

# Studies on CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent in calcium looping cycles

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**Abstract** In this work, limestone, aluminum nitrate hydrate, and glycerol water solution by combustion synthesis method were proposed to prepare a synthetic CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent for CO<sub>2</sub> capture in calcium looping cycles. The effects of the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub>, cycle number, carbonation conditions, and calcination conditions on the CO<sub>2</sub> uptake by the obtained synthetic sorbent in the repeated carbonation/calcination cycles were studied in a dual fixed-bed reactor and a thermogravimetric analyzer. The optimum mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> was 90:10 in the preparation process of the synthetic sorbent, which exhibited a 0.43 g g<sup>-1</sup> of CO<sub>2</sub> uptake after 50 cycles. The main compositions of the synthetic sorbent contained the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10 were CaO and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, and the mass ratio of CaO to Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> was 74:26. The CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> increases rapidly with the carbonation time in previous 5 min and then rises slowly after 5 min. The carbonation time to reach the maximum CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> was much sooner than that of CaO derived from limestone in each cycle. The optimum carbonation temperature window of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> was 650–700 °C. CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent possessed obviously higher sintering resistance than CaO under the more severe calcination conditions in the cycles. The high CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> was attributed to its stable

porous structure in the multiple carbonation/calcination cycles.

**Keywords** CaO · Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> · Carbonation · Calcination · CO<sub>2</sub> uptake

## Introduction

Recently, CO<sub>2</sub> capture technologies have been significantly developed. Adsorption methods using solid materials are an alternative to the absorption technology in the processes of purification gases from CO<sub>2</sub> [1]. The development of solid materials with potential application for CO<sub>2</sub> capture is a topic of great scientific interest [2–4]. Calcium-based sorbents are widely used for the control of SO<sub>2</sub> emissions [5–10]. The calcium-based sorbents can be also used to capture CO<sub>2</sub>. Calcium looping, i.e., repetitive carbonation/calcination cycles of CaO, is a promising CO<sub>2</sub> capture technology for fossil fuel-fired power plants [11, 12]. The calcium looping involves a carbonation process, where CaO absorbs CO<sub>2</sub> to generate CaCO<sub>3</sub> at 650–750 °C in a carbonator, and a calcination process, where the CaCO<sub>3</sub> is calcined under oxy-combustion or steam to produce a pure CO<sub>2</sub> stream (for reclaim and storage) and CaO in a calciner at temperature above 850 °C. After the carbonation/calcination cycle, the regenerated CaO returns to the carbonator for the next CO<sub>2</sub> adsorption process [13].

However, CO<sub>2</sub> uptake capacities of the calcium-based sorbents decrease with the number of carbonation/calcination cycles [14–16]. Various methods have been used to enhance CO<sub>2</sub> uptake capacities of the calcium-based sorbents [17–19]. The CO<sub>2</sub> uptake by the synthetic calcium-based sorbents prepared by dispersing CaO precursors across the various support materials such as Al<sub>2</sub>O<sub>3</sub> [20],

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MgO [21], CaTiO<sub>3</sub> [22], SiO<sub>2</sub> [23], Y<sub>2</sub>O<sub>3</sub> [24], and cement [25] has been reported. The supporters can stabilize effectively the pore structure and improve CO<sub>2</sub> uptake capacity of the synthetic sorbent. Among those supports, Al<sub>2</sub>O<sub>3</sub> is more prospective because of the low cost and the high improvement in CO<sub>2</sub> uptake capacity of CaO. Al<sub>2</sub>O<sub>3</sub> can react with CaO to generate the various calcium aluminates such as Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> [20, 26–29], Ca<sub>9</sub>Al<sub>6</sub>O<sub>18</sub> [30], and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> [31] under the different conditions. The calcium aluminates are good supporter to improve CO<sub>2</sub> uptake capacity of CaO. The types of the calcium aluminates are determined by the synthesis methods and the raw materials including CaO precursor (such as limestone [20], nano-CaCO<sub>3</sub> [26], calcium acetate [27], Ca(NO<sub>3</sub>)<sub>2</sub> [28], calcium naphthenate [29] and Ca(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> [30]), Al<sub>2</sub>O<sub>3</sub> precursor (such as Al(NO<sub>3</sub>)<sub>3</sub> [20], aluminum sol [26], aluminum acetylacetonate [29]), and dispersant/solvent (2-propanol [20, 27], citric acid [28, 31], xylene [29])). Li et al. [20] used Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and CaO into 2-propanol water solution to prepare CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent (the mass ratio of CaO to Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> = 75:25) by drying and subsequent calcination, which achieved 0.41 g g<sup>-1</sup> of CO<sub>2</sub> uptake after 50 cycles. Zhou et al. [30] used Ca(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> to produce CaO/Ca<sub>9</sub>Al<sub>6</sub>O<sub>18</sub> sorbent (the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> = 90:10) and found that its CO<sub>2</sub> capture capacity was 0.51 g g<sup>-1</sup> after 28 cycles. Zhang et al. [31] used CaCO<sub>3</sub>, citric acid, and aluminum nitrate by citrate preparation route and four step heating mode to fabricate CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> = 91:9), which retained 0.34 g g<sup>-1</sup> of CO<sub>2</sub> uptake after 100 cycles.

