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High performance CaO-based sorbents for pre- and post-combustion CO_2 capture at high temperature

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Abstract

Synthetic CO_2 sorbent materials of $CaO/Ca_{12}Al_{14}O_{33}$ of different compositions were prepared using a simple hydrothermal method and low-cost hydroxides starting precursors. The products were characterized by X-ray diffraction, scanning electron microscopy, BET analysis and crushing tests. Sorption kinetics and chemical stability during carbonation/ calcination multi-cycling in pre- and post-combustion conditions were investigated by thermo gravimetric analysis. Long-term stability of the hydrothermally prepared sorbents is attributed to the formation of a stable frame of mayenite ($Ca_{12}Al_{14}O_{33}$) which reduces the sintering of the active CaO phase. Among all sorbents, the one with composition 27/73 wt % $CaO/Ca_{12}Al_{14}O_{33}$ is considered a promising CO_2 sorbent with stable capture capacity (21g-CO_2/100g sorbent) in severe calcination conditions and high mechanical strength.

1. Introduction

One of the most promising technologies for efficiently separating CO_2 from a process or combustion gas is based on sorption of CO_2 at high-temperature on solid sorbents. High-temperature CO_2 sorbents can be used in two different CO_2-capture technologies:

> - Post-combustion CO_2 capture for energy generation and industry processes
> - Pre-combustion CO_2 capture for energy generation and/or hydrogen production

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Among the high temperature solid sorbents, CaO-based sorbents are considered to be the most promising candidates because of their relatively low cost, high availability, fast kinetics and high theoretical CO_2 capture capacity of 0.786 g CO_2/g CaO [1-4]. The majority of research in the field of CaO-based CO_2 sorbents has focused on natural sorbents, such as limestone and dolomite. However, the CaO-containing natural materials suffer from rapid decrease in CO_2 uptake over multi- cycles of carbonation/calcination due to sintering and pore closure [5-9]. In addition, natural CaO sorbents have sub-optimal mechanical properties leading to high attrition rates and consequently, elutriation of fine materials when used in fluidized bed reactor systems [4, 10, 11]. Therefore, due to the limitations of the natural sorbents, development of synthetic sorbents with high and stable CO_2-capacity over repeated carbonation/calcination cycles as well as high mechanical stability has become an important research topic.

Many new synthetic high temperature CaO-based sorbents have been reported to overcome the sintering of CaO particles and to improve cyclic carbonation conversion CaO-based sorbents [12]. Incorporation of inert materials such as Al_2O_3 [13], $Ca_{12}Al_{14}O_{33}$ [14] , ZrO_2 [15],$CaTiO_3$ [16], rice husk ash [17], enhances the long-term stability of CaO. The inert supporting materials should both reduce grain sintering and improve the mechanical stability of the material. Among those solid supports, mayenite ($Ca_{12}Al_{14}O_{33}$) is considered to be the most promising support for high-temperature CO_2 sorbents. Various synthesis methods for $CaO/Ca_{12}Al_{14}O_{33}$ sorbents have been reported in the literature [14, 18-21]. Recently, the authors of this paper presented a new synthesis for $CaO/Ca_{12}Al_{14}O_{33}$ sorbent based on the decomposition of $Ca_3Al_2O_6$ at high temperature. The sorbent prepared by a modified Pechini method showed a high CO_2 sorption capacity up to 29g-CO_2/100g sorbent for more than 140 carbonation/calcination cycles [20] . However, because of the high preparation cost of the synthesis method, the application of this material at large-scale is challenging. Therefore the later work, presented in this paper, focused on the development of a simpler and more cost-effective synthesis method for high-performance CO_2-capture sorbents based on largely available and cheap precursors.

2. Experimental

2.1. Preparation of sorbents

Several sorbents were synthesized with different CaO-to-$Ca_{12}Al_{14}O_{33}$ weight ratios ($CaO/Ca_{12}Al_{14}O_{33}$ = 27/73, 37/63, 47/53 and 73/27 wt %) by hydrothermal method using $Ca(OH)_2$ and AlOOH as precursors. Stoichiometric amounts of the precursors were weighed and mixed together in isopropanol using magnetic stirrer to make homogeneous slurry. Isopropanol was removed by heating the slurry at 363 K. After evaporation of the isopropanol, the powder was transferred to 50 or 600 cm³ stainless steel autoclaves. The precursor powders were mixed with water at a weight ratio liquid/solid = 3. The slurry was heated to 423 K for 5 h (pressure 3-4 bars). The product from the autoclave was then cooled and dried in a heating cabinet at 383 K. The dried powders from hydrothermal synthesis were then pelletized using uniaxial pressing (50 MPa) and calcined at 1273 K for 1 h to obtain the final CaO and $Ca_{12}Al_{14}O_{33}$ phases. Sorbent pellets were then crushed and sieved to the desired size fractions depending on the characterization methods.

