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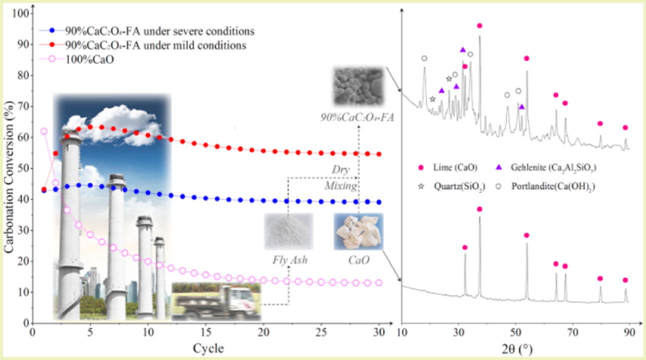
Performance of Coal Fly Ash Stabilized, CaO-based Sorbents under Different Carbonation–Calcination Conditions

Feng Yan,[†] Jianguo Jiang,*[,†,‡,§] Kaimin Li,[†] Sicong Tian,[†] Ming Zhao,[†] and Xuejing Chen[†]

[†]School of Environment, Tsinghua University, Beijing 100084, China
[‡]Key Laboratory for Solid Waste Management and Environment Safety, Ministry of Education, Beijing 100084, China
[§]Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing 100084, China

Supporting Information



ABSTRACT: The rapid deactivation of CaO sorbents due to sintering currently presents a major barrier to calcium looping for CO_2 capture. In this work, we report an easy method for synthesizing highly stable CaO-based sorbents through mechanical mixing of a calcium precursor and coal fly ash (solid waste from coal-fired plants). To investigate the stable performance of as-synthesized sorbents, the effects of calcium precursors and carbonation–calcination conditions were studied and discussed. The synthetic sorbent derived from calcium oxalate (90%CaC_2O_4-FA-2h) showed the best performance and demonstrated a CO_2 uptake of 0.38 g(CO_2) g(CaO)$^{-1}$ after 30 cycles. Even under the most severe calcination condition (at 920 °C in pure CO_2), this sorbent maintained a stable capture capacity, with a final CO_2 uptake of 0.27 g(CO_2) g(CaO)$^{-1}$ and an average decay rate of only 0.29% per cycle. Characterization of the sorbents confirmed that the formation of dispersed inert phase (gehlenite, $Ca_2Al_2SiO_7$) was responsible for this high cyclic CO_2 uptake and strong sintering resistance. This strategy significantly enhances the high temperature stability of CaO-based sorbents through in situ reuse of coal fly ash, and is thus an effective approach to CO_2 capture from the large point source.

KEYWORDS: *CO_2 capture, Calcium looping, Coal fly ash, Calcium precursor, Sintering resistance*

INTRODUCTION

CO_2 capture and storage (CCS) has been identified as a promising midterm strategy for mitigation of the continuous increase in atmospheric CO_2 concentrations,[1] which contributes significantly to global warming and climate change.[2] Generally, the process of CO_2 capture accounts for 50%–80% of the total cost in CCS,[3] thus it is necessary to develop applicable CO_2 capture methods from both technical and economic points of view. Currently, amine scrubbing is a classical CO_2 capture technology and has been used in some demonstration projects; however, this method presents some intrinsic problems: the corrosive nature of the solvents, relatively high costs, and severe efficiency penalty.[4] Comparatively, the calcium looping, based on carbonation–calcination cycles of CaO-based sorbents,[5] exhibits a number of advantages for its high theoretical capacity of 0.78 g(CO_2) g(CaO)$^{-1}$ and low costs of CO_2 avoided (estimated at $29 t$CO_2$$^{-1}$).[6] Additionally, it has wide applicability to energy storage systems through chemical heat pumps[7] and enhanced hydrogen production through steam methane reforming.[8]

The sorption capacity of natural CaO, derived from limestone or dolomite, usually reduces rapidly to 10% of its theoretical capacity after multiple cycles,[9] however, which limits the commercial application of CaO-based sorbents.[10] Hence, efforts have been made to reduce reactivity decay rates through pretreatments, such as hydration,[11] thermal treatment,[12] surfactant assisted,[13] ethanol/water modification,[14] or acetic acid modification.[15] Because unsupported CaO structures are unstable, a similar decay with limestone is observed for pure CaO derived from other calcium precursors,[16] especially under realistic calcination conditions (temperature > 900 °C and pure CO_2 atmosphere).[17] Another promising strategy is dispersion of CaO into inert materials with high Tammann temperature (T_T), such as Al_2O_3,[18−20] MgO,[21] SiO_2,[22,23] ZrO_2,[24] and $MnCO_3$.[25] Although wet-process methods, including carbon templating,[18] coprecipitation,[19,21] sol–gel,[26] ultrasonic spray pyrolysis,[27] and wet mixing,[28] can uniformly disperse the inert materials and effectively minimize sintering of CaO-based sorbents, simple synthesis techniques and the use of inexpensive raw materials remain a research hotspot.

