

## Enhanced cyclic stability of CO<sub>2</sub> adsorption capacity of CaO-based sorbents using La<sub>2</sub>O<sub>3</sub> or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as additives

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**Abstract**—To improve the stability of CaO adsorption capacity for CO<sub>2</sub> capture during multiple carbonation/calcination cycles, modified CaO-based sorbents were synthesized by sol-gel-combustion-synthesis (SGCS) method and wet physical mixing method, respectively, to overcome the problem of loss-in-capacity of CaO-based sorbents. The cyclic CaO adsorption capacity of the sorbents as well as the effect of the addition of La<sub>2</sub>O<sub>3</sub> or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> was investigated in a fixed-bed reactor. The transient phase change and microstructure were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FSEM), respectively. The experimental results indicate that La<sub>2</sub>O<sub>3</sub> played an active role in the carbonation/calcination reactions. When the sorbents were made by wet physical mixing method, CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> was much better than CaO/La<sub>2</sub>O<sub>3</sub> in cyclic CO<sub>2</sub> capture performance. When the sorbents were made by SGCS method, the synthetic CaO/La<sub>2</sub>O<sub>3</sub> sorbent provided the best performance of a carbonation conversion of up to 93% and an adsorption capacity of up to 0.58 g-CO<sub>2</sub>/g-sorbent after 11 cycles.

Key words: CO<sub>2</sub> Capture, CaO, Adsorption Capacity, Carbonation/Calcination Cycles, Sol-gel-combustion-synthesis (SGCS)

### INTRODUCTION

It is now widely acknowledged that the combustion of fossil fuels contributes to the emission of CO<sub>2</sub> in the atmosphere, which in turn contributes to the greenhouse effect. One potential approach is the capture of CO<sub>2</sub> from flue gas followed by its sequestration in geological formations or perhaps ocean storage [1-4]. The purpose of CO<sub>2</sub> capture is to produce a concentrated stream of CO<sub>2</sub> suitable for compression and piping to a storage site. But the flue gas stream contains low concentrations of CO<sub>2</sub>, so it is necessary to produce a nearly pure CO<sub>2</sub> stream suitable for sequestration. The post-combustion CaO-based high temperature carbonation/calcination cycle method [5] and chemical looping combustion method [6,7] have recently been identified to be two of the best candidates for future R&D as an emerging concept in carbon capture by the Technology Task Force of the European Technology Platform for Zero Emission Power Plants. The former method can be applied by using the existing technologies, because many of the components in these systems are commercially available [8,9]. The carbonation of CaO is a reversible reaction:



This reversible reaction (reaction 1) has the potential to be used in a clean, economically feasible CO<sub>2</sub> separation process under moderate conditions, for generation of electricity. Unfortunately, it is widely accepted that the adsorption capacity of the CaO-based sorbents decays through long-term capture and release cycles [10-12]. The carbonation conversion of natural limestone decreases quite quickly to about 20% after 10 cycles [13]. This problem, an indication of poor

reversibility of the carbonation/calcination cycles of CaO/CaCO<sub>3</sub>, is a major challenge for the future application of CaO-based technology for capturing CO<sub>2</sub> and needs to be solved. Therefore, it is necessary to improve the reversibility of the CaO-based sorbents for extended operation cycles.

Some researchers focused on increasing the porosity and surface area of the CaO-based sorbents to overcome the loss-in-capacity problem after multiple carbonation/calcination cycles. Hughes et al. [14] increased the pore volume and pore surface area of limestone by a process of steam hydration conducted at 150 °C and 475 kPa. They found that the steam hydration/activation method can improve the long-term performance of the CaO-based sorbents. A CaO conversion of this sorbent was 52% when the cyclic adsorption was tested at 750 °C after 20 cycles. Gupta et al. [15] synthesized high surface area CaO sorbents from precipitated calcium carbonate. They suggested that a mesoporous structure with porosity in the 5-20 nm pore size range will be less susceptible to pore blockage, thus providing higher CO<sub>2</sub> capture capacity and better stability. When the CaO derived from the precipitated calcium carbonate was subjected to an adsorption test at 700 °C, the CaO conversion of this sorbent was up to 95% after two cycles.

