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Development of high-temperature CO_2 sorbents made of CaO-based mesoporous silica

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ABSTRACT

This study develops a modified CaO-based mesoporous CO_2 sorbent with high sorption capacity (about 10 mol/kg sorbent) and long-term durability. Highly ordered mesoporous SBA-15 molecular sieves used as carriers were successfully synthesized through direct-synthesis by using non-ionic surfactants as the structure-directing agent under strong acidic conditions. Calcium ions using calcium acetate as the precursor were finely dispersed onto prepared carriers using an impregnation method. Calcium oxide was obtained under calcination at high temperature. Analytical techniques, such as X-ray diffraction patterns, nitrogen physisorption isotherms, scanning electron microscopy/energy dispersive spectrometer, and transmission electron microscopy, were used to characterize the synthesized mesoporous materials. The thermo-gravimetric analysis was used to test the performance of CO_2 capture using prepared CaO-modified sorbents. The property and carbon dioxide sorption ability of the substrates and sorbents were examined and discussed. Carbon dioxide was effectively adsorbed, concentrated, and separated using the reasonable reaction paths. Durability tests showed that the CO_2 adsorption ratio remains at 80% after 40 cyclic runs under a carbonation temperature at 700 °C and calcination temperature at 910 °C, respectively. The results showed that the structural stability of the sorbents was improved sufficiently under high temperature and cyclic sorption–desorption operations.

1. Introduction

It is well known that CO_2 plays the major role in global warming and the greenhouse effect, leading to serious climate change. The demand for mitigation of CO_2 emissions is now widely accepted. CO_2 capture and storage from fossil-fuel power plants is critical in mitigating the long-term impact. However, it has been shown that the sequestration of CO_2 in power plants is very costly and consumes lots of energy. The optimization of energy and economic systems has high investigative importance.

Selective CO_2 sorption using natural or synthetic materials has been proven a potential pathway for high temperature applications. Accordingly, sorbent materials with high sorption capacity, long-term durability, fast sorption/desorption kinetic and good mechanical strength properties are desired for the economic viability of CO_2 capture systems.

Lithium oxides were once considered effective CO_2 sorbents. Studies proved that Li_4SiO_4 with a CO_2 sorption capacity up to 8 mol/kg was better than Li_2ZrO_3 of 6.8 mol/kg [1,2]. However, both materials encountered diffusion limitations at the realistic size for industrial applications [3,4].

Recently, numerous studies focused on calcium oxide due to their low cost and wide availability in natural minerals. The large adsorption capacity and capability at high operating temperatures makes the Ca-based material a potential CO_2 sorbent. CaO is carbonated at high temperature into $CaCO_3$, which is regenerated into CaO upon thermal decarbonation. The exothermic carbonation reaction and endothermic calcination reaction of calcium oxide with CO_2 (Eq. (1)) form a cyclic process. Therefore, a reversible looping cycle may offer great potential for CO_2 capture at higher temperatures and lower CO_2 capture system cost:

$$\mathrm{CaO}_{(s)} + \mathrm{CO}_{2(g)} \Leftrightarrow \mathrm{CaCO}_{3(s)}\ \Delta H^{\circ}_{600^{\circ}\mathrm{C}} = -171.2\,\mathrm{kJmol^{-1}}(\text{carbonation}) \quad (1)$$

However, the major challenge of this cycle in practical applications is a sharp decay in total reversibility with the number of carbonation/calcination cycles. This deactivation results from the formation of a product layer around half hundred microns and the lack of void space for the growth of this product layer. It has also been reported that the adsorption capacity for CaO-based sorbents decays as a function of the number of cycles [5–7].

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Recently, many methods have been proposed for improving the uptake capacity and the life cycle performance of a CaO-based sorbent, such as reactivation by steam hydration, incorporation of inert materials, and modification of the pore structure. Manovic and Anthony [8,9] reactivated CaO using a steam hydration process. This increased the pore volume and improved the sorbent cyclic performance.

