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Calcium Oxide Based Sorbents for Capture of Carbon Dioxide at High Temperatures

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Calcium oxide is a promising sorbent for the capture of carbon dioxide. In this work, CaO sorbents were prepared using different precursors, including $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CaO, $\text{Ca}(\text{OH})_2$, CaCO_3 , and $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Of these, the sorbent prepared from calcium acetate (CaAc_2 –CaO) resulted in the best uptake characteristics for CO_2 . This sorbent had a higher BET surface area and larger pore volume than the other sorbents. According to SEM images, this sorbent exhibits a “fluffy” structure, which probably contributes to its high surface area and large pore volume. This sorbent also showed almost 100% carbonation, at temperatures between 550 and 800 °C. Moreover, the carbonation progressed dominantly during an initial short period. Under numerous carbonation/decarbonation cycles, the CaAc_2 –CaO sorbent demonstrated the best reversibility, even in the presence of 10 vol % water vapor. During a 27-cycle operation, the sorbent maintained fairly high conversion of 62 mol % at 700 °C. Pore size distribution measurements indicate that the pore volume decreased as the experimental cycles continued. Silica was doped on the CaAc_2 –CaO sorbent in various weight percentages, but the resultant sorbents did not exhibit better performance under cyclic operation than those without Si dopant.

1. Introduction

Carbon dioxide is the major contributor of greenhouse gases. To mitigate the greenhouse gas impact, it is critical to sequester CO_2 from fossil-fuel power plants, which account for about one-third of all anthropogenic CO_2 emissions.¹ Yong et al.² and Aaron et al.³ reviewed the separation of CO_2 from flue gas. The reversible carbonation and decarbonation reactions of calcium oxide and CO_2 to produce calcium carbonate provide a viable approach for CO_2 capture and separation from high-temperature gas streams, such as flue gas and gas streams encountered in coal gasification, fuel cell applications, and chemical heat pumps.^{4–6}

Recently, researchers have concentrated techniques for enhancing the uptake capacity and reversibility of CaO sorbent. To apply CaO for thermal energy storage, Aihara et al.⁷ synthesized a reactant of CaO and calcium titanate in a molar ratio of 1:1. The molar conversion of CaO was about 60% after 10 carbonation/decarbonation cycles. Gupta and Fan⁴ managed to achieve high CaO sorbent performance by synthesizing it from precipitated calcium carbonate that was prepared from calcium hydrate. In an effort to develop a hydrogen production process, Japanese researchers enhanced the reactivity and durability of CaO sorbents by an intermediate hydration treatment during multicycle operations. More than 85% carbonation of the sorbents was achieved after seven cyclic operations at 700 °C under partial CO_2 pressures of 6.0 and 9.0 MPa. The sorbents that were not treated by hydration exhibited much lower carbonation conversions.^{8,9} Reddy and Smirniotis⁶ studied the promotion effect of doping alkali metals on CaO sorbents. They observed that the uptake capacity of the sorbents was significantly enhanced when cesium was used as a dopant. Moreover, it was noticed that the sorbents have zero affinity to N_2 and O_2 .

The objective of this research is to develop high-performance sorbents for CO_2 uptake at high temperatures by using various

CaO precursors. The reversibility of the sorbents was tested at suitable reaction conditions. The effect of doping silica on sorbent performance was also studied.

2. Experimental Section

Sorbent Preparation. CaO sorbents were synthesized by calcination of the following precursors: calcium nitrate tetrahydrate (Fisher), calcium oxide (Aldrich), calcium hydroxide (Fisher), calcium carbonate (Fisher), and calcium acetate monohydrate (Fisher). Each precursor was heated from 50 to 750 °C at a ramp rate of 10 °C/min and kept at 750 °C for 30 min to attain full calcination of precursor to CaO. During the entire calcination progress, the sample was kept under helium atmosphere. In this work, CaO sorbents loaded with various weight percentages of silica were synthesized as follows: In a typical synthesis, calcium acetate precursor corresponding to 1 g of CaO was added to a 100-mL beaker containing 80 mL of DI water. After the calcium acetate was completely dissolved under continuous stirring at 70 °C, the appropriate amount of silica (based on silica and CaO only) to result in doping levels ranging from 10 to 50 wt % was then added into the calcium acetate solution. The mixture was then kept under vigorous stirring at 70 °C until the slurry evaporated to dryness. The product was then ground to fine powder and calcined to SiO_2 /CaO with the same calcination procedure as that described previously.

