3.1. Determination of the Operating Temperature Window for the HotPSA.
3.1.1. Quasi-equilibrium Curves of Carbonation/Calcination of CaO Sorbents. The quasi-equilibrium temperatures resulting from the carbonation of calcined sorbent (T_{carb}) and the calcination of carbonated CaO (T_{cal}) for four CaO sorbents were obtained (see Table S1 of the Supporting Information) and plotted in Figure 4, together with the selected literature data. The following observations can be made from the figure: (1) In general, the quasi-equilibrium CO_2 partial pressures from the calcination of carbonated CaO, CHC15-SG, and CHC15-PM sorbents are in general agreement with eq 1 that was obtained from the decomposition of

pure $CaCO_3$, while the quasi-equilibrium CO_2 partial pressure from the calcination of the carbonated CA5-WM sorbent shows a significant discrepancy with eq 1, particularly at low temperatures, as shown in Figure 4b. (2) The quasi-equilibrium CO_2 partial pressure corresponding to the calcination of the carbonated sorbent was always lower than that corresponding to the carbonation of the calcined sorbent at the same temperature, or the quasi-equilibrium temperature corresponding to the calcination of the carbonated sorbent was always higher than that corresponding to the carbonation of the calcined sorbent at the same CO_2 partial pressure. It is also noted that the difference is much smaller for CaO than that for the other synthetic sorbents, suggesting that the quasi-equilibrium of the CaO sorbent depends upon the sample type and procedure to obtain the data. (3) It is evident from panels c and d of Figure 4 and Table S1 of the Supporting Information that CHC15-SG and CHC15-PM had nearly the same quasi-equilibrium CO_2 partial pressures. This would be due to the same chemical compositions and source of CaO of the two synthetic sorbents. The results indicate that the quasi-equilibrium pressure or temperature is more sensitive to the composition than to the mixing method.

3.1.2. Kinetics of Carbonation/Calcination of CaO Sorbents. The kinetic parameters for the carbonation and calcination reactions can be calculated below by fitting the reaction rate equation based on the grain model.[34,35]

$$R' = \frac{dX}{dt(1 - X)} = 3r(1 - X)^{-1/3} = 56k_s(P_{CO_2} - P_{CO_2}^{eq})^n S \tag{2}$$

At the initial time $t = 0$, eq 2 becomes

$$R' = \frac{dX}{dt} = 3r_0 = 56k_s(P_{CO_2} - P_{CO_2}^{eq})^n S_0 \tag{3}$$

In logarithmic form, with $k_s = A \exp(-E/RT)$, eq 3 becomes

$$\ln(r_0) = n\ln(P_{CO_2} - P_{CO_2}^{eq}) + \ln(S_0) + \ln\left(\frac{56}{3}A\right) - \frac{E}{RT} \tag{4}$$

Assuming zero reaction order when $P_{CO_2} - P_{CO_2}^{eq} > 10$ kPa,[21] eq 4 can be rearranged as

$$\ln(r_0) = \ln\left(\frac{56}{3}AS_0\right) - \frac{E}{RT} \tag{5}$$

where r_0 is the initial specific reaction rate in the carbonation/calcination reactions, A is the pre-exponential factor, S_0 is the initial surface area of CaO or $CaCO_3$, and E is the activation energy for the carbonation or calcination reaction, which was determined by the slope of a plot of $\ln(r_0)$ versus $1000/T$, as shown in Figure 5.
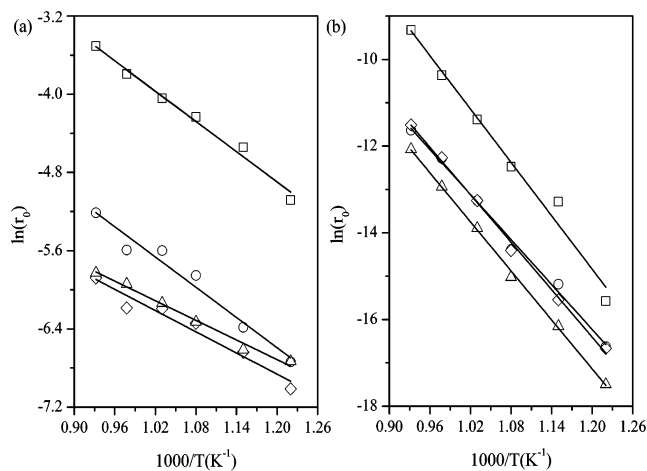

Figure 5. Arrhenius plots for (a) carbonation at 550−800 °C in 50 vol % CO_2 (N_2 balance) for 30 min and (b) calcination at 550−800 °C in 100% N_2 of the CaO sorbents (□, CaO; ○, CA5-WM; ◇, CHC15-SG; and △, CHC15-PM).

