



Batch fluidized bed test of SATS-derived CaO/TiO₂-Al₂O₃ sorbent for calcium looping



Weiwei Peng^{a,b}, Zuwei Xu^a, Haibo Zhao^{a,b,*}

^aState Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China

^bChina-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China

HIGHLIGHTS

- A hierarchical structure CaO/TiO₂-Al₂O₃ sorbent in core-shell microarchitecture is made.
- CaO/TiO₂-Al₂O₃ sorbent maintains almost 100% of the initial CO₂ capture amount after 10 cycles.
- CaO/TiO₂-Al₂O₃ sorbent shows appreciable attrition resistance in fluidization environment.
- CaO/TiO₂-Al₂O₃ sorbent provides a possible path to realize industrial application.

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ABSTRACT

High CO₂ capture capacity and attrition resistance are of great significance for CaO-based CO₂ sorbents during successive carbonation/calcination cycles. In this study, a novel self-assembly template synthesis (SATS) method is proposed to manufacture a hierarchical structure CaO/TiO₂-Al₂O₃ sorbent, where Ca-rich, Al₂O₃-supported and TiO₂-stabilized in a core-shell microarchitecture. Preparation experiments, including crushing strength and attrition tests of fresh CaO-based CO₂ sorbents, confirm the operational feasibility of sorbents to conduct carbonation/calcination cycles in a batch fluidized bed. After 10 cyclic tests, it is interesting that CaO/TiO₂-Al₂O₃ sorbent achieves superior CO₂ capture capacity and favorable cyclic stability of 0.78 mol CO₂/mol CaO, which maintains almost 100% of the initial CO₂ capture amount. As for attrition resistance, CaO/TiO₂-Al₂O₃ sorbent performs an appreciable crushing strength of 1.46 N and shows a low attrition loss with almost no variation of particle size distribution even after 10 cycles. All the tests are also conducted for CaO and CaO/Al₂O₃ sorbents for comparison, and the CO₂ capture capacity and attrition resistance of the SATS-derived CaO/TiO₂-Al₂O₃ sorbent are highlighted. In addition, it is concluded that the CaO/TiO₂-Al₂O₃ sorbent performs prospective raw material cost in repeated carbonation/calcination cycles, which provides a possible path to realize industrial application.

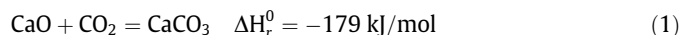
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1. Introduction

Anthropogenic emission of CO₂ from the combustion of fossil fuels is the main contributor to global warming and climate change. To mitigate the climate change, CO₂ capture and storage (CCS) processes is reported to be one of the most widely considered scenarios by capturing CO₂ generated in industrial processes [1]. And developing post-combustion CO₂ capture technologies is believed as one of the most promising CCS technologies due to

its feasibility utilization in the existing power plants after a small retrofit [2,3]. However, the currently available amine scrubbing is not widely popularized nowadays because of its unacceptably high cost, large energy penalty, environmental and health risk [4].

An alternative to amine scrubbing is the commonly termed calcium looping (Ca-L) technology, which aims at reducing CO₂ capture costs and energy penalties associated with the separation of CO₂ [5,6]. The Ca-L technology takes advantage of the reversible carbonation of CaO, during which CO₂ contained in flue gas is absorbed by CaO to form CaCO₃, and then CO₂ is released and captured when the reverse process of the reaction, named calcination, takes place in another reactor [7]. Theoretically reversible carbonation/calcination reactions are showed as follows:



* Corresponding author at: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China. Tel.: +86 27 8754 2417x8208; fax: +86 27 8754 5526.

E-mail addresses: clpengweiwei@163.com (W. Peng), xu_zuwei@163.com (Z. Xu), klinsmannzhhb@163.com, hzhao@mail.hust.edu.cn (H. Zhao).

Moreover, the reversible chemical reaction of CaO-based CO₂ sorbents is widely applied in both post-combustion process and pre-combustion process to realize advanced zero emission power generation technologies, steam methane reforming processes or water gas shift reaction for enhanced hydrogen production or syngas production, and this reversible chemical reaction can be also used in energy storage systems in chemical heat pumps [8,9].

CaO-based CO₂ sorbents are developed fast in recent years because of their low material cost, high availability, fast kinetics and high theoretical CO₂ capture capacity of 0.786 g CO₂/g CaO. The major challenge in developing Ca-L technology is the problem of loss-in-capacity, i.e. the loss in initial CO₂ capture capacity in successive carbonation/calcination cycles, the main reason for loss-in-capacity phenomenon can be identified in severe sintering at high temperatures during the calcination process, leading to a reduction of available surface area for reaction [10]. In addition, commercial CaO-based CO₂ sorbents have sub-optimal mechanical properties, contributing to high attrition rates and consequently, elutriation of fine materials when used in fluidized bed reactor systems [11,12]. Approaches to improve CO₂ capture capacity of CaO-based CO₂ sorbents include thermal pre-activation, water and steam reactivation, production of synthetic sorbents, and so on [13–15]. Among various improvement methods, synthesizing CaO-based composite materials is regarded as one of most efficient methods because the support is beneficial to suppress sorbent sintering, attrition and agglomeration, and consequent elutriation [16,17].

In our previous work [18], a tailor-made core-shell CaO/TiO₂-Al₂O₃ sorbent is synthesized by a novel self-assembly template synthesis (SATS) method. SATS method, which is based on nano/micron-particle coating technology, allows a customized hierarchical structure (typically, core-shell composite) derived from the self-assembly of different particles. The hydration between inorganic oxide particles and water can produce hydroxyl groups, and the surface of particles is charged due to hydroxyl dissociation. The particle surface potential (zeta potential) can be regulated by the pH value, whereby unlike particles (here nano-TiO₂ and micron-Al₂O₃) can be charged with opposite potential. CaO/TiO₂-Al₂O₃ sorbent is based on the self-assembly between nano-TiO₂ and micron-Al₂O₃, where nano-TiO₂ particles are coated on the surface of micron-Al₂O₃ particles to inhibit the interaction of active phase CaO with the main support Al₂O₃. It is concluded that CaO/TiO₂-Al₂O₃ sorbent performs superior and durable CO₂ capture capacity of 0.82 mol CO₂/mol sorbent after 20 cycles in TGA under mild calcination condition and retains a high-capacity and long-life performance of 0.63 mol CO₂/mol sorbent after 104 cycles in TGA under severe calcination condition, which shows high reactivity, thermal stability, mechanical strength and resistance to sintering.

