The effect of hydrothermal treatment on the structure and CO$_2$ uptake capacity of CaO-based sorbents

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CaO-based sorbents were successfully synthesized by a hydrothermal method at two different temperatures (80 and 220^{0}C) in order to investigate their effect on structure and CO$_2$ uptake capacity of CaO-based sorbents. The pertinent structural, morphological and textural properties were investigated by SEM, XRD, TGA and N$_2$ adsorption at 77K. Multi-cyclic carbonation/decarbonation experiments showed that the CaO-based sorbent synthesized at 80^{0}C possesses a higher CO$_2$ adsorption capacity compared with the sample synthesized at 220^{0}C.

1. Introduction

New or improved methods of CO$_2$ capture, combined with advanced power systems and industrial process designs, should reduce CO$_2$ capture cost and energy requirements [1]. Cyclic CO$_2$ capture using solid CaO-based sorbents is a great alternative technology for capturing CO$_2$. This technology is mainly based on a simple reversible reaction: carbonation of CaO with CO$_2$ and decarbonation of CaCO$_3$ to obtain concentrated CO$_2$ (CaO looping) [2]. Previous studies on the durability test of the calcium looping cycle have shown that carbonation conversion rapidly declines over multiple cycles due to a loss of surface area as well as an increase of particle size through sintering [3].

The development of synthetic CO$_2$ sorbents is currently a subject of intense research, aiming to (i) increase the specific surface area, thus the long term reactivity and/or (ii) improve its mechanical stability, therefore extending the sorbent lifetime, which is imperative for developing an economically viable sorbent [3].

This work is focusing on the preparation and characterization of two novel CaO-based sorbents as well as the investigation of their reactivity towards CO$_2$. The CaO-based sorbents were synthesized by a hydrothermal method using calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O) as precursor in the presence of cetyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG) co-surfactants, followed by drying and calcination. Hydrothermal reactions were conducted at two different temperatures (80 and 220^{0}C), while the carbonation/decarbonation cycling performance of the materials was measured in the course of up to 4 cycles.

2. Experimental

All reagents were used without any further purification. Briefly, 1.0 g of PEG particles (Aldrich, average Mn (10.000)) and 0.46g sodium hydrate (Mallinckrodt) were dissolved in 120 mL ddH$_2$O under vigorous stirring followed by the addition of 1.40 g of cetyltrimethylammonium bromide (CTAB) (Sigma). After stirring for 1 h at room temperature, 7.86 g of Ca(NO$_3$)$_2$·4H$_2$O (Sigma Aldrich) was added under vigorous stirring. The mixture was stirred for 24 h and then transferred to Teflon-lined autoclaves. Hydrothermal reactions were conducted at 80 ^{0}C / 48 h for the first sample, which was called Sample_80 and at 220 ^{0}C/4 d for the second sample called Sample_220 and then allowed to cool down to room temperature naturally. The products were collected by filtration and washed by ddH$_2$O and ethanol several times. Finally, the white powders obtained were calcined in air at 600 °C for 5 h with a heating rate of 9 ^{0}C/min.

The powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Rigaku R-AXIS IV Imaging Plate Detector mounted on a Rigaku RU-H3R Rotating Copper Anode X-ray Generator (λ = 1.54 Å).

SEM images of the developed materials were obtained using a Jeol JSM 7401F Field Emission Scanning Electron Microscope (SEM). The materials were subjected to gold coating prior to SEM imaging.

The nitrogen adsorption/desorption isotherms at 77 K were measured in an automated volumetric system (AUTOSORB-1, Quantachrome Instruments). Prior to measurement, the samples were outgassed at 250 °C for 12 h.

The infrared spectra (IR) spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR equipped with a N_2 purging system and a LN2-cooled wide range Mercuric Cadmium Telluride detector.