Another possibility for enhancing the stability of sorbents under cyclic runs can be achieved by the incorporation of inert materials. MgO is commonly seen in the incorporation of CaO-based sorbents for it is inert under the conditions where CO_2 is adsorbed onto CaO. However, more inert materials in the sorbent for practical application are unfavorable due to the increase of tank capacity and operating costs. Roesch et al. [10] synthesized CaO sorbents doped with alkali metals which enhanced the surface basicity of sorbents. They observed a significant improvement compared with CaO when Cs-doped material was used in CO_2 sorption. Salvador et al. [11] reactivated limestone by impregnation with 0.5 wt% NaCl. The conversion of NaCl-doped sample was higher than that of CaO after several cycles. Aihara et al. [12] synthesized CaO-based sorbents with inert $CaTiO_3$ in an equal molar ratio by an alkoxide method or physically mixing $CaTiO_3$ with $CaCO_3$, producing conversion improvement.

CaO on supports with high surface area such as alumina (Al_2O_3) or mayonite ($Ca_{12}Al_{14}O_{33}$) has also been proposed. Li et al. [13,14] prepared this tailored CaO-based sorbent by adding $Al(NO_3)_3{\cdot}9H_2O$ into the desired solution, followed by calcination. A constant capacity of 5 mol/kg for 13 cycles was observed and a conversion of 41% was still retained when the tailored sorbent was over 50 cyclic runs. The stabilization was attributed to the presence of $Ca_{12}Al_{14}O_{33}$ as a binder which inhibited the sintering of CaO particles. Martavaltzi and Lemonidou [15,16] improved the capacity of the mixed $CaO/Ca_{12}Al_{14}O_{33}$ using CaO derived from calcined calcium acetate, and 9 mol/kg (a conversion ratio of 40%) was achieved in the first five cycles with a moderate loss of 15% after 45 cycles. Wu et al. [17] prepared nano- and micro-CaO/Al_2O_3 using nano- and micro-$CaCO_3$ precursors, respectively. Nano-CaO/Al_2O_3 displayed a maximum adsorption capacity of 6 mol/kg and the conversion ratio retained at 68.3%, with both higher than those of micro-CaO/Al_2O_3.

However, some additives might be destructive or disadvantageous to the stability of sorbents. Lu et al. [18] prepared the sorbent by adding silica to a calcium acetate solution followed by evaporation and calcination. The material was tested and exhibited no enhancement in stability and reversibility of CaO. Hasler et al. [19] showed a decline in performance when $SrCO_3$ were added into limestone using physically mixing or a coprecipitation method.

Pore structure modification is another strategy for enhancing the stability of sorbents. The precipitated calcium carbonate (PCC) is the typical way and has been studied. Gupta and Fan [20] developed a mesoporous structured CaO derived from the precipitated $CaCO_3$ which was synthesized by reacting Ca^{2+} ions with ${CO_3}^{2-}$ ions in water. It proved that PCC had better reactivity than CaO obtained from the calcination of natural limestone due to the less pore plugging in the larger pores.

The study of mesoporous silica molecular sieves has attained considerable attention in recent years due to their high surface area, large pore volume and good performance as effective sorbents. The specific porous structure allows easier diffusion of target molecules into the active sites. Accordingly, the excellent textual properties lead to the development of new adsorbents.

The discovery of SBA-15 by Zhao et al. [21] in 1998 is a significant progress in the field of mesoporous materials. This silica molecular sieve was fabricated using triblock copolymer surfactants as template under hydrothermal condition. The hexagonally arranged and highly ordered SBA-15 materials possess many advantages such as easy synthesis, tunable pore size, and thick pore wall. The good thermal and mechanical stability also allows its use in high temperature chemical reactions. All aforementioned specifics of SBA-15 make it currently of high interest in many applications.

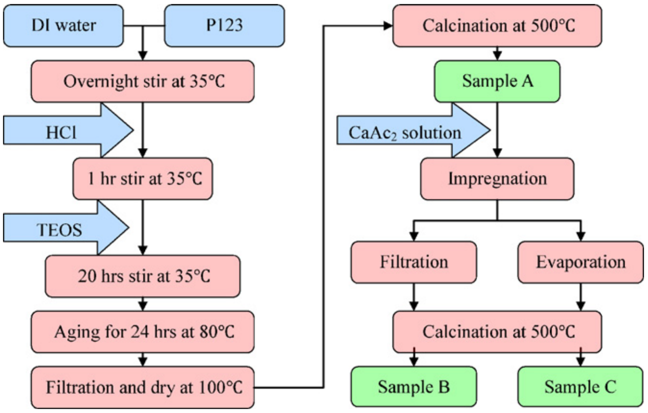

Fig. 1. Experimental scheme for preparing CaO/SBA-15.