As is well known, fluidized bed reactor is widely used in solid fuel combustion, gasification and pyrolysis because of its advantages of high heat transfer and mass transfer as well as continuous operation, while it is pointed out bed material suffers from a series of loss-in-performance (such as sorbent deactivation, solid attrition and mechanical strength loss), caused by the particles sintering and inter-particle surface collisions when operating in fluidized bed reactors. Loss-in-performance causes mass loss of sorbents and leads to elutriation of fine particles that leave the reactor with the gas flow [19,20].

Nowadays, a large number of cyclic tests of synthetic sorbents are conducted in a TGA reactor, where is not exposed to attrition, as in a fluidized bed. Moreover, some results of cyclic tests in fluidized beds are not satisfactory as expected, which is mainly reflected in undesired CO₂ capture capacity and poor physical mechanical strength. Fennell et al. [21] studied the attrition rate of the particles of five limestones in a fluidized bed, and it is found

that most limestones lost approximately 10% of their mass over the course of a typical experiment, moreover, the carbonation conversion of limestone dropped to a very low level after a few cycles, which only retained 20–30% of initial CO₂ capture capacity. Coppola et al. [22] compared the performance of six European limestones during Ca-L cycles both in a lab-scale fluidized bed and in a thermo-gravimetric apparatus, and they concluded that the CO₂ capture capacity of the sorbents measured in TGA tests was generally larger than that measured in fluidized bed reactor. Symonds et al. [23] also made a comparison between pilot-scale fluidized bed and TGA, and found that sorbent reactivity was considerably lower during the pilot-scale fluidized bed testing, meanwhile, the initial rapid kinetically controlled CO₂ capture stage was dramatically reduced and CO₂ capture efficiency was substantially reduced during the diffusion-controlled stage.

In this work, CaO/TiO₂-Al₂O₃ sorbent is manufactured by the SATS method and then is tested in a laboratory batch-operated fluidized-bed reactor, in which Ca-L facility is operated under the conditions with sufficient fluidization. In addition, physical characterizations including mechanical strength, attrition/agglomeration rate and morphology feature, and raw material cost analysis are also assessed. All of the tests are also conducted for CaO sorbent and CaO/Al₂O₃ sorbent to compare their performance on a lab-scale basis so that selecting the high-performance CaO-based CO₂ sorbent for further larger-scale testing.

2. Experimental section

2.1. Materials

In this study, calcium acetate monohydrate power (Sinopharm Chemical Reagent Co.Ltd., Shanghai, China) is used as calcium precursor. Commercial α -Al₂O₃ powder (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) with larger than 200 meshes (i.e., particle size <75 μ m) is selected as the main component of the support. The flame-synthesized TiO₂ nanoparticles made in our laboratory (as minor component of the support) are deposited on the surface of Al₂O₃ by electrostatic self-assembly in precursors to modify and stabilize the CaO-based sorbent [24].

2.2. Preparation of sorbents

Pure CaO sorbent and CaO/Al₂O₃ sorbent (80 wt%: 20 wt%) are manufactured by calcination method and wet impregnation method, respectively. CaO/TiO₂-Al₂O₃ sorbent (80 wt%: 5 wt%: 15 wt%) is obtained by a novel self-assembly template synthesis (SATS) method. During the preparation process, all sorbents are calcined in a muffle furnace at 950 °C for 2 h. Finally, all of the as-prepared samples are annealing cooled, grinded and screened. At last, samples with a particle size range of 200–300 μ m are selected. The detailed experimental procedures have been introduced in our previous work [18].

2.3. Cyclic carbonation/calcination test

2.3.1. Experimental conditions

Prior to the start of carbonation/calcination cycles, physical property parameters of sorbents are initially studied. True density of CaO, CaO/Al₂O₃ and CaO/TiO₂-Al₂O₃, which are measured by AccuPyc 1330 automatic true density analyzer (Micromeritics Instrument Corp), are 2469.3, 2704.8 and 3018.2 kg/m³, respectively. The results of physical property parameters of CaO-based CO₂ sorbents are listed in Table 1, where ρ_f , μ_f , u_{mf} and L_{mf} present density of fluidization gas, dynamic viscosity of gas flow, minimum fluidization velocity and inlet gas flow rate with the minimum flu-

Table 1
Physical property parameters of CaO-based CO₂ sorbents under different temperatures.

	CaO		CaO/Al ₂ O ₃		CaO/TiO ₂ -Al ₂ O ₃	
	700 °C 10%CO ₂ + 90%N ₂	900 °C N ₂	700 °C 10%CO ₂ + 90%N ₂	900 °C N ₂	700 °C 10%CO ₂ + 90%N ₂	900 °C N ₂
ρ_f (kg/m ³)	0.3708	0.291	0.3708	0.291	0.3708	0.291
μ_f 10 ⁻⁶ (kg/m/s)	40.7	46.1	40.7	46.1	40.7	46.1
u_{mf} (m/s)	0.0224	0.0199	0.0218	0.0303	0.0275	0.0243
L_{mf} (ml/min)	219.3	160.9	240.2	176.3	268.1	215.1

idization velocity, respectively. Finally, gas flow of 800 ml/min is chosen as superficial gas velocity in our study to satisfy bubbling fluidization with three to five times of minimum fluidization velocity.

2.3.2. Cyclic carbonation/calcination process in a batch fluidized Bed

A laboratory batch fluidized bed reactor is used to investigate the CO₂ capture capacity and the repeated stability of CaO-based CO₂ sorbents. As illustrated in Fig. 1, the reactor mainly consists of the gas control unit, the reaction unit, and the gas detection unit. The gas control unit provides 10 vol.% CO₂ (balanced with N₂) or pure N₂ as the fluidization gas. The fluidization gas is introduced into the fluidized bed from the bottom of reactor. The reaction unit includes a stainless reaction tube with a length of 892 mm placed into an electrical furnace. A porous plate with a diameter of 26 mm is set in the tube at 400 mm from the bottom. The reactor temperature is measured by a type K thermocouple at about 10 mm above the porous plate. CaO-based CO₂ sorbents are introduced through the hopper on the top of the reactor before cyclic test. All gaseous products leaving the reactor are first led to filter to remove fine particles, and then to an electric cooler to remove the steam, and finally to a gas analyzer, i.e., the gas detection unit, to determine the concentration of CO₂, which is further recorded by a computer every second. The detailed introduction of this reactor can refer to our previous publications [25–27].