Characterizations. X-ray diffraction (XRD) measurements were employed for the identification of phases of the synthesized CaO sorbents. The XRD analyses were conducted on a Siemens D500 powder X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source (wavelength = 1.5406 Å). An aluminum holder was used to support the samples in the XRD measurements.

BET surface area and pore size distribution measurements were performed using nitrogen adsorption and desorption isotherms at –196 °C on a Micromeritics ASAP 2010 volumetric adsorption analyzer. The CaO sorbents were degassed at 300 °C for at least 3 h in the degassing port of the apparatus before the actual measurements. The adsorption isotherms of nitrogen for BET measurements were collected at –196 °C by

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using six values of pressure ranging from about 30 to 186 mmHg. The pore size distribution measurements were obtained using the BJH method.

Particle size distribution measurements of the sorbent material were performed with a laser scattering particle distribution analyzer (Malvern Mastersizer S series) and a Malvern dispersion unit controller.

Scanning electron microscopy (SEM) measurements were performed on selected sorbents to obtain information on morphology using a Hitachi S-4000 field-emission scanning electron microscope. The samples were prepared by placing CaO sorbents on double-sided carbon tape mounted on the sample holder.

Carbonation–Decarbonation. Carbonation/decarbonation experiments were conducted with a Perkin-Elmer Pyris-1 thermogravimetric analyzer (TGA), a Perkin-Elmer thermal analysis gas station (TFGS), and Pyris v3.8 software from Perkin-Elmer. The microbalance of the Pyris-1 TGA operates as a high-gain electromechanical servo system that permits detection of changes in weight as small as $0.1\ \mu\text{g}$ as a function of time. To maintain the TGA balance accuracy, a helium flow (prepurified, Wright Bros, Inc.) of 45 mL/min was used as the balance purge gas to flow over the sample. The TFGS has four gas channels and can automatically switch on any of them to introduce gas over the sample according to the reaction program. The shifts between CO_2 and sheath helium together with their flows were accurately maintained by the TFGS and the reaction program.

All steps of the carbonation and decarbonation experiments, including heating the sample, cooling the sample, and shifting gases between CO_2 (99.5%, Wright Bros, Inc.) and helium were programmable and were operated batchwise. A suitable amount of sorbent was placed in a platinum sample pan and heated to the carbonation temperature at a ramp rate of $10\ ^\circ\text{C}/\text{min}$. Once the sample had reached the carbonation temperature, the program was automatically switched to the carbonation process. One minute after the carbonation progress had begun, a 20 mL/min flow of the reactant gas CO_2 was automatically switched into the system to replace the 20 mL/min flow of sheath helium. When the carbonation process had completed, the temperature was increased at a ramp rate of $10\ ^\circ\text{C}/\text{min}$ or decreased at $15\ ^\circ\text{C}/\text{min}$ to the programmed decarbonation temperature. One minute after the carbonation progress had completed, the 20 mL/min flow of CO_2 was replaced by a 20 mL/min flow of helium. When the decarbonation process had finished, the temperature was increased at a ramp rate of $10\ ^\circ\text{C}/\text{min}$ or decreased at $15\ ^\circ\text{C}/\text{min}$ to the carbonation temperature. A new carbonation/decarbonation cycle began when the temperature was achieved. In this work, the typical carbonation time was set at 300 min to achieve a relatively high uptake capacity of CO_2 , and the decarbonation time was set at 30 min to allow the sorbent to be decarbonated completely. The decarbonation time was intentionally kept this short to prevent possible sintering of the sorbents. During the entire process, the sorbent weight and the temperature were continuously recorded.

