Enhanced CO_2 Adsorption Capacity and Stability using CaO-based Adsorbents Treated by Hydration

Shengping Wang, Hui Shen, Shasha Fan, Yujun Zhao, Xinbin Ma, and Jinlong Gong
Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and
Technology, Tianjin University, Tianjin 300072, China

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The synthesis of highly efficient CaO-based sorbents using $Ca(Ac)_2$ as a precursor and ethanol as a modification agent for CO_2 capture is described. This adsorbent has several characteristics such as large surface area and pore volume and small particle size. The influence of ratio of ethanol and water on CO_2 adsorption capacity was evaluated considering that the ethanol concentration could affect the pore structure of sorbents. The results showed that CaO modified by ethanol solution had a higher carbonization and better stability. Particularly, when the volume ratio of ethanol and water was 3, a performance of adsorption capacity of 74% and conversion of 94% was observed. CaO modified by ethanol solution had a superior performance due to the decrease of grain size and the formation of loose porous structure. The influence of steam on stability of adsorbents at high temperatures was examined, and it was found that with the existence of steam diffusion, the capacity of the sorbent could remain at a higher level and the stability was evidently improved. After 18 cycles of adsorption/desorption process, the capacity remained as high as 65%. It was proposed that dynamic and cyclic steam injection was favorable for preventing the sintering of sorbents and facilitating the diffusion of CO_2. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3586–3593, 2013
Keywords: CO_2, ethanol, CaO, adsorption, steam

Introduction

Carbon dioxide (CO_2) as a major anthropogenic greenhouse gas has attracted global interests of scientific and practical communities for the occurring of global climate changes and environmental impacts. Thus, worldwide efforts have been made to lower the level of carbon dioxide in the atmosphere.[1] Furthermore, many industrial processes such as hydrogen production[2–7], enhanced steam methane reforming[5,8,9] and water–gas shift reaction[10–12] also require the removal of the CO_2 in flue gases. Solid calcium-based sorbents have attracted numerous attention in high-temperature carbon capture owing to their unique advantages[13] such as higher adsorption capacity and selectivity compared to physical adsorbents (the theoretical amount of CO_2 adsorption is 0.786 g CO_2 g^{-1}CaO at 100% CaO conversion[14]), adequate adsorption/desorption rate, rich raw materials, and simple reaction mechanism utilizing a reversible chemical reaction ($CaO + CO_2 \leftrightarrow CaCO_3$[11]). The capacity and stability of calcium-based sorbents, however, would drop sharply with increasing the number of cycles owing to sintering or agglomeration of CaO particles and formation of $CaCO_3$ product layer at high temperatures.[15–19] This is normally attributed to the low Tammann temperature of CaO (i.e., 561°C)[20] compared to the reaction temperature of above 600°C and larger molar volume of $CaCO_3$ than CaO.[21,22] The inherent drawbacks would severely restrict the large-scale application of CaO for high-temperature CO_2 capture looping process.

Numerous efforts have been made to understand the intrinsic disadvantages of the CaO sorbent and to improve its capacity and stability. The calcium-based sorbents are usually mainly derived from natural CaO compounds such as limestone and dolomite. However, qualitative investigation for natural CaO is carried out with difficulty owing to its complex and varied components resulting from the different sources of raw materials. Thus, research focus has been partially placed on the synthesis of calcium-based sorbents in a controllable manner to determine the components and quantity in the sorbents. Specifically, different precursors demonstrate different physical structures, which would directly affect the performance of sorbents.[23,24] It was suggested that the CaO sorbents prepared from organic calcium salt precursors had better adsorption capacity than inorganic ones, especially calcium propionate, calcium acetate, and calcium gluconate.[23,25] On the other hand, to further improve adsorption performance of sorbents, a variety of methods to modify the freshly prepared sorbents have been reported.[26–29] Li et al.[30] used an ethanol solution to modify CaO sorbents derived from limestone, and obtained an ∼85% carbonation conversion in the first cycle and an ∼51% carbonation conversion in the 15th cycle for carbonation at 700°C and calcination at 920°C.

It is worth mentioning that sorbents using calcium acetate as a precursor or ethanol treatment have a comparatively high capacity. Nevertheless, the further improvement of

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Correspondence concerning this article should be addressed to X. Ma at xbma@tju.edu.cn and J. Gong at jlgong@tju.edu.cn.

capacity and stability is still desirable comparing the maximum theoretical adsorption value (78.6%) and considering commercial capacity. Accordingly, this article describes the fabrication of CaO adsorbents with high adsorption capacity and stability by ethanol modification and using $Ca(Ac)_2$ as precursor for CO_2 capture at high temperatures. On the basis of adsorption capacity of CaO derived from calcium acetate, we attempted to regulate the pore structure of sorbents for further improving adsorption uptake and stability by ethanol modification. Experimental phenomena in calcinations/carbonation cycles were discussed applying thermo gravimetric analyzer (TGA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Fundamental understanding of modifying mechanism of sorbents with ethanol treatment was also presented.