Solid waste rich in Al_2O_3 and SiO_2 is a cheap and abundant resource that may mitigate sintering, and is thus an attractive

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alternative inert material. Wet mixing in distilled water or acetic acid is usually used to synthesize CaO-based sorbents, which are then stabilized by kaolin,[29,30] rice husk ash,[31] bentonite,[32] attapulgite,[33] and cement,[28,34,35] and a better cyclic capture capacity is achieved with these stabilizers (Table 2). Nevertheless, dry-process methods incorporating a direct solid-state mixing or reaction appears to be more convenient and energy-efficient. Li et al.[36] synthesized MgO-stabilized, CaO-based sorbents through overnight ball-milling of calcium acetate and magnesium oxalate, with a capture capacity enhanced from 0.27 to 0.53 g(CO_2) g(sorbent)$^{-1}$ after 50 cycles (calcination at 758 °C in He atmosphere). Quantities of coal fly ash (FA) generated in Chinese coal-fired power plants reached 532 million tons in 2013, yet a substantial amount of ash is still disposed of in landfills or as road sub-base, and contributes to a serious environmental problem.[37] However, SiO_2 and Al_2O_3 are the main components of coal fly ash, generally accounting for more than 70 wt %,[38] and the main phase composition of quartz and mullite (Figure S1) is thermostable,[39] making it an ideal source of inert material.

In this work, coal fly ash was introduced into CaO-based sorbents through dry mixing followed by calcination, to enhance the sintering resistance. Cyclic carbonation−calcination tests were performed to investigate the effect of coal fly ash and calcium precursor on cyclic CO_2 sorption performance of the synthetic CaO-based sorbents. Subsequently, the sorbent with the best stability was chosen to evaluate the influence of carbonation−calcination conditions on CO_2 capture characteristics, including the CO_2 partial pressure, carbonation temperature and calcination temperature. These investigations helped us to identify the major influence of operational conditions and compare the results with previously reported CaO-based sorbents. Because power plants are one of the main anthropogenic sources of CO_2 emission (accounting for ∼40%),[40] highly effective sorbents based on local resources could both enhance the utilization of coal fly ash and realize CO_2 capture at the large point source.

EXPERIMENTAL SECTION

Sorbent Preparation. Coal fly ash sampled from a coal-fired power plant (Hebei, China) was first calcined for 2 h at 950 °C in air, then ground and sieved to obtain the particle size of less than 74 μm (FA-2h). The chemical composition of "FA-2h" and the synthetic CaO-based sorbents were determined using X-ray fluorescence analysis (XRF, Shimadzu XRF-1800, Japan, Table S1). Five common calcium precursors were used to find the most suitable, including calcium oxide (CaO, 98 wt %, Sinopharm China), calcium hydroxide ($Ca(OH)_2$, 95 wt %, Sinopharm China), calcium carbonate ($CaCO_3$, 99 wt %, Sinopharm China), calcium acetate monohydrate ($CaAc_2\cdot H_2O$, 98 wt %, Sinopharm China), and calcium oxalate monohydrate ($CaC_2O_4\cdot H_2O$, 99 wt %, Sinopharm China). Each calcium precursor was physically dry-mixed with "FA-2h" in an agate mortar for 10 min, and the mixture was then thermally treated for 2 h at 950 °C in air to obtain CaO-based, fly ash-stabilized sorbents. All sorbent samples were designated by their synthesis conditions, e.g., "90%CaC_2O_4-FA-2h" for 90 wt % of CaO in the sorbents, calcium precursor of $CaC_2O_4\cdot H_2O$ and 2 h of thermal treatment.

Sorbent Testing. The cyclic CO_2 capture capacity of the sorbents (8−10 mg) was investigated using a thermal gravimetric analyzer (TGA, Mettler-Toledo, TGA/DSC 2, Switzerland) with a high-sensitivity balance (<0.1 μg). The reaction conditions, including the temperature, time, and gas flow, were automatically controlled by the Mettler STARe software (version 13.0). First, the temperature of the TGA was raised to the carbonation temperature (600, 650, 700, 750, or 800 °C) at a rate of 30 °C min^{-1} under a N_2 flow of 60 mL min^{-1}. Once the carbonation temperature was reached, the sorbent was subjected to a 100 vol % CO_2 flow of 60 mL min^{-1} and maintained at the temperature for 25 min. The temperature was then increased to 920 °C at a rate of 60 °C min^{-1} and calcination was performed at 920 °C for 5 min under the same atmosphere as carbonation. Subsequently, a new cycle started by reducing the temperature at a rate of −60 °C min^{-1} to the carbonation temperature. Additionally, a constant N_2 flow of 20 mL min^{-1} was used as a protective flow over the microbalance. The cyclic CO_2 uptake (X, g(CO_2) g(sorbent)$^{-1}$) was calculated on the basis of continuous mass change, assuming that mass change was caused only by the formation and decomposition of calcium carbonate.

