

CO₂ Uptakes of a Compound Sorbent in Calcination/Carbonation

Looping Cycle

Huichao Chen¹, Changsui Zhao^{1*}, Yingjie Li²

1: School of Energy and Environment, Southeast University, Nanjing 210096, PR China

2: School of Energy and Power Engineering, Shandong University, Jinan 250061, PR China

Abstract

This study focuses on the CO₂ uptakes of a compound sorbent in calcinations/carbonation looping cycle. The sorbent possesses great flexibility in regard to particle size and exhibits high CO₂ uptakes with the sintering resistant behavior greatly improved. Multiple carbonation/calcination cycle tests of the sorbent result in a decay in carbonation conversion depending on reaction condition and the number of cycles. There is a combination of 700°C and 0.5MPa especially suitable for the sorbent to achieve high cyclic CO₂ capture capacity, by 35% increase for 10 cycles and 79% increase for 50 cycles compared with the limestone in the flow of 15% CO₂ in N₂ and an average conversion of 0.86 after 50 cycles is established. Characterization results (XRD, pore volume distribution) display that the morphological and structural properties of the compound CO₂ sorbent after multiple cycles at 700°C and 0.5MPa do not reveal significant differences, which could explain the superior performance of the sorbent. The active component of the material is CaO, while the Ca₉Al₆O₁₈ and MgO provide a stable framework inhibiting deactivation of CaO.

Keywords: CO₂ Capture, Coprecipitation, Pressurized Carbonation, Calcination

1. Introduction

The issues of CO₂ emission control are receiving increasing attention due to the impact of greenhouse gases on global climate change. Affordable CO₂ control technologies have become the focus of the worldwide research. Calcium-based sorbents have been receiving widespread attention as candidates to remove the greenhouse gas CO₂ in-situ from reactors in combustors [1-2], or from fuel gases to obtain H₂-rich gases [3-6]. The CaO in these systems is to separate the CO₂ in the gases, by forming CaCO₃. CO₂ is collected in a pure form when CaCO₃ is regenerated by calcinations in a different reactor by burning a minor part of fuel with oxygen [7]. However, studies on the reversibility of the loop indicate that the carbonation is far from reversible in practice [3, 8-9] and the capture capacity of the raw CaO decays at every cycle and quickly reduces to less than 10% of the initial value [10].

It is believed that the capacity decay is mainly owing to the sintering of CaO and CaCO₃

(formed during carbonation) in the regeneration process or the physical aggregation of the crystals leading to increased particle size, or reduced surface area of the produced CaO for the carbonation reaction in the next cycle [11]. Thus, a very fast initial carbonation reaction stage ends up with low level of conversion and shifts into a very slow reaction stage, which is useless for a practical system, controlled by diffusion through the product layer of CaCO₃ [9,11].

Therefore, a lot of work has been conducted to improve the poor cyclic performance of CaO. Silaban et al. [12] have found that dolomites are superior to limestones, with better multi-cycle performance as with much MgO presence. Lysikov et al. [13], Manovic and Anthony [14], and other researchers [15] have studied the effect of thermal pretreatment on the long-term CO₂ uptake of limestones. Fennell et al. [16], Hughes et al. [17], Manovic and Anthony [18], and others [19] have modified their sorbents by hydration with water or steam. Li et al. [20-22] have modified the limestone or dolomite with

ethanol solution and acetate solution, doped KMnO_4 with CaO . Salvador et al. [23] have doped aqueous solutions of different salts with CaO such as Na_2CO_3 or NaCl . Lu et al. [24] have investigated the capacity of CaO sorbents derived from different organometallic precursors. Wu et al. [25-26] have incorporated fly ash into pellets with bed ash by wet grinding to be a CO_2 sorbent. Gupta and Fan [27] have developed a precipitated calcium carbonate (PCC) sorbent by a precipitation process. Other researchers have created synthetic sorbents by dispersing CaO across an inert matrix, e.g. Li et al. [28-29] with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and Aihara et al. [30] with CaTiO_3 to act as a structural support and further work on CaO with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ by Pacciani et al. [31]. Roesch and Lu [32-33] have prepared sorbents for CO_2 capture by a co-precipitation route, with nominal formula $\text{Ca}_{0.9}\text{M}_{0.1}\text{O}_x$, where $\text{M}=\text{Cr, Mn, Co, Cu}$ and Ce . All these methods have been tested to address this loss in capacity with varying degrees of success.