Carbonation/calcination experiments are carried out batchwise for each CaO-based CO₂ sorbent, i.e., no particles are added during the run. CaO-based CO₂ sorbents are first exposed to N₂ atmosphere for 30 min at the set-point temperature of 900 °C to ensure initial complete calcination. Then, the temperature is down to 700 °C for carbonation process with 10 vol.% CO₂ flow (balanced with N₂ flow) for 30 min. Next, the fluidization gas is switched rapidly from 10 vol.% CO₂ to N₂, following by the temperature up

to 900 °C for calcination process for 5 min. Then, the temperature is down to 700 °C again for the next carbonation/calcination cycle. The batch fluidized bed reactor is operated with a gas flow of 800 ml/min in all cases. 10 carbonation/calcination cycles are conducted for three CaO-based CO₂ sorbents. It is noted that the CO₂ capture capacity is calculated on the basis of CO₂ absorbed amount during the carbonation process.

2.4. Physical measurements

The attrition indexes of fresh sorbents are determined in a self-made abrasion tester (a stainless steel cylinder with length of 14.5 cm and diameter of 12.0 cm, equipped with a 1.5 cm baffle) [28], and are rotated on a ball-mill roller for 50 min at a rate of 10 rpm/min. The crushing strength is determined by a digital dynamometer (Shimpo, FGJ-5), taking the average value of 40 measurements of the force needed to crush a sorbent particle as the final result. The determination of particle size distribution (PSD) is conducted with a laser diffraction particle size analyzer (Malvern Mastersizer 2000), which allows testing particle size distribution with range from 0.02 to 2000 μm. The microstructure of CaO-based CO₂ sorbents is investigated by environmental scanning electron microscope (Quanta 200, FEI) with 20 kV of accelerating voltage.

3. Results and discussion

3.1. Preparation experiment

To guarantee the operational feasibility and applicability of three CaO-based CO₂ sorbents for carbonation/calcination cycles in batch fluidized bed, the preparation experiments of fresh

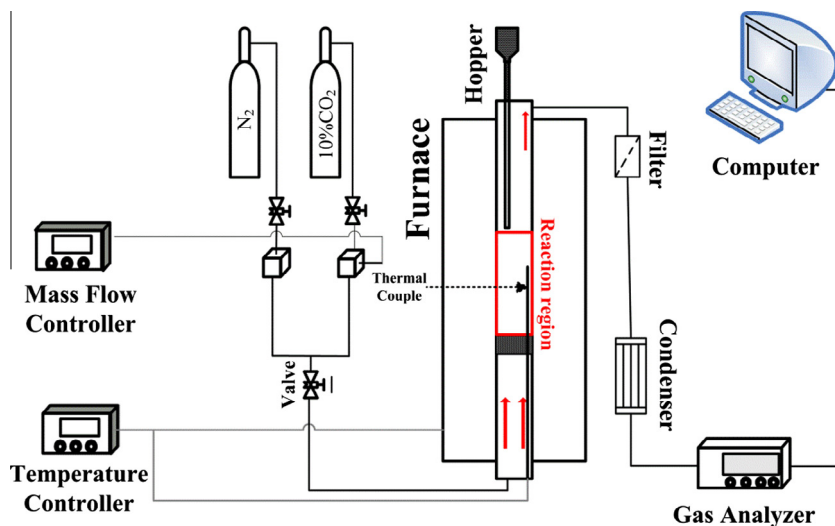


Fig. 1. A diagrammatic sketch of the batch fluidized-bed reaction system.

sorbents are deserved to study. It has been reported that solid particles with a crushing strength above 1 N have generally shown good performance with respect to attrition in continuous operation [29]. Aside from crushing strength, particle attrition rate is one of the main parameters to measure the attrition resistance. Therefore, preparation experiments, including crushing strength and attrition rate test, are conducted here to determine whether all of three fresh CaO-based CO₂ sorbents are suitable for the next carbonation/calcination cycles in fluidization environment.

As shown in Table 2, the crushing strength of fresh CaO, CaO/Al₂O₃ and CaO/TiO₂-Al₂O₃ is 1.46, 1.88 and 1.86 N, respectively, with corresponding standard deviations of 0.57, 0.28 and 0.23, respectively. In addition, CaO, CaO/Al₂O₃ and CaO/TiO₂-Al₂O₃ present an attrition index of 9.27%, 7.88% and 6.37% respectively, which perform the same changing trend as crushing strength results, indicating that CaO/TiO₂-Al₂O₃ sorbent has a better performance in mechanical durability when comparing with CaO and CaO/Al₂O₃ sorbents. The fact that fresh CaO/TiO₂-Al₂O₃ sorbent maintains high crushing strength and low attrition rate is beneficial to its excellent cyclic stability, which will be described in Section 3.2 in detail. After all, the results of preparation experiments, either crushing strength test or attrition rate test, confirm that all of values are within the range of acceptance, and all of three sorbents are suitable for next cycles in fluidization environment.

3.2. CO₂ capture performance in a batch fluidized bed

CaO, CaO/Al₂O₃ and CaO/TiO₂-Al₂O₃ sorbents are subjected to carbonation/calcination cycles in a lab-scale batch fluidized bed to test their CO₂ capture capacity and cyclic stability. Fig. 2 exhibits typical outlet profile of CO₂ concentration during cyclic tests in the lab-scale batch fluidized bed. It is noted that temperature stabilizes at 700 °C for 2 min before fluidization gas begins to change from N₂ atmosphere to 10 vol.% CO₂ (balanced with N₂) atmosphere, this operation is aiming to eliminate the evaluation error caused by temperature fluctuation. The CO₂ capture capacity of the CaO-based CO₂ sorbents is calculated on the basis of CO₂ absorption amount during the carbonation process. It is found that CO₂ diffusion plays a dominant role in first few minutes due to the long distance from gas cylinder to gas analysis meter during the carbonation process. Then CO₂ concentration increases slowly, indicating sorbent absorbs CO₂ quickly. After the carbonation process, the fluidization gas is switched rapidly from 10 vol.% CO₂ atmosphere to N₂ atmosphere. At this moment, the competition between dilution of CO₂ concentration by gas flow change and increase of CO₂ concentration by CaCO₃ decomposition occurs. The generated CaCO₃ decomposes along with fluidization gas change when CO₂ concentration is lower than the equilibrium CO₂ pressure; however, the CO₂ dilution rate exceeds the CO₂ increase rate at first 3 min, leading to CO₂ concentration decrease in Fig. 2. When CO₂ concentration reaches the minimum value of about 1.7%, temperature begins to increase from 700 °C to 900 °C, the CO₂ concentration begins to increase to a maximum value

and then decreases to 0% when temperature stabilized at 900 °C for approximately 2 min. After the calcination process lasting for 5 min, the temperature is down to 700 °C again for the next carbonation/calcination cycle.