2.2. Characterizations of sorbents

X-ray diffraction (XRD) measurements were employed for the identification of phases of the synthesized sorbents. XRD patterns of samples were obtained by a Bruker D8 Advance diffractometer using a CuKα radiation source (λ = 1.5406˚A) at 40 kV and 40 mA. The diffractograms were collected in the range 10^0 - 90^0 with a step of 0.02^0. Particle and surface morphology were studied by scanning electron microscopy (Hitachi S-4800 field emission SEM). Surface area and pore volume were determined using a N_2 adsorption analyzer (Quantachrome NOVA 4000e). The measurements were performed using nitrogen physisorption and desorption isotherms at -77 K. The sorbents were degassed at 573 K overnight prior measurements. The surface area was calculated using the Brunauer−Emmett−Teller (BET) model and the volume of pores was estimated using the Barrett−Joyner−Halenda (BJH) model. Finally, to evaluate the mechanical performance of the sorbents particles, crushing strength was measured by FGV-10X manual hand operated test stand. Abbreviations of the sorbents are presented in Table 1.

Table 1. Abbreviations of the hydrothermally prepared sorbents.

Sorbent composition (wt %)	Abbreviation
$27CaO/73Ca_{12}Al_{14}O_{33}$	27CA
$37CaO/63Ca_{12}Al_{14}O_{33}$	37CA
$47CaO/53Ca_{12}Al_{14}O_{33}$	47CA
$73CaO/27Ca_{12}Al_{14}O_{33}$	73CA

## 2.3. Testing the sorbent in thermo- gravimetric analyzer

A thermo-gravimetric analyzer (TGA, CI electronics) was used to investigate the reaction kinetics and the multi-cycling stability of the hydrothermal synthetic sorbents. High quality Verdal limestone provided by Norcem, Norway, was chosen as a reference material. All the TGA tests were performed with 25 mg of samples and the particle size fraction, 100-200 μm. CO_2 capture kinetic experiments were performed both in absence and presence of steam along with 15 vol % CO_2 in N_2 at 898 K for 10 min. The steam concentration varied from 0-50 vol % with a constant total flow of 500 cm^3/min. Multi-cycle experiments were performed under both pre- and post-combustion conditions. The gas compositions for the pre-combustion multi-cycle are based on expected CO_2 and steam concentrations for the sorption-enhanced steam methane reforming (SE-SMR) process [22]. In the pre-combustion multi-cycling, the sorbents were regenerated at 1123 K in steam-rich atmosphere. In the post-combustion multi-cycling, the steam concentration in the carbonation step was reduced to simulate a typical flue gas composition whilst the calcination was carried out in 100 % CO_2 at 1193 K. For all the tests, carbonation/ calcination cycles were repeated 40 times to determine the long term behaviour of the sorbent. The total gas flow for all the multi-cycle tests was 1000 cm^3/min. Multi-cycle testing conditions of sorbents under pre and post-combustion are summarized in Table 2.

Table 2. Testing conditions (pre and post- combustion) of the synthetic sorbents in TGA (total gas flow 1000 cm^3/min, N_2 balanced).

Pre-combustion		Post combustion	
Carbonation	Calcination	Carbonation	Calcination
873 K, 10 min	1123 K, 3 min	923 K, 10 min	1193 K, 3 min
15 vol % CO_2	21 vol % CO_2,	14.5 vol % CO_2	100 vol % CO_2
47 vol % H_2O	78 vol % H_2O	13 vol % H_2O	

3. Results and Discussions

Fig. 1a shows two XRD patterns of the as prepared dried sorbents micro powder after hydrothermal synthesis. The phases initially present in the material before calcination are calcium hydroxide, $Ca(OH)_2$ and hydrogarnet, $Ca_3Al_2(OH)_{12}$. Hydrogarnet, $(Ca_3Al_2(OH)_{12})$ is a precursor for the mayenite $(Ca_{12}Al_{14}O_{33})$ phase [23]. Indeed during calcination at 816 K [23, 24], the hydrogarnet loses water and decomposes to form the stable mayenite phase, $Ca_{12}Al_{14}O_{33}$ along with excess CaO according to the following equation (1).