The objective of this work was to produce a compound CaO -based sorbent with high CO_2 capture capacity and without problem of loss in capacity after multiple carbonation/calcinations cycles. A highly effective CO_2 sorbents containing high melting temperature of MgO and $\text{Ca}_9\text{Al}_6\text{O}_{18}$ with improvement in the sintering resistant behavior is reported.

2. Experimental

2.1 Chemicals

In this study, calcium chloride anhydrous (CaCl_2), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), aluminum chloride anhydrous (AlCl_3) and the ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) (AR, Shanghai Yijiu Chemical Cot.l.d.) have been used for coprecipitation. The polyethylene Glycol and the ammonia water (AR, Shanghai Yijiu Chemical Cot.l.d.) have been used as a disperser and a pH regulator of the solution during the coprecipitation process, respectively.

2.2 Sorbents preparation

The sorbents were synthesized with different

atomic ratio of Ca:Mg:Al as follows. The sorbents with 75wt.% of CaO and 25 wt.% of the inert materials ($10\text{wt.}\% \text{MgO} + 15\text{wt.}\% \text{Ca}_9\text{Al}_6\text{O}_{18}$) was produced with the Ca:Mg:Al atomic ratio of 10:2:0.8. The chemicals with corresponding mass were separately dissolved in 200ml distilled water in beakers and then mixed together to make a mixture solution in a glass reactor of 1000 ml (denoted by reactor 1). The $(\text{NH}_4)_2\text{CO}_3$ with enough mass to complete the coprecipitation reaction and the polyethylene Glycol (with an addition of about 1.0 wt. % of the total amount of reagents) were dissolved in 400 ml distilled water in a glass reactor of 1000 ml (denoted by reactor 2). The reactor 2 was surrounded by a water bath, which was kept at constant temperature. The solution in reactor 2 was stirred using an agitator at approximately 600-700r/min. When the temperature of the solution had stabilized after heating up to the desired temperature (80°C), the chemicals solution in reactor 1 was added into the reactor 2 with a rate of 25-50 ml /min, until the coprecipitation completed. The temperature and pH value of the solution were recorded with electrodes inline, using ammonia water to keep the pH relatively constant (9.0) during the coprecipitation process.

After the coprecipitates (using CPs for short) have been placed on the table for 24h, they were filtered and rinsed with deionized water until the pH of the rinsed water reached 7. Then rinse the coprecipitates twice with dehydrated alcohol, and put them into an oven and dry at 110°C for 2 hours under air atmosphere. After the dry fine and porous powder calcined at 950°C in air for 1 hour, the mixed powder was ground to a certain size for tests. It is found from the results of XRD analysis that the new sorbent includes only CaO , MgO and $\text{Ca}_9\text{Al}_6\text{O}_{18}$ (using C_3A for short). It is assumed that all Al_2O_3 coming from the precipitate $\text{Al}(\text{OH})_3$ reacts completely with CaO from precipitate CaCO_3 to form C_3A , and MgO was derived from precipitate MgCO_3 . Thus,

the mass ratio of CaO to (MgO+ C₃A) in the new sorbents can be calculated according to the original mass for coprecipitation. The sorbents with the average particle size (d_p) of <125 μ m and 125-400 μ m were for the tests.

2.3 Sorbent performance tests

The CO₂ uptake capacity of samples during CPR cycles was calculated by Eq. (1), and the results after repeated tests show that the mean relative error for three test runs is less than 5%.

$$X_N = (m_{\text{carb}}^N - m_{\text{cal}}^N) \cdot W_{\text{CaO}} / (m_0 \cdot c \cdot W_{\text{CO}_2}) \quad (1)$$

where, X_N is the carbonation conversion of sample, N is the number of CPR cycles, m_0 is the initial mass of sample(g), and m_{carb}^N is the mass of recarbonated sample after N cycles(g), m_{cal}^N is the mass of calcined sample after N cycles (g) and c is the content of CaO in the initial sample. W_{CaO} and W_{CO_2} are the mole mass of CaO and CO₂ (g/mol), respectively.