3. Results and discussion

(a)   *(b)*   *(c)*

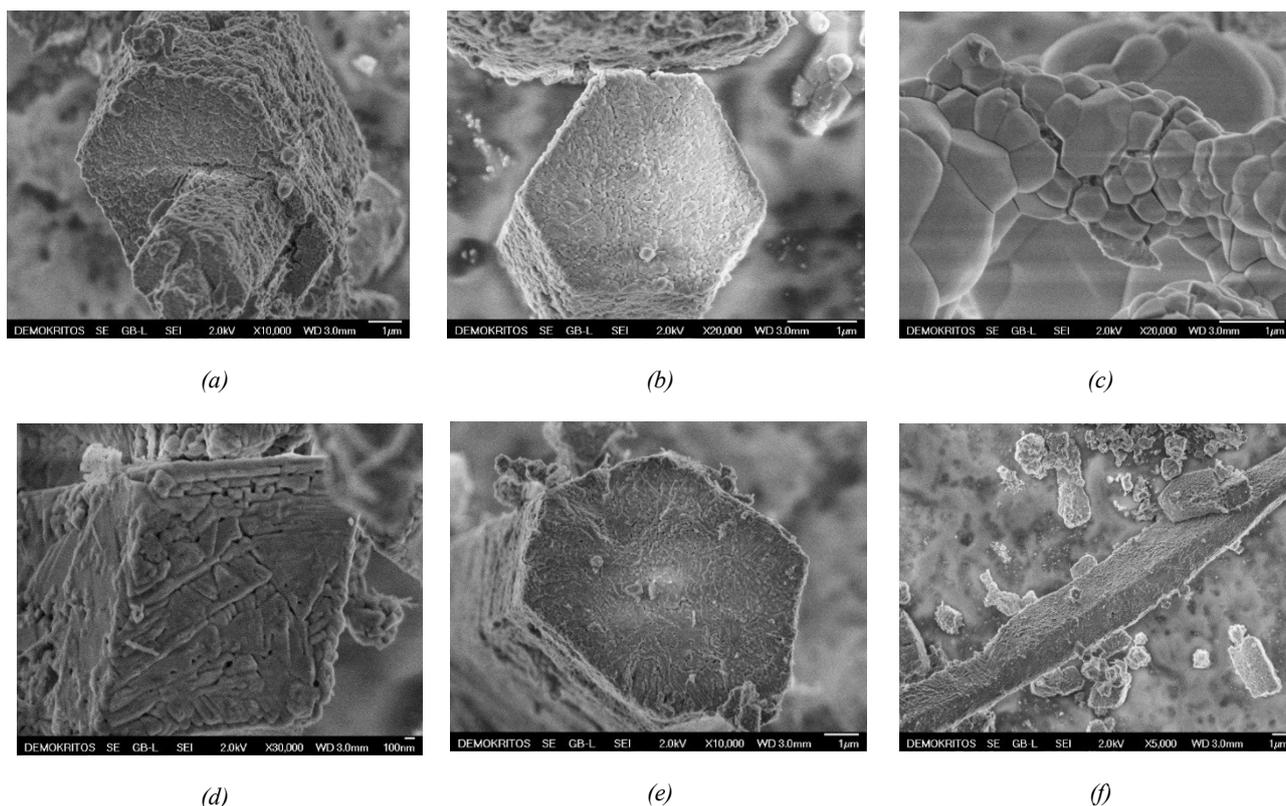*(d)*   *(e)*   *(f)*

Fig. 1. SEM images of the CaO-based sorbents hydrothermally prepared at (a-c) 80 °C and (d-f) 220 °C and calcined at 600 °C for 5h.

Fig. 1 (a-f) shows SEM images of CaO-based sorbents synthesized at different hydrothermal temperatures.

The influence of hydrothermal temperatures on the morphology of CaO-based sorbents is clearly observed. The CaO-based sorbent hydrothermally prepared at 80^0C (Fig. 1(a-c)) contains only particles with hexagonal morphologies, while the sample hydrothermally prepared at 220 °C (Fig.1 (d-f)) contains particles with: tetragonal morphology (d), hexagonal prism morphology (e) and rod-like morphology (f).

According to the XRD patterns depicted in Fig. 2a, the calcined powder of the CaO-based sorbent hydrothermally prepared at 80^0C (Sample_80) shows peaks which belong to the calcium oxide (CaO), portlandite ($Ca(OH)_2$), and calcium carbonate ($CaCO_3$) [4-9]. Similar peaks can be observed in the XRD pattern of the CaO-based sorbent hydrothermally prepared at 220 ^0C (Sample_220).