The obtained values for the activation energy and pre-exponential factor are tabulated in Table 2. It can be clearly seen that the E values were in the range obtained by other researchers in similar experimental conditions.[21,35−37] Moreover, it is shown that the activation energies obtained for the

Table 2. Kinetic and Sorption Parameters of the Carbonation/Calcination Reactions of CaO Sorbents

	CaO	CA5-WM	CHC15-SG	CHC15-PM
		Carbonation		
E (kJ mol^{-1})	43.68	43.49	30.03	28.28
A (mol m^{-2} s^{-1})	0.33	8.6×10^{-3}	7.6×10^{-4}	1.4×10^{-3}
		Decomposition		
E (kJ mol^{-1})	173.68	148.54	159.48	154.43
A (mol m^{-2} s^{-1})	2.1×10^3	2.01	3.20	6.46

three synthetic CaO sorbents are generally lower than that of the pure CaO, which could be caused by inert materials. It has been reported that the presence of inert materials could result in lower strain energy that lowers the activation energy in the synthetic sorbents.[38] The same chemical compositions and internal structures in CHC15-SG and CHC15-PM probably resulted in very similar activation energies for both the carbonation and calcination reactions. Furthermore, the low values in the activation energy (28.28−43.49 kJ/mol) for the carbonation reaction of the synthetic sorbents imply that the reaction rate in the chemical-controlled stage was not sensitive to the variation of the temperature (at least within the temperature range studied). In contrast, the calcination reaction rate of CaO sorbents showed strong dependence upon the reaction temperature because of high activation energies (148.54−173.68 kJ/mol). In other words, the reaction rate of decomposition of $CaCO_3$ should be paid more attention than the rate of carbonation when selecting or altering the operating temperature for the HotPSA, because the former is sensitive to temperature change, while the latter is already fast enough at temperatures higher than 550 °C.

3.1.3. Determination of the Operating Temperature for the HotPSA. As noted earlier, the measured quasi-equilibrium behavior of the CaO sorbents determines a temperature range at a fixed CO_2 concentration, under which the carbonation occurs. However, it is still unknown within that temperature range whether the decomposition of the CaO sorbent takes place fast enough or not, which is strongly affected by the temperature, as indicated above. Therefore, it is necessary to further investigate the calcination rate within the temperature range to refine the operating temperature. To this end, four study cases (see Table 3) with different operating temperatures

Table 3. Recommended Operating Temperatures for Different Sorbents in Various CO_2 Partial Pressures

sample	case number	CO_2 mole fraction (%)	carbonation ↔ calcination (°C)
CaO	1	10	705 ↔ 755
	2	20	755 ↔ 805
	3	30	775 ↔ 825
	4	40	795 ↔ 845
CA5-WM	1	10	690 ↔ 740
	2	20	745 ↔ 795
	3	30	775 ↔ 825
	4	40	785 ↔ 835
CHC15-SG	1	10	680 ↔ 730
	2	20	755 ↔ 805
	3	30	775 ↔ 825
	4	40	790 ↔ 840
CHC15-PM	1	10	680 ↔ 730
	2	20	755 ↔ 805
	3	30	775 ↔ 825
	4	40	790 ↔ 840

corresponding to different CO_2 mole fractions were specifically recommended for each sorbent based on the obtained "quasi-equilibrium" data of CaO sorbents. The determination of the operating temperature window for a fixed CO_2 mole fraction follows two steps: (1) the determination of the ending temperature of the carbonation mode (i.e., the starting temperature of the calcination mode), which was usually 5−10 °C lower than the quasi-equilibrium resulting from the
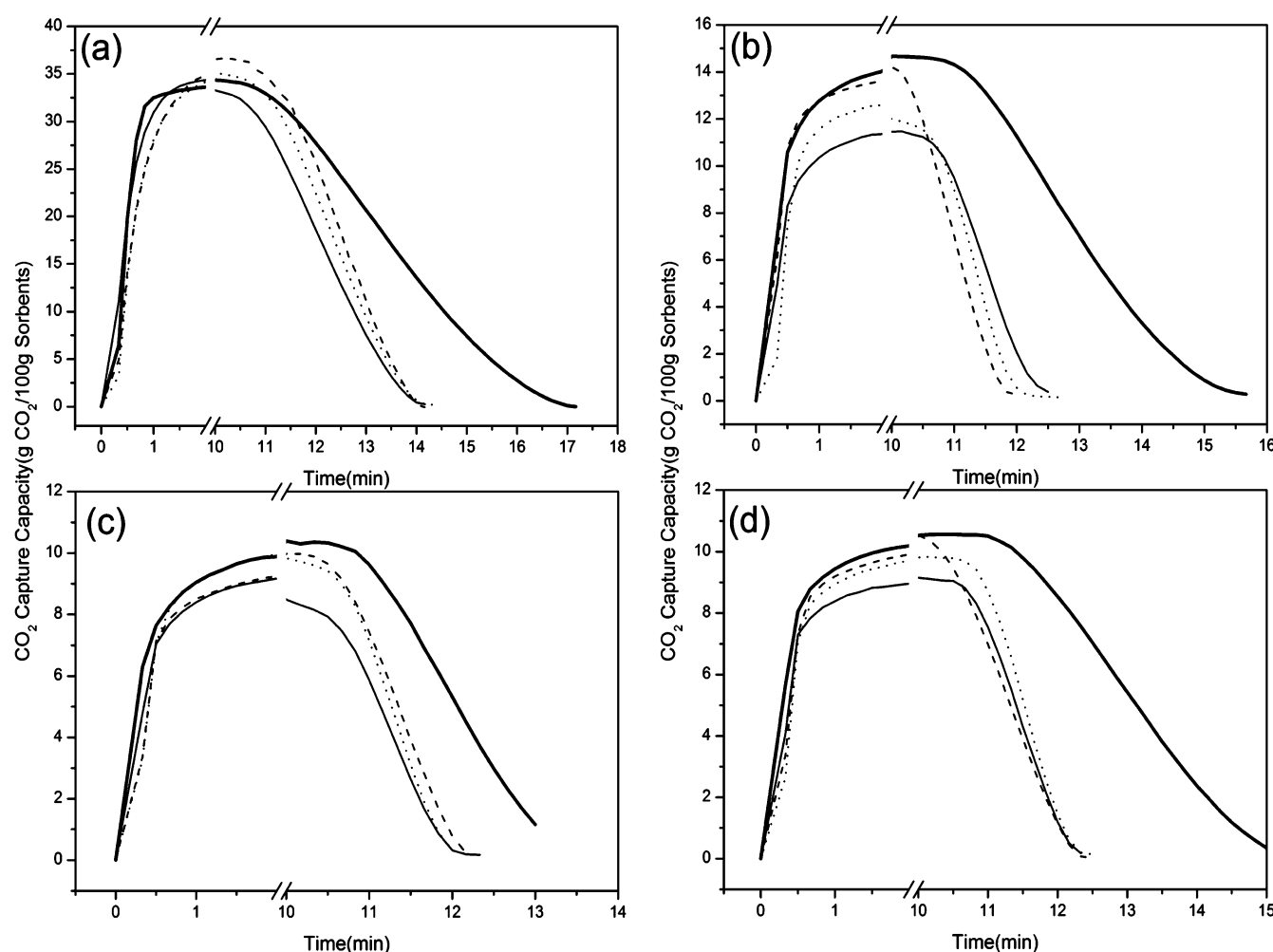
Figure 6. Carbonation and calcination of the CaO sorbents (a, CaO; b, CA5-WM; c, CHC15-SG; and d, CHC15-PM) under selected operating temperatures, with carbonation in the temperature range of 750−800 °C in 20 vol % CO_2 (N_2 balance) and calcination in the temperature range of 800−750 °C in 15 vol % steam (N_2 balance) (thick solid line, case 1; solid line, case 2; dotted line, case 3; and dashed line, case 4; for case details, see Table 3).