Other researchers designed synthetic sorbents to enhance the cyclic performance of CaO-based sorbents. Various materials were added into CaO to improve the adsorption capacity or cyclic stability of CaO-based sorbents for reversible carbonation/calcination reactions. Li et al [16] investigated the effect of adding an inert phase of Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> into CaO. They showed that a weight ratio of CaO to Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> of 75 : 25 that is subjected to calcination at 900 °C for 1.5 h is optimal for preparing this sorbent. A CaO conversion of this sorbent was 65% after 50 cycles, when it was carbonated at 650 °C. Albrecht et al. [17] suggested that incorporating finely dispersed MgO or La<sub>2</sub>O<sub>3</sub> in the CaO-based sorbent can reduce the rate of the decline

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of CaO activity during high temperature reactions. They also found that the sorbents subjected to the more severe initial calcination conditions can have higher adsorption capacity after many cycles. Liu et al. [18,19] proposed the performance of CaO sorbents derived from different precursors in the latest researches. The best performing CaO-based sorbents were obtained from D-gluconic acid. They also found that a simple wet mixing method can produce sintering-resistant sorbents from calcium and magnesium salts of D-gluconic acid.

In this paper, a few novel CaO-based sorbents were synthesized from inorganic calcium and aluminum (or lanthanum) salts as precursors. These modified sorbents were prepared by wet physical mixing method and sol-gel-combustion-synthesis (SGCS) method, respectively. The cyclic carbonation/calcination performance of these sorbents was investigated in a fixed bed reactor system. The objective of this work was to find a suitable method for each synthetic CaO-based sorbent without the problem of loss-in-capacity after many carbonation/calcination cycles.

## EXPERIMENTAL SECTION

### 1. Preparation of the Wet Physical Mixing Method

All of the precursors used in this study were analytical grade. In this method, predetermined amounts of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (or Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and the powdered pure CaCO<sub>3</sub> were added into distilled water with the weight ratio of CaO to La<sub>2</sub>O<sub>3</sub> (or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) of 80 : 20. This solution was then stirred for 15 h at room temperature and subsequently dried at 120 °C for another 5 h in a drying oven before it was calcined at 850 °C for 2 h in a muffle furnace.

### 2. Preparation of the Sol-gel-combustion-synthesis (SGCS) Method

In this method (Fig. 1), first, predetermined amounts of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (or Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were added into distilled water with the weight ratio of CaO to La<sub>2</sub>O<sub>3</sub> (or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) of 80 : 20 and the mole ratio of water to metal ions of about 40 : 1. Then the citric acid was added into the solution at a ratio, citric acid to metal ions, of 1 : 1 at room temperature. Second, the mixture was continuously stirred and kept at 80 °C in an electric-heated thermostatic water bath for a sufficient period of 7 h to allow a well-dispersed sol to be formed. Third, the sol was placed at room temperature for 18 h to form a wet gel. The wet gel was then put into a drying oven at 80 °C for 5 h and subsequently dried at 110 °C for another 12 h until the dry gel was formed. Finally, the dry gel was put into a muffle furnace quickly at 600 °C to get it burnt out before it was calcined at 850 °C for 2 h in the muffle furnace.

### 3. Experimental System

Multi-cyclic CO<sub>2</sub> capture was tested in a fixed bed, which focused on the weight changes of the carbonation/calcination reactions. The

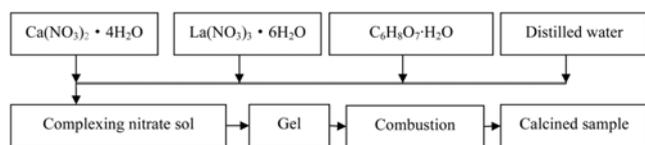


Fig. 1. The main technological process of sol-gel-combustion-synthesis (SGCS) method.

variation of sample mass was measured by a delicate electronic balance. All carbonation reactions were carried out at 850 °C in 100% CO<sub>2</sub>, while calcination reactions were at 850 °C in 100% N<sub>2</sub> at atmospheric pressure so as to be consistent with the research of Manovic and Anthony [10]. The gas flow rate was 2 L/min, and the time for carbonation and calcination was 30 and 10 min, respectively. A three-way valve was used to switch between pure N<sub>2</sub> and pure CO<sub>2</sub>. The microstructure of the samples was investigated by field emission scanning electron microscopy (FSEM, SIRION200, FEI Inc) with 20 kV of accelerating voltage under high vacuum. The phase composition of samples was determined by X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V.) with Cu K $\alpha$  radiation,  $\lambda=0.1542$  nm in the  $2\theta$  range of 15°-85° with a scanning step of 0.02°.