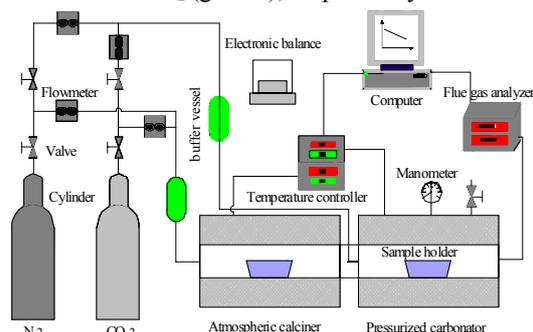


Fig. 1 Sketch of the atmospheric calcination/pressurized carbonation reactor system

2.4 Sorbent characterization

The crystalline structure of the sorbents was characterized by Rigaku X-ray diffraction (XRD) on a D/Max-2500VL/PC diffractometer using Cu K α radiation ($\lambda=1.5406\text{\AA}$).

The morphologies of the sorbents before and after the experiments were observed in a scanning electron microscope (SEM) on a FEI SIRION 200 field emission scanning electron microscope (FESEM), coupled with X-ray energy dispersive spectroscopy (X-ray EDS, GENESIS 60S) for local elemental composition determination.

Specific surface area and pore volume were

measured on ASAP 2020-M nitrogen adsorption analyzer, using nitrogen as an adsorbate at $-196\text{ }^\circ\text{C}$. The sorbents were degassed at $250\text{ }^\circ\text{C}$ overnight in the degassing port before the actual measurements. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method were applied for the determination of surface area and pore size distribution, respectively.

3 Results and discussion

3.1 Effect of carbonation condition on the carbonation conversion

To find out the flexibility in reaction conditions of the compound sorbent, different carbonation conditions were employed.

Fig.2 displays the conversion of the compound sorbent as a function of carbonation pressure and number of cycles at different carbonation temperature. It is observed in Fig.2 (a) that the conversion at $650\text{ }^\circ\text{C}$ increases rapidly with the carbonation pressure rising from 0.1MPa to 0.7MPa , with a conversion of 0.829 at 0.7MPa after 10 cycles. However, as the carbonation pressure further increases, the conversion begins to decrease slowly. The pressure of 0.7MPa is considered as an optimum value where the high cyclic conversion was achieved at $650\text{ }^\circ\text{C}$.

As the carbonation temperature increases to $700\text{ }^\circ\text{C}$ shown in Fig.2 (b), in comparison with that at $650\text{ }^\circ\text{C}$, the conversion increases at the pressure range tested and decreases more slowly with number of cycles. There is a pressure range of $0.3\text{-}0.7\text{MPa}$ among which a relative high conversion is maintained. The optimal pressure lies at 0.5MPa when the carbonation temperature is $700\text{ }^\circ\text{C}$ and a conversion of 0.946 is achieved after 10 cycles. When at $750\text{ }^\circ\text{C}$ in Fig.2(c), conversions begin to decrease a little bit faster than that at $700\text{ }^\circ\text{C}$, but slower than that at $650\text{ }^\circ\text{C}$. The pressure of 0.5MPa is distinct to be the optimal value for carbonation. As carbonation temperature further increases to $800\text{ }^\circ\text{C}$ in Fig.2(d), conversions at the pressure range tested

are a little lower than at other carbonation temperatures. However, the conversions are still much higher than that of the limestone (figures are not shown here). Based on the above discussions, it indicates that the low carbonation