calcination of carbonated CaO sorbents, and then (2) the starting temperature of the carbonation mode (i.e., the ending temperature of the calcination mode) determined on the basis of the assumption of 50 °C temperature increase during the carbonation mode. The temperature increase of 50 °C was assumed to ensure safe operation of the adiabatic fixed-bed reactor. It must be noted that, in practice, the temperature increase in the solid may vary from case to case, depending upon the heat balance of the reaction in the fixed-bed reactor.

The results in Figure 6 show a very fast reaction rate in the chemical-controlled stage of all of the CaO sorbents, which appeared to decrease with the increase of the temperature, particularly as seen in panels b and d of Figure 6. However, it can be seen that about 50−76% of the overall conversions for the CaO-based sorbents completed in 1 min, indicating that the switching time for the carbonation mode can be set as 1 min. In comparison, the decomposition rate was significantly affected by the temperature variation. It can be clearly seen that the decomposition rate in case 1 was the lowest because of the lowest calcination temperature. In this case, the decomposition can be finished in 4−5 min, which is a bit long to match with the fast chemical-controlled regime. With increasing the operating temperatures in cases 2 and 3, the decomposition

rate increased significantly, allowing for the regeneration to complete in 2−3 min. With further increasing the temperature in case 4, the decomposition rate further increased and the decomposition completed in 2 min, except the conventional CaO, which still required about 4 min to complete decomposition. With respect to the switching time for the calcination mode, it is suggestive to limit it within 2 min to minimize the number of reactors required for continuous CO_2 capture. The results indicate that this can be achieved by carefully selecting the operating temperature for the HotPSA process.

In general, it is recommended that the HotPSA operates above 750 °C because of an insufficient calcination rate below this temperature. The corresponding equilibrium pressure of 750 °C is about 0.15 atm (15 vol % mole fraction). Taking into account our previous result of the complete decomposition of the CaO sorbents in about 130 s at 750 °C in the presence of steam,[10] we think that the decomposition rate would be satisfactory within the temperature range of 750−840 °C. Correspondingly, the carbonation mode can be operated at the same temperature range under the atmosphere with a CO_2 concentration between 15 and 40%. Also, the carbonation mode of the HotPSA can be operated with higher CO_2

concentrations (i.e., >40%). In this case, the critical temperature is higher according to the equilibrium of the $CaO-CO_2$ system, corresponding to a wider operating temperature window. The decomposition rate of $CaCO_3$ is expected to be faster at higher operating temperatures. However, it is not recommended to operate the HotPSA at temperatures higher than 850 °C because that would enhance the sintering problem of the sorbent. Therefore, the HotPSA would be suitable to operate at the temperature range of 750−840 °C when the CO_2 concentration is higher than 15%.

3.2. Demonstration of the HotPSA Process in a Fixed-Bed Reactor. With the determined operating temperature of the HotPSA, the following work aims to demonstrate the concept of the HotPSA in a fixed-bed reactor by examining the temperature variation in the CaO sorbent particles during carbonation/calcination reactions in 20 vol % CO_2 (N_2 balance). This indicates whether the process can be operated autothermally under adiabatic conditions. The effect of operating variables (such as operating temperature, switching time, and sample type) on the temperature variation was also investigated.

3.2.1. Breakthrough Curve of CO_2 Capture in the Fixed-Bed Reactor. Prior to operating the fixed-bed reactor, it would be necessary to prove that the sorbent is capable of capturing all CO_2 during a period by confirming the existence of breakthrough curves. This is important because it will affect the selection of the switching time and CO_2 uptake efficiency of the HotPSA.