To investigate the influence of carbonation−calcination conditions on CO_2 capture characteristics, the TGA protocol was changed as follows. A small amount (8−10 mg) of "90%CaC_2O_4-FA-2h" was placed in a 150 μL alumina pan and heated to the carbonation temperature (700 or 750 °C) at a rate of 30 °C min^{-1} under a N_2 flow of 60 mL min^{-1}. After the carbonation temperature was reached, the atmosphere was switched to either 15 vol % or 100 vol % CO_2 flow of 60 mL min^{-1} and the temperature was maintained for 25 min. Calcination was then performed at either 750 or 900 °C for 5 min under a N_2 flow of 60 mL min^{-1}. After calcination, a new cycle was again started by reverting to the carbonation temperature and switching to the carbonation atmosphere. Besides, a set of one-cycle experiments was designed to investigate the CO_2 uptake potential under different carbonation conditions. The carbonation was performed at 700, 750, or 800 °C under either 15 vol % or 100 vol % CO_2 flow of 60 mL min^{-1} for 120 min, and then the calcination was performed at 900 °C for 5 min under a N_2 flow of 60 mL min^{-1}.

N_2 physisorption isotherms of the sorbents at 77 K were collected using a gas adsorption analyzer (Micrometrics Instrument ASAP2020 HD88, America); specific surface area was calculated using the Brunauer−Emmett−Teller (BET) method, and the pore size distribution was derived from the desorption branch of the N_2 isotherm using the Barrett−Joyner−Halenda (BJH) method. Phase composition of the sorbents was analyzed using high-resolution X-ray diffractometry (XRD, Siemens D8 Advance, Germany) using Cu Kα radiation (λ = 0.15 nm) in a 2θ range of 10−90° (scanning rate 2°/min). The surface morphology of the sorbents was observed using a scanning electron microscopy (SEM, Zeiss Merlin Compact, Germany) with a 5 kV electron beam.

RESULTS AND DISCUSSION

Effect of Coal Fly Ash Addition. Figure 1 shows the CO_2 uptake of synthetic sorbents prepared with different FA/CaO

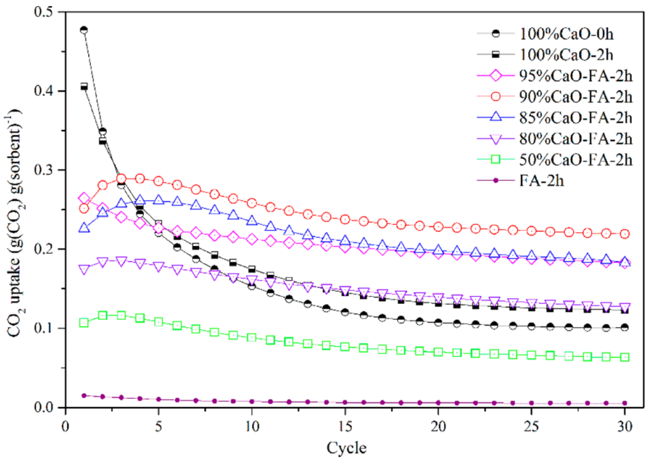

Figure 1. CO_2 uptake as a function of cycle for sorbents prepared with the indicated FA/CaO ratios. Conditions: carbonation in 100 vol % CO_2 at 750 °C for 25 min and calcination in 100 vol % CO_2 at 920 °C for 5 min.

ratios, as a function of cycle number. Unsurprisingly, the conventional CaO (100%CaO-0h) exhibited the highest initial CO_2 uptake of 0.48 g(CO_2) g(sorbent)$^{-1}$ and rapidly lost 79% of capture capacity after 30 cycles, in agreement with previous studies.[41] The capture capacity of "FA-2h" was negligible (<0.01 g(CO_2) g(sorbent)$^{-1}$) during the cyclic carbonation–calcination, indicating that "FA-2h" contained little active CaO; the XRD pattern of "FA-2h" (Figure S1) supported this conclusion. Considering the synthetic sorbents, the material with a FA/CaO mass ratio of 10:90 possessed a CO_2 uptake of 0.25 g(CO_2) g(sorbent)$^{-1}$ in the first cycle, a value markedly lower than that of conventional CaO. However, the CO_2 capture capacity of "90%CaO-FA-2h" interestingly increased to 0.29 g(CO_2) g(sorbent)$^{-1}$ after 5 cycles, and then stabilized at 0.22 g(CO_2) g(sorbent)$^{-1}$ after 30 cycles, a marked increase of 117% compared to "100%CaO-0h".

