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CO_2 capture using CaO supported mesocellular siliceous foam (MCF)

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Abstract

CaO is a promising material as an alternative CO_2 capture material which can be used at high temperature. It has advantages of wide availability in natural minerals, low cost and large sorption capacity, etc. However, CaO sinters to form large particles under long-term high temperature conditions, resulting in a rapid decrease of its surface area and the capacity of CO_2 capture. In this work, we developed a composite material called mesocellular siliceous foam (MCF)-supported CaO to enhance the stability and capacity of CaO-based materials for CO_2 capture. The crystal structure, surface morphology and porosity property of the developed composite materials were investigated. Thermogravimetric measurements were carried out to study the cyclic CO_2 capture performance of the MCF-supported CaO composites. The results showed that a part of CaO reacted with the silica wall, and the formation of Ca_2SiO_4 within the MCF framework limited the presence of CaO in the mesopores, thus inhibited the sintering of CaO. The sample of MCF-3CaO showed better performance of CO_2 capture and long-term stability, compared with the materials prepared with lower CaO content.

Key words: CO_2 capture; CaO; mesocellular siliceous foam; long-term stability

1. Introduction

1.1. Background and motivations for the study

Global warming and climate change [1, 2] are becoming serious environmental issues that will affect us all in the near future. Anthropogenic CO_2 emissions are the major source of greenhouse gases that cause global warming. Thus, carbon capture and storage (CCS) has attracted extensive attention as a practicable method to reduce CO_2 emissions [3-6]. Recently, various separation techniques for CCS have been investigated, including absorption, adsorption, membrane separation, etc. Among them, solvent-based absorption is a commercial technology for CO_2 separation. However, this technology has some drawbacks, such as high energy consumption, high cost, solvent degradation and corrosion of equipment [7, 8]. On the other hand, adsorption of CO_2 using zeolites [9-11], mesoporous silicas [12], porous carbons [13-15], and metal-organic frameworks (MOFs) [16, 17] have attracted much attention in research in this field. However, these materials are considerably less mature due to the weak interaction with CO_2 and high cost.

CaO is considered as a good alternative material in both post-combustion capture and pre-combustion capture because of the carbonation reaction of CaO with CO_2 [18-20]. Theoretically, 1 kg CaO can absorb 785 g CO_2, producing $CaCO_3$ that can be decarbonated to re-form CaO and concentrated CO_2 (so-called calcium looping cycle) [21, 22]. CaO is a low cost and wide available natural minerals. It has large sorption capacity and can be operated at high operating temperatures. All of these advantages makes CaO a potential promising CO_2 sorbent. However, there is a serious disadvantage for CaO. It sinters to form large particles in carbonation-calcination cycles, leading to a rapid decrease of its surface area and thus its reactivity toward CO_2 [23]. This characteristic is attributed to the higher carbonation and calcination temperature than the Tammann temperature of $CaCO_3$ [24].

1.2. Literature review

Recently, many studies have been carried out to solve this sintering problem. For example, adding an inert material with a high melting point, such as Al_2O_3, $CaZrO_3$, TiO_2, and MgO [25-28] can significantly improve the thermal stability of adsorbents in the multi-cyclic carbonation/calcination process. Moreover, grafting CaO onto a support material is another option to form stable sorbents. It has been reported that CaO can be supported on oxides. For example, $CaTiO_3$, $Ca_{12}Al_{14}O_{33}$, mixed calcium aluminates, $Ce_xZr_yO_z$, La_2O_3, $LaAl_xMg_yO_3$ and cement [29-33].

To increase specific surface area and total pore volume, as well as pore structure modification is another strategy for enhancing the reactivity and capacity of sorbents for CO_2 adsorption. Porous architecture can be achieved by treating CaO with ethanol/water solutions [34, 35] and organic acids [36, 37], developing novel preparation approaches such as sol−gel method [38, 39], spray-drying technique [40], mechanical activation [41], and surfactant assistance method [42, 43].

Mesoporous materials exhibit high surface areas, large pore volumes and tunable pore sizes, and thus can be applied in the fields of absorbents, catalysts, chemical sensors, drug-delivery systems, and various electrochemical devices [44]. Mesopores with excellent mass transfer for reactants, remarkable stabilities and inert properties for active sites, are considered to be able to act as excellent binders, additives and protective agents to enhance the stability of CaO in high-temperature CO_2 capture. Recently, several mesoporous material/CaO composites have been reported [45, 46].