3. Results and Discussion

CaO sorbents were prepared by calcination using various commercially available precursors, namely, calcium acetate monohydrate, calcium carbonate, calcium hydroxide, CaO, and calcium nitrate tetrahydrate. For simplicity, they are denoted as $\text{CaAc}_2\text{-CaO}$, $\text{CaCO}_3\text{-CaO}$, $\text{Ca(OH)}_2\text{-CaO}$, CaO-CaO , and $\text{Ca(NO}_3)_2\text{-CaO}$, respectively. XRD patterns of these sorbents show that they have the same peaks locating at 2θ values of

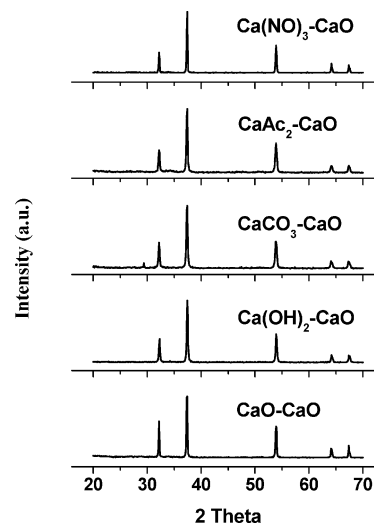


Figure 1. XRD patterns of CaO sorbents prepared from different precursors: $\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{CaAc}_2\cdot \text{H}_2\text{O}$, CaCO_3 , Ca(OH)_2 , and Aldrich CaO.

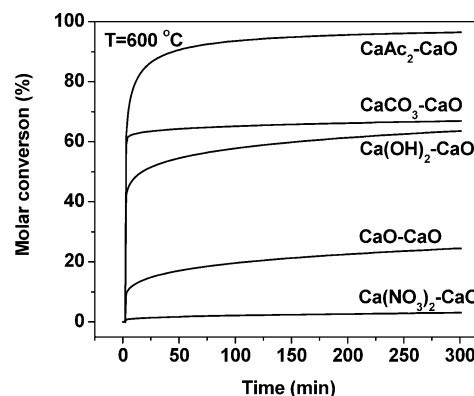
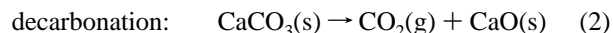
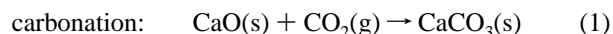


Figure 2. Uptake of CO_2 over CaO sorbents made with various precursors. Conditions: carbonation temperature, $600\ ^\circ\text{C}$; CO_2 concentration, 30 vol %; balance helium.

32.4° , 37.6° , and 54.2° (Figure 1), which are characteristic values of CaO. These indicate that the chemical compositions and crystalline phases of all of these CaO sorbents prepared from different precursors are similar. Therefore, these properties should not be the cause for any differences in carbonation and decarbonation behaviors, as discussed later.

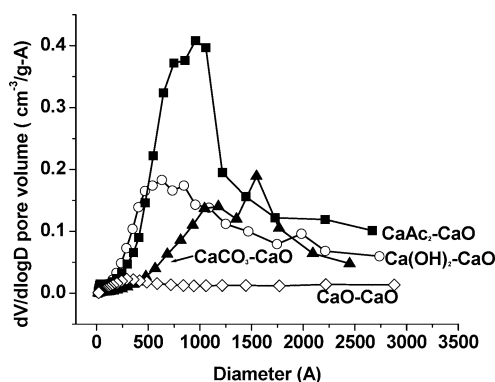
Results of 5-h carbonation reactions over these sorbents at $600\ ^\circ\text{C}$ are presented in Figure 2. The carbonation and decarbonation processes are described by the following reactions