It is necessary to prepare high active and cheap CO<sub>2</sub> sorbent in the calcium looping cycles. In this work, we used the limestone, the aluminum nitrate hydrate, and the glycerol water solution by the combustion synthesis method to fabricate the synthetic CO<sub>2</sub> sorbent. The precursor of CaO is the limestone, and it is cheaper than nano-CaCO<sub>3</sub>, calcium acetate, Ca(NO<sub>3</sub>)<sub>2</sub>, calcium naphthenate, and Ca(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>. The cost of the glycerol used in the preparation of the synthetic sorbent is also lower than that of 2-propanol, citric acid, and xylene. The glycerol as a byproduct can be also obtained from the preparation of the biodiesel fuel [32]. CaO derived from the limestone and the aluminum nitrate hydrate were dissolved in the glycerol water solution. The glycerol was inflammable. The synthetic sorbent was synthesized by Ca<sup>2+</sup> and Al<sup>3+</sup> in the glycerol water solution by the combustion. Thus, the combustion process of the solution is also the synthesis process of Ca<sup>2+</sup> and Al<sup>3+</sup>. The effects of the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub>, the cycle number, the carbonation conditions, and the calcination conditions on the CO<sub>2</sub> uptake by the obtained synthetic sorbent were studied. The microstructure of the synthetic sorbent in the calcium looping cycles was also examined.

## Experimental

A typical limestone in Shandong Province, China, was the precursor of CaO. The chemical compositions of the limestone were analyzed by X-ray fluorescence (XRF, AXIOS PW4400) as shown in Table 1. The limestone was completely decomposed into CaO at 850 °C for 20 min. CaO derived from the limestone was ground and sieved below 0.125 mm. The aluminum nitrate hydrate (analytical grade Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Shanghai Qingxi Chemical Technology Co., Ltd, China) and the glycerol (analytical grade C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>, Tianjin Kemiou Chemical Reagent Co., Ltd, China) were also used in the preparation of the synthetic calcium-based sorbent. Firstly, 60 mL glycerol was dissolved in 50 mL deionized water and stirred at 25 °C for 20 min and then, the solution was heated from 25 to 80 °C. Secondly, 10 g CaO and some Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were added in the solution and stirred at 80 °C. In order to obtain different the synthetic sorbents, the mass ratios of CaO derived from the limestone to Al<sub>2</sub>O<sub>3</sub> derived from Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were specified as 85:15, 90:10, and 95:5, respectively. CaO reacted with water to generate Ca(OH)<sub>2</sub>, which could be dissolved in the glycerol. After Ca(OH)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were completely dissolved in the glycerol water solution, the solution was sent to a muffle furnace for the combustion synthesis process. Later, the solution was combusted in the muffle furnace (800 °C) under air atmosphere for 1 h. The rapid burning of the glycerol was observed in the combustion process. Simultaneously, the calcium aluminate was synthesized by Ca<sup>2+</sup> and Al<sup>3+</sup> in the solution in the combustion process of the glycerol. Therefore, the combustion process was also synthesis process. And the synthetic sorbent was obtained after the combustion synthesis. The synthetic sorbent was ground and sieved to size <0.125 mm.

A dual fixed-bed reactor (DFR) [4] operated under atmospheric pressure was used to determine the CO<sub>2</sub> uptake by the synthetic sorbents in the carbonation/calcination cycles. The reactor mainly comprises a carbonator operated in the range of 650–725 °C and a calciner operated in the range of 850–950 °C. The sample boat containing about 1 g sample was repeatedly shifted between the carbonator and the calciner. The sample was firstly carbonated for 20 min under a gas mixer including 15 % CO<sub>2</sub> and 85 % N<sub>2</sub> in the carbonator and then was calcined for 10 min under the pure N<sub>2</sub> or CO<sub>2</sub> in the calciner. And then, the first cycle for CO<sub>2</sub> uptake was finished. At each cycle, the sample mass was weighed after the carbonation and the calcination by an electronic balance (precision accuracy is 0.1 mg). CO<sub>2</sub>

**Table 1** Chemical compositions of the limestone by XRF/mass %

CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Others	LOI <sup>a</sup>
52.08	1.32	3.32	0.53	0.03	0.02	0.47	42.23

<sup>a</sup> Loss on ignition

uptake capacity was used to describe the CO<sub>2</sub> uptake performance of the synthetic sorbent during the multiple carbonation/calcination cycles as follows:

$$C_N = \frac{m_{\text{car},N}(t) - m_{\text{cal},N}}{m_0} \quad (1)$$

where  $t$  is carbonation time, min.  $C_N$  means CO<sub>2</sub> uptake capacity of sample in the  $N$ th cycle which indicates CO<sub>2</sub> adsorption amount per unit mass of sample, g g<sup>-1</sup>.  $m_0$  represents mass of initial sample, g.  $m_{\text{cal},N}$  is sample mass after complete calcination in the  $N$ th cycle, g.  $m_{\text{car},N}(t)$  denotes sample mass after carbonation at  $t$  in the  $N$ th cycle, g.

The CO<sub>2</sub> uptake performance of the synthetic sorbent with the reaction time was studied in an atmospheric thermogravimetric analyzer (TG, Mettler Toledo TGA/SDTA851<sup>e</sup>). The uncycled and the cycled sorbents which had experienced various cycles from DFR were selected as the samples in TG. The sample mass was 5 mg. The temperature of TG increased from the room temperature to the carbonation temperature (650–700 °C) with a heating rate of 30 °C min<sup>-1</sup> and was kept 15 min at this temperature in pure N<sub>2</sub>. Then, the atmosphere was switch to the carbonation atmosphere (15 % CO<sub>2</sub> and 85 % N<sub>2</sub>). The CO<sub>2</sub> uptake capacity of the sample was computed according to Eq. 1. The CO<sub>2</sub> uptake rate of the sample was defined as follows:

$$v_N = \frac{dC_N}{dt} \quad (2)$$

where  $v_N$  denotes CO<sub>2</sub> uptake rate of sample in the  $N$ th cycle, g g<sup>-1</sup> min<sup>-1</sup>.

The phase compositions of the sample from DFR were examined by an X-ray diffraction (XRD, D/Max-III A). The apparent morphologies of the samples after different carbonation/calcination cycles sampled from DFR were detected by a scanning electron microscope (SEM, JEOL JSM-7600F). The element distributions in the surface of the sample from DFR were examined by an energy-dispersive X-ray (EDX, Oxford INCA sight X). The microstructure parameters of the sample from DFR were detected by an accelerated surface area and porosimetry system (Micromeritics, ASAP 2020-M) abased on N<sub>2</sub> adsorption method. It should be mentioned that the surface area and the pore volume of the sample were computed by BET method and BJH model, respectively.