Mesocellular siliceous foam (MCF) is a typical mesoporous material, which has attracted considerable attention in research due to its easy synthesis, tunable pore size and thick pore walls [47, 48]. The interconnected nature of the large uniform pores makes MCF a good support material, and the good thermal and mechanical stability also allow its use in high temperature chemical reactions. Therefore, MCF is considered as a potential inert supporting material which can accommodate a high loading of CaO.

1.3. Aim and objectives of this study

This research is focusing on the fabrication of novel MCF-supported CaO with the aim of enhancing the reactive stability in cyclic CO_2 capture. MCF, which provides a highly stable framework under high temperature conditions, is selected as an inert supporting material to accommodate CaO with high CO_2 sorption capacity, and to mitigate the sintering problem of CaO. Thermogravimetric studies were carried out to characterize the cyclic CO_2 capture performance of MCF-supported CaO. In addition, the effects of MCF/CaO ratio and carbonation/calcination temperature on the cyclic CO_2 capture performance were also investigated.

2. Experimental materials and procedures

2.1 Materials

Triblock copolymer P123 (poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), EO_{20}–PO_{70}–EO_{20}, M_{av} = 5800) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37.8 wt.%), ammonium fluoride (NH_4F), 1,3,5-trimethylbenzene (TMB), and tetraethyl orthosilicate (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2 Preparation of MCF-supported CaO

The pristine MCF material was synthesized according to the method reported by Schmidt-Winkel et al [49]. Typically, P123 (2.0 g) was dissolved in a HCl solution (1.6 M, 75 mL) at room temperature under stirring. Then TMB (2.0 g) and NH_4F (23 mg) were added and the mixture was heated to 40 °C. After 60 min of stirring, TEOS (4.4 g) was added, followed by 20 h of stirring at 40 °C. Afterwards, the milky mixture was transferred into an autoclave and aged at 100 °C for 24 h. The obtained material was recovered by filtration, washed carefully and dried at room temperature. The organic template was removed by calcination at 550 °C for 6 h in air to produce the MCF material.

Then, the loading of CaO onto the MCF material was achieved by wet impregnation of calcium precursor ($Ca(NO_3)_2{\cdot}4H_2O$) into the mesopores of MCF and calcination to form CaO. In a typical preparation, 2.1, 4.2, 8.4 and 12.6 g of $Ca(NO_3)_2{\cdot}4H_2O$ (corresponding to 0.5, 1, 2 and 3 g CaO, respectively) were dissolved in 50 ml of distilled water. When the precursor was completely dissolved, 1 g of MCF was then added into each of the calcium nitrate solutions while stirring. After the solvent was removed by evaporation and dried, the samples were calcined at 750 °C for 2 h in air with a heating rate of 2 °C/min. The products were designated as MCF-*x*CaO, where $x = 0.5$, 1, 2 and 3, respectively.

2.3 Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a D/Max2550 VB/PC spectrometer with Cu Kα radiation (40 kV and 40 mA). Nitrogen adsorption-desorption isotherms were measured with a Micrometrics ASAP 2020 physisorption analyzer. The samples were pretreated by degassing under N_2 purge at 200 °C for 6 h prior to measurement. The surface area of each sample was determined according to the N_2 physisorption data at –196 °C calculated by the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3 (P/P_o). The total pore volume was calculated from the adsorbed volume at $P/P_o \geq 0.97$. The pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) model. The morphologies of the as-synthesized composites were observed in a Nova NanoSEM 450 scanning electron microscope (SEM).

The CO_2 sorption property and the multicyclic carbonation/calcination performance of each sample were investigated using the TGA method by a thermogravimetric analyzer (Stanton Redcroft). In a typical measurement, the sample (5 ~ 8 mg) was placed in a small Al_2O_3 crucible and heated to 900 °C under N_2 for degassing. A complete cycle was composed of carbonation conducted under pure CO_2 stream at 700 °C and calcination conducted under pure N_2 stream at 900 °C, respectively. The gases were supplied at a constant flow rate of 50 ml min^{-1}.