The evolution of CO₂ capture capacity of three CaO-based CO₂ sorbents in fluidized bed is shown in Fig. 3(a), and the CO₂ capture capacity of a series of CaO-based CO₂ sorbents under different experimental conditions is shown in Fig. 3(b) (the TGA experiments are reported in our previous study [18]). According to Fig. 3(a), it is found that CaO/TiO₂-Al₂O₃ sorbent, which is manufactured by the SATS method, exhibits the maximum initial CO₂ capture capacity of 0.78 mol CO₂/mol CaO (mol/mol for logogram in following descriptions), compared with 0.62 mol/mol and 0.57 mol/mol for CaO/Al₂O₃ sorbent and CaO sorbent, respectively. The relative poor CO₂ capture capacity of CaO and CaO/Al₂O₃ at first cycle may be ascribed to the pre-calcination process, which results in active CaO sintering and pore surface reduction.

Then, a loss-in-capacity phenomenon of CaO and CaO/Al₂O₃ sorbent is exposed during successive cycles. The CO₂ capture capacity of CaO/Al₂O₃ is less-than-desirable, which is consistent with the results performed in TGA under severe condition with the carbonation process at 700 °C in 10 vol.% CO₂ for 20 min and the calcination process at 900 °C in pure CO₂ for 5 min in Fig. 3(b). It should be noted that the reactivity and stability of CaO-based CO₂ sorbents in TGA under severe condition and batch fluidized bed are always less desirable than that in TGA under mild condition with the carbonation process at 700 °C in 10 vol.% CO₂ for 20 min and the calcination process at 700 °C in pure N₂ for 20 min. For example, after 10 cycles, the CO₂ capture capacity of CaO/Al₂O₃ sorbent in the batch fluidized bed is 0.50 mol/mol, compared with 0.59 mol/mol in TGA under severe condition and 0.82 mol/mol in TGA under mild condition. To sum up, it is demonstrated that different reaction environments and experimental facilities play important role in final CO₂ capture performance. Moreover, these comparative results prove the significance and practicability of the studies on performance of synthetic CaO-based CO₂ sorbents in batch fluidized beds, and further benefit for the research on realization of commercialization in large-scale industrialization.

As for CaO/TiO₂-Al₂O₃ sorbent, it maintains a surprising CO₂ capture capacity of 0.78 mol/mol after 10 cycles in the batch fluidized bed, which is 46% and 36% higher than those of CaO and CaO/Al₂O₃ respectively. The CO₂ capture capacity of CaO/TiO₂-Al₂O₃ sorbent remains almost 100% of the initial CO₂ capture amount, presenting superior performance in terms of both capture capacity and cyclic stability. According to Fig. 3(b), it can be found that this high-capacity and long-life property of CaO/TiO₂-Al₂O₃ sorbent maintains in both batch fluidized bed environment and TGA environment (mild calcination condition and severe calcination condition). Even after 104 cycles, CaO/TiO₂-Al₂O₃ sorbent still attains superior CO₂ capture capacity of 0.63 mol/mol, retaining 79.4% of its initial CO₂ absorbing amount [18]. The reason for the superior CO₂ capture performance of CaO/TiO₂-Al₂O₃ sorbent is attributed to the formation of core-shell (Al₂O₃-TiO₂) structure, which inhibits the chemical reaction between active CaO phase and Al-based materials; In addition, the high melting ability and mechanical strength of synthetic sorbent are helpful to its sintering resistance and cyclic stability during multiple cycles.

The schematic of CO₂ capture capacity by CaO-based CO₂ sorbent is shown in Fig. 4(a), the area between red curves, which is filled with gray shade titled as “S”, represents the CO₂ capture capacity during the carbonation process. According to Fig. 4(b)–(d), the area between outlet CO₂ concentration and inlet CO₂ concentration (10%) of CaO/TiO₂-Al₂O₃ sorbent is obviously much larger than that of CaO and CaO/Al₂O₃, which confirms the high

Table 2

Crushing strength, standard deviation of crushing strength and attrition index of fresh CaO, CaO/Al₂O₃ and CaO/Al₂O₃-TiO₂.

	Crushing strength (N)	Standard deviation	Attrition index (%)
CaO	1.46	0.57	9.27
CaO/Al ₂ O ₃	1.88	0.28	7.88
CaO/TiO ₂ -Al ₂ O ₃	1.86	0.23	6.37

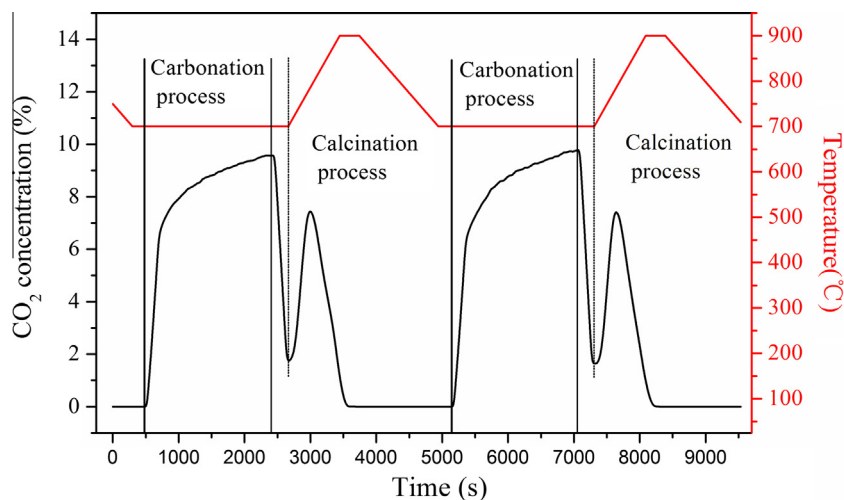


Fig. 2. Typical outlet CO₂ concentration of CaO-based CO₂ sorbent after carbonation/calcination cycles in a lab-scale batch fluidized bed.