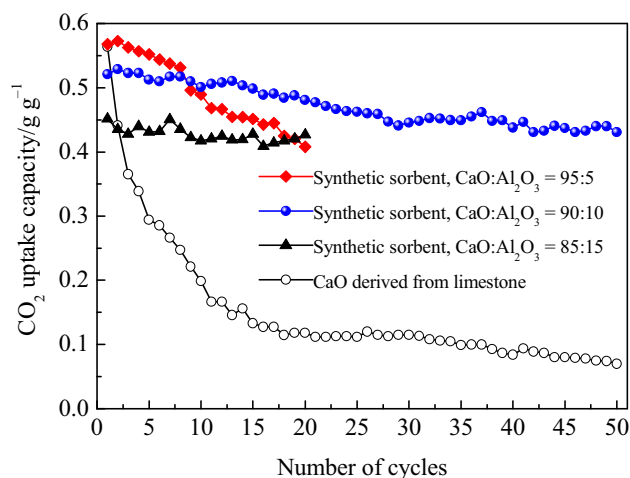
## Results and discussion

### Effect of mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> on cyclic CO<sub>2</sub> uptake by synthetic sorbent

Figure 1 shows the cyclic CO<sub>2</sub> uptake capacity of the synthetic calcium-based sorbents contained the various mass

ratios of CaO to Al<sub>2</sub>O<sub>3</sub> in the carbonation/calcination cycles in DFR. The CO<sub>2</sub> uptake capacity of the synthetic sorbent contained the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 95:5 is higher than that of the sorbent possessed the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10 in the previous eight cycles, but the CO<sub>2</sub> uptake capacity of the former is lower than that of the latter after nine cycles. The synthetic sorbent possessed the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 85:15 exhibits lower CO<sub>2</sub> uptake capacity than the sorbent possessed the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10. Thus, the optimum mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> is 90:10. The CaO content of the synthetic sorbent is less than that of the limestone. At the same time, the CO<sub>2</sub> capture activity of CaO derived from the limestone is high during the first cycle. Therefore, the CO<sub>2</sub> capture capacity of CaO is higher that that of the synthetic sorbent (the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> = 90:10) after one cycle. The CO<sub>2</sub> uptake capacity of the synthetic sorbent (the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10) drops slowly with the number of cycles. As the cycle number increases from 1 to 50, CO<sub>2</sub> uptake capacity of the synthetic sorbent (the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10) decreases by 17 %, while that of CaO drops 88 %. The CO<sub>2</sub> uptake capacity of the synthetic sorbent (the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10) after 50 cycles is 0.43 g g<sup>-1</sup>, which is about six times as high as that of CaO after 50 cycles for the same reaction conditions.

The XRD spectrum of the obtained synthetic sorbent contained the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10 is presented in Fig. 2. The XRD quantitative analysis shows that the main compositions of the synthetic sorbent contained the mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10 are CaO and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, and the mass ratio of CaO to Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is 74:26. Thus, the following researches focus on the CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26). The SEM–EDS mapping of the surface of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>

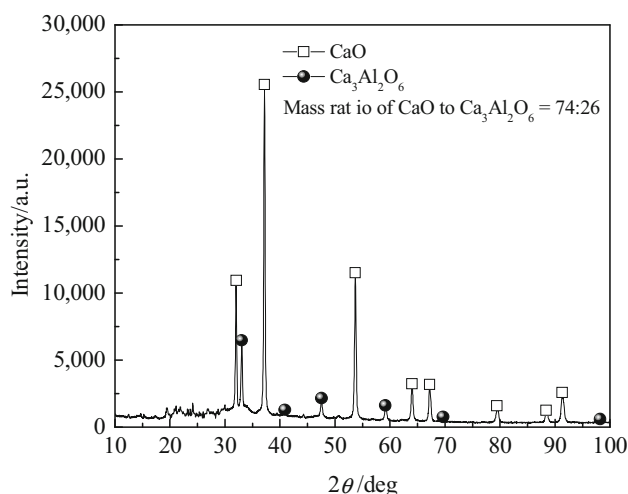


**Fig. 1** Cyclic CO<sub>2</sub> uptake by synthetic sorbent contained different mass ratios of CaO:Al<sub>2</sub>O<sub>3</sub> in DFR (carbonation: 700 °C, 15 % CO<sub>2</sub>, 20 min; calcination: 850 °C, 10 min, pure N<sub>2</sub>)

sorbent is shown in Fig. 3. Ca, Al, and O elements disperse uniformly in the surface of the initial synthetic sorbent. It suggests that CaO as the CO<sub>2</sub> sorbent and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> as the inert support are evenly mixed in the synthetic sorbent. The glycerol is soluble in the water. At the same time, Ca(OH)<sub>2</sub> generated by the hydration of CaO and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O are dissolved in the glycerol and the water, respectively. Thus, the obtained solution is the homogeneous solution. Ca<sup>2+</sup> and Al<sup>3+</sup> are distributed uniformly in the glycerol water solution. Therefore, CaO and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> uniformly distribute in the obtained synthetic sorbent after the combustion synthesis. The high CO<sub>2</sub> uptake capacity of the synthetic sorbent in the cycles is attributed to the good dispersion of CaO and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>.