Experimental

Sorbent preparation

Calcium acetate (Tianjin Fengchuan, >95%) as the precursor was first calcined at 850°C for 3 h at a ramp rate of 3°C/min from room temperature to 850°C to get full calcination of CaO. The attained CaO materials were treated in ethanol (Tianjin Kelmel, 99.99%) solution at three different temperatures (room temperature, 100°C, and 160°C, respectively). Then, the suspension was stirred vigorously for 5 min with simultaneous addition of Na_2SiO_3 (mass ratio: 5%) (Tianjin Kelmel, 99.5%). Subsequently, the mixture was continued with ultrasonic dispersion for 15 min and then stirred for 3 h. Eventually, the mixture was filtrated, washed, and dried at 80°C for 6 h. The product was grounded to fine powder and tested. The following nomenclature was used to illustrate the preparation method: CaO was followed by the treatment method, i.e., CaO/EtOH (100°C). Room temperature is shortened as RT.

Characterization

Specific surface area and pore-size distribution (PSD) measurements were performed using nitrogen adsorption–desorption isotherms on a Micromeritics Tristar volumetric adsorption analyzer. The sample of CaO-based sorbents were first degassed at 90°C to eliminate free water for 1 h in the degassing port of the apparatus. Then, the samples were continually degassed at 300°C for 12 h before the actual measurements. The adsorption and desorption isotherms of nitrogen were collected at −196°C using the values of pressure ranging from about 1 to 760 mm Hg. The specific surface area was calculated by the Brunauer–Emmet–Teller (BET) method and the PSD measurement was determined using the Barrett–Joyner–Halenda (BJH) method.

Crystalline structure and grain size of the sorbent samples were characterized by XRD on a Rigaku D/max-2500 diffractometer operating at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation ($\lambda = 1.54056$ Å), and operating in a 2θ range of 5–90° at a scanning rate of 0.02°/s.

Pore structure and surface morphology of the fresh CaO sorbents were observed with SEM using a Hitachi S4800 field-emission microscope at 5.0 kV under high vacuum. The samples were prepared by mixing CaO sorbents in ethanol solution with ultrasonic dispersion or directly solid powder preparation.

CO_2 adsorption/desorption

N_2 was used as purge gas during the calcination period and as dilution gas during the carbonation period with 99.99% purity. CO_2 used for adsorption period had a purity of 99.99%. The concentration of carbon dioxide used for adsorption tests was 50 vol %.

CO_2 adsorption/desorption performance of sorbents was measured with TGA using NETZSCH STA449F3. A small amount of sorbent (~10 mg) was used for adsorption of CO_2 at high temperature. During the adsorption process, 50 mL/min of CO_2 reactant gas along with 50 mL/min of N_2 purge gas passed over the sample. When adsorption process was completed, the program was automatically switched to the desorption process, and 50 mL/min of pure N_2 passed without CO_2 reactant gas. We chose the actual temperature of flue gas as the whole experiment carbonation temperature, considering practical application of sorbents. So, the adsorption and desorption temperature are set to 600°C and 700°C, respectively. In this work, the adsorption time was set at 45 min and desorption time was set at 20 min to allow the sorbent to adsorb and desorb completely. For steam addition experiments, the steam was introduced to the TGA system through a bubbler with N_2 by controlling the bath temperature. The different steam content was obtained by adjusting the bath temperature to obtain the desirable saturated vapor pressure. The CO_2 adsorption capacity of the sorbent is expressed in the following equation

$$\text{Adsorption capacity} = \frac{\text{mass of the adsorbed } CO_2}{\text{mass of the sorbent}} \times 100\%$$

Results and Discussion

CaO derived from $Ca(CH_3COO)_2$ calcination at different temperatures

Figure 1 shows the weight loss curve and DTG (Derivative Thermogravimetry) curve of $Ca(CH_3COO)_2$. It was clear that there were three weight loss platforms, which could be ascribed to the following reactions

$$Ca(CH_3COO)_2 \cdot H_2O = Ca(CH_3COO)_2 + H_2O \qquad (1)$$

$$Ca(CH_3COO)_2 = CaCO_3 + C_3H_6O \qquad (2)$$

$$CaCO_3 = CaO + CO_2 \qquad (3)$$

At about 100°C, $Ca(CH_3COO)_2 \cdot H_2O$ releases one molecule of crystal water. Subsequently, $Ca(CH_3COO)_2$ is broken

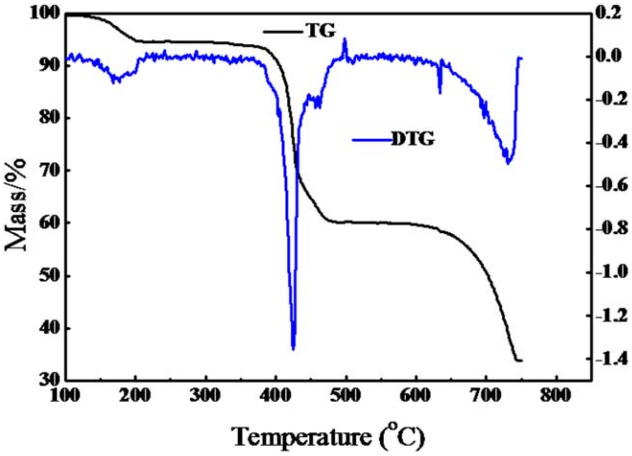

Figure 1. TG calcinations and DTG curve of $Ca(CH_3COO)_2$ in N_2 atmospheres.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