The capture of CO_2 on the prepared composites is achieved by the chemical reaction between CaO and CO_2, which is a reversible process:

$$\mathrm{CaO}_{(s)} + \mathrm{CO}_{2(g)} \Leftrightarrow \mathrm{CaCO}_{3(s)} \qquad \Delta H_{600^\circ\mathrm{C}} = -171.2\,\mathrm{kJ}\cdot\mathrm{mol}^{-1} \tag{1}$$

To compare the CO_2 capture performance of different samples in multi-cyclic carbonation/calcination process, carbonation conversion [43, 50, 51] is calculated:

$$\text{Carbonation conversion}(\%) = \frac{m_n\text{-}m_o}{m_o b}\frac{W_{\mathrm{CaO}}}{W_{\mathrm{CO_2}}} \times 100 \tag{2}$$

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From 2008 to today when my PhD students publish their work in solvent-based chemical absorption. We always use 'Capture Level'.

Some of our academic friends like 'Capture Rate'.

where m_n is the sample weight after n cycles of carbonation, m_o is the weight of the original sample after degassing, b means the content of CaO in the original sample (wt.%), W_{CaO} and W_{CO2} represent the molar mass of CaO and CO_2, respectively。

3. Results and discussion

3.1 Characterizations of the MCF-*x*CaO samples

The XRD patterns in Figure 1 show the crystalline structure of the prepared MCF-*x*CaO samples. It can be seen that the MCF-0.5CaO shows almost no diffraction peaks in the XRD pattern, while the MCF-1CaO, the MCF-2CaO and the MCF-3CaO exhibit both Ca_2SiO_4 and CaO peaks. It is suggested that MCF is composed of amorphous silica without crystalline structure. During the impregnation process, $Ca(NO_3)_2$ enters into the pores of MCF. When the mixture was calcined up to 750 °C in air, $Ca(NO_3)_2$ melts at 560 °C and subsequent decomposition occurred in the molten phase ($2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$). During the calcination of material, a part of CaO reacted to form Ca_2SiO_4 ($2CaO + SiO_2 \rightarrow Ca_2SiO_4$) [46]. As for the MCF-0.5CaO sample, although some of the CaO transformed into Ca_2SiO_4, the amorphous MCF was still the major constituent, therefore no obvious diffraction peaks are present. For the MCF-1CaO, some characteristic peaks of Ca_2SiO_4 appeared on the XRD profile, but the percentage of CaO was still very small, suggesting that almost all the CaO had transformed into Ca_2SiO_4. With the increase of the CaO/MCF stoichiometric ratio, the MCF-2CaO and the MCF-3CaO showed much more intensive CaO diffraction peaks while the Ca_2SiO_4 diffraction patterns did not change much, indicating that the formed Ca_2SiO_4 prevented the further reaction between CaO and SiO_2. Therefore, from XRD analysis, it is obvious that only the MCF-2CaO and the MCF-3CaO have the active sites of CaO which could be available for CO_2 capture.

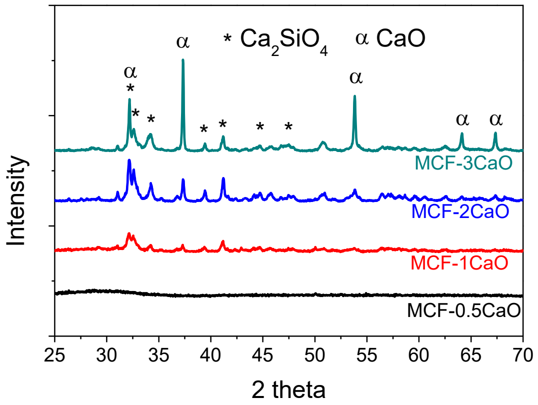

Figure 1. XRD patterns of MCF-*x*CaO samples, where *x* = 0.5, 1, 2 and 3, respectively.

The morphology of each MCF-*x*CaO sample was analyzed by SEM and the images were shown in Figure 2. The MCF-0.5CaO sample exhibited a relatively regular particle shape, with a porous surface morphology, which was similar to the original MCF material. With the increase of CaO content, the morphologies and structures of MCF-*x*CaO changed gradually. For example, for the MCF-1CaO sample, there was a slight increase in the degree of aggregation and the particle surface was more smooth and dense. However, the MCF-2CaO and the MCF-3CaO showed clearly different morphologies compared with the MCF-0.5CaO and the MCF-1CaO. For the MCF-2CaO and the MCF-3CaO, a large monolithic structure is observed including that the surface became very dense. This may be due to the presence of large amount of CaO particles outside the mesopores of MCF.