### 4. Experimental Data Analysis Method

The carbonation conversion ( $X_n$ ) and the adsorption capacity ( $C_n$ ) were calculated using the equations as follows.

$$X_n = \frac{m_n - m_0}{m_0 \cdot b} \cdot \frac{W_{CaO}}{W_{CO_2}} \quad (2)$$

$$C_n = \frac{m_n - m_0}{m_0} \quad (3)$$

Where  $m_n$  is mass of the carbonated sample after  $n$  cycle(s),  $m_0$  is mass of the calcined initial sample,  $b$  is content of CaO in the initial calcined sample.  $W_{CaO}$  and  $W_{CO_2}$  are mole mass of CaO and CO<sub>2</sub>, respectively. As a result,  $X_n$  reflects only the reversibility of CaO in the sorbent, while  $C_n$  reflects the overall performance of sorbent.

## RESULTS AND DISCUSSION

### 1. Performance of the Wet Physical Mixing Method

As the previous studies [16-21] indicated that modified sorbents often show slower decay in the initial calcium looping cycles, the carbonation conversions of the novel modified sorbents using either La<sub>2</sub>O<sub>3</sub> or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as “inert” material are higher than those of the pure CaCO<sub>3</sub> sorbent with number of cycles (Fig. 2(a)). The main reason is that the inert material usually acts as a physical barrier to prevent the sintering and aggregation of small CaCO<sub>3</sub> grains. It is also shown from Fig. 2(a) that CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> is much better than CaO/La<sub>2</sub>O<sub>3</sub> and pure CaO on cyclic CO<sub>2</sub> capture. Li et al. [16] pointed out previously that when calcination temperatures in the preparation stage are in the range of 800-1,000 °C, the inert intermediate phase of Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> is formed from calcium and aluminum precursors and it can enhance the adsorption capacity for CaO based sorbent during cyclic reactions. After 11 cycles, the carbonation conversion of CaO/La<sub>2</sub>O<sub>3</sub> sorbent is 36% and the carbonation conversion of pure CaO sorbent is 24%, while CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent provides the highest carbonation conversion of 52%. However, there is little difference in adsorption capacity between CaO/La<sub>2</sub>O<sub>3</sub> sorbent and pure CaCO<sub>3</sub> sorbent after 11 cycles from Fig. 2(b). Therefore, this simple wet physical mixing method should be suitable for the synthetic CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent but not for the CaO/La<sub>2</sub>O<sub>3</sub> sorbent.

### 2. Performance of the SGCS Method

When the sorbents were prepared by SGCS Method, changes had come to CaO/La<sub>2</sub>O<sub>3</sub> sorbent. The results in Fig. 3 clearly show