To compare the performances of all CaO sorbents, carbonation experiments were performed at $600\ ^\circ\text{C}$ under a CO_2 partial pressure of 0.3 bar. For all five sorbents, a monotonic increase in sorbent conversion was observed (Figure 2). With the exception of $\text{Ca(NO}_3)_2\text{-CaO}$, all of the other sorbents exhibited high carbonation rates during the initial stage that were followed by an abrupt shift to a relative lower rate. During the 5-h carbonation process at $600\ ^\circ\text{C}$, $\text{Ca(NO}_3)_2\text{-CaO}$ was carbonated only about 2.5% by CO_2 . Under the same carbonation conditions, CaO-CaO was carbonated about 25%; $\text{Ca(OH)}_2\text{-CaO}$, 63%; $\text{CaCO}_3\text{-CaO}$, 66%; and $\text{CaAc}_2\text{-CaO}$, 97%, or nearly 100% conversion. The $\text{Ca(NO}_3)_2\text{-CaO}$ sorbent exhibited a low

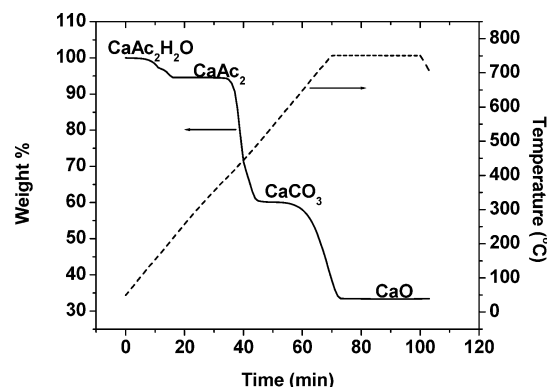
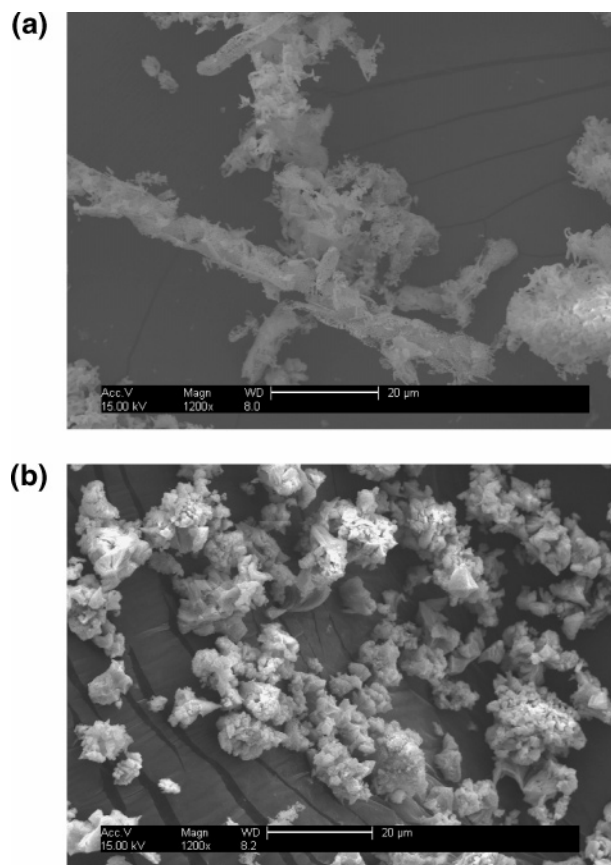
Table 1. Morphological Properties of Various Sorbents before and after Carbonation/Decarbonation Cycles at 700 °C

sorbent	number of cycles	BET surface area (m ² /g)	pore volume (cm ³ /g)
Ca(NO ₃) ₂ -CaO		n/a ^a	n/a ^a
CaO-CaO		4.2	0.02
Ca(OH) ₂ -CaO		13.9	0.15
CaCO ₃ -CaO		5.3	0.08
CaAc ₂ ·H ₂ O-CaO		20.2	0.23
CaAc ₂ ·H ₂ O-CaO	1	18.7	0.19
CaAc ₂ ·H ₂ O-CaO	2	19.0	0.19
CaAc ₂ ·H ₂ O-CaO	4	18.3	0.19
CaAc ₂ ·H ₂ O-CaO	8	14.9	0.14