The sintering resistance of synthetic sorbents could be attributed to the 2 h thermal pretreatment and effective separation of CaO particles by the inert material. According to the study by Manovic et al.,[12] CaO-based sorbents that have undergone thermal pretreatment (800–1300 °C) exhibit a lower initial capture capacity due to a decrease in pore surface area, but perform better in a longer series of cycles. The favorable influence of thermal pretreatment (see the cyclic capture capacity difference between "100%CaO-0h" and "100% CaO-2h") was explained using the pore-skeleton model,[12] which suggested that changes in the pore-skeleton; i.e., the formation of inward (hard) skeletal, protected the particle morphology and enhanced the long-term capture capacity. The inert material was confirmed to be gehlenite ($Ca_2Al_2SiO_7$) from XRD diffraction peaks (Figure 2) at 2θ = 29.15, 31.43, and 52.12° for (2 0 1), (2 1 1), and (3 1 2) reflections, respectively (JCPDS 89-6887).[42] Gehlenite, with a comparatively high melting point (1593 °C, Table S2), generally exhibits good thermal durability,[43] and thus act as a physical barrier to prevent sintering and aggregation of $CaCO_3$ nanoparticles during calcination. Therefore, the high CO_2 capture capacity of the synthetic sorbent was maintained over multiple carbonation–calcination cycles.

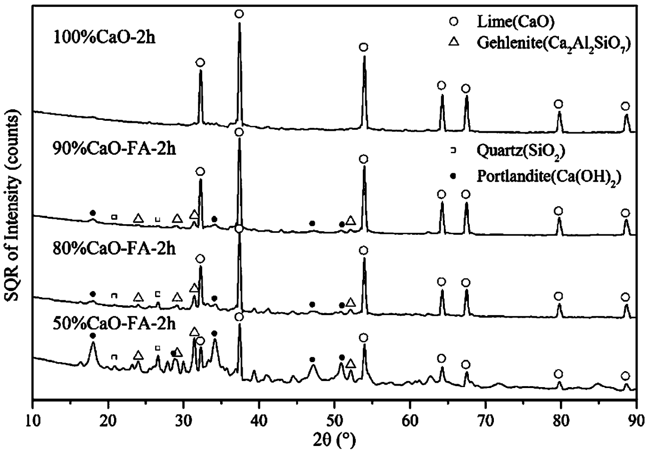

Figure 2. XRD patterns of sorbents prepared with the indicated FA/CaO ratios.

Moreover, evidence suggests that there is also an optimal FA/CaO ratio for the sorbent, below which the sorbent loses its sintering resistance[44] and above which the sorbent sacrifices its active CaO component.[45] When the mass ratio of FA/CaO was decreased to 5:95, "95%CaO-FA-2h" possessed a slightly higher initial CO_2 uptake of 0.26 g(CO_2) g(sorbent)$^{-1}$ but a more rapid decay of 30.79% after 30 cycles, implying that the coal fly ash had a limited stabilizing effect. When FA/CaO was increased to 15:85, 20:80, and 50:50, the synthetic sorbents exhibited lower capture capacity during cyclic carbonation–calcination due to (i) lower proportions of active CaO in the initial mixture and (ii) higher consumption of active CaO into gehlenite formation. The XRD patterns (Figure 2) further confirmed that the intensity of CaO reflections (JCPDS 37-1497, 2θ = 32.20, 37.35, and 53.85° for the (111), (200), and (220) reflections) decreased and the intensity of gehlenite reflections increased with increasing proportions of coal fly ash, although it is still difficult to accurately calculate the amount of active CaO that involved in carbon capture, because we cannot account for the exact amount of CaO reacted to form gehlenite. Besides, "90%CaO-FA-2h" did not show a notable formation of gehlenite over the cycles (Figure S3), thus it would not sacrifice too much active CaO to form stabilizer. Considering the cyclic CO_2 uptakes, the optimal FA/CaO ratio (between 15:85 and 10:90) is almost consistent with the theoretical value predicted by the three-dimensional percolation theory.[46]

Effect of Calcium Precursor. Figure S4a shows the first carbonation–calcination cycle curves of synthetic sorbents prepared from the 5 calcium precursors. The initial CO_2 uptake of synthetic sorbents was ranked as follows: "90%$CaAc_2$-FA-2h" > "90%$CaCO_3$-FA-2h" > "90%$Ca(OH)_2$-FA-2h" > "90% CaC_2O_4-FA-2h" > "90%CaO-FA-2h", which was in accordance with the previous study (summarized in Table S3), despite the addition of coal fly ash. Generally, the difference in specific surface area and pore size distribution made the variance of the nucleation rate of $CaCO_3$, and consequently the carbonation conversion of CaO-based sorbents.[47] As expected, "90%$CaAc_2$-FA-2h" had the highest surface area of 10.98 m^2 g^{-1} and largest pore volume of 129.93 × 10^{-3} cm^3 g^{-1} (Table 1), whereas the other sorbents were ranked, for CO_2 uptake, in the same order as surface area. It was worth noting that a two-stage reaction could be identified clearly for the synthetic sorbents, wherein an initial fast carbonation stage controlled by surface reaction and a subsequent significantly slower carbonation stage controlled