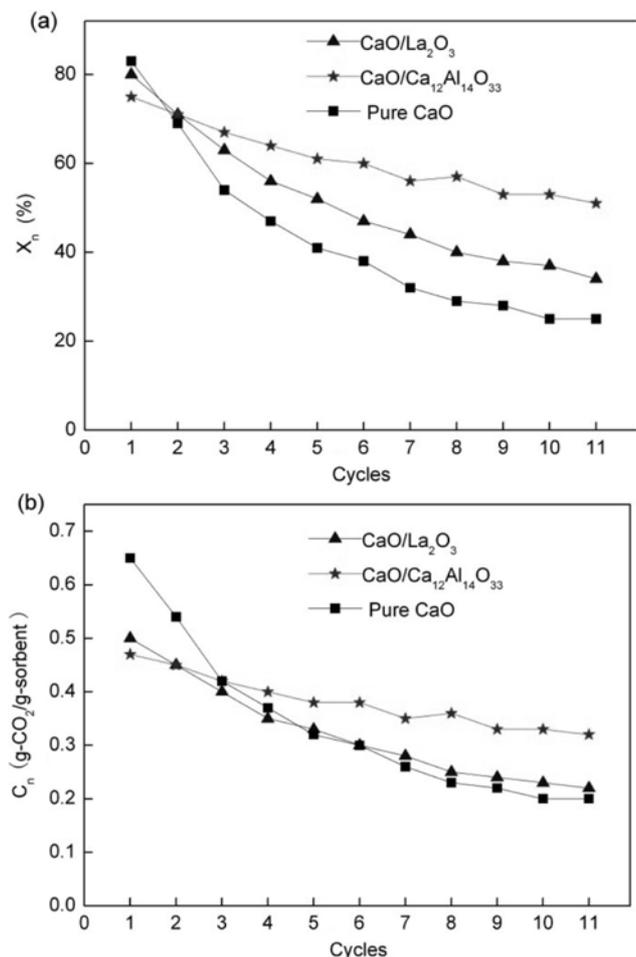


Fig. 2. The performance of the sorbents made by wet physical mixing method compared with pure CaCO<sub>3</sub>. (a) Carbonation conversion; (b) adsorption capacity.

that the adsorption capacity of the two modified sorbents can be improved to be a satisfactorily high level through the SGCS method, especially using La<sub>2</sub>O<sub>3</sub> as additive. In the severe carbonation condition of 850 °C in 100% CO<sub>2</sub>, Fig. 3(a) shows that the carbonation conversions of the CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent are about 95% within 11 cycles, which is much higher than those of the CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (SGCS) sorbent. Fig. 3(b) shows that the novel CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent is able to achieve high adsorption capacities during carbonation/calcination reactions. Its CaO adsorption capacity is up to 0.58 g-CO<sub>2</sub>/g-sorbent after 11 cycles, almost the same as after the first cycle (0.60 g-CO<sub>2</sub>/g-sorbent). As a result, when the synthetic sorbents were made by the SGCS method, the CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent had a perfect performance in improving the stability of CO<sub>2</sub> adsorption capacity during carbonation/calcination cycles.

### 3. Discussion

Li et al. [16] pointed out that during the cyclic carbonation/calcination of CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, the Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> binder does not take part in the reaction and may be considered as inert. However, unlike the Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, La<sub>2</sub>O<sub>3</sub> cannot be considered as inert for the conditions used in the present investigation. Shirsat et al. [22] reported thermo-chemistry in the decomposition of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. The decomposition reaction can be written as follows:

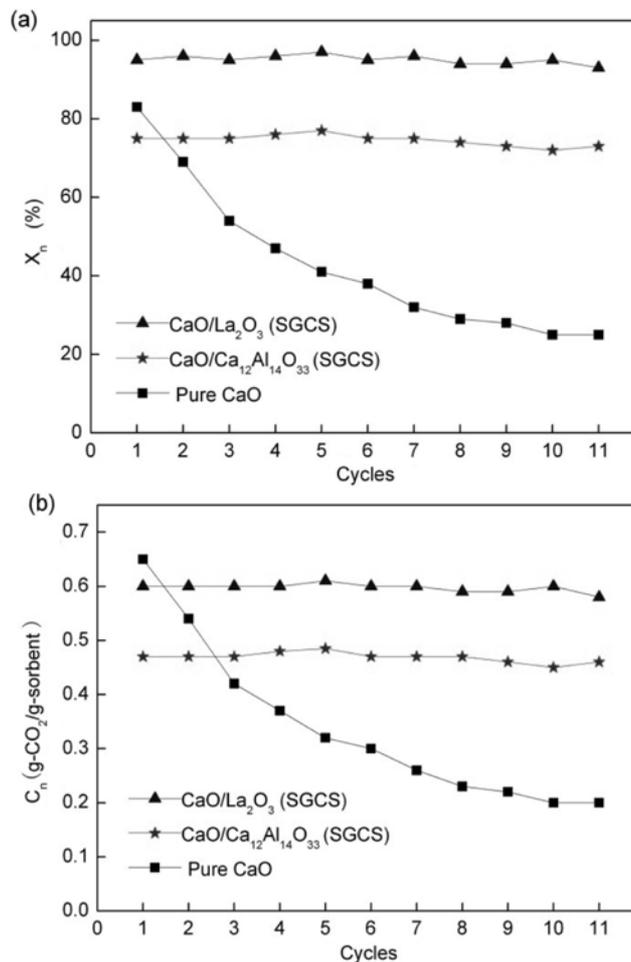


Fig. 3. The performance of the sorbents made by SGCS method compared with pure CaCO<sub>3</sub>. (a) carbonation conversion; (b) adsorption capacity.