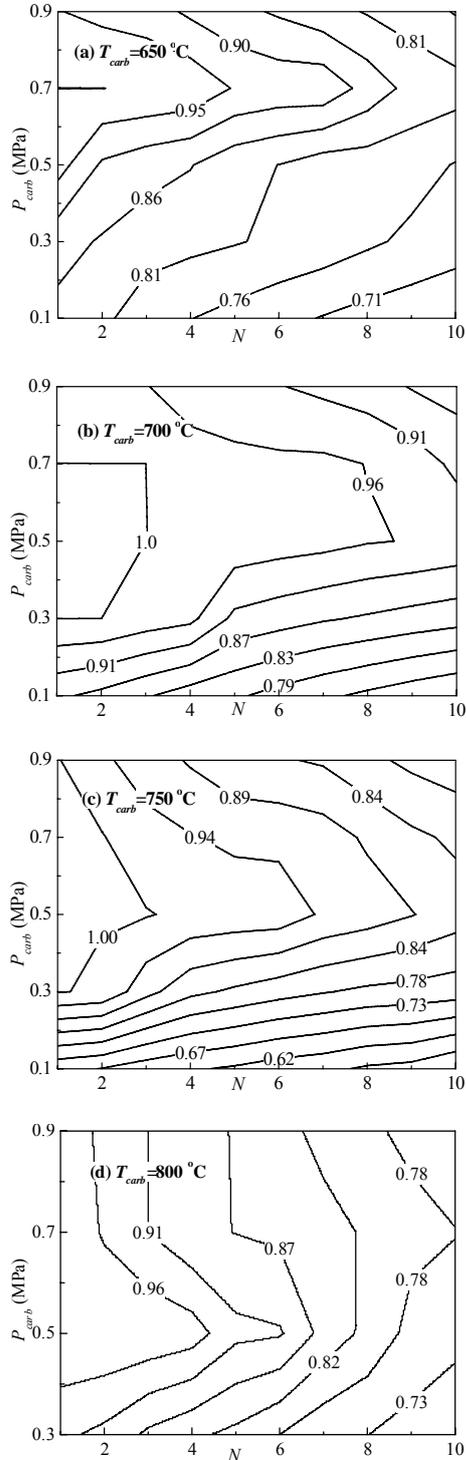


Fig. 2 Carbonation conversion of the compound sorbent as a function of pressure and number of cycle at different carbonation temperature ($d_p < 125 \mu\text{m}$)

temperature is not beneficial to intrinsic chemical reaction of $\text{CaO}-\text{CO}_2$; however, the sintering is stronger at high temperature which affects the microstructure of the produced CaO . The joint effect of carbonation temperature and pressure on sorbents' conversion can be seen more distinct in Fig.3. It is noted that there is an optimal combination of 700°C and 0.5MPa among the temperature and pressure tested, which is beneficial to reaction, and a high conversion is maintained.

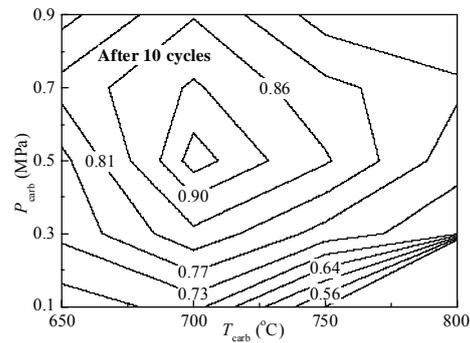


Fig. 3 Carbonation conversion of the compound sorbent after 10cycles as a function of pressure and temperature ($d_p < 125 \mu\text{m}$)

Bathia and Perlmutter [37] and Shimizu et al. [1] revealed that the carbonation reaction rate of CaO particles was considered as a first-order reaction with respect to the CO_2 partial pressure. Some tests have been conducted by varying CO_2 concentration during carbonation. Fig.4 presents the effect of CO_2 concentration in carbonation atmosphere on the conversion of the compound sorbent at 0.5MPa and 700°C . It is observed that the sorbent performance is slightly worse in a

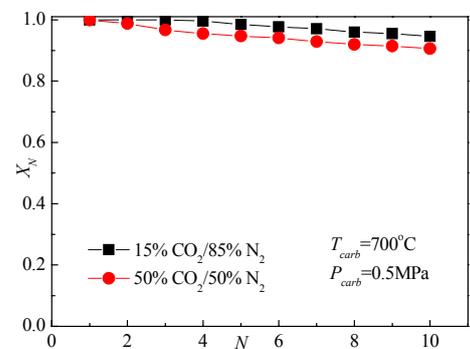


Fig. 4 Effect of CO_2 concentration in carbonation on conversion of the compound sorbent ($d_p < 125 \mu\text{m}$)