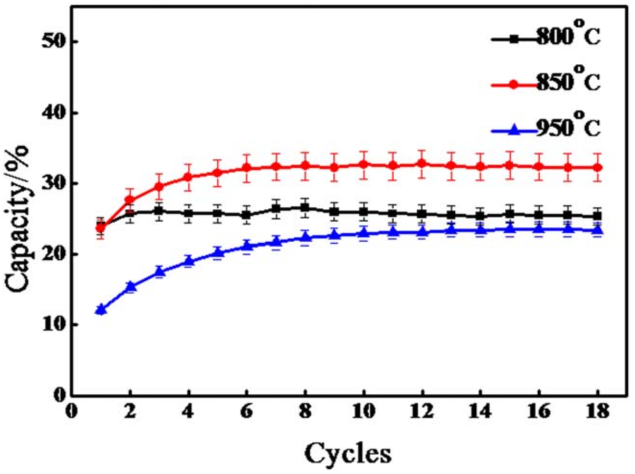

Figure 2. Adsorption capacity of CaO from $Ca(AC)_2$ calcined at different temperatures.

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down into $CaCO_3$ and C_3H_6O at 390°C. Finally, $CaCO_3$ starts to decompose to CaO at 620°C. When the temperature reaches 750°C or above, $Ca(CH_3COO)_2$ is supposed to decompose to CaO completely.

Figure 2 shows the adsorption capacity performance of the CaO sorbents derived from calcined $Ca(Ac)_2$ at different temperatures. CO_2 adsorption capacity of the sorbents were relatively low.[15] As shown in Figure 3, the fresh CaO from $Ca(Ac)_2$ exhibited a layered stack structure, which probably resulted in the lower adsorption capacities. It was also observed that the adsorption capacity did not decrease with the increasing number of cycles (Figure 2). The phenomenon could be described as thermal activation or self-activation[31]. Freshly calcined sorbents could form a kind of stable and solid structure inside the sorbents by a high-temperature treatment, which is called hard skeleton structure[31] as illustrated in Figure 4. The hard skeleton structure could support the whole sorbent and resist the sorbent collapsing during the thermal looping cycles[16], which is obviously favorable for anti-sintering ability and the stability of the sorbents. We also noted that the adsorption capacity of 950°C was lower, most likely because its sintering was too severe during high-temperature treatment. Accordingly, the temperature of 850°C was chosen to be the optimized calcination temperature of the precursor for following sorbent preparation.

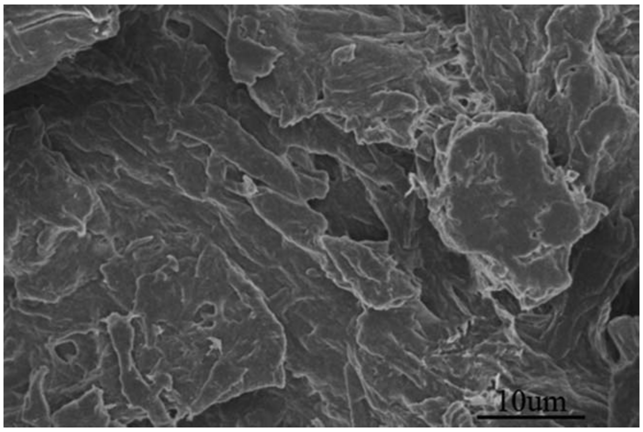


Figure 3. SEM image of CaO from $Ca(CH_3COO)_2$ calcined at 850°C.

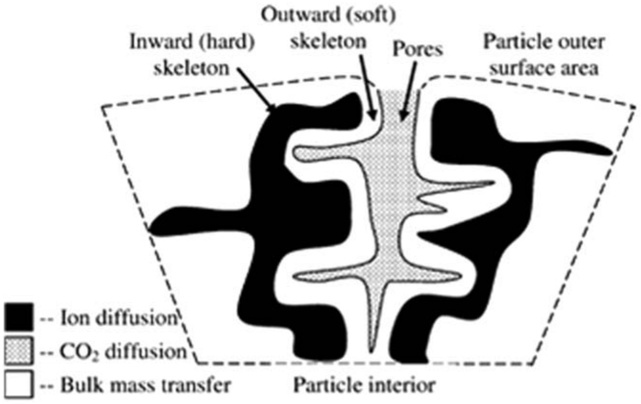


Figure 4. Schematic representation of skeleton model.[31]

CaO derived from $Ca(CH_3COO)_2$ with EtOH solution treatment

Effect of Treatment Temperature and Solvent. Figures 5a, b exhibit the adsorption capacities of CaO sorbents with EtOH solution and pure water treatment at three different temperatures. Adsorption capacities of all sorbents decreased with the number of cycles increasing. Among them, CaO/EtOH (RT) had the highest uptake capacity of 74% in the first cycle (based on the theoretically maximum adsorption capacity, which is calculated as 78.6%), and CaO conversion was calculated to be 94%. The adsorption capacity of CaO/EtOH (RT) in the following cycles was still obviously superior to other two sorbents.

Figure 5b shows the same tendency of CaO adsorption capacity with pure water treatment compared to Figure 5a. CaO/water (RT) still had a higher conversion and a better capacity. There existed a little difference from the 10th cycle compared with ethanol treatment, the superiority of CaO/water (RT) was not obvious and had almost the same capacity with that of CaO/water (100°C).