And the equilibrium pressure of CO<sub>2</sub> can be measured by the given equation as follows:

$$\ln p_{\text{CO}_2} (\text{pa}) (\pm 0.22) = -17502.2/T + 25.87 \quad (773 \leq T(\text{K}) \leq 1190) \quad (5)$$

From the above equation, when the temperature is 850 °C (1,124 K), the equilibrium pressure of CO<sub>2</sub> is 29,000 pa. As a result, in the process of carbonation of 100% CO<sub>2</sub> under 1 atm, La<sub>2</sub>O<sub>3</sub> adsorbs CO<sub>2</sub> to form the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, while in the process of calcination of 100% N<sub>2</sub> under 1 atm, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> decomposes into La<sub>2</sub>O<sub>3</sub> again.

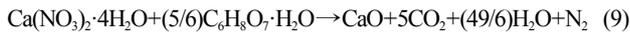
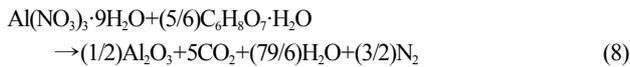
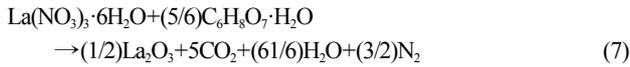
When the sorbents were made by wet physical mixing method in our research, La<sub>2</sub>O<sub>3</sub> was only mixed on the surface of CaO physically. However, Al<sub>2</sub>O<sub>3</sub> was not only physically mixed with CaO, but also had a chemical reaction with CaO as follows:



As a result, Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> could have a much more well-distributed mixing than La<sub>2</sub>O<sub>3</sub> within the CaO-based sorbents. Although both the addition of La<sub>2</sub>O<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> could delay the sintering of CaO particles to give the CaO-based sorbent higher carbonation conversions during cyclic CO<sub>2</sub> capture, the CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent

was much better than the CaO/La<sub>2</sub>O<sub>3</sub> sorbent in cyclic CO<sub>2</sub> capture performance by this simple method shown in Fig. 2.

However, since the sorbents were made by the SGCS method, the calcination of metal nitrates consisted of many physical processes and chemical reactions. In the process of the preparation, after the gel of nitrate and citric acid was ignited, metal nitrates acted as agent of oxidation while citric acted as fuel:



Reactions (7), (8) and (9) released a large amount of gas and heat, leading to the combustion of the dry gel. The particles of the product could be well-dispersed and sintered in the microstructure. Finally, even ultrafine nano-powders were produced. The well-dispersed additives in CaO particles could prevent small CaO particles from agglomeration effectively during high temperature carbonation/cal-

cination reactions; thus the adsorption capacity of the synthetic CaO-based sorbents could be highly improved by this method.

In the case of CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent, XRD analysis of this sorbent shown in Fig. 4 indicates that the initial calcined sample

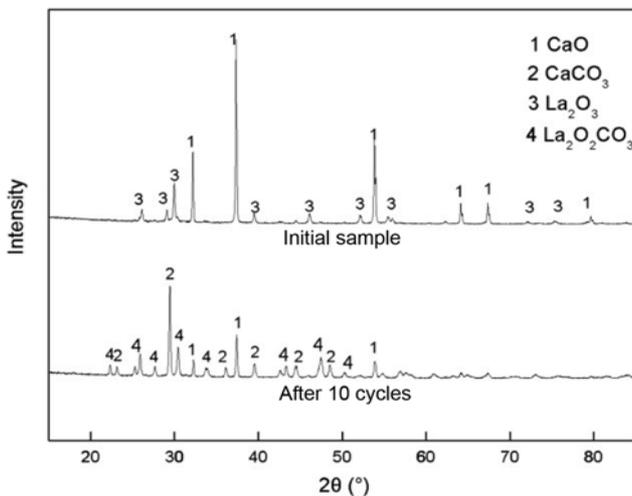


Fig. 4. XRD of the CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent.