Therefore, a CaO-based CO_2 sorbent on SBA-15 was developed in this study. CaO with high CO_2 sorption capacity was selected as the active component. SBA-15 was selected as an inert support and provided a highly stable framework under severe temperature conditions. The prepared sorbents were characterized using analytical techniques and subjected to a cyclic performance test by thermo-gravimetric analysis.

2. Experimental

In this study, all chemicals used in the synthesis, the preparation method, and the characterization techniques are described below. SBA-15 samples were first synthesized using a non-ionic-surfactant-templating approach following the procedure reported by Vinu et al. [22]. Calcium ions were then deposited on prepared SBA-15 and calcium oxide particles were obtained following the calcination. Analytical techniques were used in order to characterize all prepared samples and clearly establish the physical and chemical properties.

2.1. Materials

Poly(ethylene glycol)–*block*–poly(propylene glycol)–*block*–poly (ethylene glycol) (P123, $EO_{20}PO_{70}EO_{20}$, BASF), hydrochloric acid (HCl, 37.8%, J.T. Baker) and tetraethyl orthosilicate (TEOS, 99%, Merck) were used in the synthesis of SBA-15 as structure-directing agent, catalyst, and precursor of Si, respectively. Calcium acetate hydrate (Sigma–Aldrich) was used as the precursor of Ca. CO_2 and nitrogen were used as purge gas during the carbonation and calcination period, respectively.

2.2. Preparation method

The experimental scheme for preparing CaO/SBA-15 was shown in Fig. 1 as below. Triblock copolymer P123 as a structure-directing agent was dissolved in distilled water and stirred at 35 °C for 2 h. The required amount of HCl was then added to the clear solution as a catalyst and stirred for another 1 h at 35 °C. A given amount of TEOS as the source of Si was added drop wise to the acid solution under vigorous stirring at 35 °C. The stirring was continued for 20 h at 35 °C to form a homogeneous gel with molar composition: 0.00138 P123/0.086 TEOS/0.474 HCl/16.6 H_2O. The resultant mixture was transferred into a polypropylene bottle and aged at 80 °C for another 24 h without stirring. The aged mixtures were filtered, washed, and dried at 100 °C overnight. After calcination

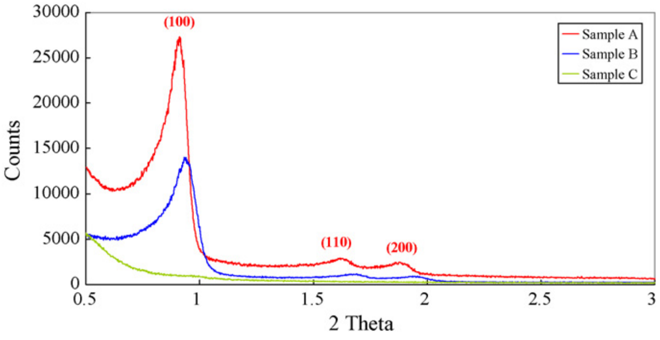

Fig. 2. XRD spectrum of prepared composites.

at 500 °C for 5 h in air, the mesoporous SBA-15 (sample A) was obtained.

17.165 g of calcium acetate (corresponding to 1 g CaO) was added to 80 ml of distilled water. After the precursor was completely dissolved under continuous stirring at 70 °C, 0.5 g of SBA-15 was then added into the calcium acetate solution. The mixture solution was kept still for 24 h after another 1 h stirring. The products were calcined to CaO/SBA-15 after the solvent was removed by filtration (sample B) and evaporation (sample C) to dryness.

2.3. Characterization

In this work, additional characterization was performed in order to clearly establish the structural properties. Analytical techniques such as X-ray diffraction patterns, nitrogen physisorption isotherms, scanning electron microscopy/energy dispersive spectrometer, and transmission electron microscopy, were used to characterize the synthesized mesoporous materials. The thermogravimetric analysis was used to test the performance of CO_2 capture by prepared CaO-modified sorbents.