^a n/a = not available.**Figure 3.** Pore size distributions of CaO sorbents prepared from CaAc₂·H₂O, CaCO₃, Ca(OH)₂, and Aldrich CaO.

uptake capacity of CO₂, or its carbonation reaction rate was extremely low under the experimental conditions. The reason for this difference is that Ca(NO₃)₂-CaO had a significantly lower BET surface area than the other sorbents. For Ca(NO₃)₂-CaO, the BET surface area was so small that could not even be obtained under our measurement conditions (Table 1). We observed that the precursor Ca(NO₃)₂·4H₂O melted and formed solid oxide upon calcination. However, the other precursors still existed as fine powders during and after the calcination process. The cause for the complete melting and sintering of Ca(NO₃)₂-CaO is that calcium nitrate tetrahydrate has a low melting temperature of about 45 °C. During calcination, the precursor melted at the very early stages and finally formed a solid solution instead of a powder. This phenomenon prevents the possible formation of pores when the precursor progressed to CaO. For CaO-CaO, the material still existed as a fine powder after calcination, which justifies its higher capacity for carbonation by CO₂ than Ca(NO₃)₂-CaO. However, CaO-CaO does not contain many pores, and its BET surface area is fairly small (4.2 m²/g), so its capacity was constrained to a low value (25%). For Ca(OH)₂ and CaCO₃, porosity was formed when the precursors decomposed by releasing H₂O or CO₂ (Table 1 and Figure 3) during calcination. Therefore, Ca(OH)₂-CaO and CaCO₃-CaO had better uptake capacities than Ca(NO₃)₂-CaO and CaO-CaO. For CaAc₂·H₂O, the dissociated water evaporated before the precursor dissolved. When this organometallic compound decomposed to CaO through multiple steps during calcination, a large volume of pores was formed.

The TGA curves of weight and temperature versus time in Figure 4 depict the decomposition process of CaAc₂·H₂O to CaO. The various weight plateaus correspond to the different decomposition steps, in order, of desorption of physically adsorbed gases and water, dehydration to calcium acetate, decomposition to calcium carbonate at above 400 °C, and subsequent decomposition to CaO at above 600 °C. This

**Figure 4.** Percent weight change of CaAc₂·H₂O during calcination. Conditions: temperature ramp, 10 °C/min; atmosphere, helium.**Figure 5.** SEM images of (a) CaAc₂-CaO and (b) Ca(OH)₂-CaO.

multistep decomposition ended in the formation of meso- and macropore structures (Figure 3). Structural differences among the sorbents are clearly illustrated by the SEM images in Figure 5. CaAc₂-CaO exhibits a porous, "fluffy" structure, whereas the Ca(OH)₂-CaO particles look more compact and solid. These SEM images revealed that, as expected, the different pore volumes and BET surface areas of the sorbents are based on their different structures, which finally determined their carbonation performances. During carbonation, CO₂ diffused more easily through the fluffy structure than through a solid layer to reach the unreacted CaO. Because these sorbents [except for Ca(NO₃)₃-CaO] have similar particle size ranges (Figure 6), it is reasonable to propose that the different carbonation performances were induced by their different pore structures and BET surface areas rather than by particle size. At 600 °C, CaAc₂-CaO exhibited about 97% conversion, the best performance among the five precursors under investigation in this research,

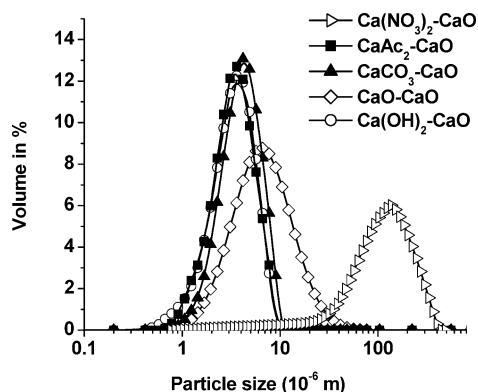


Figure 6. Particle size distributions of CaO sorbents prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CaAc}_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, CaCO_3 , and Aldrich CaO.