Table 1. Summary of the Calcium Content and Structural Parameters of Sorbents

samples	calcium content[a] (%)	BET surface area (m^2 g^{-1})	BJH pore volume (10^{-3} cm^3 g^{-1})	average pore size (nm)
FA-2h	2.80	0.44	1.28	8.6
100%CaO-2h	97.90	3.24	20.24	8.1
90%CaO-FA-2h	89.88	2.96	18.22	8.3
90% $Ca(OH)_2$-FA-2h	89.64	4.95	82.56	9.2
90% $CaCO_3$-FA-2h	89.77	5.63	59.04	16.5
90%$CaAc_2$-FA-2h	90.76	10.98	129.93	7.6
90% CaC_2O_4-FA-2h	88.97	3.85	38.25	10.0

[a] Calcium content was defined by XRF results, which is its nominal composition.

by diffusion were observed.[48] "90%$CaCO_3$-FA-2h", in particular, showed the fastest rate in the first 2 min stage, as the sorbent had the largest macropore (>50 nm) volumes (Figure S5) that provided a larger channel for the easier diffusion of CO_2.[49] Conversely, carbonation occurred gradually over the entire 25 min period for "90%CaC_2O_4-FA-2h" and "90%CaO-FA-2h", because these sorbents had small macropore volumes, leading to a low initial CO_2 uptake.

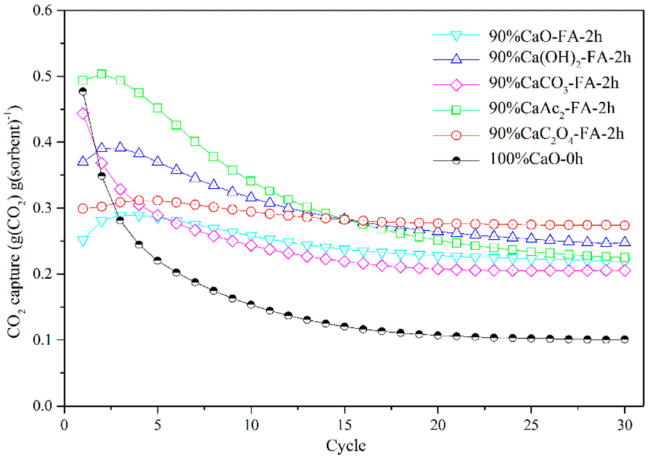

Figure 3. CO_2 uptake as a function of cycle for sorbents prepared from different calcium precursors. Operational conditions as in Figure 1.

Generally, the cyclic performance of CaO-based sorbents is different but more important for large-scale application. Figure 3 shows the CO_2 uptake of sorbents prepared from different precursors over 30 cycles of carbonation−calcination. Because the synthetic sorbents have been thermally pretreated for 2 h and physically doped with the inert material (gehlenite, Figure S6), they possessed a better cyclic stability than pure CaO sorbents. Interestingly, the CO_2 uptake of synthetic sorbents, except for "90%$CaCO_3$-FA-2h", increased slightly with cycle number over the initial cycles. This "self-reactivation" phenomenon may also be explained using the pore-skeleton model:[12] the reaction rate is slower in the first cycle, because the inward (hard) skeleton is less reactive and restricts ion diffusion; in subsequent cycles, the outward (soft) skeleton which accelerates the carbonation rate is formed and continues to grow. This expected change in carbonation rate was shown in Figure S4: the synthetic sorbents appeared to perform a two-stage carbonation reaction, and maintained an increase in the rate of fast-carbonation stage throughout multiple cycles. Subsequently, the CO_2 uptake of synthetic sorbents would be expected to decrease with cycle number, due to sintering of sorbents and closure of small pores under the severe calcination conditions, despite the mitigating effect of the inert material.[10]