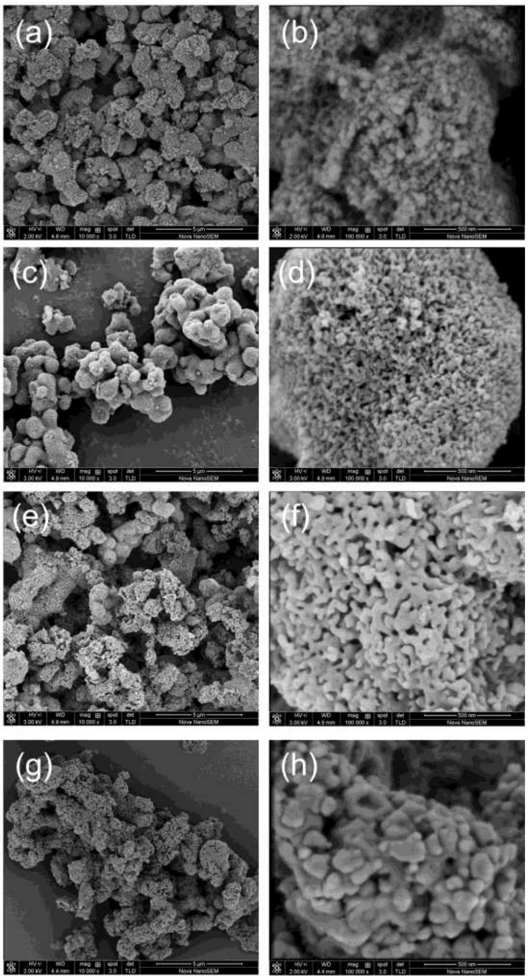

Figure 2. SEM images of each MCF-xCaO sample, (a,b) MCF-0.5CaO, (c,d) MCF-1CaO, (e,f) MCF-2CaO, (g,h) MCF-3CaO.

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The porosity properties of the MCF-*x*CaO samples were characterized by N_2 adsorption-desorption isotherms, as shown in Figure 3. The BET surface area and total pore volume of each sample are summarized in Table 1. As seen from Figure 3, each sample showed a type IV isotherm (according to IUPAC classification) which is typical in the original MCF. Meanwhile, the isotherm showed a steep hystersis loop of type H1 at relatively high pressure, which was attributed to the capillary condensation phenomenon of the large mesopores in the composite material. In addition, the samples showed very low N_2 adsorption quantities at relatively low pressure range, suggesting that a weak interaction present between the adsorbent and the adsorbate. When $P/P_0 > 0.9$, the N_2 uptakes showed a sharp rise. This type of isotherm is common in solid adsorbent with regular spherical particles, which is consistent with the SEM observation.

The BET surface area and total pore volume of the MCF-0.5CaO sample were 182.8 $m^2 \cdot g^{-1}$ and 0.69 $cm^3 \cdot g^{-1}$, respectively, much lower than those of the original MCF (approximately 600~800 $m^2 \cdot g^{-1}$ and 1.5~2.0 $cm^3 \cdot g^{-1}$). This is because the CaO content had occupied a considerable amount of space in the mesopores of MCF. With the increase of CaO content, the N_2 uptakes of MCF-*x*CaO showed a sharp decrease. Accordingly, the surface areas and total pore volumes of the MCF-1CaO, the MCF-2CaO and the MCF-3CaO were reduced to 67.4, 27.4, 12.9 $m^2 \cdot g^{-1}$ and 0.17, 0.09, 0.06 $cm^3 \cdot g^{-1}$, respectively. The N_2 adsorption-desorption isotherm of the MCF-3CaO was almost parallel to the X axis, suggesting that majority of the mesopores had been occupied by CaO. Therefore, adding more CaO would probably lead to the complete blockage of mesopores.

Table 1 BET surface area and total pore volume of each MCF-*x*CaO sample.