By analyzing the above-mentioned capacity statistics for the two modification methods, there were evident trends that the treatment of low temperature was favorable for sorbent capacity performance, especially by ethanol treatment.

Table 1 shows the textural properties of fresh sorbents on different treatment conditions. The specific surface area of the sorbent was only ~3.0 m^2/g upon calcination treatment. However, the surface area of sorbents increased with EtOH solution and pure water treatment, particularly for those at RT. From the curves of PSD in Figure 6, we learned that the sorbents with low temperature treatment had a larger surface area and pore volume; surface area of CaO at RT was 21.4 m^2/g and 14.7 m^2/g, respectively. This indicated that low temperature treatment was favorable for the formation of porous construction. Moreover, the results of PSD also conformed to the capacity curves.

Figure 6 shows that there is predominately a peak in the PSD curves, of which that of CaO/EtOH (RT) had a narrower range of PSD compared to CaO/water(RT). Moreover, predominant pore size of CaO/EtOH was in the range of 5–25 nm, mainly being mesoporous, whereas that of CaO/water was in the range of 20–70 nm. It is well known that micropores lead to a larger specific surface area with significant diffusion resistance, whereas macropores are contributive to gas diffusion and stability of sorbents with decreasing surface area.[23]

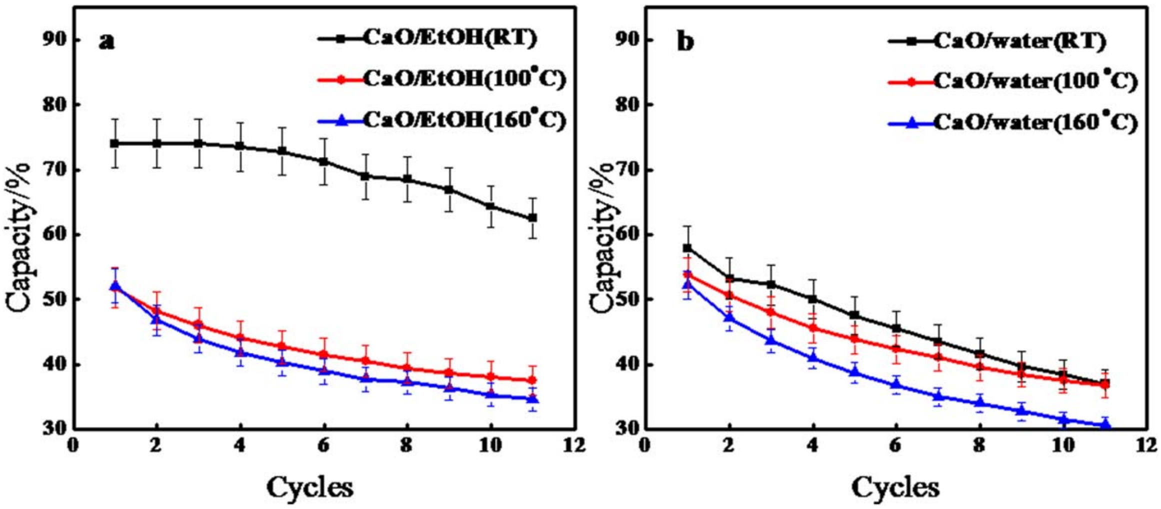


Figure 5. Adsorption capacity of CaO with solution treatment at three different temperatures: room temperature, 100°C, and 160°C.

(a) 75 vol % ethanol solution treatment and (b) pure water treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, more mesopores would make for CO_2 reaction with CaO at high temperature as it could keep the balance of gas diffusion and enough surface area for CaO reaction.

By comparison, the capacity results also demonstrated that performance of sorbents by ethanol solution modification was better than that of sorbent by pure water modification with larger specific area and pore volume. The sorbents by ethanol modification were able to maintain higher capacity after couple of cycles, meaning that CaO modified with EtOH solution had a better anti-sintering ability. The improvement in sorbents' performance could be due to the remarkable changes in sorbents' texture during the hydration process[32] (e.g., CaO reacted with H_2O to form $Ca(OH)_2$). According to solubility theory, when the solute's solubility becomes small, particle size of the deposit also turns small accompanied by change in morphology. Ethanol as a short-chain alcohol has a low surface tension, which could decrease the tension of the solid particles. Meanwhile, it has a smaller permittivity than that of water (ethanol permittivity $D = 24$, water permittivity $D = 80$). When ethanol is added to pure water, the permittivity of the whole mixed solution is reduced with a decrease in the solubility of solute and generation of high over-saturation of solute, resulting in the production of small particles.[33] As the whole CaO hydration process was at dynamic precipitate solubility equilibrium, particle size grew smaller and the appearance changed progressively with enough hydration time. The process scheme regarding the effect of ethanol addition is shown in Scheme 1. First, upon hydration, CaO particles transform into small $Ca(OH)_2$ particles and a part of $Ca(OH)_2$ dissolves with the pore structure becoming loose. With addition of ethanol, solubility decreases and smaller particles precipitate. After the dynamic precipitate cycles, the particle size of $Ca(OH)_2$ grows smaller. Upon calculation, the particle size of the sorbent was only 12.7 nm according to XRD results (Figure 7) as introduction of ethanol decreased the solute solubility at room temperature.