carbonation atmosphere of 50% CO₂/50% CO₂ than that in 15%CO₂/85% CO₂, probably due to some pore blockage [38]. At a given pressure, an increase in CO₂ concentration of carbonation atmosphere means an increase in CO₂ partial pressure; the carbonation reaction is accelerated, a fast build-up of the CaCO₃ product layer may occur. As the molar volume of the CaCO₃(36.9 cm³/g) is 2 times larger than that of CaO (16.9cm³/g), pores in the surface of CaO would be quickly filled up under high CO₂ partial pressure by fast reaction, which would hinder further carbonation. Alvarez and Abanades found a critical thickness of the product layer of CaCO₃, with the average value of about 49 nm [39]. As Bathia and Perlmutter [37] and Mess et al. [40] outlined that the slow stage reaction rate was independent of CO₂ partial pressure when the CO₂ partial pressure was far high from the equilibrium value for the CaO-CO₂-CaCO₃ system. The CO₂ uptake is mainly dependent on how the initial reaction develops. Therefore, the total CO₂ uptake is insensitive to the partial pressure of CO₂, in consistent with what Grasa and Abanades [41] have found.

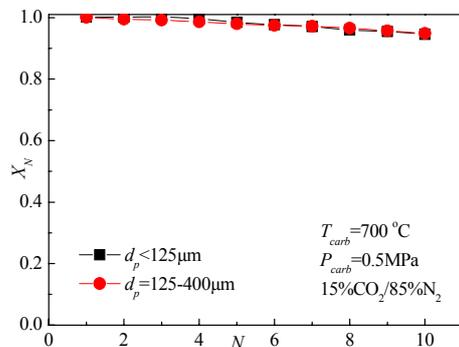


Fig. 5 Effect of particle size on conversion of the compound sorbent

To investigate the possible effect of particle size on carbonation conversions, two narrow particle size fractions ($d_p < 125 \mu\text{m}$, $d_p = 125-400 \mu\text{m}$) have been tested. Based on previous studies on the carbonation reaction of CaO [3,37,42], it was expected that the particle size would have a strong effect on the overall carbonation rates. Particles with poor

microstructure were expected to show increasing resistance to CO₂ diffusion towards the free CaO surfaces into the interior of the particle as particle sizes increased during multi-cycles. On the contrary, a complex network of pores is favorable to reaction. As seen in Fig.5, particle sizes do not influence the carbonation capacity of the sorbents that is determined only by the number of cycles. Though the particle size would affect the reaction rate at the initial fast carbonation stage that lasts for the first few minutes, a great amount complex network of pores in the sorbent favor the reaction, resulting in little difference in the final conversion. Since pores in the sorbent are abundant that the carbonation can take place to a great extent and a high conversion is achieved. It suggests that the compound sorbent shows great flexibility in particle size.

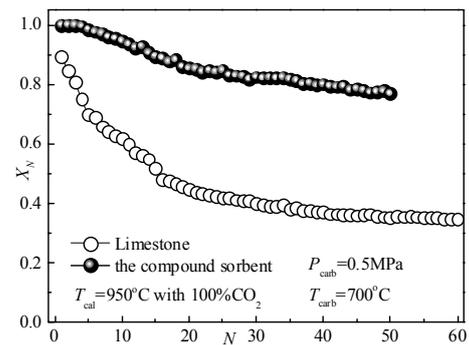


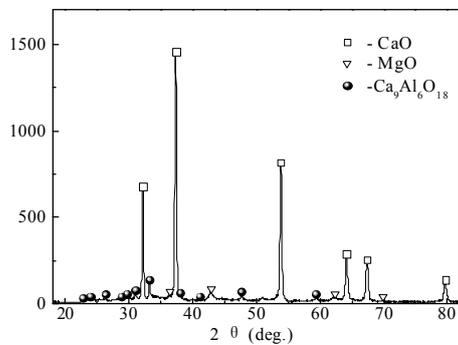
Fig. 6 Comparison of cyclic conversions of the compound sorbent and the limestone for carbonation at 700°C and 0.5MPa in 15%CO₂/85%N₂ ($d_p < 125 \mu\text{m}$)

Comparison of the cyclic carbonation conversions of the compound sorbent and the limestone at 700°C and 0.5MPa in an atmosphere of 15%CO₂/85%N₂ is illustrated in Fig.6. It is observed that carbonation conversion of the compound sorbent is much higher than that of the limestone and along the number of cycles. After 50 cycles, it achieves a conversion as high as 0.77, two times higher than the limestone, which only retains 0.36 under the same reaction condition. It reveals that the compound sorbent enhances the long-term CO₂ capture behavior of CaO-based sorbent which