#### Effect of cycle number on cyclic CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>

The CO<sub>2</sub> uptake capacities and rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent (the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO derived from the limestone with the number of cycles in TG are plotted in Fig. 4. The CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO increase rapidly with the carbonation time in the previous 5 min and then rise slowly after 5 min, as shown in Fig. 4a. Although the CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is lower than that of CaO in the first cycle at the same reaction time, the CO<sub>2</sub> uptake capacity of the former is much higher than that of CaO in the other cycles. For example, the CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> at 5 min in the 10th and the 50th cycles are 2.1 and 6.2 times as high as those of CaO for the same reaction conditions, respectively. For the same reaction time in the previous 2.5 min, the CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> remains almost the same with the number



**Fig. 2** XRD spectrum of initial synthetic sorbent contained mass ratio of CaO:Al<sub>2</sub>O<sub>3</sub> = 90:10

of cycles, whereas that of CaO decays rapidly, as illustrated in Fig. 4a. The CO<sub>2</sub> uptake rate is obtained according to Eq. 2, as presented in Fig. 4b. It is found that the carbonation time to reach the maximum CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is much sooner than that of CaO in each cycle. The CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is higher than that of CaO in previous 5 min except in the first cycle. After 5 min, the CO<sub>2</sub> uptake rate of CaO becomes almost zero, whereas CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> still remains the high reaction rate.

#### Effect of carbonation conditions on cyclic CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>

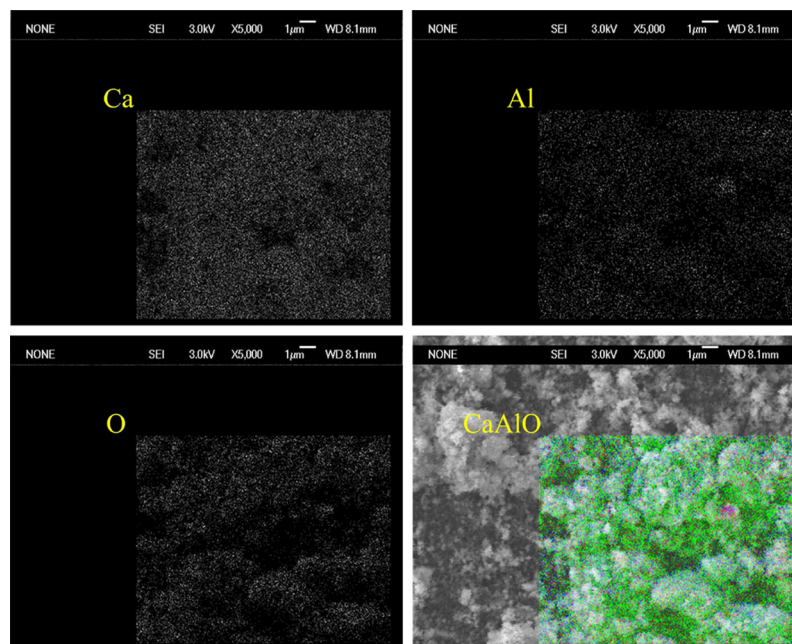
The optimum carbonation temperature window of the general calcium-based sorbent is 650–700 °C in the carbonation/calcination cycles [33, 34]. It is necessary to examine the specific carbonation temperature which is favorable to the CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>. The effect of the carbonation temperature on the cyclic CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO derived from the limestone is depicted in Fig. 5. In the range of 650–720 °C, CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> exhibits slightly higher CO<sub>2</sub> uptake capacity at 700 °C. It is found that the optimum carbonation temperature window of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is still 650–700 °C. CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> at 650, 680, and 700 °C for 20-min carbonation are 4.8, 3.1, and 4.1 times as high as those of CaO after 20 cycles, respectively.

The effect of the carbonation temperature on the CO<sub>2</sub> uptake capacities and rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO in the 10th cycle in TG are displayed in Fig. 6. The influence of the carbonation temperature on the CO<sub>2</sub> uptake capacity and rate of CaO is greater than that of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, especially in previous 5 min. For example, with the carbonation temperature increasing from 650 to 700 °C, the CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO for 3-min carbonation in the 10th cycle increase by 6 and 58 %, respectively, as shown in Fig. 6a. The time to reach the maximum CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is shortened with the carbonation temperature increasing from 650 to 700 °C in the 10th cycle, as presented in Fig. 6b. The maximum CO<sub>2</sub> uptake rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> in the range of 650–700 °C are almost the same. However, the maximum CO<sub>2</sub> uptake rates of CaO in the range of 650–700 °C exhibit great differences.

#### Effect of calcination conditions on cyclic CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>

CO<sub>2</sub> is captured by CaO in the carbonator to turn into CaCO<sub>3</sub>. In order to provide the heat of regeneration of

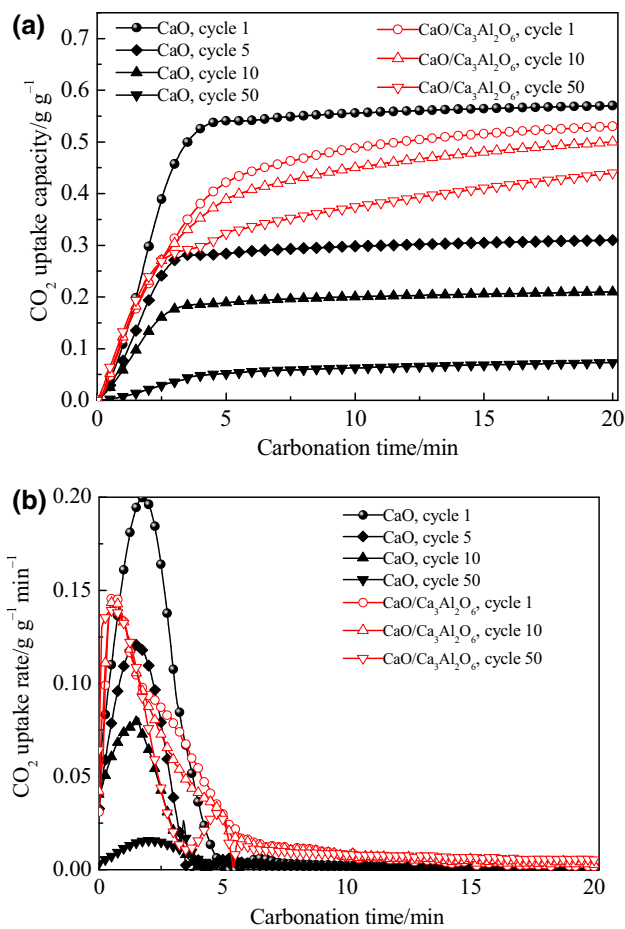
**Fig. 3** SEM-EDS mapping of initial CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent (mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26)