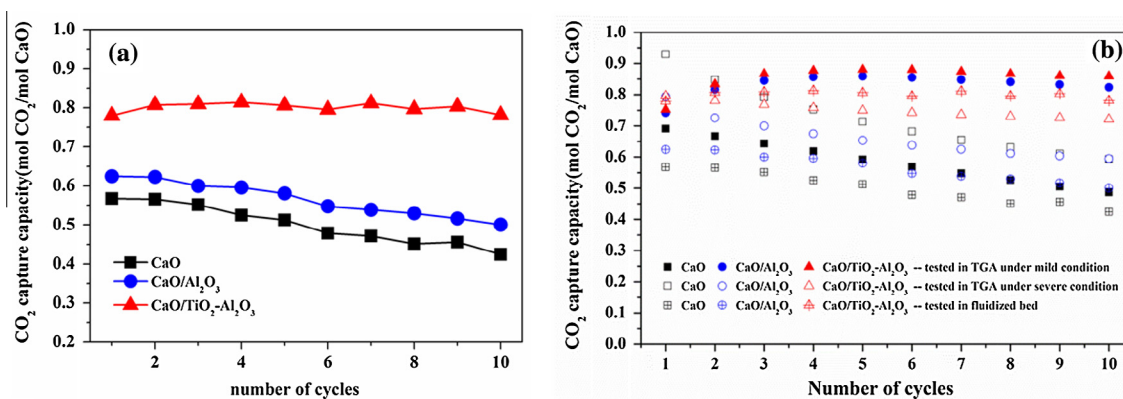


Fig. 3. Evolution of CO₂ capture capacity for CaO, CaO/Al₂O₃ and CaO/TiO₂-Al₂O₃ during 10 cycles: (a) under batch fluidized bed condition, (b) under different experimental conditions. TGA under mild condition: carbonated at 700 °C in 10 vol.% CO₂ for 20 min and calcined at 700 °C in pure N₂ for 20 min; TGA under severe condition: carbonated at 700 °C in 10 vol.% CO₂ for 20 min and calcined at 900 °C in pure CO₂ for 5 min; Batch fluidized bed: carbonated at 700 °C in 10 vol.% CO₂ for 30 min and calcined at 900 °C in pure N₂ for 5 min.

reactivity and superior CO₂ capture capacity of CaO/TiO₂-Al₂O₃ sorbent in the batch fluidized bed.

More especially, it can be found in Fig. 4(b)–(d) that outlet CO₂ concentration increases rapidly from 0% to 5% due to CO₂ diffusion caused by long distance from gas cylinder to gas analysis meter and hysteretic chemical reaction at first 3 min. Then, three CaO-based CO₂ sorbents perform significant difference on CO₂ concentration change. The vertical coordinate in Fig. 4 is the outlet CO₂ concentration, thus a higher outlet CO₂ concentration means that only few CO₂ reacts with sorbent in the reaction unit. It should be noted that the CO₂ capture performance under relatively low CO₂ concentration environment (real operating condition) in the reactor unit is of great importance for sorbent, which describes how much capacity a sorbent can utilize under real Ca-L processes. At the first cycle, it takes about 10–12 min for CaO and CaO/Al₂O₃ sorbents to reach outlet CO₂ concentration of, for example, 8%, which means a short chemically controlled initial reaction period. More especially, this time for CaO sorbent decreases obviously to 8 min at the fifth cycle and 6.8 min at the tenth cycle. And CaO/Al₂O₃ sorbent shows a similar change trend as CaO sorbent in the repeated cycles. On the contrary, it takes about 18 min for CaO/TiO₂-Al₂O₃ sorbent to reach 8% outlet CO₂ concentration even at the tenth cycle, exhibiting a high reactivity and superior CO₂ capture capacity. Thus, CaO/TiO₂-Al₂O₃ sorbent performs a better prospect under real operating conditions when comparing with CaO and CaO/Al₂O₃ sorbent.

3.3. Physical measurements

It is well-known that the textural change of CaO-based CO₂ sorbents, such as grain growth and pore closures, is contributed to the deactivation of the CaO-based CO₂ sorbents in the Ca-L process. Grasa and Abanades [30] found a structural and morphological change of sorbent occurs during cyclic reaction due to low Tamman temperature of CaCO₃. Borgwardt [31] reported that depletion of the reactivity of the sorbent is affected by sorbent sintering, which caused an increase in the density of sorbent particles, pore closure/loss and reduction of the reacting surface area. Luo et al. [32] stated that the molar volume of CaCO₃ formed in the carbonation process is much larger than that of CaO, leading to pore blocking and an increase in diffusion resistance of CO₂ through carbonation product layer. To have a comprehensive understanding on three CaO-based CO₂ sorbents, the morphological images of sorbents after 10 tests are examined by environmental scanning electron microscope (ESEM), as shown in Fig. 5.

In our previous study [18], it was reported that fresh CaO-based CO₂ sorbents have developed porous structure, which provides a larger surface area for CO₂ capture, however, it has been found that a significant change in porosity and morphology appeared after multiply cycles in TGA.

As shown in Fig. 5, the ESEM result of CaO-based CO₂ sorbents in the batch fluidized bed performs a similar change trend as that in TGA reactor. From Fig. 5(a), CaO sorbent loses coarse surface and