As shown in Figure 7, the carbonation of about 100 g of CA64 particles was conducted in three different cases at 770
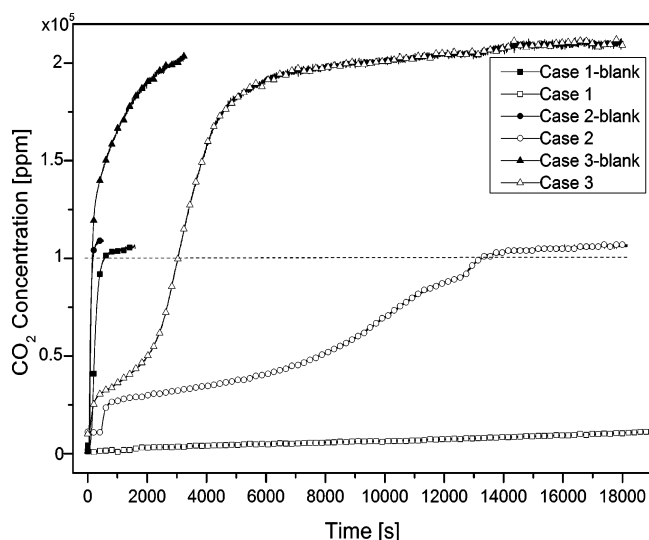

Figure 7. Breakthrough curve of CA64 in the fixed-bed reactor under case 1, 10% CO_2/N_2, 200 mL/min, and 770 °C; case 2, 10% CO_2/N_2, 500 mL/min, and 770 °C; and case 3, 20% CO_2/N_2, 500 mL/min, and 770 °C. All of the blank tests were conducted under the same atmosphere but different temperature (25 °C).

°C. Also, three corresponding blank tests were conducted at room temperature under the corresponding atmosphere. Because there is no reaction between CaO and CO_2 at room temperature, the CO_2 concentration increased sharply when switching on the CO_2 valve in all blank tests. In comparison, at 770 °C, the reaction between CaO and CO_2 occurred, so that the CO_2 concentration initially increased very slowly.

Particularly, in case 1, all CO_2 was captured by CA64 particles during the 5 h carbonation because no breakthrough during that time was observed. With increasing the total flow rate to 500 mL/min in case 2, the CO_2 concentration in the exiting gas increased slowly to 100 000 ppm after about 3.5 h of carbonation. Similarly, the breakthrough time of CA64 was further shortened to about 1.5 h with increasing the CO_2 fraction to 20% in case 3, in agreement with the previous work.[39] Interestingly, in cases 2 and 3, the molar ratios between CaO and CO_2 fed into the reactor within the breakthrough time were very close to each other (2.45 and 2.33, respectively). Therefore, it is indicated that the HotPSA is achievable to capture all CO_2 in a specified period by controlling the molar ratio of CaO/CO_2. The total mass flow rate of the gas mixture was selected to be 500 mL/min in the following tests.

3.2.2. Effect of the Operating Temperature on the Temperature Variation of the CaO Particle. The cyclic variation of the temperature of the CaO-based particles during operation was monitored, which is an indication of the sustainability of the process. Figure 8 presents the effect of the operating temperature (700−790 °C) on the temperature variation of CaO-based particles over 20 carbonation/calcination cycles with the switching time of 1 min in 20 vol % CO_2 (N_2 balance). It can be clearly seen that, when the operating temperatures were lower than 770 °C, the temperature variation diminished after a few cycles. The decay in the temperature increase can be ascribed to the insufficient decomposition rate of $CaCO_3$. Consequently, less CaO was regenerated for subsequent CO_2 capture, leading to a reduced temperature increase next cycle. On the other hand, the slow decomposition of $CaCO_3$ also resulted in a slight increase in the ending temperature in the calcination mode in the initial few cycles, which, however, decreased noticeably as the cycle continued. The initial increase in the ending temperature was caused by the faster carbonation rate than the calcination. Subsequently, the convective energy loss from solid to gas decreased the ending temperature of the calcination mode. Thus, the HotPSA is not applicable if being operated within the temperature between 700 and 750 °C because of the insufficient decomposition rate, which is consistent with the previous TGA results.