CaCO<sub>3</sub> and produce a pure CO<sub>2</sub> stream (>95 %, dry) for sequestration and recycling in the industrial application, the oxy-combustion of fuel is employed in the calciner. Therefore, the calcination of the carbonated sorbent was carried out in the atmosphere of the almost pure CO<sub>2</sub>. It is necessary to investigate the CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> for calcination under pure CO<sub>2</sub>. Figure 7 shows the temperature and the atmosphere in the calcination on the cyclic CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO derived from the limestone. The previous research reported that improving the calcination temperature intensified the sintering of the calcium-based sorbents and it decreased the CO<sub>2</sub> uptake capacity [15, 35, 36]. As the calcination temperature rises, CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO both exhibit a drop in the CO<sub>2</sub> uptake capacity due to the sintering, but the sintering resistances of the two sorbents are obviously different. With increasing the calcination temperature from 850 to 950 °C under pure N<sub>2</sub>, CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO after 20 cycles decay by 14 and 37 %, respectively. Moreover, the high CO<sub>2</sub> concentration in the calcination atmosphere aggravates the sintering [37]. When calcination temperature is 950 °C, CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO calcined under pure CO<sub>2</sub> after 20 cycles are 12 and 40 % lower than those of the two sorbents calcined under pure N<sub>2</sub>, respectively. Accordingly, CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO after 20 cycles under the severe calcination conditions (950 °C, pure CO<sub>2</sub>) are about 25 and 62 % lower, respectively, compared with those of the two sorbents under the moderate calcination conditions (850 °C, pure N<sub>2</sub>).

The effects of the calcination conditions on the CO<sub>2</sub> uptake capacities and rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO to Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO in the 10th cycle in TG are depicted in Fig. 8. The higher temperature and CO<sub>2</sub> concentration in the calcination process lead to drop in the CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO at the same carbonation time in the 10th cycle, but CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> retains the higher CO<sub>2</sub> uptake capacity under the severe calcination conditions. For example, when the moderate conditions (850 °C, pure N<sub>2</sub>) are changed into the severe conditions (950 °C, pure CO<sub>2</sub>), the CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO at 3 min in the 10th cycle drops by approximately 24 and 61 %, as plotted in Fig. 8a. When the calcination conditions become more severe, the CO<sub>2</sub> uptake rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO in the 10th cycle decrease and the time to reach the maximum CO<sub>2</sub> uptake rates is also prolonged, as illustrated in Fig. 8b. It is found that the CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is much higher than that of CaO under the more severe calcination conditions at the same carbonation time in the 10th cycle. The results from DFR and TG indicate that CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent possesses obviously higher sintering resistance than CaO under the more severe calcination conditions.

The precursors, the preparation method, and CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) are compared with those of CaO/calcium aluminates reported in the literature, as presented in Table 2. It can be found that CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent prepared from the limestone, the aluminum nitrate hydrate, and the glycerol water solution by the combustion

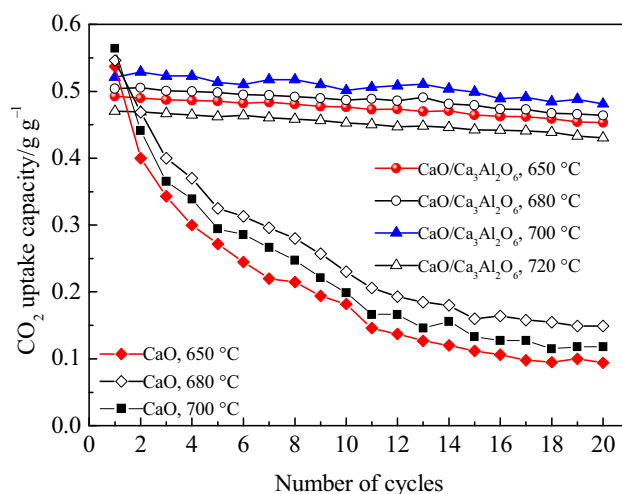


**Fig. 4** CO<sub>2</sub> uptake capacities and rates of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO in various cycles with reaction time in TG (carbonation: 700 °C, 15 % CO<sub>2</sub>, 20 min; calcination: 850 °C, 10 min, pure N<sub>2</sub>). **a** CO<sub>2</sub> uptake capacity, **b** CO<sub>2</sub> uptake rate