The elemental quantitative analysis was determined on an induced coupled plasma-mass spectrometer (ICP-MS, Agilent). In a typical analysis, 5 mg of samples were dissolved in 10 ml acid mixture of HNO_3, $HClO_4$, and HF (5:3:2, v/v). The mixture was digested in a high-pressure bomb system at 170 °C for 5 h until a clear digested solution was obtained. After that, the resultant solution was transferred into a PTFE beaker and heated gently on a hot plate to evaporate the residual acid solvent. The residue was diluted by 2% HNO_3 (v/v) to 50 ml for ICP-MS analysis.

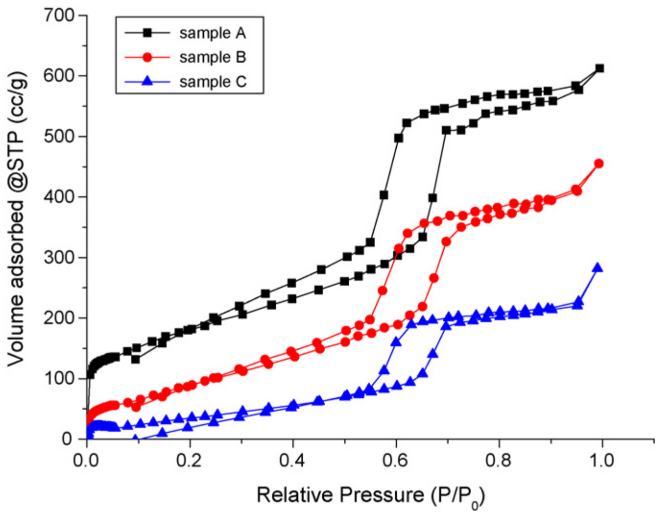

Fig. 3. N_2 sorption/desorption isotherms of samples A–C.

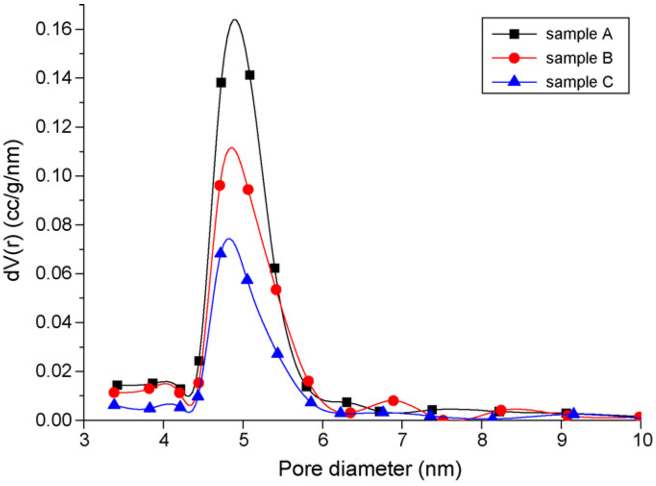

Fig. 4. Pore size distribution of samples A–C.

The surface area and porous structure were inferred from a surface analyzer of Quantachrome Nova 4200 Series. Samples were pretreated by degassing at 300 °C for 3 h prior to measurement. The surface area was determined according to N_2 physisorption data at 77 K calculated by the BET (Brunauer–Emmett–Teller) method in the relative pressure range of 0.05–0.3. The pore size distribution was obtained using the BJH (Barrett–Joyner–Halenda) model assuming cylindrical geometry for the pores using a Harkins–Jura expression for the multilayer thickness. The total pore volume was taken from the volume of N_2 adsorbed at a relative pressure $P/P_0 = 0.995$ single point.

The morphologies of prepared samples were observed in scanning electron microscopy of Hitachi S-4800, coupled with X-ray energy dispersive spectrometer of Horiba Emax-Energy 7593 h for local elemental qualitative analysis. The pore and channel morphologies of the synthesized mesoporous materials were observed on a transmission electron microscopy (TEM, Philips TECNAI 20).

The crystalline structure of samples were characterized by X-ray diffraction of Bruker Axs D8 Advance using Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, and 40 mA). Typically, the data were collected from 0.5° to 3° (2θ) with a step size of 0.002° and at a rate of 0.5 s/step.