Table 1. Textural Properties of CaO Sorbents with Different Temperature and Solvent Treatment

Sorbents	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Particle Size (nm)
CaO/EtOH(RT)	21.4	0.121	12.7
CaO/EtOH (100°C)	6.6	0.021	>100
CaO/EtOH (160°C)	2.8	0.013	>100
CaO/water (RT)	14.7	0.095	33.1
CaO/water (100°C)	4.2	0.014	>100
CaO/water (160°C)	2.8	0.001	>100
CaO/calcination	3.0	0.008	63.2

XRD patterns of CaO sorbents modified with different solution conditions show that $Ca(OH)_2$ (corresponding to JCPDS #84–1274) together with a small amount of $CaCO_3$ impurity was observed in all the samples. By analysis of XRD patterns using the Debye–Scherrer equation, the grain size of CaO/EtOH (RT) and CaO/water (RT) was about 12.7 nm and 33.1 nm, respectively, while the others were all above 100 nm. According to CO_2 adsorption mechanism over CaO-based materials, there are two stages of reaction: a fast reaction (chemical-reaction controlled) stage and a slow

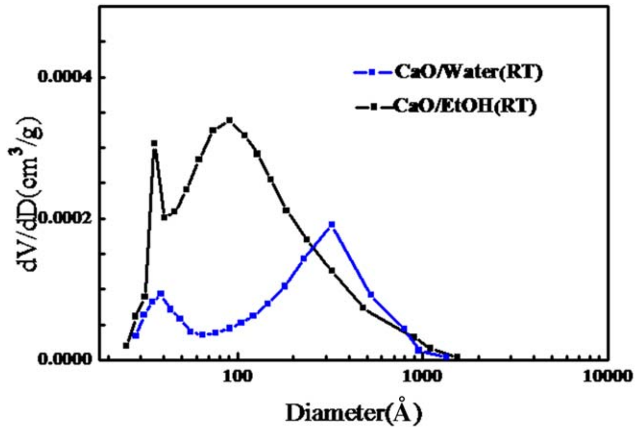
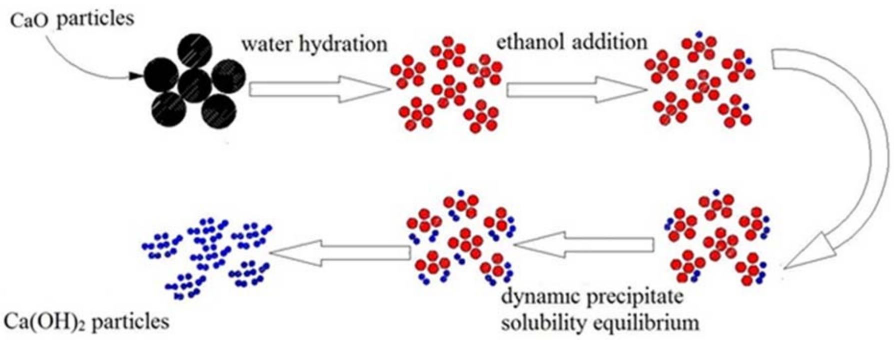


Figure 6. Pore-size distribution of CaO sorbents at RT.

(a) Treatment by ethanol at room temperature and (b) Treatment by water at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. The hydration process with the addition of ethanol.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction (gas-diffusion controlled) stage.[7] The layer-structured $CaCO_3$ is formed at the outside of the adsorbents during the fast reaction stage. Then, the $CaCO_3$ product layer prevents the diffusion of CO_2 into the particle to react with inner CaO as pores are blocked or collapse and the surface of sorbents is covered. Consequently, the whole process then transforms to be diffusion controlled. For this reason, the sorbent would perform better if the particle size is small (e.g., <50 nm), which allows carbonation to take place at the rapid reaction-controlled regime in contrast to diffusion-controlled regime with larger sorbent particles.[14] Then, the particle-size calculation of CaO sorbents modified with different solution conditions was in line with the adsorption capacity results of sorbents, and CaO/EtOH (RT) had the smaller particle size and higher capacity.

As also shown in Figure 8, it was distinct that sorbents with different solution treatment had evidently different morphology structure. CaO/EtOH (RT) exhibited a porous and fluffy structure, which was apparently in favor of CO_2 adsorption with providing the spacious CO_2 diffusion pathway to reach the inner unreacted CaO,[34] especially in diffusion-controlled stage. Surface morphology presented that there were lots of pores and a network of larger inner pores around the outer surface of the particle. CaO/water (RT), however, possessed a bit of dense structure, which had a large and solid base with many fine fragments.

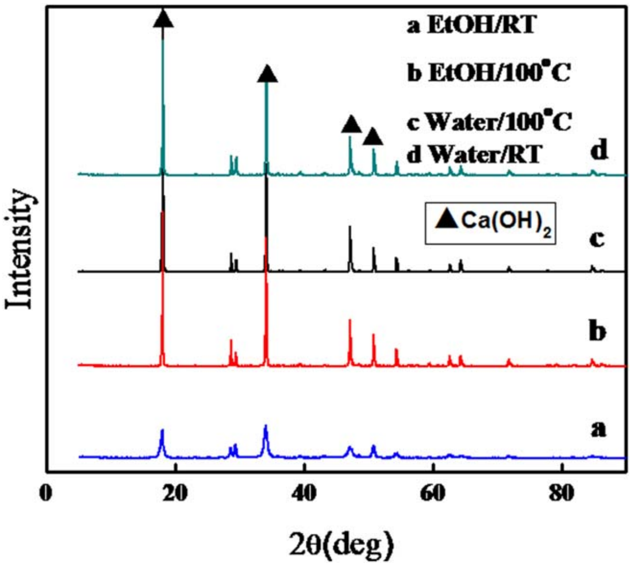


Figure 7. XRD patterns of CaO sorbents modified with different solution conditions.