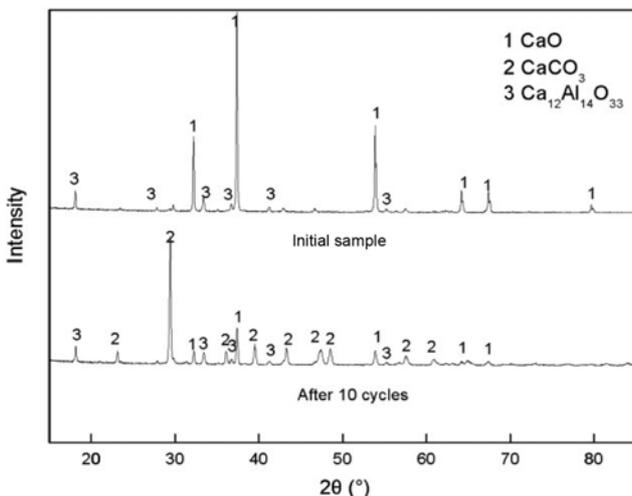


Fig. 5. XRD of the CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (SGCS) sorbent.

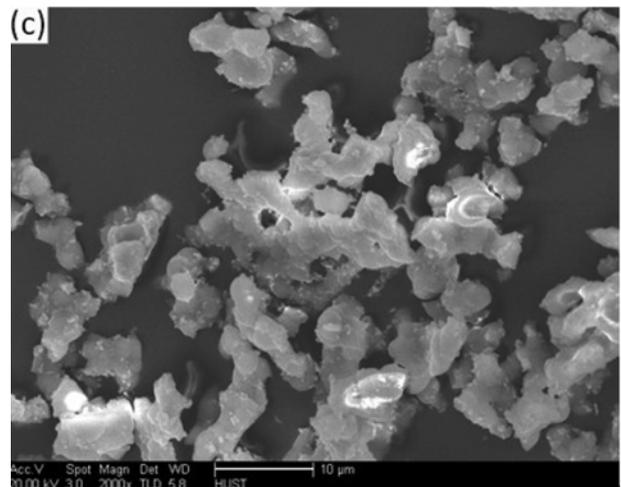
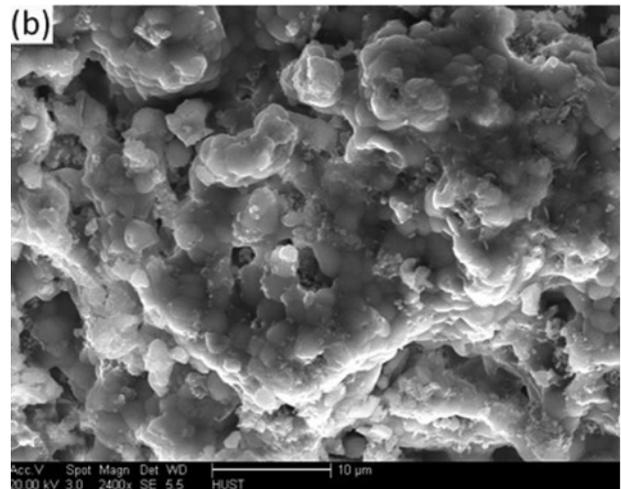
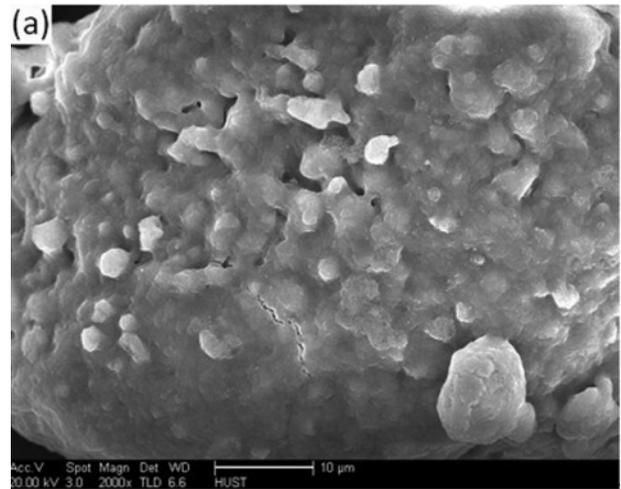


