Korean J. Chem. Eng., **28**(4), 1042-1046 (2011)
DOI: 10.1007/s11814-010-0469-z

Enhanced cyclic stability of CO_2 adsorption capacity of CaO-based sorbents using La_2O_3 or $Ca_{12}Al_{14}O_{33}$ as additives

Cong Luo, Ying Zheng†, Ning Ding, and Chuguang Zheng

State Key Laboratory of Coal Combustion, Department of Energy and Power Engineering,
Huazhong University of Science and Technology, Wuhan 430074, China

(*Received 13 April 2010 • accepted 27 October 2010*)

Abstract−To improve the stability of CaO adsorption capacity for CO_2 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_2O_3 or $Ca_{12}Al_{14}O_{33}$ 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_2O_3 played an active role in the carbonation/calcination reactions. When the sorbents were made by wet physical mixing method, $CaO/Ca_{12}Al_{14}O_{33}$ was much better than CaO/La_2O_3 in cyclic CO_2 capture performance. When the sorbents were made by SGCS method, the synthetic CaO/La_2O_3 sorbent provided the best performance of a carbonation conversion of up to 93% and an adsorption capacity of up to 0.58 g-CO_2/g-sorbent after 11 cycles.

Key words: CO_2 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_2 in the atmosphere, which in turn contributes to the greenhouse effect. One potential approach is the capture of CO_2 from flue gas followed by its sequestration in geological formations or perhaps ocean storage [1-4]. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 suitable for compression and piping to a storage site. But the flue gas stream contains low concentrations of CO_2, so it is necessary to produce a nearly pure CO_2 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:

$$CaO+CO_2 \rightleftharpoons CaCO_3 \tag{1}$$

This reversible reaction (reaction 1) has the potential to be used in a clean, economically feasible CO_2 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 $CaO/CaCO_3$, is a major challenge for the future application of CaO-based technology for capturing CO_2 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_2 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 $Ca_{12}Al_{14}O_{33}$ into CaO. They showed that a weight ratio of CaO to $Ca_{12}Al_{14}O_{33}$ 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_2O_3 in the CaO-based sorbent can reduce the rate of the decline

---

†To whom correspondence should be addressed.
E-mail: zhengying@mail.hust.edu.cn

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-basd 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 $La(NO_3)_3{\cdot}6H_2O$ (or $Al(NO_3)_3{\cdot}9H_2O$) and the powdered pure $CaCO_3$ were added into distilled water with the weight ratio of CaO to La_2O_3 (or $Ca_{12}Al_{14}O_{33}$) 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 $La(NO_3)_3{\cdot}6H_2O$ (or $Al(NO_3)_3{\cdot}9H_2O$) and $Ca(NO_3)_2{\cdot}4H_2O$ were added into distilled water with the weight ratio of CaO to La_2O_3 (or $Ca_{12}Al_{14}O_{33}$) 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_2 capture was tested in a fixed bed, which focused on the weight changes of the carbonation/calcination reactions. The variation of sample mass was measured by a delicate electronic balance. All carbonation reactions were carried out at 850 °C in 100% CO_2, while calcination reactions were at 850 °C in 100% N_2 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_2 and pure CO_2. 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 Kα radiation, λ=0.1542 nm in the 2θ range of 15°-85° with a scanning step of 0.02°.

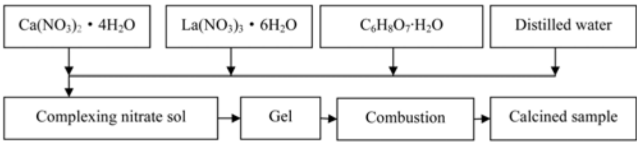

Fig. 1. The main technological process of sol-gel-combustion-synthesis (SGCS) method.