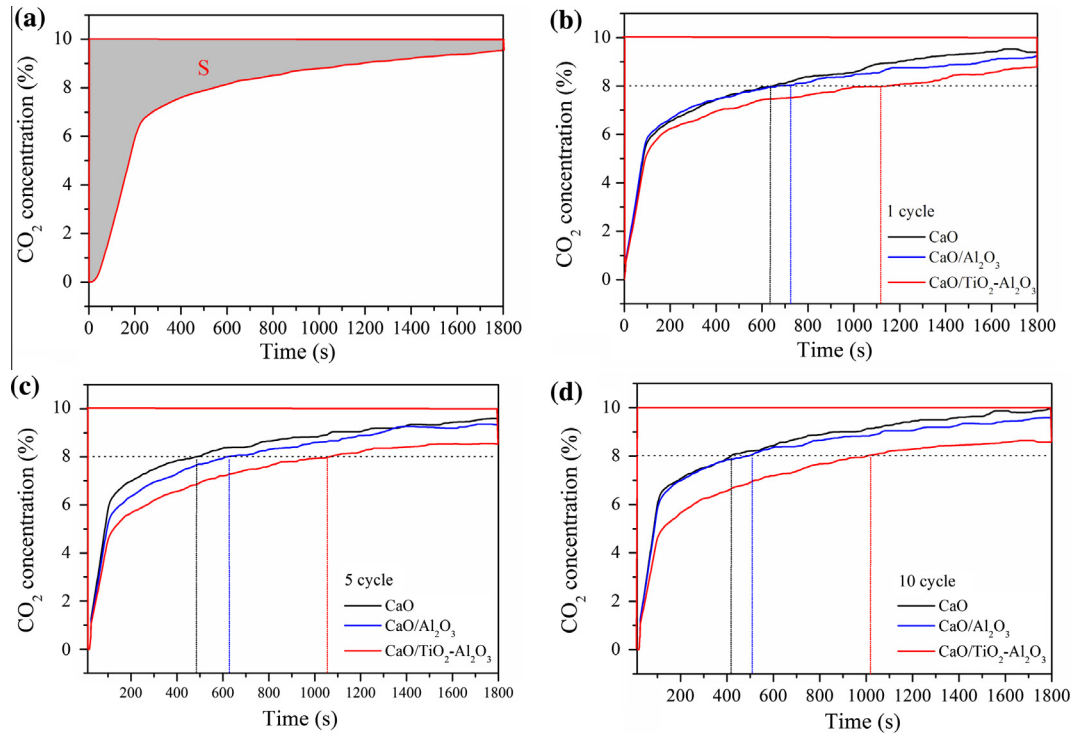


Fig. 4. (a) Schematic of CO₂ capture capacity by CaO-based CO₂ sorbent; and outlet CO₂ concentration curves of three sorbents at different cycle: (a) first cycle, (c) fifth cycle, and (d) tenth cycle. Carbonated at 700 °C in 10 vol.% CO₂ for 30 min and calcined at 900 °C in pure N₂ for 5 min in the batch fluidized bed.

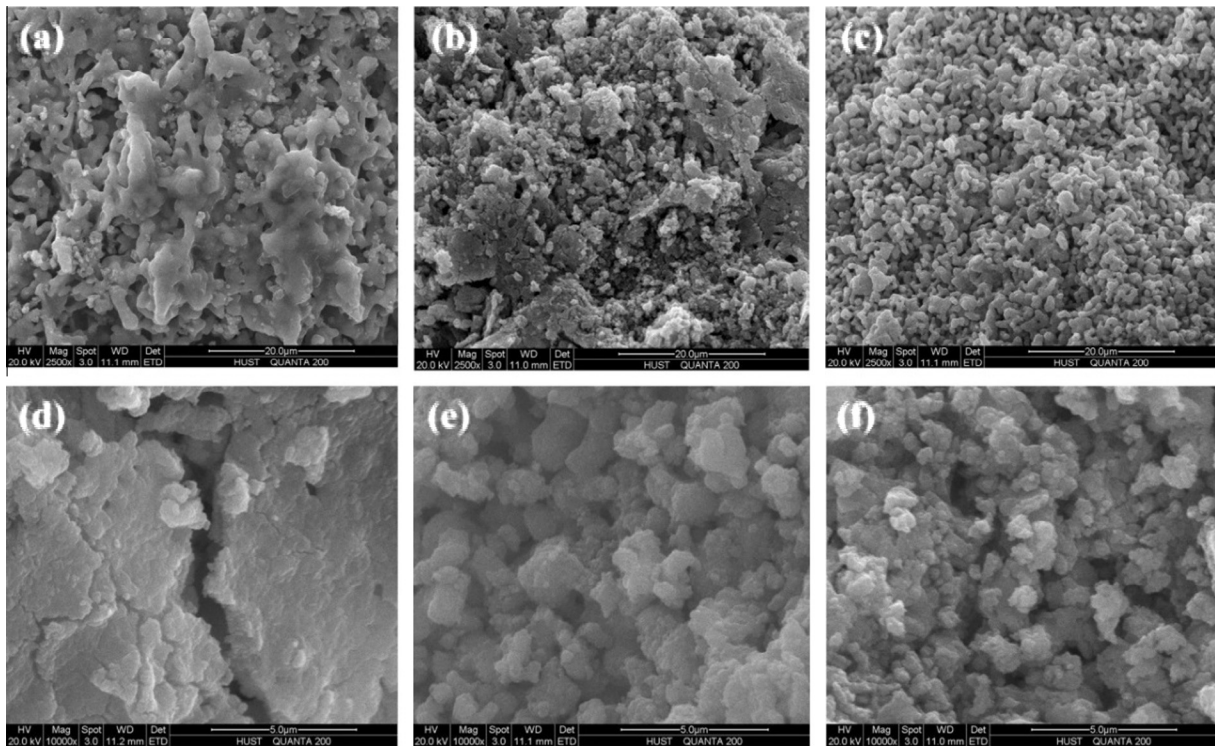


Fig. 5. ESEM images of three CaO-based CO₂ sorbents: the upper row shows used sorbents with the magnifying power of 2500 (a, b and c); the lower row shows used sorbents with the magnifying power of 10,000 (d, e and f); the left column presents CaO sorbent (a, d); the middle column presents CaO/Al₂O₃ sorbent (b, e); the right column presents CaO/TiO₂-Al₂O₃ sorbent (c, f). Each sorbent experienced 10 cyclic tests in the batch fluidized bed.

porous morphology after 10 cycles, demonstrating that CaO sorbent suffers from a serious sintering in the batch fluidized bed, which is also confirmed by clear crack and aggregation

phenomenon appeared in Fig. 5(d). It can be seen that all of the support materials adding (Al₂O₃ or TiO₂-Al₂O₃) play a key role in suppressing sintering of synthetic sorbents, but there are

considerable differences in terms to the degree of improvements. As for $\text{CaO}/\text{Al}_2\text{O}_3$ sorbent in Fig. 5(b) and (e), it shows a less serious sintering phenomenon of particles when comparing with CaO sorbent, but it also appears an increased particle density and partial pore blocking. This acceptable performance is benefited from high melting and strong mechanical strength as a result of adding Al-based support. In contrast, $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$ sorbent in Fig. 5(c) and (f) maintains a rich and quite uniform porous structure, the interconnected pore distribution and unique core-shell structure ensures high reactivity, satisfactory mechanical properties and sintering resistance, which is contributed to prominent CO_2 capture capacity during multiply carbonation/calcination cycles in the batch fluidized bed.