(a) EtOH treatment at RT, (b) EtOH treatment at 100°C, (c) pure water treatment at 100°C, and (d) pure water treatment at RT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

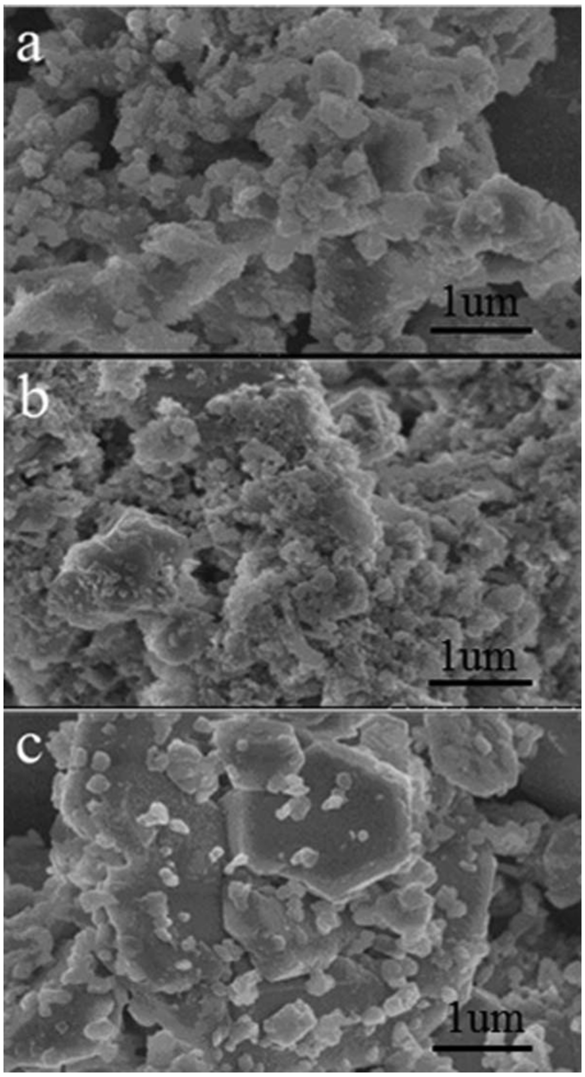


Figure 8. SEM images of fresh sorbents.

(a) Treatment by ethanol solution (75 vol %) at room temperature, (b) Treatment by pure water at room temperature, and (c) Treatment by ethanol solution (75 vol %) at 100°C.

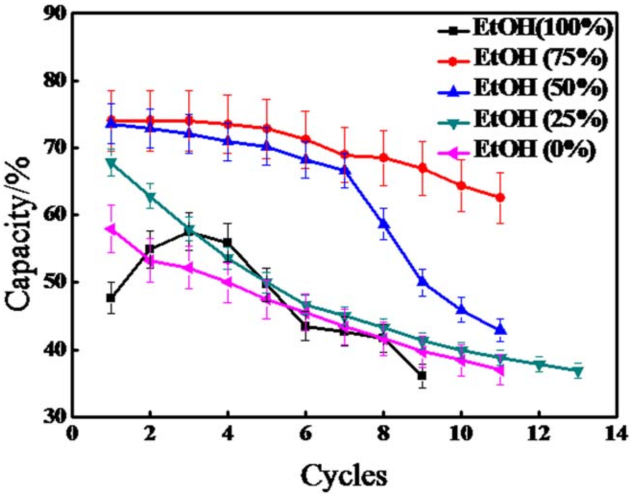


Figure 9. 19) Adsorption capacity curves at different ratios of EtOH and water.

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Effect of Ethanol Concentration. The volume ratio of EtOH and water has a great impact on the sorbents performance, as shown in Figure 9. With the increase of the concentration of ethanol, CO_2 uptake and stability of sorbents both rose. When EtOH volume ratio reached 50%, the sorbent adsorption capacity and stability improved noticeably. Especially, CaO/EtOH (75 vol %) displayed the best adsorption performance and stability at high temperature. In the first cycle, the sorbent of CaO/EtOH (75 vol %) had a nearly 74% capacity with ~94% conversion. Upon increasing the number of cycles, the sorption uptake capacity and conversion decreased slightly to 62.5% and ~ 80%, respectively.

XRD patterns of the sorbents treated by different concentrations of ethanol are shown in Figure 10. No significant differences were observed, but $Ca(OH)_2$ with a small amount of $CaCO_3$ impurity was detected. The particle size of sorbents decreased gradually with the increase of ethanol concentration. CaO modified with EtOH solution (75 vol %) had a grain size of 12.7 nm. As mentioned above, addition of ethanol would decrease the solute solubility of the mixed solution, resulting in smaller precipitate particles and further higher capacity.