4. Experimental Data Analysis Method

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

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

$$C_n = \frac{m_n - m_0}{m_0} \tag{3}$$

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_2, 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_2O_3 or $Ca_{12}Al_{14}O_{33}$ as "inert" material are higher than those of the pure $CaCO_3$ 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 $CaCO_3$ grains. It is also shown from Fig. 2(a) that $CaO/Ca_{12}Al_{14}O_{33}$ is much better than CaO/La_2O_3 and pure CaO on cyclic CO_2 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 $Ca_{12}Al_{14}O_{33}$ 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_2O_3 sorbent is 36% and the carbonation conversion of pure CaO sorbent is 24%, while $CaO/Ca_{12}Al_{14}O_{33}$ sorbent provides the highest carbonation conversion of 52%. However, there is little difference in adsorption capacity between CaO/La_2O_3 sorbent and pure $CaCO_3$ sorbent after 11 cycles from Fig. 2(b). Therefore, this simple wet physical mixing method should be suitable for the synthetic $CaO/Ca_{12}Al_{14}O_{33}$ sorbent but not for the CaO/La_2O_3 sorbent.

2. Performance of the SGCS Method

When the sorbents were prepared by SGCS Method, changes had come to CaO/La_2O_3 sorbent. The results in Fig. 3 clearly show

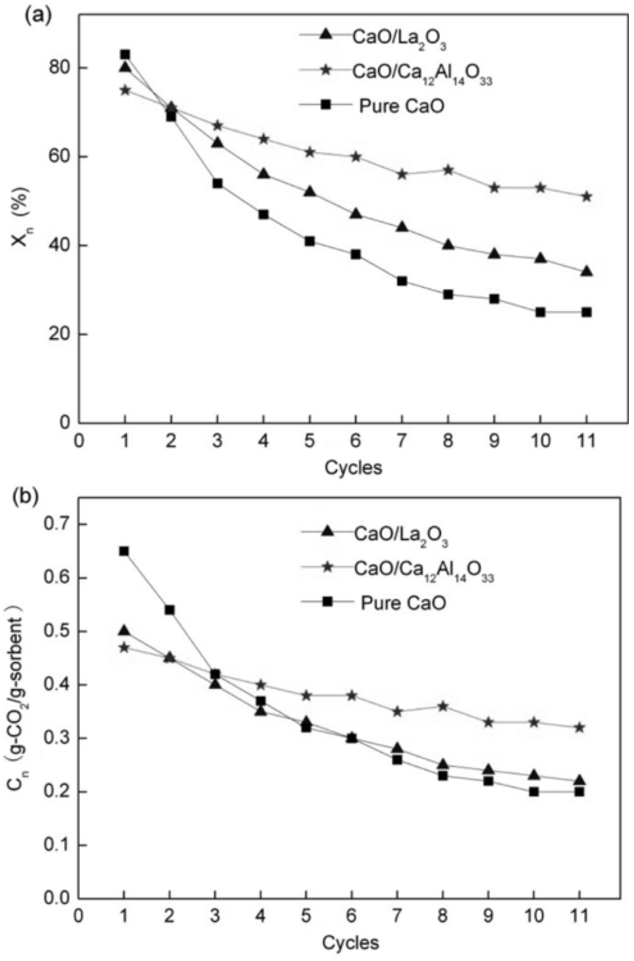

Fig. 2. The performance of the sorbents made by wet physical mixing method compared with pure $CaCO_3$. (a) Carbonation conversion; (b) adsorption capacity.