Because the fast-carbonation stage proceeded rapidly in the first cycle and the self-reactivation effect was not significant for "90%$CaCO_3$-FA-2h", it exhibited a fast decay in conversion with increasing cycle number; i.e., a CO_2 uptake of 0.44 and 0.21 $g(CO_2)$ $g(sorbent)^{-1}$ for the first and 30th cycles, respectively. "90%CaO-FA-2h" was relatively stable, with an average decay rate of 0.43% per cycle; however, the CO_2 uptake was only 0.22 $g(CO_2)$ $g(sorbent)^{-1}$ after 30 cycles, due to the small pore volume of the initial structure. For the other three sorbents, the CO_2 uptake after 30 cycles was ranked "90% CaC_2O_4-FA-2h" > "90%$Ca(OH)_2$-FA-2h" > "90%$CaAc_2$-FA-2h" (0.27, 0.25, and 0.23 $g(CO_2)$ $g(sorbent)^{-1}$, respectively), which was opposite to the ranking found for initial CO_2 uptake. In the study by Grasa et al.,[17] CaO derived from CaC_2O_4 showed marginally better performance after 80 cycles under severe calcination conditions than CaO derived from $CaAc_2$; Li et al.,[36] in contrast, reported that CaO derived from $CaAc_2$ showed considerably better long-term CO_2 capture performance due to the decomposition process, which produced small CaO crystals with a unique porous structure. We are not able to state which calcium precursor is better, or the difference depends on cyclic sorption conditions; however, we chose CaC_2O_4 as the calcium source throughout the rest of this study, because it exhibited the best stability and the highest final CO_2 uptake in our investigation. Actually, decomposition process of CaC_2O_4 was similar to that of $CaAc_2$ and also resulted in smaller CaO grains than normal CaO (Figure S7a,b). "90% CaC_2O_4-FA-2h" was observed to consist of smaller particles with more particle gaps than "100%CaO-0h" after 30 cycles (Figure S7c,d), indicating that sintering of CaO over the multiple carbonation−calcination cycles was minimal, due to the antisintering effect of the inert material (gehlenite).

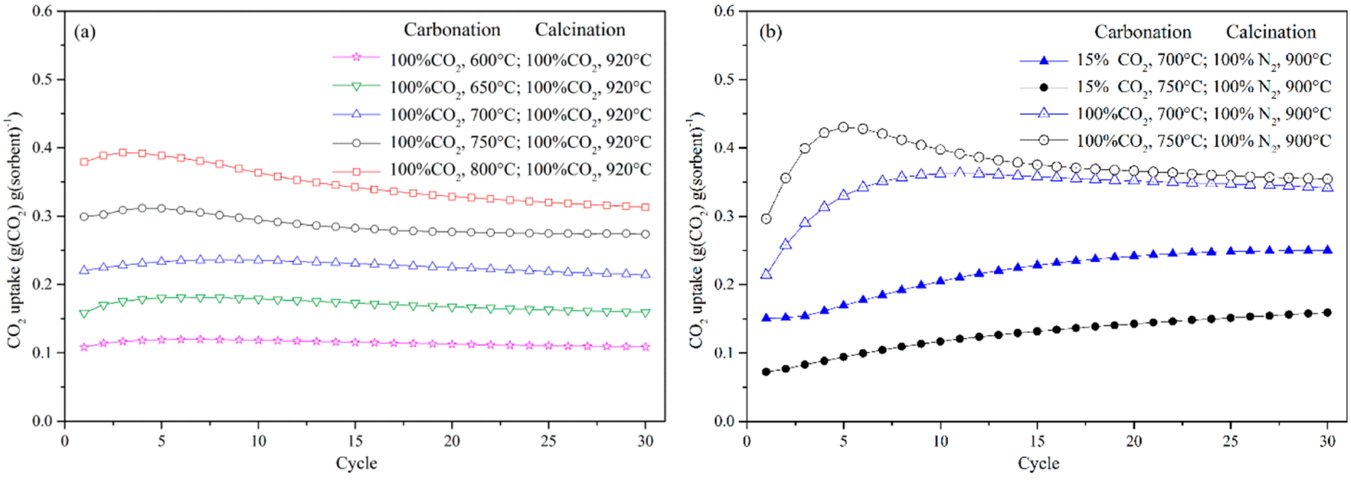

Figure 4. CO_2 uptake as a function of cycle for "90%CaC_2O_4-FA-2h" under different (a) carbonation temperature and (b) CO_2 partial pressure (carbonation for 25 min and calcination for 5 min).

Effect of Carbonation–Calcination Conditions. Carbonation temperature and CO_2 partial pressure has an important effect on carbonation conversion of CaO-based sorbents, based on the equilibrium partial pressure of CO_2 over CaO (Figure S9).[50] For example, a carbonation temperature no higher than 778 °C would be required for a CO_2 volume fraction of 15% remaining in the flue gas. On the other hand, the minimum temperature of the calcination reaction should be up to 900 °C, assuming an operating CO_2 pressure of 101 kPa suitable for compression and subsequent storage. Figure S10 shows the one-cycle carbonation (120 min) and calcination reaction curves of "90%CaC_2O_4-FA-2h" under different carbonation conditions. In a pure CO_2 atmosphere, the sorption rate and sorption capacity were enhanced as temperature increased from 700 to 800 °C, and the CO_2 uptake was 0.40, 0.51, and 0.53 $g(CO_2)\ g(sorbent)^{-1}$ after 120 min of carbonation, respectively. Generally, the fast carbonation stage is within 1 min duration,[22] so we separated the whole carbonation process into two stages: the fast stage (0–1 min) and the slow stage (1–120 min). The calculation showed that the sorption rate and the sorption capacity were enhanced as the increasing temperature both in the fast stage and in the slow stage. Considering a CO_2 partial pressure of 15%, the carbonation conversion at a temperature of 700 °C was significantly higher than that at 750 °C, which was consistent with the results reported by Li et al. that a carbonation temperature of 660–710 °C was optimal for cyclic CO_2 capture in 15% CO_2.[31]