$$7Ca_3Al_2(OH)_{12} \rightarrow Ca_{12}Al_{14}O_{33} + 9CaO + 42H_2O \qquad (1)$$
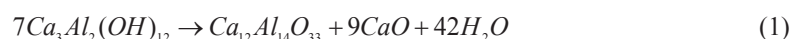
Decomposition of the hydrogarnet phase was confirmed by XRD diffraction after calcination at 1273 K for 1 h (Fig. 1b). For all synthesized powders, only the two oxide phases calcium oxide and mayenite were detected.
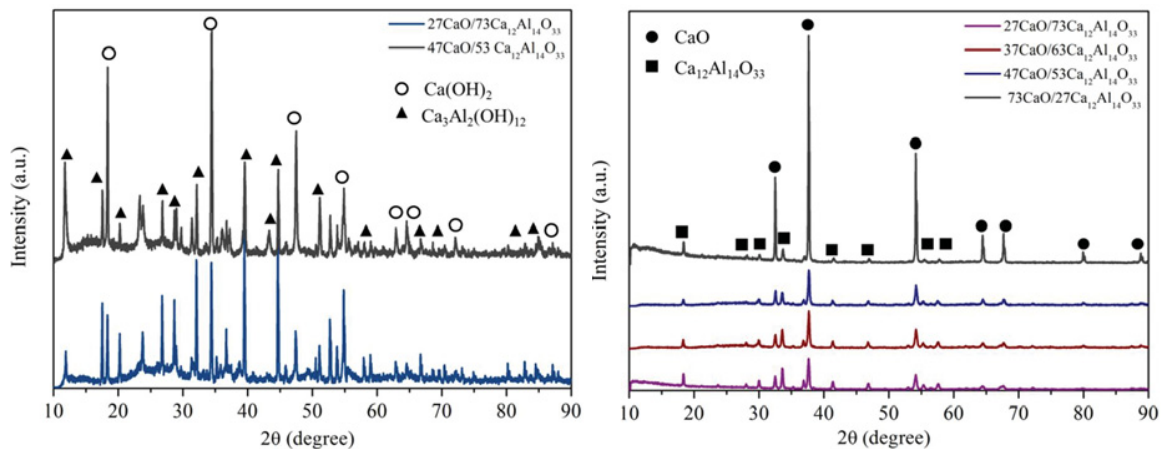
Fig. 1. (a) X-ray diffraction patterns of two different as-synthesized dried hydrothermal sorbents: ○ $Ca(OH)_2$, ▲ $Ca_3Al_2(OH)_{12}$; (b) X-ray diffraction patterns of calcined hydrothermal (1273 K , 1 h) sorbents with different $CaO/Ca_{12}Al_{14}O_{33}$ ratios: ● CaO, ■ $Ca_{12}Al_{14}O_{33}$.

The textural properties of the samples were determined by isothermal adsorption of nitrogen, and applying BET to obtain the surface area (SA) and BJH for the pore volume (PV) as listed in Table 3.

Table 3. BET surface area and total pore volume of the calcined synthetic and natural sorbents.

Sorbent	BET surface area (m^2/g)	BJH pore volume (cm^3/g)
27CA	9.2	0.08
37CA	10.7	0.09
47CA	13.1	0.09
73CA	11.4	0.09
Limestone (Verdal), calcined	11.8	0.13

All the synthetic sorbent particles show a BET surface area comparable to the fresh calcined limestone but a lower pore volume. A maximum of surface area was measured for the 47CA sorbent, and no correlation to the CaO percentage can be established. Likewise, the pore volume values show almost no variation for different compositions.

To assess the effect of steam on the sorption properties of the sorbent, carbonation kinetics determination were performed on the 27CA sorbent varying the steam content in the carbonation atmosphere. The results, in Fig. 2, show a significant improvement of the sorption kinetics and capture capacity with the addition of steam. In general, CO_2 uptake profile of CaO-based sorbent comprises two different regimes, one with the fastest rate, at the beginning of the carbonation reaction, which is kinetically controlled, followed by slower reaction regime, which is diffusion limited. During that fast stage, reaction takes place on the free surface of CaO and the whole process is only limited by the kinetics of the reaction between CaO and CO_2. In the diffusion controlled regime, the reaction between CO_2 and CaO is physically limited due to the increasing steric hindrance for CO_2 to penetrate the carbonate layer and reach the unreacted CaO core [25]. For the hydrothermal sorbents, the CO_2-uptake of the sorbent in dry conditions is very slow from the beginning of the carbonation step. After 10 min the total CO_2-uptake is only 7 g-CO_2/100g sorbent. Introducing 15 vol % steam in the carbonation atmosphere enhanced the sorption kinetics and the final CO_2-uptake of the solid. Increasing further the steam content extended the duration of the kinetically limited regime and reduced the diffusion-limited sorption. Above 40 vol % the CO_2-uptake is almost entirely kinetically limited