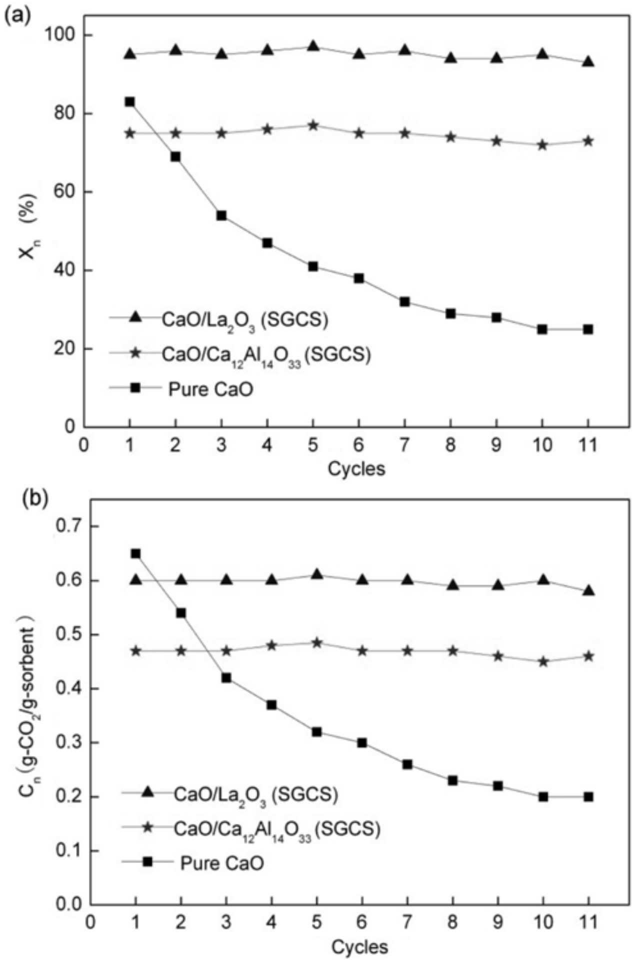

Fig. 3. The performance of the sorbents made by SGCS method compared with pure $CaCO_3$. (a) carbonation conversion; (b) adsorption capacity.

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_2O_3 as additive. In the severe carbonation condition of 850 ºC in 100% CO_2, Fig. 3(a) shows that the carbonation conversions of the CaO/La_2O_3 (SGCS) sorbent are about 95% within 11 cycles, which is much higher than those of the $CaO/Ca_{12}Al_{14}O_{33}$ (SGCS) sorbent. Fig. 3(b) shows that the novel CaO/La_2O_3 (SGCS) sorbent is able to achieve high adsorption capacities during carbonation/calcination reactions. Its CaO adsorption capacity is up to 0.58 g-CO_2/g-sorbent after 11 cycles, almost the same as after the first cycle (0.60 g-CO_2/g-sorbent). As a result, when the synthetic sorbents were made by the SGCS method, the CaO/La_2O_3 (SGCS) sorbent had a perfect performance in improving the stability of CO_2 adsorption capacity during carbonation/calcination cycles.

3. Discussion

Li et al. [16] pointed out that during the cyclic carbonation/calcination of $CaO/Ca_{12}Al_{14}O_{33}$, the $Ca_{12}Al_{14}O_{33}$ binder does not take part in the reaction and may be considered as inert. However, unlike the $Ca_{12}Al_{14}O_{33}$, La_2O_3 cannot be considered as inert for the conditions used in the present investigation. Shirsat et al. [22] reported thermo-chemistry in the decomposition of $La_2O_2CO_3$. The decomposition reaction can be written as follows:

$$La_2O_2CO_3 \rightleftharpoons La_2O_3+CO_2 \tag{4}$$

And the equilibrium pressure of CO_2 can be measured by the given equation as follows:

$$\ln p_{CO_2}(pa)(\pm 0.22) = -17502.2/T + 25.87 \; (773 \leq T(K) \leq 1190) \tag{5}$$

From the above equation, when the temperature is 850 ºC (1,124 K), the equilibrium pressure of CO_2 is 29,000 pa. As a result, in the process of carbonation of 100% CO_2 under 1 atm, La_2O_3 adsorbs CO_2 to form the $La_2O_2CO_3$, while in the process of calcination of 100% N_2 under 1 atm, $La_2O_2CO_3$ decomposes into La_2O_3 again.

When the sorbents were made by wet physical mixing method in our research, La_2O_3 was only mixed on the surface of CaO physically. However, Al_2O_3 was not only physically mixed with CaO, but also had a chemical reaction with CaO as follows:

$$7Al_2O_3+12CaO \rightarrow Ca_{12}Al_{14}O_{33} \tag{6}$$

As a result, $Ca_{12}Al_{14}O_{33}$ could have a much more well-distributed mixing than La_2O_3 within the CaO-based sorbents. Although both the addition of La_2O_3 and $Ca_{12}Al_{14}O_{33}$ could delay the sintering of CaO particles to give the CaO-based sorbent higher carbonation conversions during cyclic CO_2 capture, the $CaO/Ca_{12}Al_{14}O_{33}$ sorbent was much better than the CaO/La_2O_3 sorbent in cyclic CO_2 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:

$$La(NO_3)_3{\cdot}6H_2O+(5/6)C_6H_8O_7{\cdot}H_2O \rightarrow (1/2)La_2O_3+5CO_2+(61/6)H_2O+(3/2)N_2 \quad (7)$$

$$Al(NO_3)_3{\cdot}9H_2O+(5/6)C_6H_8O_7{\cdot}H_2O \rightarrow (1/2)Al_2O_3+5CO_2+(79/6)H_2O+(3/2)N_2 \quad (8)$$

$$Ca(NO_3)_2{\cdot}4H_2O+(5/6)C_6H_8O_7{\cdot}H_2O \rightarrow CaO+5CO_2+(49/6)H_2O+N_2 \quad (9)$$

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

In the case of CaO/La_2O_3 (SGCS) sorbent, XRD analysis of this sorbent shown in Fig. 4 indicates that the initial calcined sample

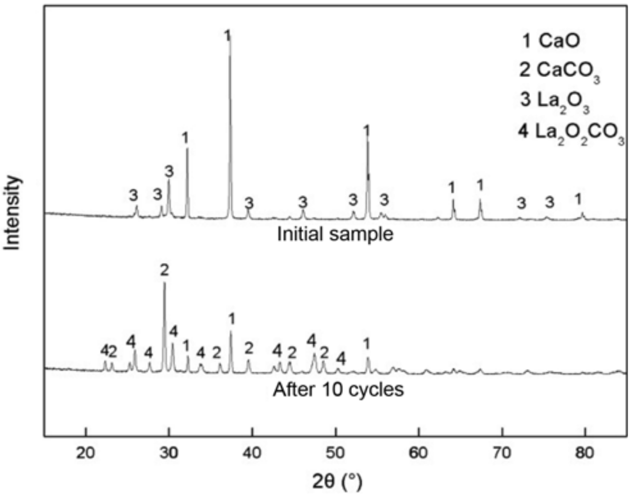

Fig. 4. XRD of the CaO/La_2O_3 (SGCS) sorbent.

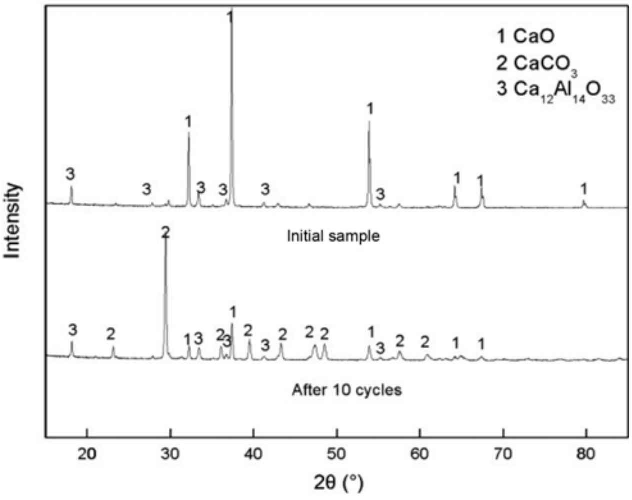

Fig. 5. XRD of the $CaO/Ca_{12}Al_{14}O_{33}$ (SGCS) sorbent.