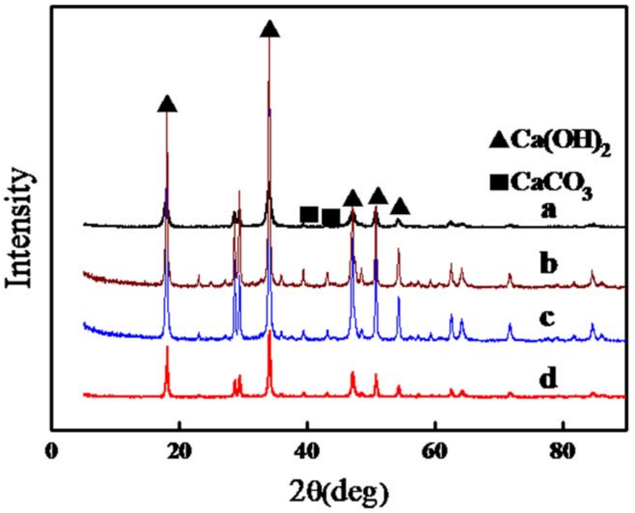

Figure 10. XRD patterns of (a) CaO modified with pure water at RT, (b) CaO modified with EtOH solution at RT (25 vol %), (c) CaO modified with EtOH solution (50 vol %), and (d) CaO modified with EtOH solution (75 vol %).

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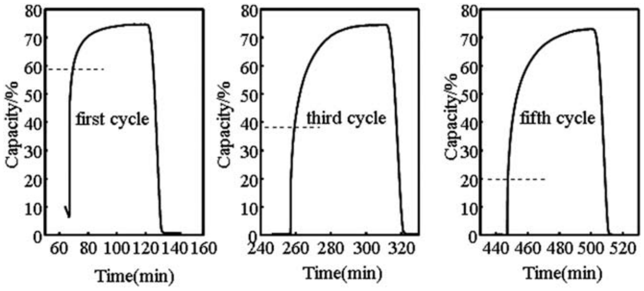

Figure 11. Adsorption curves comparison of the three specific cycles.

To further interpret the effect of particle size on performance of sorbents, we chose CaO/EtOH (75 vol %) as a model sample. Adsorption curves of three specific cycles during carbonation/calcination process are illustrated in Figure 11. As mentioned earlier, small particles are favorable for the carbonization of sorbents due to the diffusion-controlled effect. In particular, when particle size is sufficiently small, the whole process finally turns to chemical-controlled stage.[35–37] As shown in Figure 11, during the whole adsorption/desorption cycles, cycle curves did not perform notably different from one another. According to the criterion of dividing the fast- and slow-reaction stages, which is proposed by Wu and Lan,[38] a dividing line of the two reaction stages is marked in Figure 11. About 80% of the whole adsorption uptake was obtained during the fast reaction stage in the first cycle. What profoundly manifested that the particle size of freshly prepared sorbent by ethanol modification was very small, which was crucial to 20) increasing the capacity of sorbents. However, less than 60% of the whole adsorption uptake took place during the fast stage in the third cycle while the remaining adsorption uptake finished during the slow stage. In addition, in the fifth cycle, the trend was more apparent and only less than 30% of the whole uptake finished during the fast stage. The decrease of uptake in the fast reaction stage indicated that the particle size of the sorbent gradually became larger and larger as the cycle number increased, further resulting in the decrease of adsorption capacity.

Figure 12 shows difference in surface morphology of the sorbents treated with different volume ratios of EtOH solution. When treated with pure water, the sorbents possessed a dense structure, which had a large and solid base with many fine fragments. With the increase of the concentration of ethanol up to 75 vol %, the structure of sorbents became loose and porous, resulting in the enhancement of adsorption capacity and stability. However, the sorbent with pure ethanol treatment displayed a skeleton-like appearance, which could explain why the capacity curve exhibited an unusual trend. Accordingly, we speculated that in pure ethanol solution, there only existed a weak chemical interaction between hydroxyl group of ethanol molecule and oxygen atom of CaO without water molecule. The change in polarity of hydroxyl group for ethanol likely took effect in the morphology and adsorption performance of modified CaO. As ethanol had the weaker polarity and larger radius compared to water and could not react with CaO, the sorbent treated by