Nowadays, the commercialization of Ca-L technology faces two severe technical problems. One is a well-known problem of loss-in-capacity, the other is the attrition resistance. The attrition resistance property is reported to be a significant problem, because the poor attrition performance induces mass loss from the reactor and causes a marked increase of the sorbents makeup, and finally reduces the economics of the whole system. Therefore, the attrition resistance of sorbents (including pore size distribution and mechanical durability) should be assessed to provide a reference for realizing industrial application.

The particle size distribution (PSD) of three CaO-based CO_2 sorbents is determined by a laser diffraction particle size analyzer to test the attrition/agglomeration rate. The extent of attrition/agglomeration is estimated by comparing the PSD values before and after cyclic tests. As shown in Fig. 6, all of CaO-based particles mainly distribute in range from 100 μm to 400 μm , especially gathered in 200–300 μm . According to Fig. 6(a), CaO sorbent shows the mass distribution shifts from 200–300 μm to both 80–200 μm (primary proportion) and 700–900 μm (minor proportion), indicating that particles suffer from obvious attrition and slight agglomeration. On the other hand, $\text{CaO}/\text{Al}_2\text{O}_3$ and

$\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$ contain a large amount of particles in the size range of 200–300 μm by comparing their fresh and used particles, meaning these two particles exhibit inconspicuous fragmentation. Nevertheless, $\text{CaO}/\text{Al}_2\text{O}_3$ shows partial agglomeration, which exhibits in increasing particle size between 500 μm and 1200 μm . Therefore, the findings may be summarized as follows: $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$ is the most attrition resistant sorbent, followed by $\text{CaO}/\text{Al}_2\text{O}_3$, and CaO is the most readily attrition sorbent. Furthermore, the attrition/agglomeration rate at a larger scale is deserved to research in depth.

Mechanical durability is the other indicator to measure attrition resistance performance, and it is important to develop a sorbent with a high mechanical strength to reduce the overall make-up in the system. Crushing strength can be used as a fast screening method for evaluating the mechanical durability of CaO-based CO_2 sorbents. The crushing strength of each sorbent with a particle size range from 200 μm to 300 μm is taken as the average value of 40 measurements of the force needed to crush a CaO-based particle.

The result in Fig. 7 shows that the crushing strength of the three CaO-based CO_2 sorbents decrease with the increase of cyclic numbers, and that the standard deviation of the measurement also decreases. In details, the crushing strengths of fresh CaO , $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$ are 1.46, 1.88 and 1.86 N, respectively, compared to 0.66, 1.21 and 1.46 N for used CaO , $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$, respectively. The effects of support material, including Al_2O_3 and $\text{TiO}_2\text{-Al}_2\text{O}_3$, on the enhancement of the crushing strength of sorbents are revealed here. More specifically, $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$ sorbent shows the highest crushing strength and keeps a high mechanical stability, which are beneficial to the attrition resistance capacity. However, the crushing strength of CaO-based CO_2 sorbents referred in this study should be significantly improved to satisfy the industrial demand when comparing with other solid particles such as oxygen carriers.

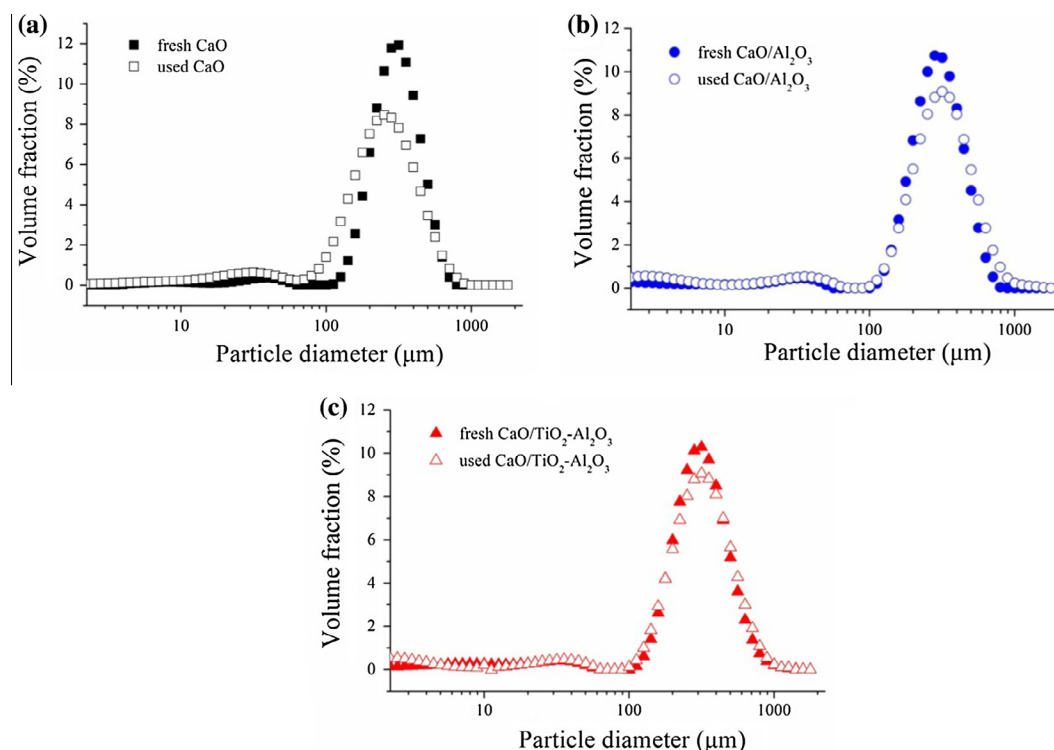


Fig. 6. Particle size distributions of CaO-based CO_2 sorbents: (a) fresh and used CaO ; (b) fresh and used $\text{CaO}/\text{Al}_2\text{O}_3$; (c) fresh and used $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$.