(linear sorption) and attains a maximum capacity of 21g-CO_2/100g sorbent corresponding to the maximum theoretical CO_2-capacity of the solid for full conversion of CaO into $CaCO_3$.
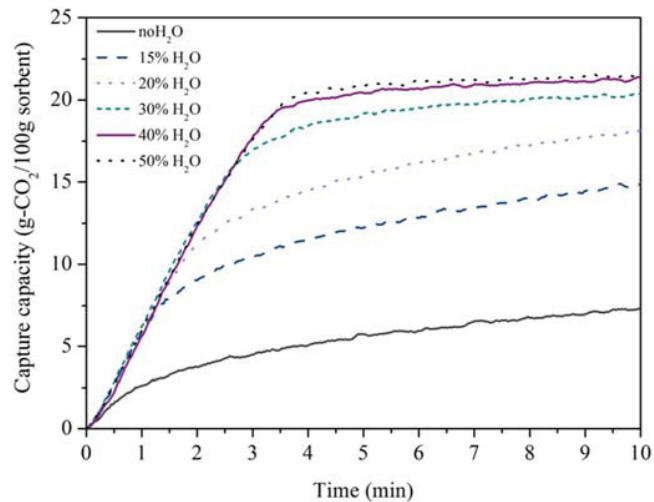

Fig. 2. CO_2 uptake profiles with 15 vol % CO_2 (with 0 - 50 vol % H_2O, balanced in N_2) at 898 K.

It can be affirmed then that steam plays an important role in the mass transfer phenomena for this reaction. Nevertheless, the mechanism of the steam enhanced carbonation reaction of CaO with CO_2 is quite unclear. Fig. 2 indicates that the steam has a positive effect on diffusion limited regime. For natural sorbents, Broda et al. also observed that steam did not affect the initial reaction rate in the kinetically controlled stage but enhances the diffusion in the $CaCO_3$ product layer [26]. A similar effect is observed here, however, the surface area and pore size of the synthetic sorbent particles are not significantly different from the values for the calcined limestone, meaning that the slow reaction kinetics in dry carbonation atmosphere cannot be explained by the microstructure of the synthetic particles. It is believed that in the CaO/mayenite sorbents, the mayenite ($Ca_{12}Al_{14}O_{33}$) plays an active role on the diffusion of the CO_2 in the particle and contributes to a more efficient conversion of the CaO into $CaCO_3$. Indeed, the $Ca_{12}Al_{14}O_{33}$ structure is a cage-like structure which can accommodate free excess oxygen due to the presence of hydroxides in the structure [27]. That excess oxygen can diffuse in the structure along the oxygen network giving high oxide ion conductivity [28, 29]. However, this oxygen conductivity is very sensitive to the presence of water vapour at high temperatures [30]. Similarly, the role of water vapour and its interaction with the $Ca_{12}Al_{14}O_{33}$ support is not yet clearly understood but might contribute to the diffusion of CO_2 and /or carbonate ions in the solid material.