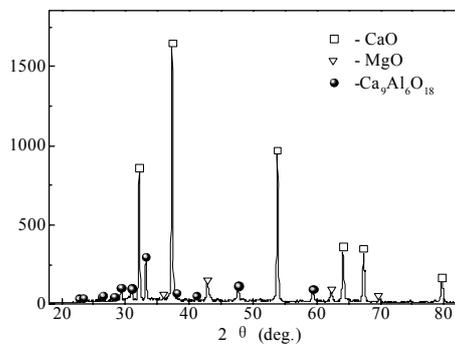
highlights the predominance of the compound sorbent over the limestone.

3.3 Microstructure analysis

To find out the mechanism of the compound sorbent to achieve high conversion, the XRD spectrums were conducted. Fig.7 illustrates the diffraction patterns of the sorbent after initial calcination and after 10 cycles at 700°C and 0.5MPa. It is clear that the crystal structures of the sorbents under different conditions are identical only including the CaO, MgO and Ca₉Al₆O₁₈. It is worthwhile to mention that the little difference in intensity and peak breadth of XRD spectrums of CaO suggests very little change in the grain size of CaO after 10 cycles. It attributes to the presence of MgO and C₃A, which act as structural support to prevent grain growth and increase the sintering temperature of the sorbent with these high melting point materials well dispersed. Based on Fig.7 and Eq.(2), the grain size of CaO after initial calcination and after 10 cycles at 700°C and 0.5MPa was calculated to be 28.9 nm and



(a) After initial calcination



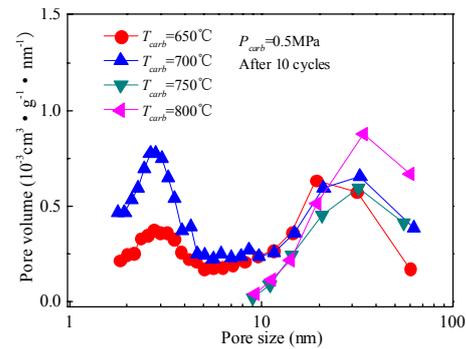
(b) After 10 cycles at 700°C and 0.5MPa

Fig.7 XRD spectrums of the compound sorbent

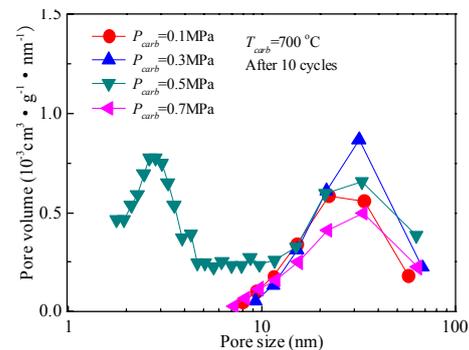
32.3nm, respectively. This small grain size of the solid favors the gas-solid reaction and it is part of the reason why the high activity of the sorbent is retained.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where, D is the grain size of CaO derived from different sorbents, nm, β is peak breadth of half height in XRD spectra, λ is X-ray wavelength, 0.15406 nm, θ is Bragg angle, degree, and k is Scherrer constant.



(a) Effect of carbonation temperature

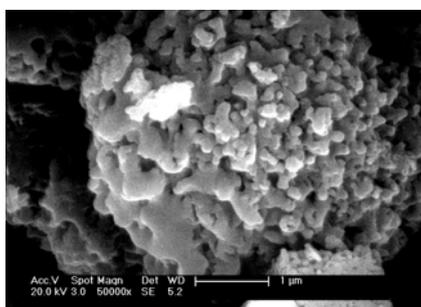


(b) Effect of carbonation pressure

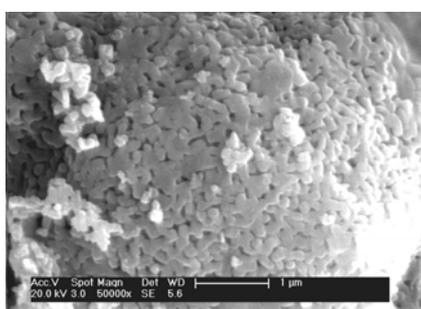
Fig. 8 Effect of carbonation temperature and pressure on pore volume distribution of the compound sorbent after 10 cycles