Sample	MCF-0.5CaO	MCF-1CaO	MCF-2CaO	MCF-3CaO
BET surface area ($m^2 \cdot g^{-1}$)	182.8130	67.4418	27.4300	12.9117
Total pore volume ($cm^3 \cdot g^{-1}$)	0.690551	0.166678	0.086684	0.057772

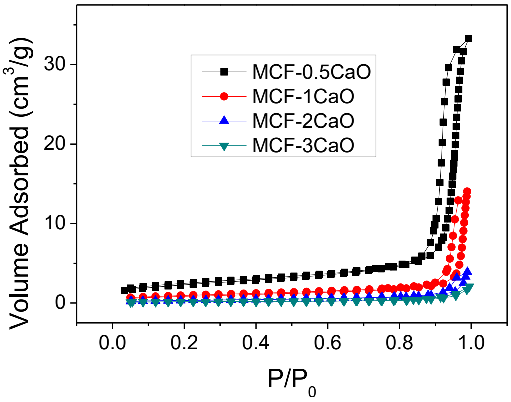

Figure 3. N_2 adsorption-desorption isotherms for each MCF-xCaO sample, where x = 0.5, 1, 2 and 3, respectively.

3.2 CO_2 capture capability and long-term stability of each MCF-*x*CaO sample

In this section, the long-term stability and resistance to thermal sintering were investigated for the developed CaO based materials. The durability performance of each sample was tested by means of multicyclic carbonation/calcination process. Prior to the multi-cyclic test, the sample was calcined in situ in the TGA furnace by heating up to 900 °C in pure N_2, aiming to degas and decarbonate the sample. Then the temperature was cooled to 700 °C prior to the carbonation stage. A complete cycle was composed of carbonation in pure CO_2 at 700 °C for 30 min and calcination in pure N_2 at 900 °C for 15 min, respectively. After calcination, the temperature was cooled to 700 °C again to continue with the carbonation stage of a new cycle. About 20-cycle stability tests for the MCF-2CaO and the MCF-3CaO were carried out. TGA results for the MCF-2CaO and the MCF-3CaO were shown in Figure S1. Because the MCF-0.5CaO and MCF-1CaO showed nearly no CO_2 capture, we only conducted three cycles of carbonation/calcination operation for these two materials (Figure 4).

According to the CO_2 uptake in each carbonation process and equation 2, the carbonation conversions of the MCF-xCaO samples were calculated and showed in

Figure 4. The CO_2 uptakes of both the MCF-0.5CaO and the MCF-1CaO were nearly zero because of the irreversible reaction between CaO and silica under high temperature. As shown in the XRD results (Figure 1), almost all the CaO component had transformed into Ca_2SiO_4 during the synthesis of the MCF-0.5CaO and the MCF-1CaO. For the samples of the MCF-2CaO and the MCF-3CaO, the CO_2 capture performances were much better. For example, the carbonation conversions were 22.2% and 31.5%, respectively for the MCF-2CaO and the MCF-3CaO. Moreover, both the MCF-2CaO and the MCF-3CaO showed better long-term stability compared with the original CaO, and the carbonation conversions were 15.8% and 27.5% after 20 carbonation/calcination cycles, respectively. It is suggested that that a part of CaO within the silica pores were transformed into inert Ca_2SiO_4, which in turn prevented the contact of CaO and silica. In addition, the inert Ca_2SiO_4 reacted with original MCF forming a stable framework which could effectively limit the sintering of CaO under long-term high temperature conditions [46, 50]. Therefore, the multi-cyclic stability of the CaO-based composites was significantly enhanced for the MCF-2CaO and the MCF-3CaO samples.

During the 20 carbonation/calcination cycles, the MCF-2CaO and MCF-3CaO still experienced a slow decay, and the carbonation conversions were reduced 28.2% and 12.7%, respectively. In comparison, CaO showed much significant decay in multicyclic carbonation/calcination process. Li *et al.* [50] reported that the carbonation conversion of CaO rapidly decayed from 68% to 12% after 50 carbonation/calcination cycles. Similarly, Sun *et al.* [51] reported that CaO derived from natural limestone displayed a large activity loss of 51.2% from the carbonation conversion of 64.4% to 31.4% after 20 carbonation/calcination cycles. The MCF-3CaO exhibited better stability than the MCF-2CaO in terms of the stability of CO_2 capture. It is suggested that in the long-term high temperature process, some CaO particles in the MCF-2CaO sample were transformed into Ca_2SiO_4, resulting in the reduction of active CaO species. However, for the MCF-3CaO sample with more CaO content, more active CaO sites were available for CO_2 capture.