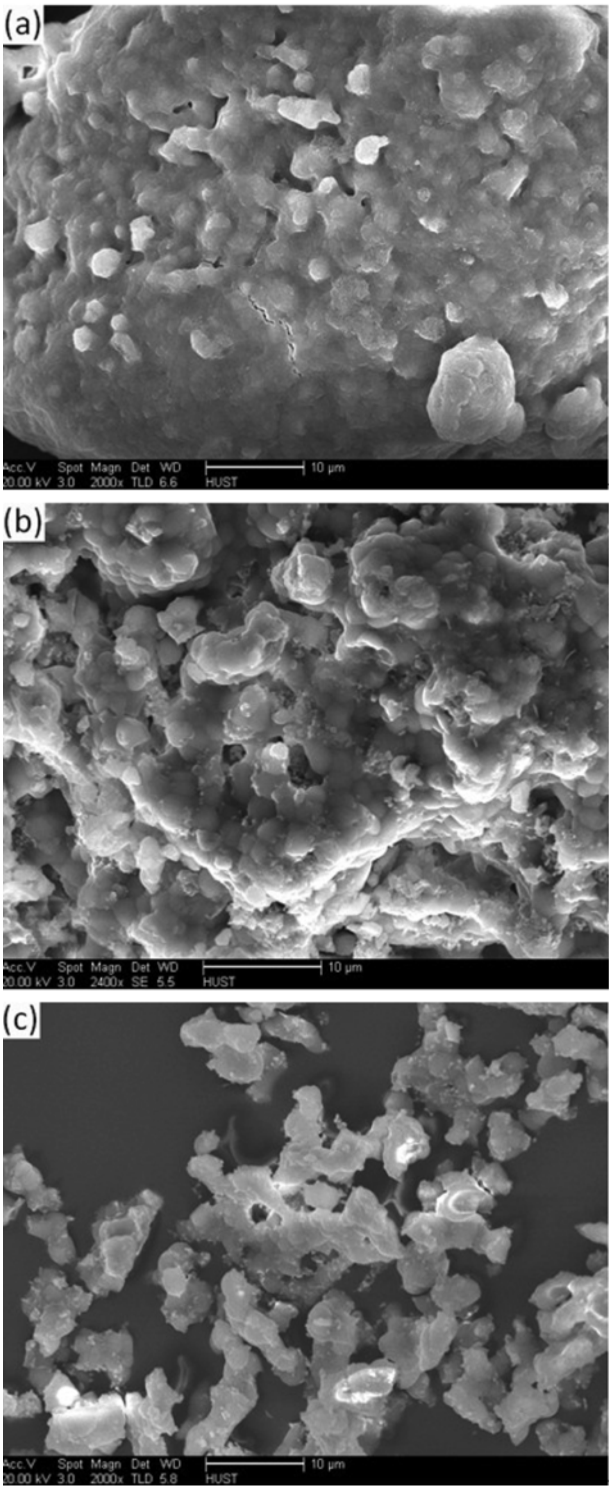

Fig. 6. FSEM photos of the sorbents made by SGCS method compared with pure $CaCO_3$. (a) pure $CaCO_3$ after 7 carbonation/calcination cycles; (b) $CaO/Ca_{12}Al_{14}O_{33}$ (SGCS) sorbent after 11 carbonation/calcination cycles; (c) CaO/La_2O_3 (SGCS) sorbent after 11 carbonation/calcination cycles.

exists only in two main materials: CaO and La_2O_3. After 10 cycles, this sample also exists only in two main materials: $CaCO_3$ and $La_2O_2CO_3$. But in the case of CaO/$Ca_{12}Al_{14}O_{33}$ (SGCS) sorbent, Al_2O_3 reacted with CaO into a stable framework of $Ca_{12}Al_{14}O_{33}$. XRD analysis of this sorbent shown in Fig. 5 indicates that the $Ca_{12}Al_{14}O_{33}$ binder does not take part in the cyclic reactions. This is the difference between the addition of La_2O_3 and $Ca_{12}Al_{14}O_{33}$, which results in the different performance in the cyclic CO_2 capture. Therefore, La_2O_3, acts as CO_2 transferor, which makes CO_2 molecules go through the $CaCO_3$ product layer much easier during carbonation process, and has a superior performance than $Ca_{12}Al_{14}O_{33}$ 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 $CaCO_3$ sorbent after many carbonation/calcination cycles. There are little visible pores on the surface of the pure $CaCO_3$ sorbent due to severe sintering after seven carbonation/calcination cycles in Fig. 6(a). The blockage and collapse of pores of the $CaCO_3$ increases the hindrance to the passage of CO_2 during the carbonation process. As a result, the CaO adsorption capacity of the pure $CaCO_3$ 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_2 diffusion within the sorbents.