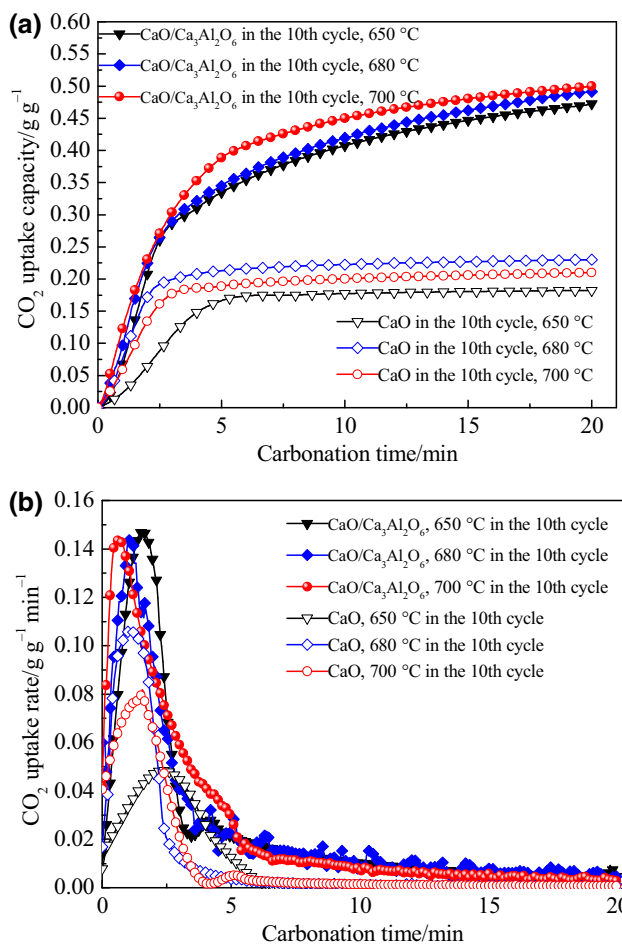
synthesis exhibits higher CO<sub>2</sub> uptake capacity than some synthetic sorbents such as CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> [20, 26, 27] and CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> [31]. The materials such as the limestone and the glycerol in the preparation of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent are also not costly, compared with those in the preparation of the synthetic sorbent reported in the references. Thus, the obtained CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent by the combustion synthesis is a promising CO<sub>2</sub> sorbent in the calcium looping technology.

#### Microstructure analysis

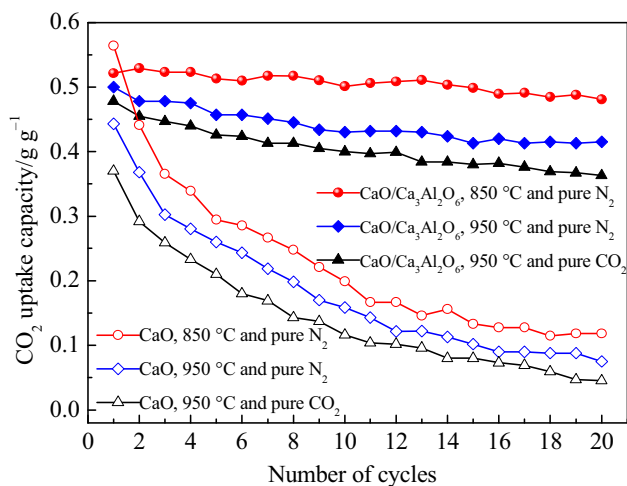
The apparent morphologies of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO after 1 and 10 cycles detected by SEM analysis are presented in Fig. 9. Compared with that of CaO, the surface of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> appears more porous and loose than that of CaO after the same cycles. As the number of cycles rises from 1 to 10,



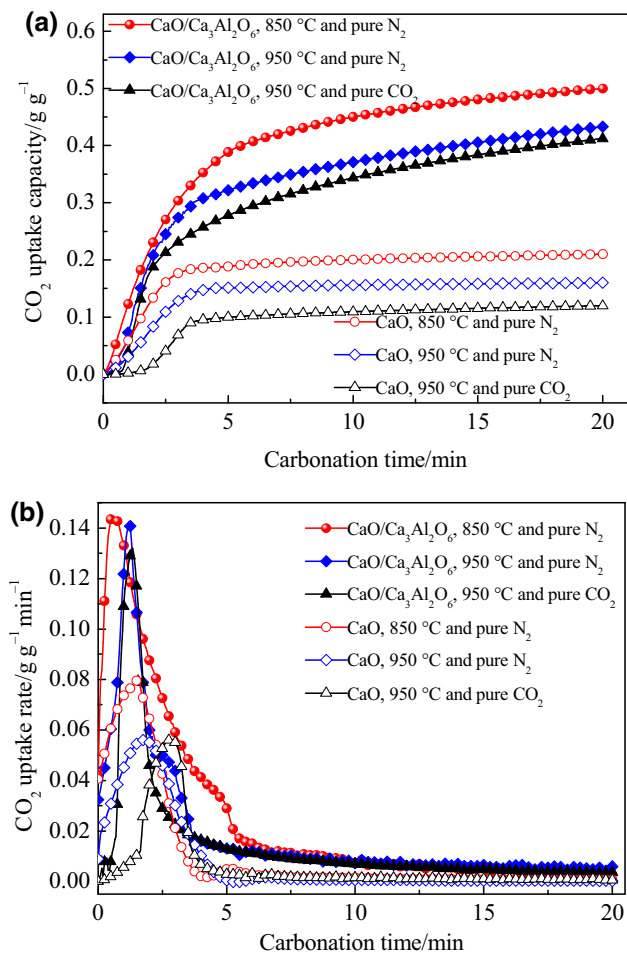
**Fig. 5** Effect of carbonation temperature on CO<sub>2</sub> uptake capacities of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO in DFR (carbonation: 15 % CO<sub>2</sub>, 20 min; calcination: 10 min, 850 °C, pure N<sub>2</sub>)



**Fig. 6** CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> contained mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO at various carbonation temperatures in the 10th cycle with carbonation time in TG (carbonation: 15 % CO<sub>2</sub>, 20 min; calcination: 10 min, 850 °C, pure N<sub>2</sub>). **a** CO<sub>2</sub> uptake capacity, **b** CO<sub>2</sub> uptake rate