It is noted that for the MCF-3CaO adsorbent, the capacity of CO_2 adsorption is

Formatted: No underline, Underline color: Auto around 4 mmol CO_2 per gram of adsorbent. This value of CO_2 uptake is higher than some reported data, for example, 2.3 mmol g^{-1} CO_2 adsorption was reported using an organic acid modified CaO pellets (adsorption temperature: 650 °C; desorption temperature: 850 °C and 15 vol.% CO_2 in N_2 at atmosphere pressure) [52], and 3.0 mmol g^{-1} CO_2 adsorption was obtained using CaO/meso-SiC material with adsorption and desorption temperature at 690 and 850 °C, respectively (15 vol.% CO_2 in N_2 at atmosphere pressure) [53]. However, higher CO_2 adsorption capacity (up to 13.9 mmol g^{-1}) were also reported by other researchers [30, 54, 55]. We suggested that a large amount of inert silica material was present inside the developed material, resulting the relatively low CO_2 uptake per gram of the adsorbent. Thus further medication of the adsorbent developed in this work is suggested in terms of increasing the capacity of CO_2 uptake and possible molecular modelling work can be carried out to support the development of CO_2 adsorbent.

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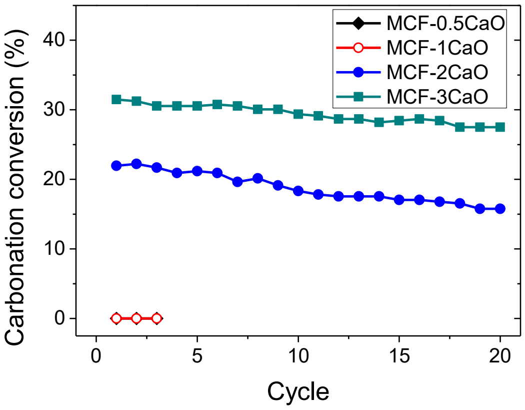

Figure 4. The carbonation conversion of MCF-supported CaO sorbents in 20 carbonation/calcination cycles. Carbonation: 700 °C, 30 min, pure CO_2; Calcination: 900 °C, 15 min, pure N_2.

3.3 Influence of adsorption conditions

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Therefore, the MCF-3CaO sample is considered to be a better candidate for CO_2 capture. It was selected to further investigate its CO_2 capture properties under varied situations. Carbonation temperature and calcination temperature are two important operation factors during the CO_2 capture process; these two parameters were investigated using the MCF-3CaO sample. When calcination temperature was fixed at 900 °C, carbonation temperature varied from 700 °C to 650 °C and 750 °C, respectively. 5-cycle carbonation/calcination tests through TGA method and the results were shown in Figure S2. The carbonation conversions were calculated and shown in Figure 5. It is obvious that the carbonation temperature strongly influenced the carbonation conversion. With the increase of carbonation temperature from 650 °C to 750 °C, the carbonation conversion increased from 26.3% to 36.8%. In addition, the stabilities of MCF-3CaO under different carbonation temperatures were also improved, the carbonation conversions after 5 cycles were 23.5%, 30.5% and 35.2%, respectively at 650, 700 and 750 °C.

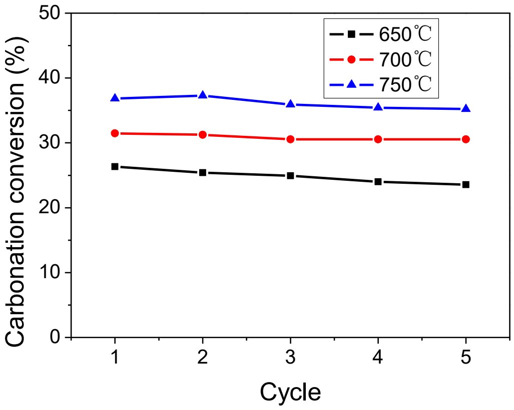

Figure 5. 5-cycle carbonation/calcination stability of MCF-3CaO under different carbonation temperatures.