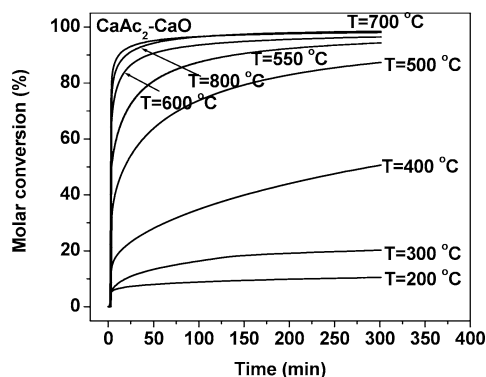


Figure 7. Effect of temperature on carbonation of $\text{CaAc}_2\text{-CaO}$. Conditions: carbonation temperatures, 200, 300, 400, 500, 550, 600, 700, and 800 °C; CO_2 concentration, 30 vol %; balance helium.

during the 5-h carbonation process of CO_2 . This high performance can be ascribed to its large surface area and pore volume. To appreciate its performance, one should note that 97% is a significantly high uptake of about 76 wt % CO_2 per unit mass sorbent.

Except for $\text{Ca}(\text{NO}_3)_2\text{-CaO}$, which began the carbonation at a relatively low rate in the initial stage, the other sorbents began with a rapid reaction that was followed abruptly by a much slower one. During the slow reaction regime, the reaction rate decreased because CO_2 had to diffuse through the formed CaCO_3 layer to reach the unreacted CaO. It is suggested that the shift of the reaction mechanism happened when the surface of sorbent was covered and small pores were blocked by the formation of a nonporous carbonate product layer. This layer significantly hinders the inward diffusion of CO_2 . According to our results, the ratio between the carbonation rate of the fast reaction regime and that of the slow regime is as much as 2 orders of magnitude. Hyatt et al.¹⁰ and Barker et al.¹¹ have also reported the limitation of CO_2 diffusion through carbonated sorbent surfaces.

Because $\text{CaAc}_2\text{-CaO}$ exhibited the best performance for the capture of CO_2 among the sorbents studied, we selected it to examine the effect of temperature on carbonation behavior. A set of experiments was conducted at temperatures ranging from 200 to 800 °C (Figure 7). During the carbonation reactions, the CO_2 partial pressure was fixed at 0.3 bar (30 kPa). This pressure is as about 1.4 and 10 times high as the CO_2 equilibrium pressure of the carbonation/decarbonation reaction at 800 °C (22 kPa) and 700 °C (3 kPa), respectively. It is far greater than the equilibrium pressures at temperatures lower than 700 °C. Thus, the reversible reactions will proceed with carbonation if enough time is given to allow the CO_2 diffused through the

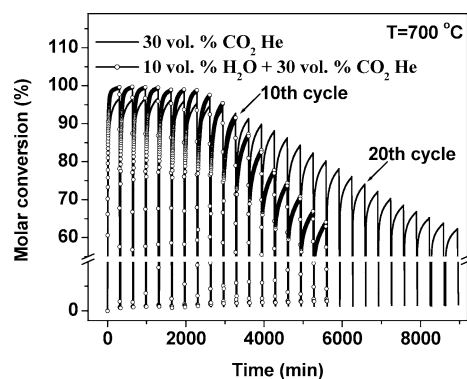


Figure 8. Extended carbonation/decarbonation cycles over $\text{CaAc}_2\text{-CaO}$ (27 cycles without water and 17 cycles with water). Conditions: carbonation and de carbonation temperature, 700 °C; gas concentrations: (a) 30 vol % CO_2 , balance helium; (b) 10 vol % H_2O + 30 vol % CO_2 , balance helium.