With increasing the operating temperature to 770 and 790 °C, the temperature increase of all CaO-based particles became stable over 20 cycles, although the decay in the temperature increase was observed in the initial few cycles. It indicates that, at 770 and 790 °C, the operation of the HotPSA could be self-sustained. However, it is worthy to point out that, at 790 °C, the temperature increase (∼3.4 °C on average) was clearly lower than that at 770 °C (∼9 °C on average). It means a lower conversion of CaO at 790 °C than at 770 °C because the temperature increase resulted from the carbonation of CaO and CO_2. This can be explained on the basis of the thermodynamic equilibrium CO_2 partial pressure of CaO over the temperature. A higher operating temperature corresponds to a higher equilibrium pressure of CO_2 ($P_{CO_2}^{eq}$), leading to a lower driving force ($P_{CO_2} - P_{CO_2}^{eq}$) that is in a linear relationship with the decomposition rate of $CaCO_3$.[3,40] Therefore, an optimum operating temperature exists within the range of 750−840 °C for a fixed CO_2 concentration, taking into account the conversion of CaO. It is suggested the the HotPSA operates at 770 °C when the CO_2 fraction is 20%, achieving relatively higher CO_2 uptake and autothermal operation over 10 cycles.
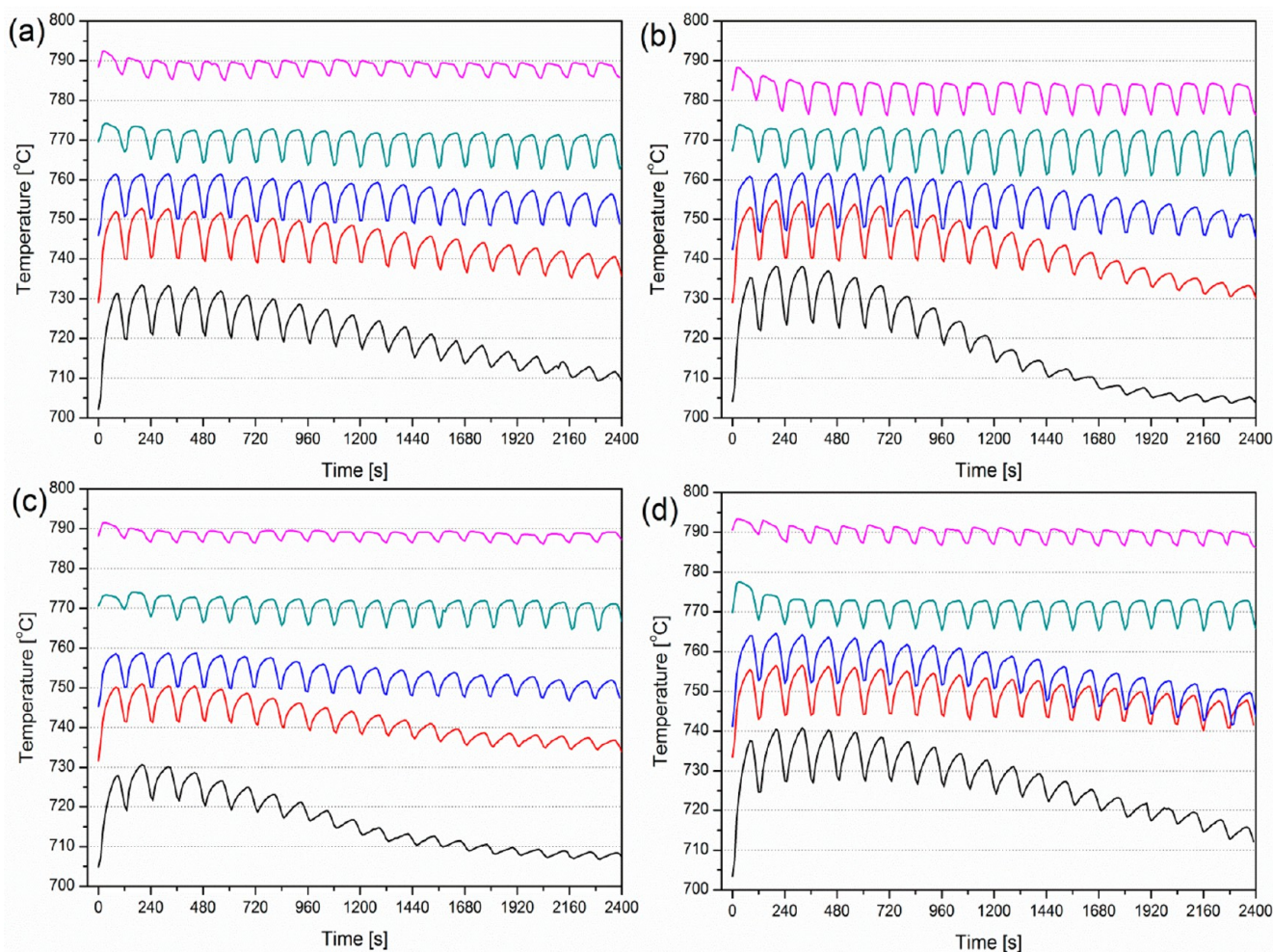
Figure 8. Variations of the temperature of (a) CA43, (b) CHC50, (c) CA64, and (d) CHC90 over 20 carbonation/calcination cycles with the switching time of 1 min at starting temperatures of 700−790 °C, with carbonation in 20% CO_2 (N_2 balance) at 700−790 °C and calcination in 100% N_2 at 700−790 °C.

On the basis of this result, the process was operated at 770 °C in the following work.

It should be mentioned that different quasi-equilibrium behaviors of different CaO-based sorbents seem to have a negligible effect on the temperature variation of the sorbent at the same operating temperature of 770 °C. It is thought that this is because the chemical reaction is not the only factor affecting the temperature variation in the particles, and other factors (e.g., mass and heat transfers and similar kinetic parameters) may play an important role in the operation of the fixed-bed reactor.

3.2.3. Effect of the Switching Time on the Temperature Variation of the CaO Particle. Figure 9 presents the effect of the switching time (1−5 min) on the temperature variation of the CaO-based particles over two single carbonation/calcination cycles at 770 °C. It is shown that the temperature of all CaO-based particles increased significantly in a short period after feeding CO_2 into the reactor, which should be attributed to the fast carbonation reaction between CaO and CO_2. Then, the temperature started to decrease gradually as time elapsed when the switching time of the carbonation mode was longer than 1 min. This can be attributed to the greater heat loss from solid to gas than the heat generated from the diffusion-controlled regime of carbonation. This temperature decrease was found to disappear with the switching time of 1

min. It is suggested that the chemical-controlled stage of carbonation usually finished within 1 min, in accordance with the previous TGA results.[10,41] Then, in the calcination mode, the decomposition of $CaCO_3$ occurred under a lower CO_2 partial pressure, resulting in a significant decrease in the sample temperature. Subsequently, the sample temperature gradually increased to a certain temperature. This phenomenon was pronounced when the switching time was longer than 3 min. This was caused by heat transfer from gas because the rapid decomposition of $CaCO_3$ dropped the sample temperature below the gas temperature. With a decreasing switching time, the heat-transfer phenomenon became much less pronounced at the switching time of 2 min and disappeared at the switching time of 1 min.