The adsorption capacity and the multiple cyclic adsorption/desorption performance was measured by a thermogravimetric analyzer of NETZSCH TG 209 *F1 Iris*. In a typical experiment the appropriate amount of samples (in 50% volume of container) were distributed in a small Al_2O_3 crucible and heated to 950 °C at 15 °C/min under N_2 for degas. A complete cycle was composed of carbonation and calcination steps at 700 and 910 °C, respectively. During a carbonation step 100% CO_2 was supplied at a constant gas flow rate of 20 ml/min for 1 h. After that, only N_2 at a flow rate of 20 ml/min was conducted into the reactor for a calcination step.

In order to compare the adsorptive performance during each cyclic runs, the adsorption ratio (as presented in Eq. (2)) was defined as the mol amount CO_2 per mol CaO (in the initial mass of sorbent)

Table 1
The textural properties of prepared samples.

Samples		BET		
		Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cc/g)
A	SBA-15	659	5.27	0.830
B	CaO/SBA-15	367	5.05	0.667
C	CaO/SBA-15	155	4.75	0.432

adsorbed in the isothermal carbonation step:

$$\text{Adsorption ratio} = \frac{\text{mol amount of adsorbed CO}_2}{(MX/56) \times 100\%} \qquad (2)$$

where M is the initial mass of sorbent, and X is the content of CaO in the sorbent.

3. Results and discussion

Fig. 2 presents the XRD patterns of SBA-15 and Ca-modified SBA-15. Sample A shows three well-resolved peaks attributed to (1 0 0), (1 1 0), and (2 0 0) at low-angle range which is typical highly ordered SBA-15 with 2D hexagonal *p6mm* symmetry [23]. However, the