solid CaCO_3 layer to reach unreacted CaO, until 100% CaO conversion is achieved. Therefore, the difference among the CaO conversions at different temperatures was caused by kinetics rather than thermodynamics. When the temperatures were equal to or less than 300 °C, the reaction rates were fairly low. These low rates indicate that the reactions are kinetically controlled at low temperatures. When the carbonation was conducted at 400 or 500 °C, the carbonation curves smoothly shifted from the first regime to the second regime. This suggests that the reaction mechanism was transferring from kinetic control to diffusion control or that the reaction was being controlled by both mass diffusion and kinetics. When the carbonation temperatures were between 550 and 800 °C, conversions increased to more than 94% after 5 h of carbonation. These observations indicate that the range of 550–800 °C is a suitably wide operating window for the carbonation of CO_2 over $\text{CaAc}_2\text{-CaO}$. Within this window of operating temperatures, the carbonation capacities of the $\text{CaAc}_2\text{-CaO}$ are quite large compared to those at lower temperatures. It is observed that the curves evolved into a plateau stage shortly after the carbonation began. More than 90% of this carbonation occurred within the first 10 min of the fast reaction period (Figure 7). The fast carbonation should be ascribed to the large BET surface area and pore volume of $\text{CaAc}_2\text{-CaO}$. This high rate offers a great opportunity for CaO in industrial applications. During the initial stage, the diffusion resistance obviously did not limit the reaction rate much because a large area of sorbent was under exposure to the gas phase.

Good reversibility is a must for sorbent applications. $\text{CaAc}_2\text{-CaO}$ was chosen to test sorbent durability, and 700 °C was selected as the operating temperature for both carbonation and decarbonation. At 700 °C, both reactions proceeded quickly. By using the same temperature for carbonation and decarbonation, repetitive heating and cooling of the sorbent between cyclic operations was avoided. The precursor of calcium acetate monohydrate was calcined for 3 h at 700 °C under oxygen to obtain better sorbent reversibility, although its carbonation capacity was slightly reduced in the first cycles. Figure 8 shows that the carbonation conversion of the $\text{CaAc}_2\text{-CaO}$ sorbent remained stable, even with 10 vol % water (vapor) present in the feed gas, at 93% after 10 cycles at 700 °C. When the process reached the 10th cycle, the CO_2 uptake capacity began to decrease slowly in the subsequent cycles. However, after 27 cycles, the sorbent still maintained a relatively high conversion (about 62%). The high conversion was ascribed to the sorbent's fluffy structure, large BET surface area, and large pore volume. The decreasing of the conversion through reaction cycles was

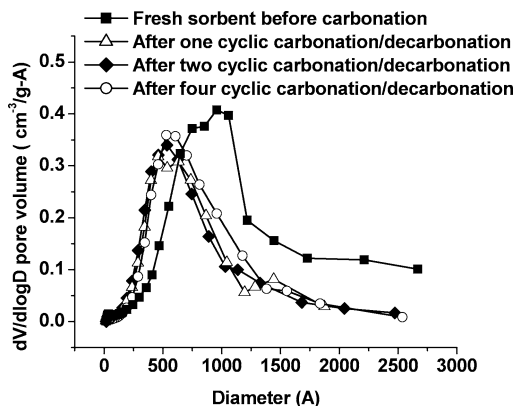


Figure 9. Pore size distribution of $\text{CaAc}_2\text{-CaO}$ sorbent after carbonation/decarbonation at 700 °C.

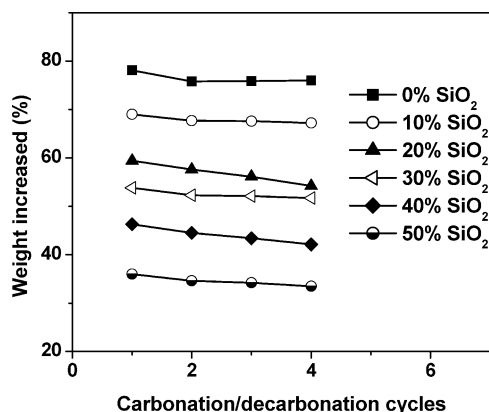


Figure 10. Maximum carbonation values over $\text{CaAc}_2\text{-CaO}$ sorbents doped with 0 to 50 wt % SiO_2 . Conditions: carbonation and decarbonation temperature, 700 °C; CO_2 concentration, 30 vol %; balance helium.