The long term multi-cycling of the synthetic sorbents and the Verdal limestone in pre-combustion conditions are shown in Fig. 3. Sorbents, 27CA and 37CA present a stable capture capacity up to 40 cycles. In practice, the CO_2 capture capacity of 27CA and 37CA sorbents attain the theoretical maximum of 21g-CO_2/100g sorbent and 29g-CO_2/100g sorbent respectively, corresponding to a full conversion of the available CaO in the solid. Sorbent 47CA has a higher initial capture capacity (36g-CO_2/100g sorbent) at the beginning of cycling but shows a linear decay in sorption capacity down to 31g-CO_2/100g sorbent after 40 cycles. However, it should be noted that after 40 cycles, all the tested sorbents show a sorption capacity up to 3 times the capacity of the limestone cycled in the same conditions. Meanwhile, the CO_2 capacity of the Verdal limestone during repeated carbonation/ calcination cycles is 11g-CO_2/100g sorbent after 40 cycles and is expected to continue decreasing over the next 50 cycles before stabilizing around 6g- CO_2/100 g sorbent as in the post-combustion multi-cycling (Fig. 5).
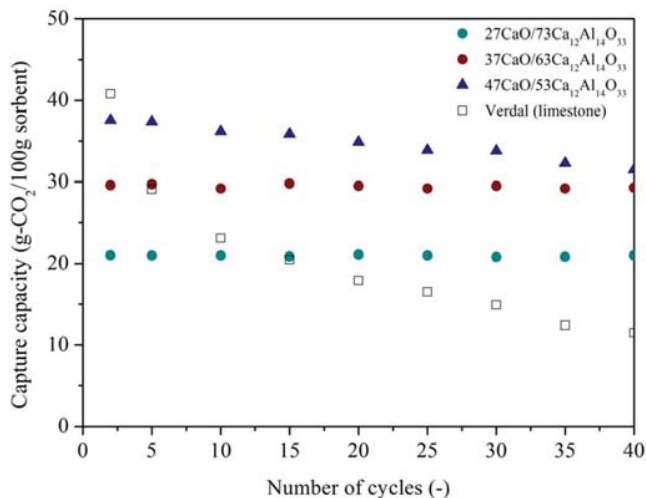
Fig. 3. CO_2 capture capacity of synthetic and natural sorbents over 40 cycles under pre-combustion condition. Carbonation: 873 K for 10 min; 15 vol % CO_2, 47 vol % H_2O balanced in N_2. Regeneration: 21 vol % CO_2, 78 vol % H_2O, balanced in N_2, 1123 K for 3 min. Verdal limestone is included as reference.

Fig. 4 shows CO_2 uptake profiles for the natural limestone (Verdal) and the synthetic sorbents during multi-cycling in pre-combustion condition. After 40 cycles, the CO_2 uptake of the limestone is low and the diffusion-controlled regime becomes prominent due to the extended sintering of the CaO and the reduction of pore volume in the sample. On the other hand, the sorption profiles of 27CA and 37CA sorbent remains unchanged even after 40 cycles, confirming the high stability of the sorbent.
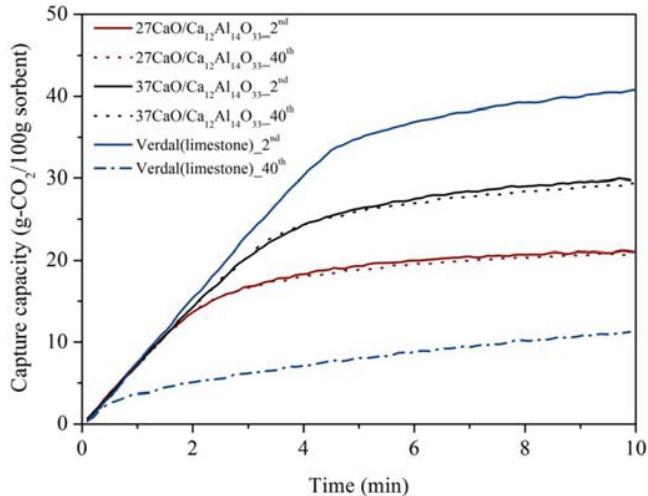

Fig. 4. CO_2 uptake profiles under pre-combustion condition: Carbonation: 873 K for 10 min, 15 vol % CO_2, 47 vol % H_2O, balanced in N_2.

Multi-cycling in TGA under post combustion conditions of three different sorbents (37CA, 47CA and 73CA) along with Verdal limestone is shown in Fig. 5. A similar trend has been observed under pre- and post- combustion condition. Increasing the $Ca_{12}Al_{14}O_{33}$ content in the sorbent stabilizes the structure of the material and reduces the sintering of the CaO phase during multi-cycling as evidenced by an almost constant sorption capacity (35g CO_2/100g sorbent) during the first 20 cycles for 47CA. However, in 47CA, the $Ca_{12}Al_{14}O_{33}$ does not totally prevent