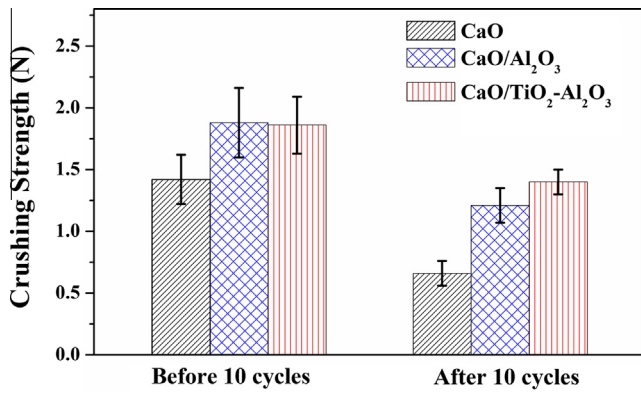


Fig. 7. Crushing strength results for CaO, CaO/Al₂O₃, CaO/TiO₂-Al₂O₃ before and after 10 cyclic tests in batch fluidized bed. Carbonated at 700 °C in 10 vol% CO₂ for 30 min and calcined at 900 °C in pure N₂ for 5 min.

3.4. Raw material cost analysis

In recent years, more and more researches are focusing on the development of a simpler and more cost-effective synthesis method for high-performance CO₂ capture sorbents based on largely available and cheap precursors. Although the fabrication process of pure CaO (sample A), CaO/Al₂O₃ (sample B) and CaO/Al₂O₃-TiO₂ (sample C) uses different method (calcination method, wet impregnation and SATS method, respectively), the main fabrication cost is from the two hours calcination process in muffle furnace at high temperature of 950 °C rather than the simple stirring process in water bath kettle, and this two hours calcination process is the same for these three sorbents. In addition, the fabrication cost also depends on production scale, technological level, and device characteristic and so on, for which is difficult to have a precise measure and calculation. Thus, we focus on the analysis of raw material cost to provide a reference for comprehensive evaluation of three sorbents. It is believed that a cheap raw material will be helpful to save make-up cost and operation cost, especially under the condition of continuous long-term operation in large-scale factory.

Raw material cost of three CaO-based CO₂ sorbents based on different cycle numbers are listed in Table 3. The unit prices of raw materials is derived from the industry information website about manufacturers, suppliers and products (www.made-in-china.com), and the costs of CaO-based CO₂ sorbent for per mol CO₂ capture capacity based on different CO₂ capture amount at certain cycle are estimated. Although the impact of TiO₂ additive on manufacturing cost of CaO/TiO₂-Al₂O₃ is worth considering, its mass fraction only accounts for 5%, which results in a small

Table 3
Raw material costs of three CaO-based CO₂ sorbents based on different CO₂ capture amount at certain cycle.

	Ca(AC) ₂ ·H ₂ O	μm-Al ₂ O ₃	nm-TiO ₂	Raw material cost
Unit price (\$/kg)	1.50	0.50	20.00	/
Pure CaO sorbent (\$/kg CO ₂)				
1 cycle	10.53	/	/	10.53
5 cycle	11.76	/	/	11.76
10 cycle	14.28	/	/	14.28
CaO/Al ₂ O ₃ sorbent (\$/kg CO ₂)				
1 cycle	9.53	0.26	/	9.78
5 cycle	10.35	0.28	/	10.63
10 cycle	12.00	0.32	/	12.32
CaO/TiO ₂ -Al ₂ O ₃ sorbent (\$/kg CO ₂)				
1 cycle	7.70	0.16	2.00	9.85
5 cycle	7.50	0.15	2.00	9.65
10 cycle	7.70	0.16	2.00	9.85

proportion in overall raw material cost. It is noted that the raw material costs of CaO/TiO₂-Al₂O₃ sorbent do not show a distinct advantage at first cycle, however, after 10 cyclic tests, the advantage of SATS-derived CaO/TiO₂-Al₂O₃ sorbent in raw material cost contribution is highlighted with a considerable value of 9.85 \$/kg CO₂, compared with CaO of 14.28 \$/kg CO₂ and CaO/Al₂O₃ of 12.32 \$/kg CO₂. Manovic and Anthony [33] reported that amine scrubbing is one of the post-combustion CO₂ capture technologies ready for commercialization, however, the costs using this process for large power plants are still unacceptable. Moreover, the use of liquid amines is associated with environmental and health risks. Qin et al. [34] researched that the cost for 1 ton of sorbent using limestone, Ca(OH)₂, calcium acetate, calcium lactate, and calcium gluconate as the calcium precursor is around 157–318 \$, 149–248 \$, 1107–2165 \$, 2384–2968 \$, and 2926–6953 \$, respectively when taking the theoretical decomposition ratio of calcium precursor/CaO and composition of sorbent pellets cement (75 wt.% CaO and 25 wt.% as the support and binder) into account. Thus, the SATS-derived CaO/TiO₂-Al₂O₃ sorbent performs competitive advantage when comparing with other post-combustion methods and other synthetic CaO-based CO₂ sorbents. It can be predicted that the SATS-derived CaO/TiO₂-Al₂O₃ sorbent proves its particularly prominent raw material cost advantage during long cyclic tests.

4. Conclusion

A comprehensive study has been undertaken to investigate the CO₂ capture capacity and attrition resistance of CaO sorbent (made by calcination method), CaO/Al₂O₃ sorbent (made by wet impregnation method) and CaO/TiO₂-Al₂O₃ sorbent (made by self-assembly template synthesis method) in a batch fluidized bed. The CaO/TiO₂-Al₂O₃ sorbent is based on the self-assembly between nano-TiO₂ and micron-Al₂O₃, where nano-TiO₂ particles are coated on the surface of micron-Al₂O₃ particles to inhibit the interaction of active phase CaO and the main support Al₂O₃. It is found that CaO/TiO₂-Al₂O₃ sorbent possesses a high-capacity and long-life performance of 0.78 mol/mol after 10 carbonation/calcination cycles, which is consistent with our previous results in TGA under. In addition, the result of ESEM proves its high sintering resistance to maintain abundant available surface area and stable textural structure for CO₂ capture reaction, which confirms the advantage of novel SATS method. Besides addressing the loss-in-capacity of CaO-based CO₂ sorbent, attrition resistance is the other important parameter that should be paid attention, especially in the fluidized bed environment. And the pore size distribution and mechanical durability results show that the CaO/TiO₂-Al₂O₃ sorbent exhibits high mechanical strength, durable anti-attrition performance and favorable long-life stability. Finally, the raw material analysis shows that CaO/TiO₂-Al₂O₃ sorbent has competitive advantage for further continuous long-term operation in large-scale factory.

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