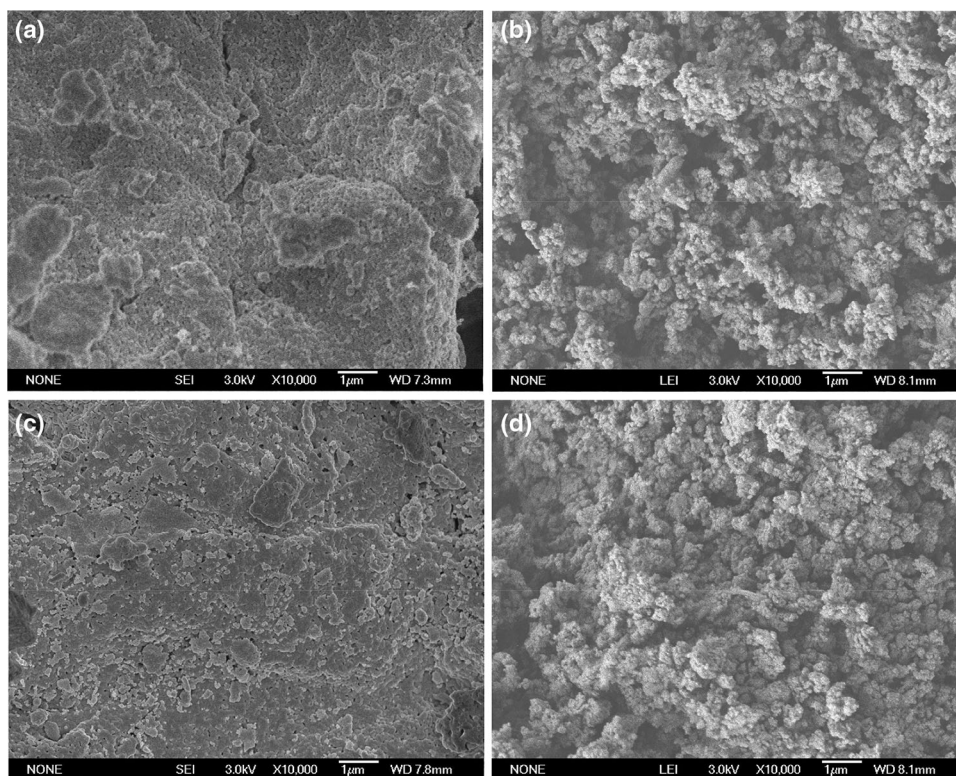
**Fig. 7** Effect of calcination temperature and atmosphere on CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26 and CaO in DFR (carbonation: 700 °C, 15 % CO<sub>2</sub>, 20 min; calcination: 10 min)



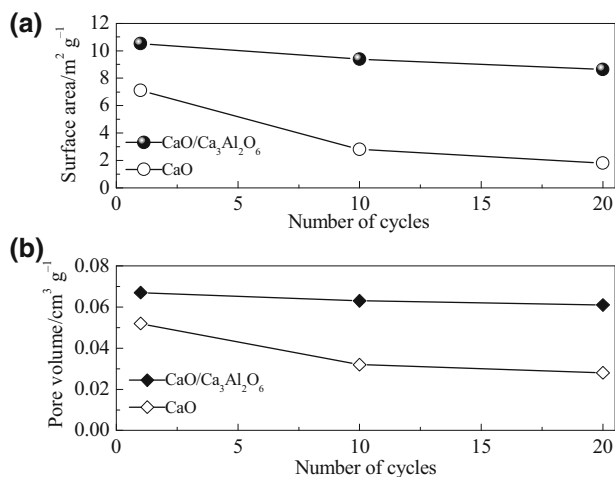
**Fig. 8** CO<sub>2</sub> uptake by CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO in the 10th cycle under various calcination conditions in TG (carbonation: 700 °C, 15 % CO<sub>2</sub>, 20 min; calcination: 10 min). **a** CO<sub>2</sub> uptake capacity, **b** CO<sub>2</sub> uptake rate

**Table 2** Comparison of CO<sub>2</sub> uptake between CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> obtained in this work and other CaO/calcium aluminates presented in literature

Synthetic sorbent (mass ratio of CaO:Al <sub>2</sub> O <sub>3</sub> )	Precursors prepared method	Carbonation conditions	Calcination conditions	CO <sub>2</sub> uptake/g g <sup>-1</sup>
CaO/Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> (90:10) [in this work]	Limestone, Al(NO <sub>3</sub> ) <sub>3</sub> , glycerol, combustion synthesis method	700 °C, 15 % CO <sub>2</sub> , 20 min	850 °C, N <sub>2</sub> , 10 min	0.43 (after 50 cycles)
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> (87:13) [20]	CaO, Al(NO <sub>3</sub> ) <sub>3</sub> , 2-propanol, mixing method	700 °C, 20 % CO <sub>2</sub> , 30 min	850 °C, N <sub>2</sub> , 5 min	0.41 (after 50 cycles)
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> (66:34) [26]	Nano-CaCO <sub>3</sub> , aluminum sol, mixing method	650 °C, 33 % CO <sub>2</sub> , 40 min	800 °C, N <sub>2</sub> , 5 min	0.18 (after 50 cycles)
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> (92:8) [27]	Calcium acetate, Al(NO <sub>3</sub> ) <sub>3</sub> , 2-propanol, mixing method	690 °C, 33 % CO <sub>2</sub> , 30 min	850 °C, N <sub>2</sub> , 5 min	0.36 (after 45 cycles)
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> (90:10) [28]	Ca(NO <sub>3</sub> ) <sub>2</sub> , Al(NO <sub>3</sub> ) <sub>3</sub> , citric acid, sol-gel combustion synthesis method	850 °C, 100 % CO <sub>2</sub> , 30 min	850 °C, N <sub>2</sub> , 10 min	0.47 (after 11 cycles)
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> (82:18) [29]	Calcium naphthenate, aluminum acetylacetonate, xylene, single nozzle flame spray pyrolysis method	700 °C, 100 % CO <sub>2</sub> , 30 min	700 °C, He, 30 min	0.40 (after 100 cycles)
CaO/Ca <sub>9</sub> Al <sub>6</sub> O <sub>18</sub> (90:10) [30]	Ca(C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ) <sub>2</sub> , Al(NO <sub>3</sub> ) <sub>3</sub> , mixing method	650 °C, 15 % CO <sub>2</sub> , 30 min	800 °C, N <sub>2</sub> , 10 min	0.51 (after 28 cycles)
CaO/Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> (91:9) [31]	CaCO <sub>3</sub> , citric acid and Al(NO <sub>3</sub> ) <sub>3</sub> , four step heating method	650 °C, 20 % CO <sub>2</sub> , 30 min	850 °C, N <sub>2</sub> , 10 min	0.41 (after 50 cycles)