the sintering and the capacity gradually decreases after the 20th cycle. The material with the lowest CaO-content shows a stable sorption capacity during the 40 cycles with a total sorption capacity of 26g-CO_2/100g sorbent, which is more than 4 times the final CO_2-uptake of the limestone.
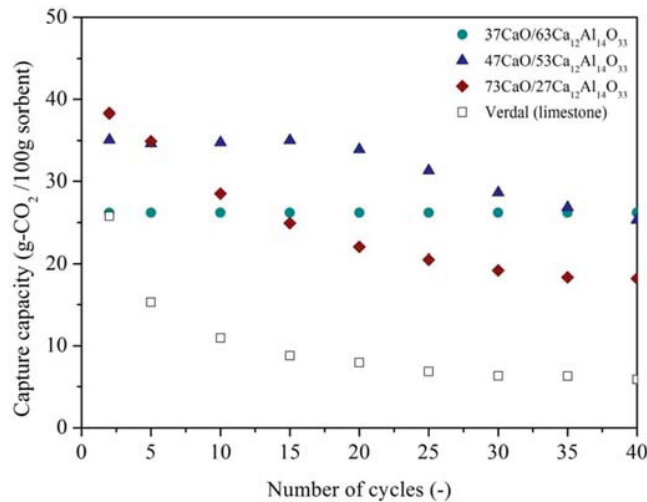

Fig. 5. CO_2 capture capacity of synthetic and natural sorbents during 40 cycles under post -combustion condition. Carbonation: 923 K for 10 min; 14.5 vol % CO_2, 13 vol % H_2O balanced in N_2. Regeneration: 100 vol % CO_2, at 1193 K for 3 min). Verdal limestone is included as reference.

The two TGA multi-cycles showed that there is an optimal $Ca_{12}Al_{14}O_{33}$ content in the solid to prevent the sintering of the CaO phase and maintain stable sorption capacity throughout the whole multi-cycling test. The optimal content for hydrothermal sorbents for stable CO_2 capture is below 40 wt % CaO in the calcined sorbent composition. Increasing the CaO content in the starting material will reduce the minimum diffusion distance between each CaO particle which will eventually lead to a sintering of the CaO phase and a loss of sorption capacity during cycling (Fig. 3 and 5).

Scanning electron microscopy of the as prepared hydrothermal powder (a), the calcined particles before (b) and after cyclic carbonation/ calcination in pre-combustion condition (c) and post- combustion condition (d) is shown in Fig. 6(a-d).The starting powder is made of plate-like particles corresponding to the dried hydroxides (Fig. 6a). After calcination, the plate-like particles have been converted into irregularly shaped particles with a defined microstructure of sub-micron particles finely dispersed on the surface of larger particles, Fig. 6b. From past experience on previous system, it is known that during the conversion of $Ca_3Al_2O_6$ to CaO and $Ca_{12}Al_{14}O_{33}$, the excess CaO diffuses on the surface of the $Ca_{12}Al_{14}O_{33}$ phase where it becomes available for reacting with CO_2 [20]. A similar behaviour is expected to take place during decomposition of the hydrogarnet [$Ca_3Al_2 (OH)_{12}$] phase. The submicron CaO particles are homogeneously distributed on the solid binder material creating a porous layer which remains largely unchanged even cycling in severe calcination conditions for extended period of time Fig. 6(c-d).

Another important criterion when developing synthetic sorbents is the mechanical strength of the particles. Indeed, in order to reduce the elutriation of fine material during solid circulation and reduce the overall make up in the system, it is important to develop a material with a high resistance to attrition. Crushing strength can be used as a fast screening method for evaluating the mechanical strength of particulate materials. For each sorbent composition 100 particles with a particle size (0.8mm < dp <1mm) were crushed. For comparison, the strength of fresh limestone (uncalcined and calcined) was also measured. The average crushing strengths are summarized in Table 4.
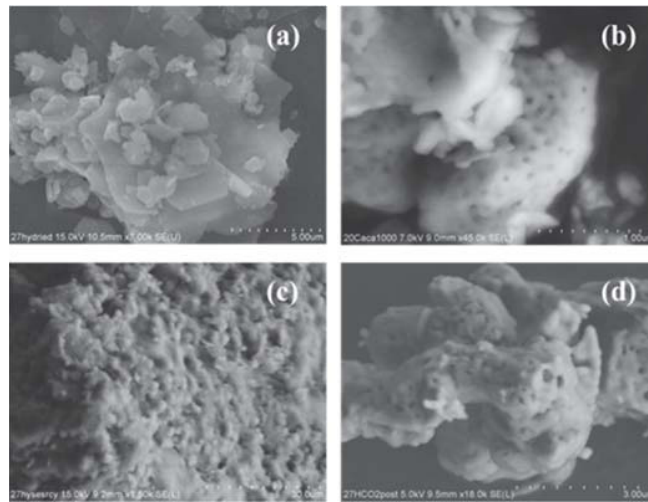
Fig. 6. SEM images of hydrothermally prepared sorbents: (a) as prepared 27CA hydrothermal dried powder; (b) 27CA after calcination at 1273 K for 1 h; (c) 27CA after 40 cycles (d) 37CA sorbent after 40 cycles.