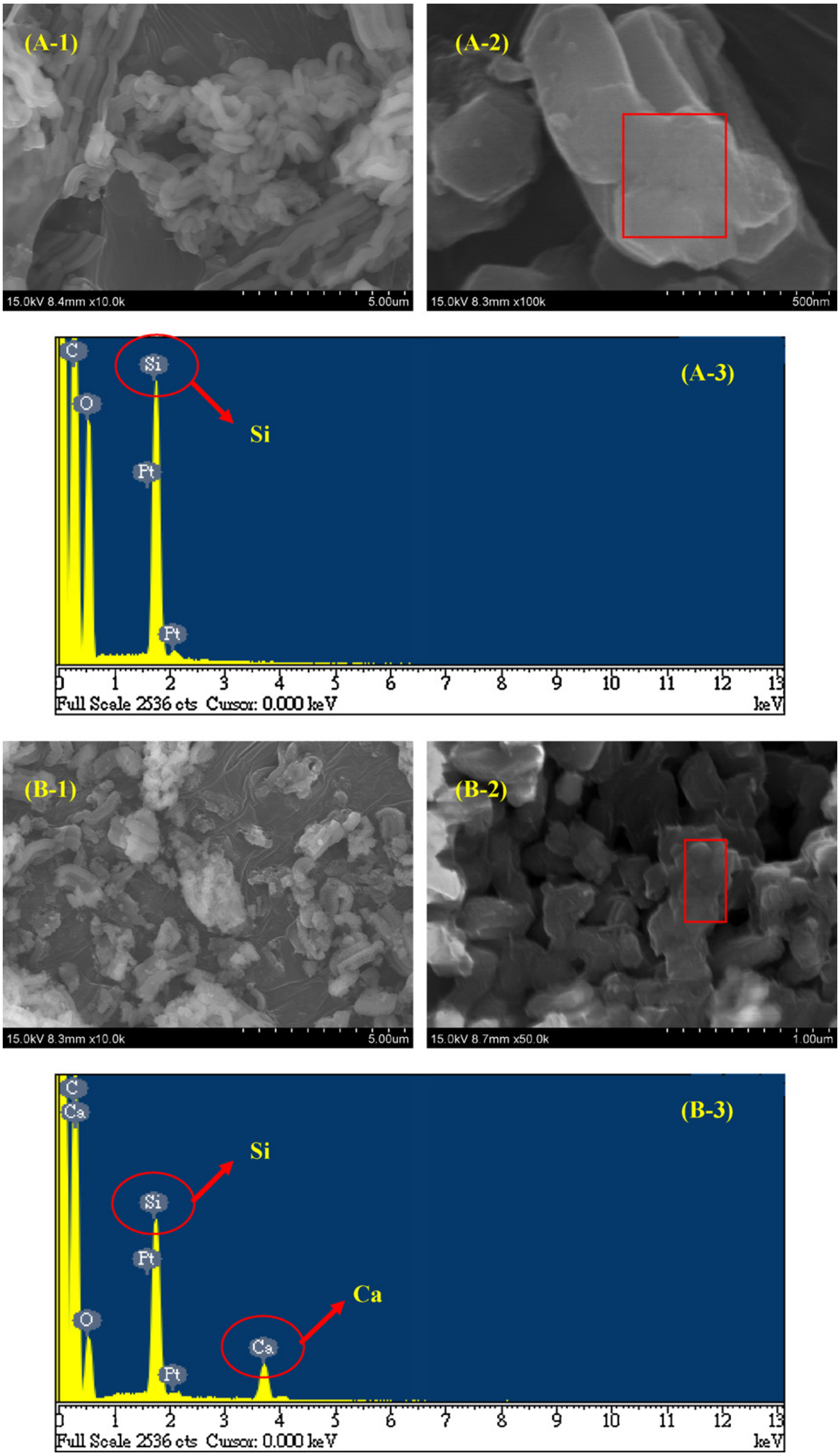

Fig. 5. SEM images and EDX spectra of prepared composites: (a) sample A, (b) sample B, and (c) sample C.

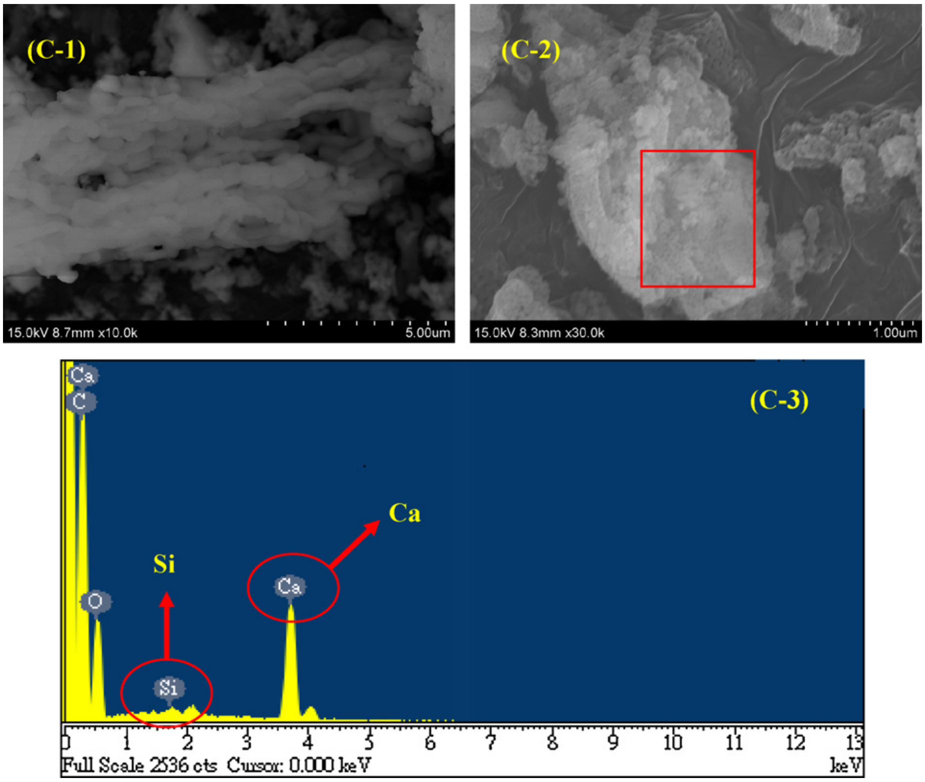

Fig. 5. (*Continued*).

intensity of three characteristic peaks decrease with the increase in calcium content, which indicates that pore clogging by calcium oxide particles have partly destroyed the ordered structure of SBA-15.