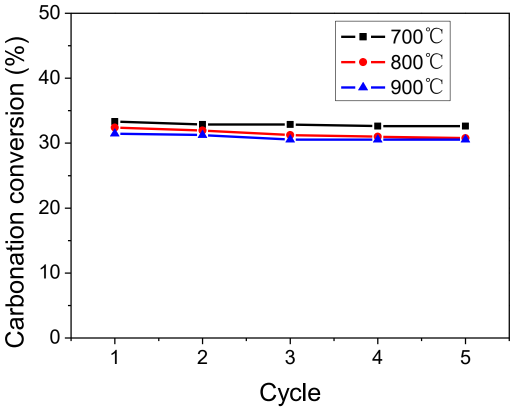

Figure 6. 5-cycle carbonation/calcination stability of MCF-3CaO under different calcination temperatures.

The calcination temperature was investigated at 700, 800 and 900 °C, and the carbonation temperature was constant at 700 °C. The TGA results of 5-cycle carbonation/calcination tests and the calculated carbonation conversions were exhibited in Figure S3 and Figure 6, respectively. It can be seen that the variation of calcination temperature had little influence on the carbonation conversion of the MCF-3CaO. The influence was mainly on the reaction rate because higher calcination temperature would promote the decomposition of $CaCO_3$.

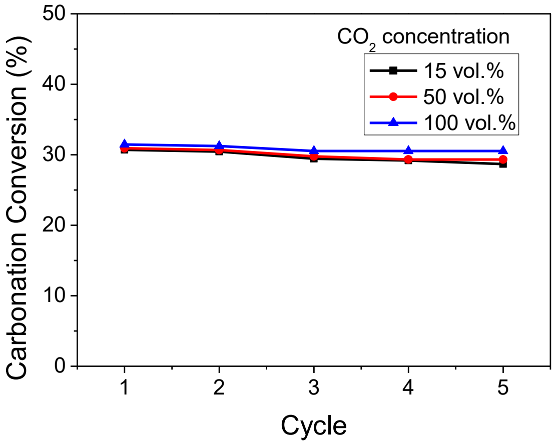

Figure 7. 5-cycle carbonation/calcination stability of MCF-3CaO under different CO_2 concentrations at 900 °C for carbonation and 700 °C for calcination .

The influence of CO_2 concentration was also investigated, while the carbonation temperature was fixed at 700 °C and the calcination temperature was constant at 900 °C, respectively. 15 vol.% and 50 vol.% CO_2 in N_2 were used to test the capture ability and long-term stability of MCF-3CaO, as shown in Figure S4 and Figure 7. The results revealed that the capture capacity and long-term stability of MCF-3CaO were almost the same when 15 vol.%, 50 vol.% and 100 vol.% CO_2 were investigated, suggesting that the MCF-3CaO could be employed in low concentration CO_2 capture process. Therefore, the MCF-3CaO is a potential promising sorbent for the capture of CO_2 from flue gases.

4. Conclusions

In this work, a method of preparing novel MCF-supported CaO composites was proposed for CO_2 capture. It showed that the interaction between CaO and silica support forming Ca_2SiO_4 was key to prepare a CO_2 adsorbent with better stability in cycles of CO_2 adsorption/desorption. ~~In a long term high temperature process, a part~~

~~of CaO reacted with the silica wall to form Ca_2SiO_4. MCF and Ca_2SiO_4 constructed a stable framework which was suggested to prevent the sintering of CaO during CO_2 capturing process.~~We also concluded that certain amount of CaO should be incorporated into the MCF material in order to have a better performance of CO_2 capture, due to the interaction with support. The~~ The sample of~~ MCF-3CaO ~~showed a good carbonation conversion of~~with 31.5% carbonation conversion showed only slightly reduce of CO_2 adsorption after 20 cycles of carbonation/calcination process (carbonation temperature: 700 °C and calcination temperature: 900 °C). ~~when carbonation temperature was 700 °C and calcination temperature was 900 °C. After 20 cycles of carbonation/calcination process, the carbonation conversion showed slightly reduce to 27.5%. Moreover, the MCF-3CaO also exhibited good capture performance when 15 vol.% CO_2 was used.~~The investigation of process conditions using the MCF-3CaO showed that the adsorption temperature (carbonation) had a clear influence on CO_2 capture, while small influence was obtained from calcination temperature and CO_2 concentration.

Acknowledgement

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