a)   *b)*
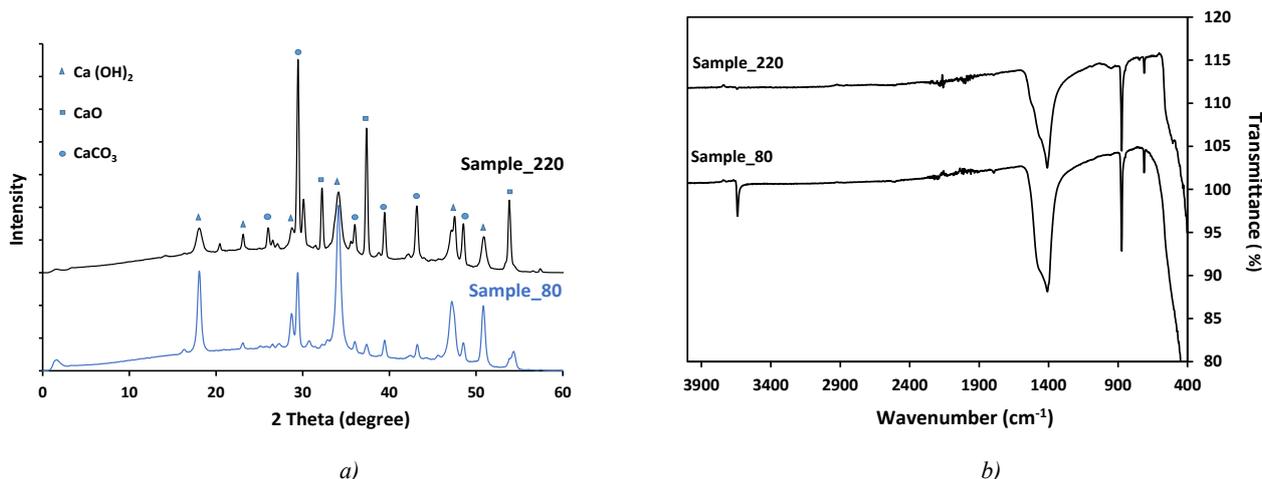
Fig. 2. (a) X-ray diffraction patterns and (b) Infrared spectra of CaO-based sorbents hydrothermally prepared at 80 °C (Sample_80) and at 220 °C (Sample_220) calcined at 600 °C for 5h.

According to FTIR spectrum presented in Figure 2(b), after calcination at 600 ^{0}C, the CaO-based sorbent hydrothermally prepared at 80 ^{0}C (Sample_80) shows a sharp peak at 3639 cm^{-1} (due to the easy rehydration of CaO to Ca(OH)$_2$) that can be ascribed to the stretching vibration of bulk OH groups of the hydroxide [10]. The appearance of the strong peak at 1405 cm^{-1} (due to the symmetric stretching vibration of uni- or bidentate carbonate) and weak peak at 873 cm^{-1} demonstrates the presence of carbonate species [11-13]. This is due to exposure of highly reactive surface area of CaO to air during calcination which resulted in the formation of considerable amount of CO$_2$ and H$_2$O, which are adsorbed on the surface of CaO in the form of free –OH and carbonate species. This indicates that surface –OH and lattice oxygen of CaO do provide oxygen which is more

assessable on high surface area samples [14, 15]. Carbonate band is also observed at at 711 cm^{-1} (C-O stretching) [16].

Similar peaks can be observed in the FTIR spectrum of the CaO-based sorbent hydrothermally prepared at 220 ^{0}C (Sample_220). In addition a small peak at 746 cm^{-1} was observed attributed to the carbonate band [17].

The N$_2$ adsorption/desorption isotherms at 77 K of the as-prepared samples are presented in Fig. 3. The analysis of the respective data showed a BET specific surface area of 11.67 m^2/g (Sample_220) and 47.02 m^2/g (Sample_80), respectively. The as-prepared samples exhibit a typical type IV isotherm with hysteresis, characteristic for mesoporous materials. It can be seen that the surface area of the as-prepared samples was highly dependent upon the fabrication procedure adopted.
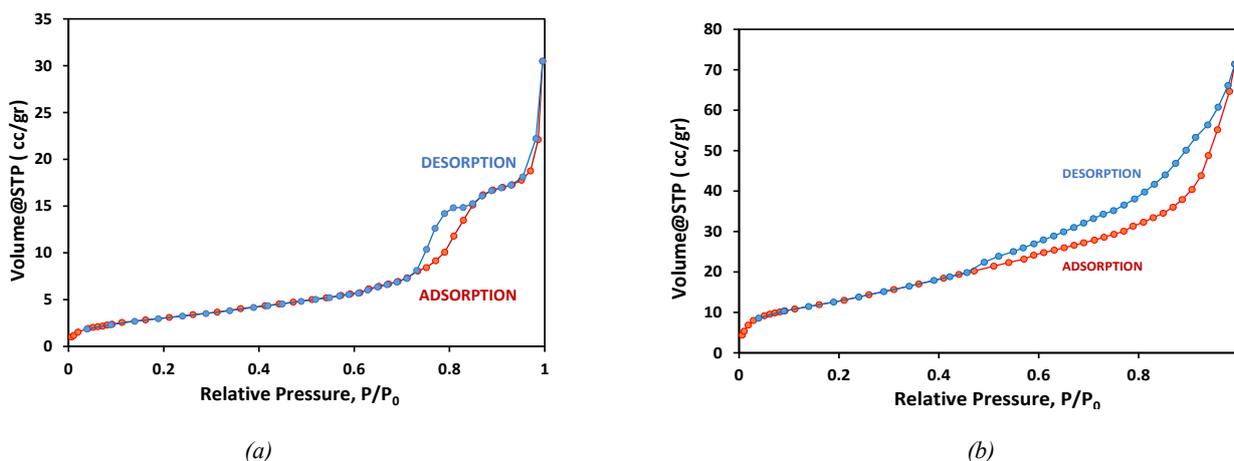