The porosity of the prepared samples was measured by N_2 physisorption method. It is well understood that the location of inflection point is related to a pore in mesoscale and the sharpness of these curves reveals the uniformity of the mesopore size distribution [24]. Fig. 3 shows the adsorption/desorption isotherms of SBA-15 and CaO/SBA-15. All samples display the type IV isotherms (according to the IUPAC classification) with H1 hysteresis loops at higher relative pressures. This is due to capillary condensation and desorption of nitrogen which indicate a typical mesoporous material with larger pore sizes and narrow size distributions [25]. The inflection points are similar but the sharpness of the steeps is decreased with the increasing amount of modified calcium ions. Fig. 4 displays the pore size distribution of SBA-15 and CaO/SBA-15. For calcium oxide loaded SBA-15 samples, the pore diameter and the peak intensities also decrease. The result indicates that the mesostructure is maintained but the pore size and pore volume is decreased due to the blockage of mesopore channels by the calcium oxide particles.

The textural properties of the three samples are summarized in Table 1. It is clear that the CaO dispersed on SBA-15 makes the specific surface area and pore size to decrease because the CaO blocks the mesopore channels. A decrease in their pore volume values is also observed. When a large amount of CaO is loaded onto a SBA-15 sample, most of the CaO particles take places within the ordered support channels. ICP data shows the Ca elemental concentration results for different samples. The Ca-wt% of sample B and sample C are 6.02 and 48.6, respectively. It was found that the Ca content varies due to different solvent removing procedures such as filtration and evaporation. According to the results, a higher Ca content is loaded by using evaporation method. This explains why

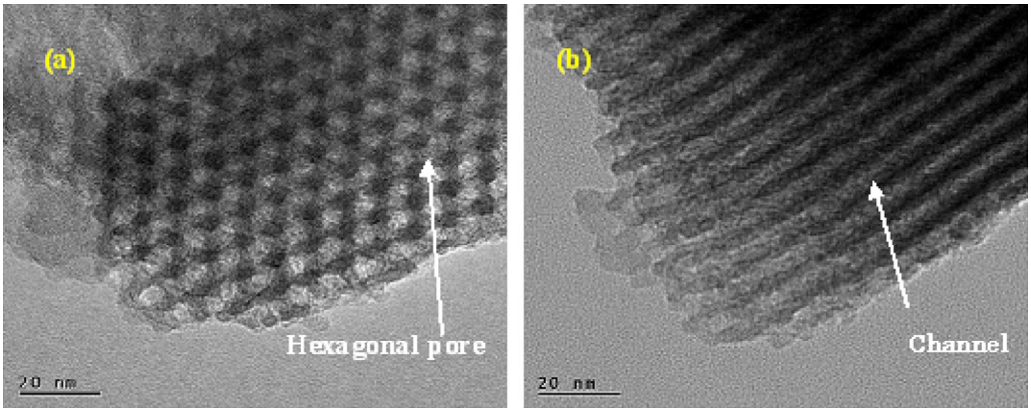

Fig. 6. TEM images of SBA-15 (sample A).

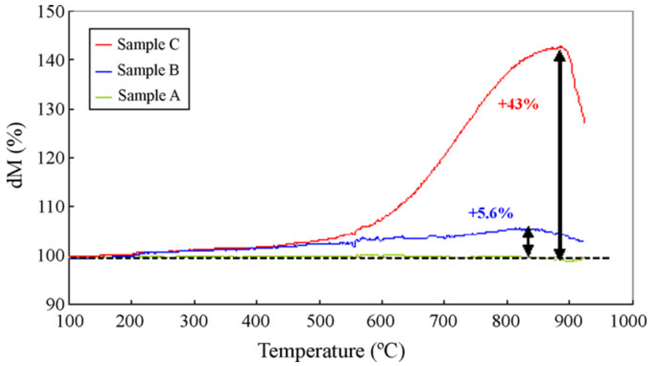

Fig. 7. TG analysis of prepared SBA-15 and CaO/SBA-15 materials.

specific surface area and pore volume of sample B is smaller than sample A.

The particle morphology of various samples can be observed in Fig. 5. The SEM images (A-1 and A-2 of Fig. 5) clearly show the long fibrous aggregates which are the typical shape of SBA-15 and extend tens of micrometers. Compared with the SEM images of B-1 and B-2, the overgrowth of calcium oxide on the external surface is clearly seen in C-1 and C-2 of Fig. 5 with high amounts of calcium oxide. The EDX Spectra show the Ca loading on the support. It also demonstrates that a higher Ca content is obtained from the solvent removals using an evaporation method over a filtration method.