Figure 4 shows the cyclic performance of "90%CaC_2O_4-FA-2h" under different carbonation conditions. Although a higher carbonation temperature (in the range of 600–800 °C) increased capture capacity in pure CO_2, a more rapid decay of CO_2 uptake was also observed, i.e., a decay of −0.5% (600 °C), −0.7% (650 °C), 2.9% (700 °C), 8.6% (750 °C), and 17.4% (800 °C) after 30 cycles, respectively (Figure 4a), indicating that increasing carbonation temperature would intensify the sintering of sorbents (Figure S8a–e). Considering long-term capture capacity, a carbonation temperature of 700–750 °C was recommended for the synthetic sorbents during cyclic CO_2 capture. When the CO_2 partial pressure was lowered to the realistic concentration in flue gas (~15%), the CO_2 uptake decreased sharply with decreasing CO_2 partial pressure, leaving a CO_2 uptake of 0.26 $g(CO_2)\ g(sorbent)^{-1}$ after 120 min of carbonation at 700 °C (Figure S10). Figure 4b further shows the effect of CO_2 partial pressure on the cyclic CO_2 uptake under temperatures of 700 and 750 °C. The cyclic stability was significantly enhanced in 15% CO_2, and there was no obvious decay over 30 cycles while a slight decay was observed for carbonation in pure CO_2 after 10 cycles. Because of the self-reactivation effect, the CO_2 uptake interestingly increased throughout the 30 cycle carbonation–calcination, and achieved a final capacity of 0.25 $g(CO_2)\ g(sorbent)^{-1}$ after 30 cycles at a carbonation temperature of 700 °C (15% CO_2).

In real fluidized-bed combustion (FBC) capture plants, higher concentrations of CO_2 (>90%) are needed to produce concentrated CO_2 streams, thus a calcination temperature of >900 °C will be required.[50] However, both high temperatures[51] and high CO_2 concentrations will promote sintering[51] and produce a net decrease in surface area and pore volumes in all cases, which will inhibit the gas–solid reaction. It is therefore necessary to consider the effect of temperature and CO_2 partial pressure during calcination on the cyclic stability of synthetic sorbents. Ridha et al.[30] proposed that the temperature of 920 °C was more adequate for calcination than 900 °C, though calcination at 920 °C resulted in ~9% lower CO_2 uptake for the next cycle. Grasa et al.[9] suggested that a calcination temperature above 950 °C accelerated the decay in CO_2 uptake of CaO. However, it was unnecessary to use such a high calcination temperature in practice, and 920 °C was chosen instead for a calcination atmosphere composed of pure CO_2.

As expected, CO_2 uptake in the first cycle was independent of calcination conditions, and determined by carbonation conditions. However, CO_2 uptake increased substantially in subsequent cycles, when the calcination atmosphere was changed from pure CO_2 to pure N_2 (Figure 5). This increase in CO_2 uptake in the initial cycles may be ascribed to the self-reactivation effect, whereas this effect was counteracted by sintering under severe calcination conditions (Figure S8c,d,g,h). Besides, when the calcination atmosphere was pure CO_2, the "recarbonation" process will increase cyclic capacity as is reported;[52] however, it is far from offsetting the rapid decay of CO_2 uptake. Because the sorbents before calcination were still found in the $CaCO_3$ phase (Tammann temperature = 524 °C), which is more readily sintered than CaO (Tammann temperature = 1170 °C), significant sintering of sorbents would be expected to occur mainly under severe calcination conditions (in pure CO_2 at ~900 °C). In contrast, sintering of sorbents is significantly mitigated for calcination conducted in pure N_2, because sorbents decarbonate as soon as the atmosphere is changed, and sorbents already exist in the CaO phase when the temperature reaches ~900 °C. As for the effect of calcination temperature, a similar trend in cyclic CO_2 uptake was observed between calcination temperatures of 750 and 900 °C, leading to final CO_2 uptakes of 0.38 and 0.35 $g(CO_2)\ g(sorbent)^{-1}$, respectively. Because sorbents decarbonate as soon as the atmosphere is changed to pure N_2 atmosphere, increasing the calcination temperature will not sharply intensify the sintering of sorbents (in CaO phase), and thus the net effect of calcination temperature (in the range 750–900 °C) was negligible.