In general, heat transfer between solid and gas should be minimized to avoid a temperature gradient in the reactor. It seems that it is effective to minimize the heat transfer by controlling the switching time. Also, shortening the switching time did not offset the CO_2 uptake too much. For instance, the temperature increase of CHC90 at 1 min switching time was similar to that at a longer switching time, implying that the diffusion-controlled stage did not contribute too much to the conversion of CaO.[41] Thus, the switching time for the carbonation and calcination modes could be set as 1 min,
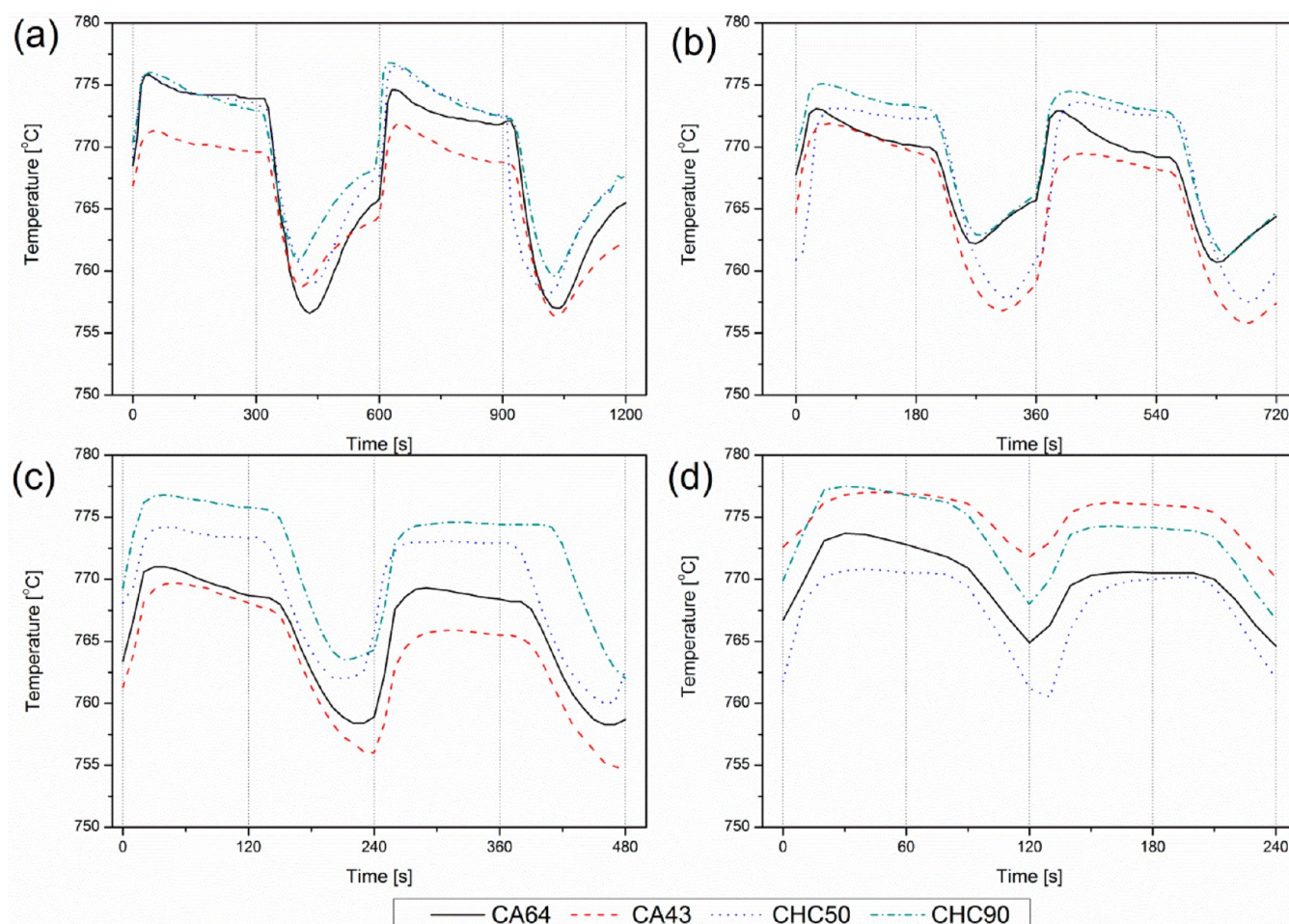
Figure 9. Variations of the temperature in CaO-based particles over two carbonation/calcinations cycles with a switching time of (a) 5 min, (b) 3 min, (c) 2 min, and (d) 1 min, with carbonation in 20 vol % CO_2 (N_2 balance) at 770 °C for 1−5 min and calcination in N_2 at 770 °C for 1−5 min.

while the switching time for the calcination mode could be set between 1 and 2 min.