caused by pore blockage and collapse, which induced greater CO_2 diffusion resistance because of the lower surface area and smaller pores. The results in Table 1 and Figure 9 show the evolution of the BET surface area and pore volume with the progression of carbonation/decarbonation cycles. When the number of reaction cycles increased, the BET surface area and pore volume of the sorbent decreased. When water vapor was present in the system, the uptake capacity decreased faster than in the case without vapor. This is probably due to the water “helping” the collapse of pore structure or longer durations at higher temperature inducing damage to the fluffy nature of the sorbent.

Sintering results in a lower surface area and decreases the uptake capacity of the sorbent. However, it is significant only when the operating temperature is above the Tammann temperature, which is estimated as 0.52 times the sorbent melting point temperature (K). “Refractory” dopants are expected to prevent sorbent sintering.⁷ For CaO , SiO_2 , and CaCO_3 , the melting temperatures are 3171, 3223, and 1603 K, respectively. Therefore, their Tammann temperatures correspond to 1649, 1676, and 834 K. Thus, sintering of the former two compounds will not occur at 973 K (700 °C), whereas that of the latter will.

CaO sorbents with five different weight percentages of SiO_2 , namely, 10, 20, 30, 40, and 50 wt % (based on CaO and SiO_2 only), were studied in this work. Figure 10 gives the maximum weight gained by the $\text{CaAc}_2\text{-CaO}$ and $\text{SiO}_2\text{-CaAc}_2\text{-CaO}$ sorbents in cyclic carbonation/decarbonation processes at 700 °C. The maximum weight gained by per unit mass sorbent decreases (from 80% to below 40%) as the weight of dopant is

increased. The reason for this is that the silica contributes to sorbent weight but the CO_2 amount captured by it is negligible (results not shown). Durability performances of the $\text{SiO}_2\text{-CaAc}_2\text{-CaO}$ sorbent were not better than those of the $\text{CaAc}_2\text{-CaO}$ sorbent (Figure 10). Hence, the presence of refractory silica, which is considered to reduce the effect of sintering and enhance durability, did not materially promote the overall performance of the undoped CaO . Thus, we propose that sintering effects should not be the main factor in the decreasing carbonation performance. The dominant factor causing the deterioration of carbonation should be the closure of pores and decrease of surface area during the repetitive carbonation and decarbonation cycles. Therefore, although SiO_2 might effectively prevent CaCO_3 from sintering, it has a limited impact on the overall sorbent reversibility performance.

4. Conclusions

In this work, five precursors were used to synthesize CaO sorbents for CO_2 uptake. The CaO sorbent prepared from calcium acetate monohydrate was identified as the best candidate for the capture of CO_2 . In a wide operating window of 550–800 °C, this sorbent achieved high carbonation of more than 94 mol %. When the carbonation temperature was 700 °C, about 90% of the sorbent carbonated with CO_2 within the first 10 min. $\text{CaAc}_2\text{-CaO}$ also showed a capability of maintaining its reversibility over multiple carbonation/decarbonation cycles, even in the presence of 10 vol % water vapor. In a 27-cycle carbonation/decarbonation experiment, in which the carbonations were conducted under 0.3 bar CO_2 (balanced in helium) and at 700 °C and the decarbonations were conducted under helium and at 700 °C, the sorbent maintained a fairly high conversion of 62%. Both rapid and high uptake capacities of CO_2 , together with the good regenerability observed over these sorbents, were ascribed to their large BET surface areas and meso- and macroporous structures. Such a structure was brought about in the progress of precursor decomposition during calcination. When refractory silica was doped on these sorbents, it did not noticeably enhance their durabilities. This indicates that the main factor in the decaying carbonation performance of these sorbents in multiple carbonation/decarbonation cycles is the blockage and collapse of the pore structure rather than sorbent sintering effects.

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