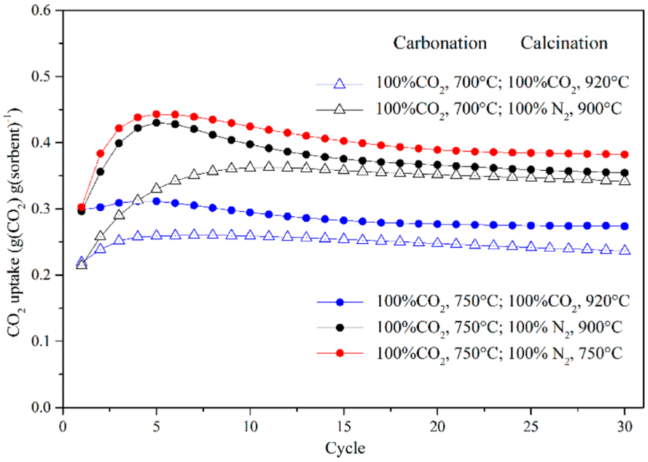

Figure 5. CO_2 uptake as a function of cycle for "90%CaC_2O_4-FA-2h" under different calcination conditions (carbonation for 25 min and calcination for 5 min).

In general, CO_2 uptake and cyclic stability of CaO-based sorbents was mainly influenced by the calcium precursor, carbonation conditions and calcination conditions, as discussed above. However, the synthetic sorbents showed comparatively high CO_2 uptake and good cyclic stability compared to other CaO-based sorbents even in the most severe carbonation–

Table 2. Synthetic CaO-based Sorbents Stabilized by Solid Waste: Effectiveness and Stability over Cycles of Carbonation and Calcination

		carbonation			calcination				CO_2 uptake		
support	CaO content (wt %)	T (°C)	t (min)	CO_2[a] (%)	T (°C)	t (min)	CO_2[a] (%)	N, cycles	X_1 g(CO_2) g(sorbent)$^{-1}$	$X_{residue}$[b] g(CO_2) g(sorbent)$^{-1}$	loss[c] (%)
FA[d]	90	800	25	100	920	5	100[j]	30	0.38	0.31	0.58
	90	750	25	100	920	5	100[j]	30	0.30	0.27	0.29
	90	750	25	100	750	5	0	30	0.30	0.38	−0.87
	90	750	25	100	900	5	0	30	0.30	0.35	−0.65
	90	700	25	100	900	5	0	30	0.21	0.34	−1.98
	90	700	25	15	900	5	0	30	0.15	0.25	−2.20
kaolin[29]	91[e]	700	30	15	950	10	100[j]	25	0.47	0.24	1.96
		700	30	15	850	10	0	25	0.47	0.40	0.60
Kaolin[30]	90[f]	650	20	15	920	10	100[j]	30	0.24	0.13	1.47
husk ash[31]	84[e]	700	15	15	980	20	0	20	0.35	0.20	2.05
		700	15	15	850	20	0	50	0.45	0.27	0.78
bentonite[32]	81[e]	850	10	100	850	10	0	35	0.41	0.25	1.11
	81[g]	850	10	100	850	10	0	35	0.46	0.22	1.49
attapulgite[33]	77[e]	700	25	15	950	10	100[j]	20	0.50	0.31	1.90
		700	25	15	900	10	0	20	0.53	0.40	1.23
cement[28]	77[e]	850	10	100	850	10	0	30	0.53	0.36	1.09
cement[34]	75[e]	650	30	15	900	10	0	18	0.35	0.23	1.89
cement[35]	75[h]	650	30	15	900	10	100[j]	18	0.51	0.32	2.07
	75[h]	650	30	15	900	10	0	70	0.48	0.36	0.36
	75[i]	650	30	15	900	10	0	70	0.43	0.31	0.40

[a] Atmospheric CO_2 content was adjusted by N_2. [b] X_1 and $X_{residue}$ refer to CO_2 uptake in the first and last cycle, respectively. [c] The average change in CO_2 uptake capacity per cycle: $(1 - X_{residue}/X_1)/N \times 100\%$. [d] The calcium precursor was CaC_2O_4. [e] The calcium precursor was $Ca(OH)_2$. [f] The calcium precursor was $Ca(Ac)_2$. [g] The CaO precursor was $CaCO_3$. [h] The CaO precursor was calcium L-lactate hydrate. [i] The CaO precursor was calcium D-gluconate monohydrate. [j] There was a slight increase in CO2 uptake, so-called "recarbonation", during the switch from carbonation to calcination in pure CO_2 atm.

calcination conditions (Table 2). This result thus provides an easy and promising approach to scaled-up high temperature CO_2 capture, considering both economic and environmental points of view.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00355.

> Characterization of "FA-2h" and synthetic sorbents, including chemical composition, XRD patterns, N_2 physisorption isotherms, pore size distributions, cyclic CO_2 uptakes, and SEM images; comparison of CO_2 uptakes of CaO sorbents derived from different calcium precursor (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*Prof. Dr. Jianguo Jiang. Tel./Fax.: +86 01062783548. E-mail: jianguoj@mail.tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

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