3.2.4. Effect of the Sample Type on the Temperature Variation of the CaO Particle. The sample type would affect the temperature variation of the sorbent in the HotPSA, because of different reactivity in different samples. Figure 10 shows the variation of the temperature increase associated with carbonation of various CaO particles over 20 carbonation/calcination cycles at 770 °C with the switching time of 1 min. Except for CHC90, all other CaO particles showed an increase in the temperature increase over the initial 6 cycles, which gradually became stable over the next 14 cycles. CHC90 showed a decrease in the temperature increase over the initial three cycles, which then became stable. It appears that the stability in the temperature variation of the sorbent was not affected by the sample type, and no consistent trend of the temperature increase with respect to sample type was observed. This phenomenon was resulted from the inconsistent starting temperature in every run in the fixed-bed reactor, which might cause the irregular variation in the sorbent temperature.

3.2.5. Long-Term Carbonation/Calcination Cycles. When the operating temperature and switching time were determined, it is necessary to run the process in long-term cycles. Figure 11 presents the temperature variation of CaO-based particles over 100 cycles in the fixed-bed reactor with the switching time of 1 min. It can be clearly seen that the sample temperature dropped slightly within the first 10 cycles and then became quite stable
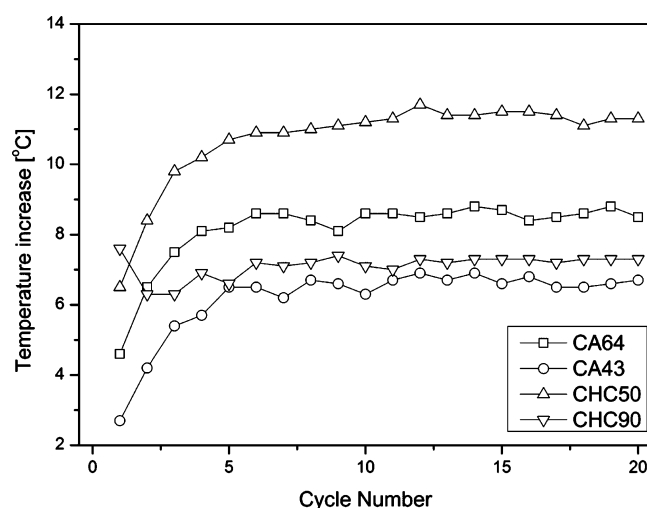

Figure 10. Variations of the temperature increase of CaO-based sorbents over 20 carbonation/calcination cycles, with carbonation in 20 vol % CO_2 (N_2 balance) for 1 min and calcination in N_2 for 1 min. The operating temperature is 770 °C.

over the next 90 cycles. This further confirms that, at 770 °C, the HotPSA can sustain its operation over 100 cycles. Also, the decomposition rate of $CaCO_3$ matched that of the carbonation reaction because the temperature increase in the carbonation
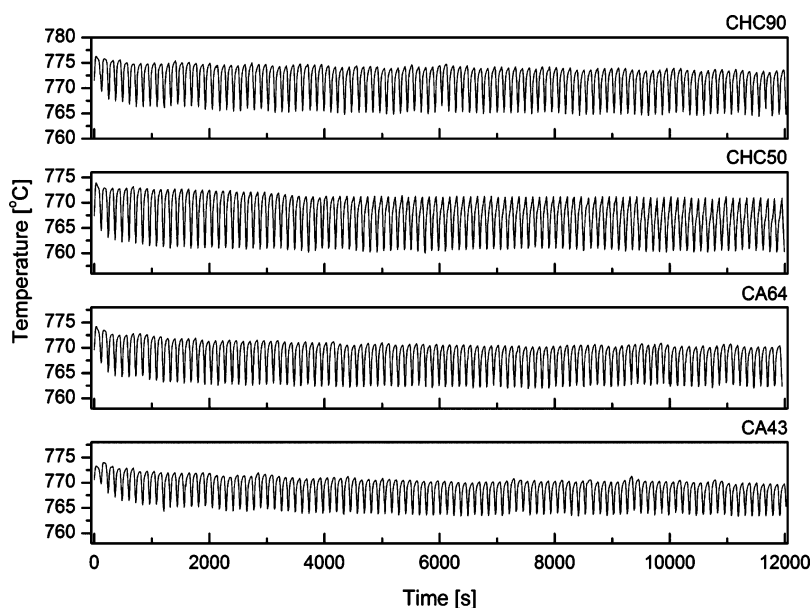
Figure 11. Long-term carbonation/calcination cycles of the CaO-based particles in the fixed-bed reactor with the switching time of 1 min, with carbonation at 770 °C in 20 vol % CO_2 (N_2 balance) and calcination at 770 °C in N_2.

mode was consistent over cycles, as seen in Figure 11. Under such conditions, however, the CO_2 uptake of CHC90 was not very high. As presented in Figure S2 of the Supporting Information, it can be clearly seen that the CO_2 uptake of CHC90 reduced from about 2.3 g of CO_2/100 g of sorbent at the first cycle to ~1 g of CO_2/100 g of sorbent at the 100th cycle. The amount of CO_2 released from decomposition of $CaCO_3$ appeared to remain at a certain level over the 100 cycles, which contributed to the continuous operation of the process. With this CO_2 capture capacity, a reactor with the volume of 300 m^3 is able to capture 5 tons of CO_2/min, assuming that the bed void is 0.5 and the sorbent density is 3.34 tons/m^3.