Structural properties such as pore volume distribution of the compound sorbent after 10 cycles are shown in Fig.8, to facilitate the comparison with the effect on the microstructure by different carbonation temperature and pressure. As can be seen in Fig.8 (a) that after 10 cycles at 0.5MPa, the sorbent possesses abundant mesopores of 2-10nm carbonated at 650 and 700°C, and no significant difference in pores of 10-100nm are found at 650-800°C. As

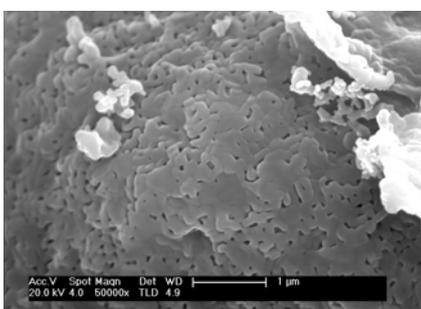
pores of 2-10nm are the important passages for CO₂ transfer to the active CaO and the space for CO₂ retention, they play an important role in the extent of CO₂-CaO reaction. Therefore, it explains why the sorbents exhibit higher conversion at 650-700°C and 0.5MPa. As in Fig.



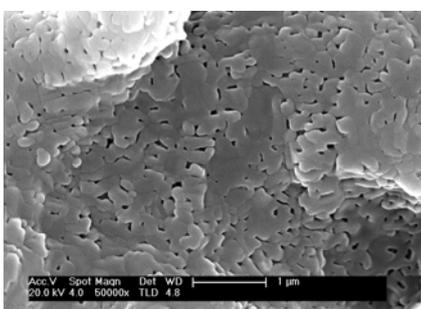
(a) Initial calcination



(b) After 10 cycles at 0.5MPa and 700°C



(c) After 10 cycles at 0.5MPa and 800°C



(d) After 10 cycles at 0.9MPa and 700°C

Fig.9 SEM images of the compound sorbent under different reaction conditions

8(b), there is also no great change in pores of 10-100nm for the sorbent carbonated at 0.1-0.7MPa, but abundant pores of 2-10nm are found for the sorbent carbonated at 0.5MPa and 700°C which indicates the highest conversion can be achieved at this condition.

Fig. 9 shows the images of the compound sorbent after initial calcination and after 10 cycles at different carbonation temperature and pressure, which are intuitional to understand the microstructure and the structural changes of the sorbent under the different reaction conditions.

Observations of the particles by SEM indicate some change in pore structure from a complex network of micropores and mesopores after initial calcination in Fig.9 (a), to plenty of connected but a little more open pores after 10 cycles at 0.5MPa and 700°C in Fig.9 (b). As the carbonation temperature increases to 800°C, a fraction of grain growth leads to abundant more open pores as shown in Fig. 9(c), in consistent with that in Fig.8(a). With carbonation pressure elevated to 0.9MPa in Fig.9 (d), pore structure of sorbent is similar as Fig.9 (c), but pores are relatively larger. It suggests that the compound sorbent is more tolerant to high temperatures than limestone (not shown here) thus retaining its CO₂ sorption ability, though with somewhat sintered at high temperature and pressure.

4 Conclusions

A compound sorbent with high CO₂ capture capacity and long-term life is produced by coprecipitation process. The sorbent shows great flexibility in particle sizes and the conversion is insensitive to CO₂ partial pressure. The highest CO₂ capture capacity of the sorbent is achieved at 700°C and 0.5MPa in an atmosphere of 15%CO₂/85%N₂, with slow decay over long-term cycles. SEM images and XRD spectrums of the sorbent after initial calcination and after 10 cycles at 700°C and 0.5MPa show very little change in the microstructure after the repeated carbonation /calcination cycles resulting from somewhat

sintering. The stability performance of the sorbent, especially carbonated at 700°C and 0.5MPa is guaranteed by the uniform dispersion of MgO and Ca₉Al₆O₁₈ binder among CaO particles based on the coprecipitation process. The Ca₉Al₆O₁₈ and MgO provide a stable framework inhibiting sintering of CaO. The CaO derived from the sorbent fulfills the target of the study (The average conversion of 0.86 for 50 cycles) even though it shows a slow decrease in its sorption ability from the first to the last cycle.

Acknowledgments

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