Table 4. Crushing strength measured on natural (calcined/ uncalcined) and synthetic (calcined) sorbents.

Sorbent		Median crushing strength (N)
Verdal (limestone)	uncalcined	7.0
Verdal (limestone)	calcined	1.6
27CA	50MPa_1273 K_1 h	5.4
37CA	50MPa_1273 K_1 h	3.5
47CA	50MPa_1273 K_1 h	3.4
73CA	50MPa_1273 K_1 h	1.7

As reported in the literature [11, 31], the limestone particles are significantly weaker after calcination. All tested sorbent show a higher crushing strength than the calcined natural sorbent. Increasing the mayenite content increases the crushing strength of the synthetic sorbents. The hydrothermal sorbent with the highest CaO content shows a maximum crushing strength which is more than 3 times higher than the calcined Verdal limestone.

4. Conclusions

New CaO-based synthetic sorbents were prepared by simple hydrothermal method using low cost calcium and aluminium hydroxide precursors. All these sorbents were composed of active CaO and inert support material, $Ca_{12}Al_{14}O_{33}$. Compared to natural limestone, hydrothermally prepared synthetic sorbents exhibit much higher CO_2 capture capacity over multiple carbonation/ calcination cycles, which is due to the inert support material that effectively prevents sintering of the $CaCO_3$ during calcination. Synthetic sorbent with an optimum ratio around 30 wt% CaO is considered optimum in terms of stable CO_2 capture capacity (21g-CO_2/100g sorbent during multi-cycles (40 cycles), high sorption kinetics in presence of water vapour and high mechanical strength.

Acknowledgment

References

[1] J.C. Abanades, D. Alvarez, Conversion limits in the reaction of CO_2 with lime, Energy Fuels, 17 (2003) 308-315.

[2] B. Feng, W. Liu, X. Li, H. An, Overcoming the problem of loss-in-capacity of calcium oxide in CO_2 capture, Energy Fuels, 20 (2006) 2417-2420.

[3] N. Florin, P. Fennell, Synthetic CaO-based sorbent for CO_2 capture, Energy Procedia, 4 (2011) 830-838.

[4] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, The calcium looping cycle for large-scale CO_2 capture, Progress in Energy and Combustion Science, 36 (2010) 260-279.

[5] J.C. Abanades, G. Grasa, M. Alonso, N. Rodriguez, E.J. Anthony, L.M. Romeo, Cost structure of a postcombustion CO_2 capture system using CaO, Environmental Science & Technology, 41 (2007) 5523-5527.

[6] N.H. Florin, A.T. Harris, Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents, Chem. Eng. Sci., 63 (2008) 287-316.

[7] D. Alvarez, J.C. Abanades, Pore-size and shape effects on the recarbonation performance of calcium oxide submitted to repeated calcination/recarbonation cycles, Energy Fuels, 19 (2004) 270-278.

[8] P.S. Fennell, R. Pacciani, J.S. Dennis, J.F. Davidson, A.N. Hayhurst, The effects of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand, Energy Fuels, 21 (2007) 2072-2081.

[9] G.S. Grasa, J.C. Abanades, CO_2 capture capacity of CaO in long series of carbonation/calcination cycles, Ind.Eng.Chem. Res., 45 (2006) 8846-8851.

[10] A. Coppola, F. Montagnaro, P. Salatino, F. Scala, Attrition of limestone during fluidized bed calcium looping cycles for CO_2 capture, Combust. Sci. Technol., 184 (2012) 929-941.

[11] Z. Chen, J.R. Grace, C. Jim Lim, Limestone particle attrition and size distribution in a small circulating fluidized bed, Fuel, 87 (2008) 1360-1371.

[12] S. Choi, J.H. Drese, C.W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, ChemSusChem, 2 (2009) 796-854.

[13] S.F. Wu, Q.H. Li, J.N. Kim, K.B. Yi, Properties of a nano CaO/Al_2O_3 CO_2 sorbent, Ind. Eng. Chem. Res., 47 (2007) 180-184.