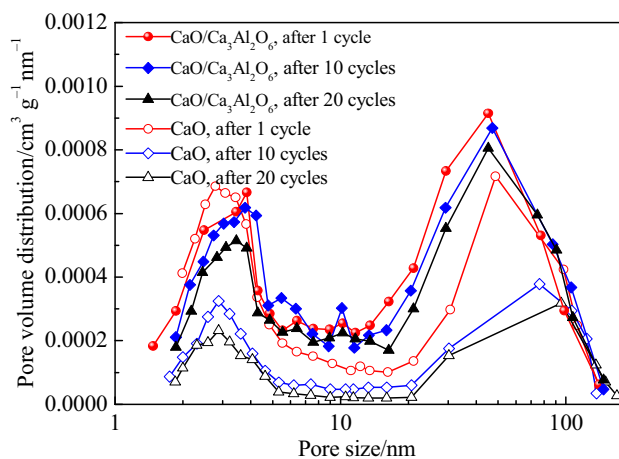


**Fig. 9** SEM images of  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  (mass ratio of  $\text{CaO}:\text{Ca}_3\text{Al}_2\text{O}_6 = 74:26$ ) and  $\text{CaO}$  with number of cycles (carbonation:  $700^\circ\text{C}$ , 15 %  $\text{CO}_2$ , 20 min; calcination: 10 min,  $850^\circ\text{C}$ , pure  $\text{N}_2$ ). **a**  $\text{CaO}$  after 1 cycle, **b**  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  after 1 cycle, **c**  $\text{CaO}$  after 10 cycle, **d**  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  after 10 cycle



**Fig. 10** Surface area and pore volume of  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  (mass ratio of  $\text{CaO}:\text{Ca}_3\text{Al}_2\text{O}_6 = 74:26$ ) and  $\text{CaO}$  with number of cycles (carbonation:  $700^\circ\text{C}$ , 15 %  $\text{CO}_2$ , 20 min; calcination: 10 min,  $850^\circ\text{C}$ , pure  $\text{N}_2$ ). **a** Surface area, **b** Pore volume

lots of pores in the surface of  $\text{CaO}$  are blocked due to the sintering, but the surface of  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  still retains the porous structure. The combustion products ( $\text{CO}_2$  and water vapor) are quickly released from the synthetic sorbent in



**Fig. 11** Pore volume distributions of  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  (mass ratio of  $\text{CaO}:\text{Ca}_3\text{Al}_2\text{O}_6 = 74:26$ ) and  $\text{CaO}$  with number of cycles (carbonation:  $700^\circ\text{C}$ , 15 %  $\text{CO}_2$ , 20 min; calcination: 10 min,  $850^\circ\text{C}$ , pure  $\text{N}_2$ )

the combustion synthesis step, which maybe leads to the formation of the porous structure. The stable porous structure of  $\text{CaO}/\text{Ca}_3\text{Al}_2\text{O}_6$  is favorable for maintaining the high cyclic  $\text{CO}_2$  uptake capacity.



The surface areas and the pore volumes of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO in 20 cycles are shown in Fig. 10. The surface area and the pore volume of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> keep more stable than those of CaO with the cycle number. As the cycle number increases from 1 to 20, the surface areas of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO drop about 18 and 75 %, respectively. After 20 cycles, the surface area and the pore volume of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> are approximately 4.8 and 2.2 times as high as those of CaO, respectively. The high and stable surface area and pore volume of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent in the cycles facilitate the high cyclic CO<sub>2</sub> uptake capacity.

The pore volume distributions of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) and CaO in 20 cycles are depicted in Fig. 11. There are two peaks in the pore volume distribution curves of the two sorbents. One peak is in 2–5 nm, and another peak is in 20–100 nm. It is found that volume of pores in the entire measured range for CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> decreases slightly, whereas that for CaO drops rapidly. The small pores are prone to be blocked in the CO<sub>2</sub> uptake by the sorbent, whereas the pores in 20–100 nm in diameter are important felids for CO<sub>2</sub> uptake [38, 39]. As the cycle number increases from 1 to 20, the volumes of pores in 20–100 nm in diameter for CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaO decrease by 9 and 57 %, respectively. It reveals that Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is good supporter and maintains stable in the pore structure of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> during the multiple cycles. Therefore, CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO:Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> = 74:26) can retain high CO<sub>2</sub> uptake activity in the cycles.

## Conclusions

The limestone, the aluminum nitrate hydrate, and the glycerol water solution as the materials were used to prepare a new CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent by the combustion synthesis. CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent contained the mass ratio of CaO to Al<sub>2</sub>O<sub>3</sub> = 90:10 exhibits higher CO<sub>2</sub> uptake capacity, and its main compositions are CaO and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (the mass ratio of CaO to Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is 74:26). The CO<sub>2</sub> uptake capacity of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> sorbent after 50 cycles can retain 0.43 g g<sup>-1</sup>, which is about six times as high as that of CaO derived from the limestone for the same reaction conditions. The CO<sub>2</sub> uptake rate of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is much higher than that of CaO during previous 5 min after two cycles. The optimum carbonation temperature window of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> is 650–700 °C. CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> shows higher sintering resistance than CaO under the more severe calcination conditions. After 20 cycles, the surface area and the pore volume of CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> are about 4.8 and 2.2 times as high as those of CaO, respectively. CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> possesses more pores in the range of 20–100 nm

in diameter during the cycles, which is helpful to maintain high CO<sub>2</sub> uptake capacity. CaO/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> obtained by the combustion synthesis is promising as a high active CO<sub>2</sub> sorbent in the calcium looping cycles.

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