3.3. Practical Operation of the HotPSA Process for Continuous CO_2 Capture. In a continuous industrial process, the carbonation and calcination modes can be accomplished in a system of fixed-bed reactors operating in parallel. The operational diagrams for the HotPSA process to complete a single PSA cycle in two cases are depicted in Figure 12. A twin fixed-bed reactor system would be used to operate the HotPSA process when the switching time for both carbonation and calcination modes is 1 min, as shown in Figure 12a. If the switching time for the calcination mode increases to 2 min to allow for more complete decomposition of $CaCO_3$, at least

three beds operating in parallel are needed to complete a full PSA cycle, as shown in Figure 12b. In step 1, reactor 1 operates in the carbonation mode, while the other two are in the calcination mode. In step 2, reactor 1 is switched to the calcination mode, while reactor 2 comes into play for CO_2 capture. Reactor 3 is still in the calcination mode. After 2 min of calcination, reactor 3 is ready for CO_2 capture in step 3. In the meanwhile, reactor 2 is in the calcination mode. Another cycle continues by resuming step 1. It must be noted that a purge step between the carbonation and calcination modes may be required if the CO_2 stream produced in the calcination mode is largely diluted by the residual flue gas introduced in the carbonation mode.

In addition, pure N_2 was used in this work to dilute CO_2 in the calcination mode. In practical operation, however, pure steam is required to dilute CO_2 in the calcination mode because steam is easier to separate than other gases. One concern regarding to the use of steam is that the steam temperature is generally much lower than the operating temperature of the HotPSA, which may result in significant heat loss from solid to gas during calcination. One possible solution is to maximize the relative strength of heat conduction and heat convection by controlling the particle size. Also, the heat loss because of the introduction of low-temperature steam must be compensated from high-temperature feeding gas in the carbonation mode. The high-temperature feeding gas in the carbonation mode can be obtained from pre-combustion systems (~600 °C and 20 bar) and/or post-combustion systems (~800 °C, 1 bar, and flue gas after superheaters). However, the startup of the whole process relies on the heat convective process during the carbonation mode. The minimized heat convection indicates that the startup of the process would be slow. Also, the decrease of particle size would increase the pressure drop through the fixed-bed reactor. Therefore, there is a trade-off when selecting the particle size of the sorbent for the HotPSA process. On the other hand, efforts could be made to increase the temperature of steam as close as possible to the operating temperature of the HotPSA process to minimize energy loss. This could be
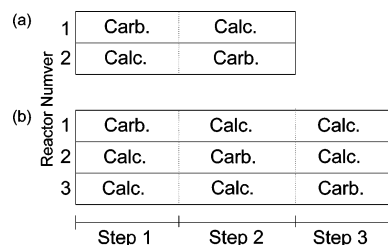

Figure 12. Operational diagram of the HotPSA process for continuous CO_2 capture in cases of (a) 1 min of switching for carbonation and calcination modes and (b) 1 min of switching for the carbonation mode and 2 min of switching for the calcination mode.

achieved by recycling the exiting gases from the carbonation and calcination modes to preheat the low-temperature steam.

Alternatively, the process could operate under sub-atmospheric pressure. In other words, the CO_2 concentration in the calcination mode will be diluted by depressurization. In this way, the energy loss from solid to gas in the calcination mode could be ignored. However, vacuum pressure swing adsorption (VPSA) is much more complicated than a typical PSA process. Future work will investigate the calcination under steam or vacuum to achieve minimal energy loss.

4. CONCLUSION

This work was carried out to experimentally demonstrate the feasibility of the HotPSA process in a fixed-bed reactor. On the basis of the experimental results, the main conclusions can be drawn as follows: (1) The quasi-equilibrium behavior of the synthetic CaO sorbents is clearly dependent upon the sample type, CO_2 partial pressure, and procedure of obtaining data. (2) The activation energy was found to be 148.5−173.68 kJ/mol for the calicnation of the carbonated sorbent and 28.28−43.68 kJ/mol for the carbonation of the calcined sorbent. (3) The operating temperature window for the HotPSA process is 750−840 °C for CO_2 concentrations higher than 15%. (4) The temperature variation in the CaO sorbent particle diminished when the operating temperature was below 770 °C in 20% CO_2 (N_2 balance). (5) Heat transfer in the fixed bed can be minimized by controlling the switching time for the carbonation and calcination modes within 1 and 2 min, respectively. (6) The process could operate stably over 100 cycles at 770 °C at the switching time of 1 min in 20% CO_2 (N_2 balance).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental data of the quasi-equilibrium CO_2 partial pressure of the CaO sorbent and carbonation and calcination profiles of handmade particle and powder of CHC15-PM. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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NOMENCLATURE

A = pre-exponential factor for carbonation/calcination (mol m^{-2} s^{-1})
E = activation energy for carbonation/calcination of CaO sorbents (kJ mol^{-1})
k_d = reaction rate constant of decomposition of $CaCO_3$ (s^{-1})
k_s = reaction rate constant (mol m^{-2} s^{-1})
n = reaction order

P = total pressure in the fluidized bed
P_{CO_2} = CO_2 partial pressure (kPa)
$P_{CO_2}^{eq}$ = equilibrium CO_2 partial pressure (kPa)
r_0 = reaction rate r at time zero (s^{-1})
r = reaction rate in the carbonation/calcination reaction (s^{-1})
R = universal gas constant (8.314 × 10^{-3} kJ mol^{-1} K^{-1})
R' = specific reaction rates of carbonation/calcination (s^{-1})
S = surface area of the solid reactant (m^2 g^{-1})
S_0 = surface area of the solid reactant at time 0 (m^2 g^{-1})
t = time (s)
T = temperature (K)
X = conversion of the solid reactant to the solid product (%)

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