[14] C.S. Martavaltzi, A.A. Lemonidou, Parametric study of the $CaO−Ca_{12}Al_{14}O_{33}$ synthesis with respect to high CO_2 sorption capacity and stability on multicycle operation, Ind. Eng. Chem. Res., 47 (2008) 9537-9543.

[15] R. Koirala, K.R. Gunugunuri, S.E. Pratsinis, P.G. Smirniotis, Effect of zirconia doping on the structure and stability of CaO-based sorbents for CO_2 capture during extended operating cycles, The Journal of Physical Chemistry C, 115 (2011) 24804-24812.

[16] S.F. Wu, Y.Q. Zhu, Behavior of $CaTiO_3$/Nano-CaO as a CO_2 Reactive Adsorbent, Ind. Eng. Chem. Res., 49 (2010) 2701-2706.

[17] Y. Li, C. Zhao, Q. Ren, L. Duan, H. Chen, X. Chen, Effect of rice husk ash addition on CO_2 capture behavior of calcium-based sorbent during calcium looping cycle, Fuel Process. Technol., 90 (2009) 825-834.

[18] C. Luo, Y. Zheng, N. Ding, C. Zheng, Enhanced cyclic stability of CO_2 adsorption capacity of CaO-based sorbents using La_2O_3 or $Ca_{12}Al_{14}O_{33}$ as additives, Korean J. Chem. Eng., 28 (2011) 1042-1046.

[19] Z.-s. Li, N.-s. Cai, Y.-y. Huang, Effect of preparation temperature on cyclic CO_2 capture and multiple carbonation−calcination cycles for a new Ca-based CO_2 sorbent, Ind. Eng. Chem. Res., 45 (2006) 1911-1917.

[20] J. Mastin, A. Aranda, J. Meyer, New synthesis method for CaO-based synthetic sorbents with enhanced properties for high-temperature CO_2-capture, Energy Procedia, 4 (2011) 1184-1191.

[21] Z.-s. Li, N.-s. Cai, Y.-y. Huang, H.-j. Han, Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide absorbent, Energy Fuels, 19 (2005) 1447-1452.

[22] K. Johnsen, H.J. Ryu, J.R. Grace, C.J. Lim, Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as -acceptor, Chem. Eng. Sci., 61 (2006) 1195-1202.

[23] K. Sato, S. Fujita, K. Suzuki, T. Mori, High performance of Ni-substituted calcium aluminosilicate for partial oxidation of methane into syngas, Catal. Commun., 8 (2007) 1735-1738.

[24] J.M. Rivas-Mercury, P. Pena, A.H. de Aza, X. Turrillas, Dehydration of $Ca_3Al_2(SiO_4)_y(OH)_{4(3−y)}$ studied by neutron thermo diffractometry, J. Eur. Ceram. Soc., 28 (2008) 1737-1748.

[25] J.S. Dennis, R. Pacciani, The rate and extent of uptake of CO_2 by a synthetic, CaO-containing sorbent, Chem. Eng. Sci., 64 (2009) 2147-2157.

[26] M. Broda, V. Manovic, E.J. Anthony, C.R. Müller, Effect of pelletization and addition of steam on the cyclic performance of carbon-templated, CaO-based CO_2 sorbents, Environmental Science & Technology, 48 (2014) 5322-5328.

[27] H. Boysen, M. Lerch, A. Stys, A. Senyshyn, Structure and oxygen mobility in mayenite ($Ca_{12}Al_{14}O_{33}$): a high-temperature neutron powder diffraction study, Acta Crystallographica Section B, 63 (2007) 675-682.

[28] M. Lacerda, J.T.S. Irvine, F.P. Glasser, A.R. West, High oxide ion conductivity in $Ca_{12}Al_{14}O_{33}$, Nature, 332 (1988) 525-526.

[29] J.T.S. Irvine, M. Lacerda, A.R. West, Oxide ion conductivity in $Ca_{12}Al_{14}O_{33}$, Mater. Res. Bull., 23 (1988) 1033-1038.

[30] J.T.S. Irvine, A.R. West, $Ca_{12}Al_{14}O_{33}$ — A possible high-temperature moisture sensor, J. Appl. Electrochem., 19 (1989) 410-412.

[31] X. Yao, H. Zhang, H. Yang, Q. Liu, J. Wang, G. Yue, An experimental study on the primary fragmentation and attrition of limestones in a fluidized bed, Fuel Process. Technol., 91 (2010) 1119-1124.