CONCLUSIONS

Modified CaO-based sorbents using La_2O_3 or $Ca_{12}Al_{14}O_{33}$ as additives are synthesized by SGCS method and wet physical mixing method in the present work. Unlike $Ca_{12}Al_{14}O_{33}$, La_2O_3 is not a completely inert material without the ability of adsorbing CO_2. But when the sorbents are made by wet physical mixing method, $Ca_{12}Al_{14}O_{33}$ can have a much more well-distributed mixing than La_2O_3 in CaO particles; thus CaO/$Ca_{12}Al_{14}O_{33}$ sorbent provides a relatively higher CO_2 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_2O_3 retard the sintering of CaO particles but also adsorb CO_2 in the carbonation process. Therefore, La_2O_3, acts as CO_2 transferor, which makes CO_2 molecules go through the $CaCO_3$ product layer much more easily during the carbonation process, and has a superior performance than $Ca_{12}Al_{14}O_{33}$ theoretically for CaO-based sorbents when both of them are prepared into even ultrafine powders. The synthetic CaO/La_2O_3 (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_2/g-sorbent after 11 cycles.

ACKNOWLEDGEMENTS

This work is supported by the National Basic Research Program of China (No. 2011CB707301), the National Natural Science Foundation of China (No. 50936001, 51021065), and Analytical and Testing Center of HUST for XRD and FSEM measurements.

REFERENCES

1. S. Bachu, *Prog. Energy Combust.*, **34**, 254 (2008).
2. Y. Seo, S. H. Jo, H. J. Ryu, D. H. Bae, C. K. Ryu and C. K. Yi, *Korean J. Chem. Eng.*, **24**, 457 (2007).
3. W. J. Choi, J. B. Seo, S. W. Cho, S. W. Park and K. J. Oh, *Korean J. Chem. Eng.*, **26**, 705 (2009).
4. B. Khoshandam, R. V. Kumar and L. Allahgholi, *Korean J. Chem. Eng.*, **27**, 766 (2010).
5. J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, *Prog. Energy Combust.*, **36**, 260 (2010).
6. H. J. Ryu, D. Shun, D. H. Bae and M. H. Park, *Korean J. Chem. Eng.*, **26**, 523 (2009).
7. Q. L. Song, R. Xiao, Z. Y. Deng, L. H. Shen and M. Y. Zhang, *Korean J. Chem. Eng.*, **26**, 592 (2009).
8. F. Fan, Z. S. Li and N. S. Cai, *Korean J. Chem. Eng.*, **26**, 1414 (2009).
9. H. J. Ryu, Y. C. Park, S. H. Jo and M. H. Park, *Korean J. Chem. Eng.*, **25**, 1178 (2008).
10. V. Manovic and E. J. Anthony, *Ind. Eng. Chem. Res.*, **48**, 8906 (2009).
11. V. Manovic and E. J. Anthony, *Ind. Eng. Chem. Res.*, **49**, 6916 (2010).
12. B. Feng, W.-q, Liu, X. Li and H. An, *Energy Fuels*, **20**, 2417 (2006).
13. J. C. Abanades and D. Alvarez, *Energy Fuels*, **17**, 308 (2003).
14. R. W. Hughes, D. Lu, E. J. Anthony and Y. Wu, *Ind. Eng. Chem. Res.*, **43**, 5529 (2004).
15. H. Gupta and L.-S. Fan, *Ind. Eng. Chem. Res.*, **41**, 4035 (2002).
16. Z.-S. Li, N.-S.Cai and Y.-Y. Huang, *Ind. Eng. Chem. Res.*, **45**, 1911 (2006).
17. K. O. Albrecht, K. S. Wagenbach, J. A. Satrio, B. H. Shanks and T. D. Wheelock, *Ind. Eng. Chem. Res.*, **47**, 7841 (2008).
18. W. Liu, B. Feng, Y. Wu, G. Wang, J. Barry and D. Costa, *Environ. Sci. Technol.*, **44**, 3093 (2010).
19. W. Liu, N. W. Low, B. Fen, G. Wang and D. Costa, *Environ. Sci. Technol.*, **44**, 841 (2010).
20. C. Luo, Y. Zheng, N. Ding, Q. Wu, G. Bian and C. Zheng, *Ind. Eng. Chem. Res.*, **49**, 11778 (2010).
21. L. Li, D. L. King, Z. Nie and C. Howard, *Ind. Eng. Chem. Res.*, **48**, 10604 (2009).
22. A. N. Shirsat, M. Ali, K. N. G. Kaimal, S. R. Bharadwaj and D. Das, *Thermochim. Acta*, **399**, 167 (2003).