TEM images show the morphology of 2D hexagonal pores arrays and channels at mesoscale for SBA-15. A clearly hexagonal array of well defined pores with uniform pore size about 6 nm and long range coverage was observed in Fig. 6. It represents that a typical SBA-15 with highly ordered structure as described in literature [23] was successfully synthesized in this study.

The CO_2 uptake capacity is examined in a TGA instrument using 100% CO_2 at 700 °C and a constant gas flow rate of 20 ml/min for 1 h. Desorption at 910 °C for 30 min under pure N_2 flow is then followed. The weight increase corresponds to the amount of CO_2 adsorption. Fig. 7 depicts the weight change of samples in terms of wt% with increasing temperature. Sample C exhibits a 43 wt% increase in sorption capacity (equal to 9.8 mol/kg sorbent) from SBA-15 during the carbonation step. On the other hand, the CO_2 adsorption ability of sample B is much smaller than that of sample C, which shows only 5.6 wt% increase in sorption capacity (1.3 mol/kg sorbent). This result could interpret the superior capacity of sample C compared to sample B. ICP data clearly shows that the Ca loading amount of sample C is larger than sample B. This result reveals that more CaO active sites were obtained on sample C to react with CO_2 to form $CaCO_3$.

It is obviously that sample C exhibits a high sorption rate at the beginning of the carbonation reaction. A maximum sorption rate is observed at the temperature of 700 °C according to the reflection point in the curve. When the temperature is over 700 °C, the CO_2 sorption rate is slowed down due to a competition between the adsorption and desorption processes. In the calcination regime, the $CaCO_3$ is gradually decomposed to CaO and CO_2 when the temperature is over 900 °C.

The stability is much more important than capacity for a sorbent used in CO_2 uptake. Therefore, the durability performance of sample C is examined and depicted in Fig. 8. A maximum adsorption ratio of 97% can be observed on 2nd cyclic run for sample C which conserves a nearly 80% utilization efficiency even after 40 cycles. The SBA-15 as supports of the sample C has provided a stable framework inhibiting deactivation of CaO. The result reveals that the CaO-modified SBA-15 can possess a high sorption capacity with long-term durability. It is promising to use this composite material as a high energy CO_2 sorbent in the carbon capture and storage technology.

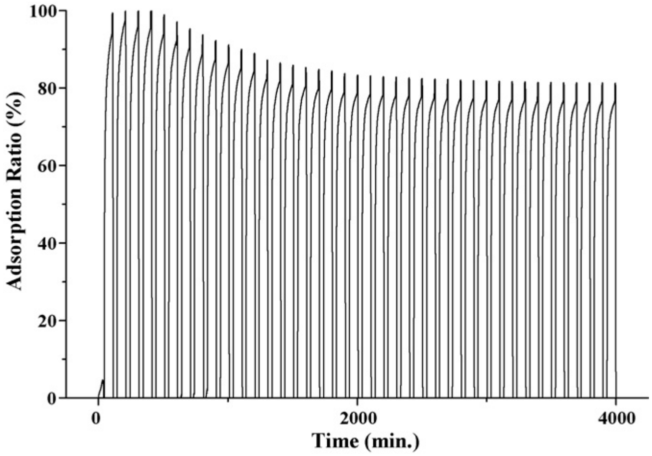

Fig. 8. Multiple cyclic runs over sample C under a carbonation temperature at 700 °C and calcination temperature at 910 °C, respectively.

4. Conclusions

This study presented typical SBA-15 molecular sieves used as carriers successfully synthesized through direct-synthesis using non-ionic surfactants as the structure-directing agent under strong acidic conditions. The modified CaO-based mesoporous CO_2 sorbents were then prepared. The highly ordered mesoporous structure with high surface area and large pore volume was validated using analytical techniques such as XRD, N_2 physisorption isotherms, SEM/EDX, and TEM. Carbon dioxide was effectively adsorbed, concentrated, and separated through the reasonable reaction paths using thermo-gravimetric analysis. Durability tests show that the CO_2 adsorption ratio remained at 80% after 40 cyclic runs under a carbonation temperature at 700 °C and calcination temperature at 910 °C, respectively. The results show that the structural stability of the sorbents was improved sufficiently under high temperature and cyclic sorption–desorption operations.

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