Fig. 6. FSEM photos of the sorbents made by SGCS method compared with pure CaCO<sub>3</sub>. (a) pure CaCO<sub>3</sub> after 7 carbonation/calcination cycles; (b) CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (SGCS) sorbent after 11 carbonation/calcination cycles; (c) CaO/La<sub>2</sub>O<sub>3</sub> (SGCS) sorbent after 11 carbonation/calcination cycles.

exists only in two main materials: CaO and La<sub>2</sub>O<sub>3</sub>. After 10 cycles, this sample also exists only in two main materials: CaCO<sub>3</sub> and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. But in the case of CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (SGCS) sorbent, Al<sub>2</sub>O<sub>3</sub> reacted with CaO into a stable framework of Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. XRD analysis of this sorbent shown in Fig. 5 indicates that the Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> binder does not take part in the cyclic reactions. This is the difference between the addition of La<sub>2</sub>O<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, which results in the different performance in the cyclic CO<sub>2</sub> capture. Therefore, La<sub>2</sub>O<sub>3</sub> acts as CO<sub>2</sub> transferor, which makes CO<sub>2</sub> molecules go through the CaCO<sub>3</sub> product layer much easier during carbonation process, and has a superior performance than Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> for CaO-based sorbents theoretically when both of them are prepared into ultrafine well-dispersed powders.

Fig. 6 shows the microstructure of the modified sorbents and the pure CaCO<sub>3</sub> sorbent after many carbonation/calcination cycles. There are little visible pores on the surface of the pure CaCO<sub>3</sub> sorbent due to severe sintering after seven carbonation/calcination cycles in Fig. 6(a). The blockage and collapse of pores of the CaCO<sub>3</sub> increases the hindrance to the passage of CO<sub>2</sub> during the carbonation process. As a result, the CaO adsorption capacity of the pure CaCO<sub>3</sub> drops sharply with the number of cycles. The surface of the modified sorbents made by SGCS method seems porous in Fig. 6(b), expansive and loose in Fig. 6(c). It can be found that the conglomeration of CaO particles does not occur after 11 carbonation/calcination cycles within the modified sorbents. This structure is beneficial to the CO<sub>2</sub> diffusion within the sorbents.

## CONCLUSIONS

Modified CaO-based sorbents using La<sub>2</sub>O<sub>3</sub> or Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as additives are synthesized by SGCS method and wet physical mixing method in the present work. Unlike Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, La<sub>2</sub>O<sub>3</sub> is not a completely inert material without the ability of adsorbing CO<sub>2</sub>. But when the sorbents are made by wet physical mixing method, Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> can have a much more well-distributed mixing than La<sub>2</sub>O<sub>3</sub> in CaO particles; thus CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent provides a relatively higher CO<sub>2</sub> adsorption capacity after multiple carbonation/calcination cycles.

However, when the sorbents are made by SGCS method, the particles of the product can be well-dispersed and sintered in the microstructure, which subsequently can prevent small CaO particles from agglomeration effectively. Moreover, not only can La<sub>2</sub>O<sub>3</sub> retard the sintering of CaO particles but also adsorb CO<sub>2</sub> in the carbonation process. Therefore, La<sub>2</sub>O<sub>3</sub> acts as CO<sub>2</sub> transferor, which makes CO<sub>2</sub> molecules go through the CaCO<sub>3</sub> product layer much more easily during the carbonation process, and has a superior performance than Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> theoretically for CaO-based sorbents when both of them are prepared into even ultrafine powders. The synthetic CaO/La<sub>2</sub>O<sub>3</sub> (SGCS made) sorbent provides the best performance of a carbonation conversion of up to 93% and an adsorption capacity of up to 0.58 g-CO<sub>2</sub>/g-sorbent after 11 cycles.

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