(a)   *(b)*

Fig. 3. N$_2$ adsorption/desorption isotherms of CaO based sorbents hydrothermally prepared at (a) 80 °C (Sample_80) and (b) 220 °C (Sample_220) calcined at 600 °C for 5h.

The carbonation/decarbonation cycling performance of the materials was measured in a thermogravimetric analysis instrument (SETARAM SETSYS Evolution 18

Analyzer). Specifically, the TGA measurements were performed on ~10 mg of each sample in an Al$_2$O$_3$ crucible. The carbonation reaction took place at 600°C under 100%

CO_2 atmosphere (gas flow: 16 ml/min), while the decarbonation reaction was conducted at 800^oC under 100% Ar flow (gas flow: 100 ml/min). The steps that were followed for each measurement were four, including an activation step before the first carbonation-decarbonation cycle, which involved the calcination of each material at 900^oC under 100% Ar flow in order to render the material free of any hydrated or carbonated phases.

The results of CO_2 capture performance of the materials studied are comparatively shown in Fig. 4 and Table 1.
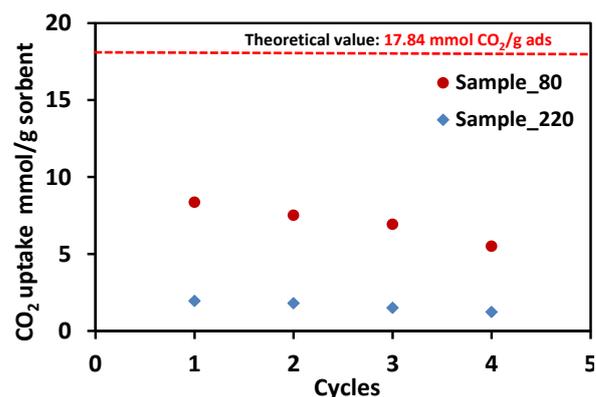

Fig. 4. Evaluation of the as-prepared CaO-based samples up to 4 carbonation-decarbonation cycles.

Table 1. CO_2 uptake capacity and maximum efficiency (%) of CaO-based sorbents

Sample	Hydrothermal temperature	BET surface area (m^2/g)	CO_2 adsorption capacity (mmol CO_2/g sorbent)				Max. Efficiency (%)*
			1st cycle	2nd cycle	3rd cycle	4th cycle	
Sample_80	80 ^0C	47	8.36	7.51	6.92	5.50	47
Sample_220	220 ^0C	11	1.95	1.8	1.5	1.22	11

*Max. Efficiency = (max. measured capture capacity)/(theoretical capacity of pure CaO) %
Theoretical capacity of pure CaO = 17.84 mmol/g CaO

According to Fig. 4 and Table. 1, the CaO-based sorbent synthesized at 80 ^0C possesses a higher CO_2 adsorption capacity (8.365 mmol CO_2/g sorbent) compared with the sample synthesized at 220 ^0C which exhibited a CO_2 adsorption capacity of 1.951 mmol CO_2/g sorbent for the first carbonation/decarbonation cycle. This is in agreement with previous studies which showed that the sorption capacity of CO_2-sorbent materials depends on the surface area of the material [6].

4. Conclusions

The chosen hydrothermal synthesis temperature has a strong effect on the structure and CO_2 uptake capacity of the prepared CaO-based sorbents. By decreasing the hydrothermal temperature from 220 to 80 ^{o}C, a higher CO_2 uptake capacity of the CaO-based sorbent was observed. Furthermore, temperature drives morphological changes in the samples.

Acknowledgements

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