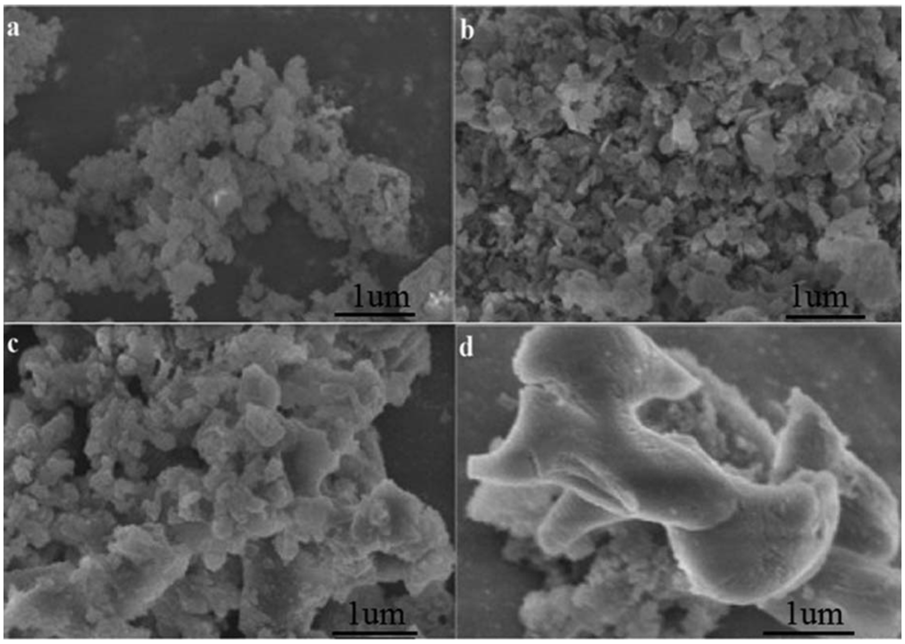

Figure 12. SEM images of CaO modified with different concentration solution.

(a) CaO modified with 25 vol % EtOH solution, (b) CaO modified with 50 vol % EtOH solution, (c) CaO modified with 75 vol % EtOH, (d) CaO modified with pure EtOH.

pure ethanol performed differently from others in the absence of water molecule.

Effect of Steam. To further improve the stability of sorbent, we investigated the steam e22) effect on the performance of the sorbents. As shown in Figure 13, when no steam was injected into CO_2 gas during the whole adsorption process, capacity of the sorbent declined slowly all along, and then after the 10th cycle, the performance was still on an evident downward trend. Yet, stability of the sorbent significantly enhanced along with steam injection into the mixture gas. In the case of the sorbent CaO-Steam-*a,* the performance remained constant and after 18 cycles of adsorption/desorption process, capacity of the sorbent remained above 65%. The sorbent CaO-Steam-*b* displayed nearly identical performance with CaO-steam-*a* in the first six cycles. However, from the seventh cycle, the capability of sorbent tended to drop slowly. We suggested that the steam could not durably hinder the sintering of sorbent particles if the steam quantity was insufficient. Therefore, it showed that the steam mass fraction had an important influence on the adsorption capacities of samples.

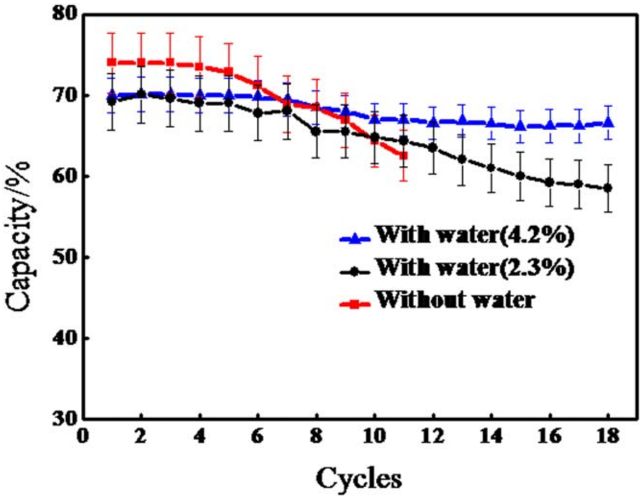

Figure 13. Adsorption capacity curves with the different steam treatment.

(a) During the whole adsorption process, 4.2% steam was injected into CO_2 gas, (b) During the whole adsorption process, 2.3% steam was injected into CO_2 gas, and (c) During the whole adsorption process, no steam was injected into CO_2 gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

With regard to the mechanism of steam enhancing stability, it is plausible that product layer break-up during the diffusion control stage mainly results in surface area recovery and performance improvement,[39] and the presence of H_2O molecules in the mixture gas is favorable for CO_2 penetration into product layer. It is possible that small H_2O molecules could penetrate into $CaCO_3$ product layer easier than larger CO_2 molecules, and the existence of hydroxyl group could transform the internal structure of the sorbents to produce porous structure. Subsequently, it is easier for CO_2 molecules to diffuse into the inner CaO.[40]

Conclusions

We had shown that CaO-based sorbents using $Ca(Ac)_2$ as the precursor and being modified by ethanol solution had a higher adsorption capacity and better stability, which had an initial capacity of 74%. Water and ethanol had a synergistic effect in excellent performance of sorbents, in which ethanol played a key role. Addition of ethanol directly resulted in decrease of the mixed solution solubility and precipitate particle size as ethanol molecules had a smaller permittivity and surface tension. With the volume ratio of ethanol increasing, capacity of sorbents also rose evidently because of small particle size of the produced $Ca(OH)_2$ and loose porous structure. Nevertheless, pure water or ethanol modification would both result in poor capacity. Meanwhile, effect of steam on the sorbent stability was also evaluated. When steam was injected into mixture gas, the whole performance conversion and stability improved apparently. It was suggested that the existence of smaller H_2O molecules was favorable for the penetration of CO_2 into $CaCO_3$ product layer. Then, CO_2 could react with inner CaO effectively and finally lead to an improvement in stability of sorbents. The sorbents demonstrated the competitive CO_2 adsorption performance in the presence of steam diffusion, which could maintain an adsorption capacity of above 65% after 18 cycles. The experimental results provide the commercial application possibility of the sorbents for calcium looping process. This work could also provide guidance for pore structure modification of other types of calcium-based sorbents.

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