Microwave-assisted synthesis of stable SBA-15 mesoporous supports for CaO-based sorbents suitable for CO_2 capture

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Abstract

This study is focused on the microwave-assisted synthesis of SBA-15 materials and the optimization of the experimental conditions (crystallization time and temperature) to achieve a stable support for CaO-based sorbents suitable for "calcium looping cycle" CO_2 capture. Calcium was introduced by incipient wetness impregnation, giving two SBA-15 samples with 10 wt-% and 20 wt-% Ca loading. The final Ca-based SBA-15 sorbents were characterized using thermogravimetric analysis (TGA-DSC), X-Ray diffraction (XRD), nitrogen sorption measurements and tested in the carbonation-calcination cycles (lab-scale uint and TG).

Three synthetic non-supported CaO sorbents were also prepared by sol-gel method and the help of structurants and also studied in CO_2 capture process, being the influence of the final calcination temperature and the nature of the carbon matrixes used evaluated.

The results obtained in the lab-scale CO_2 capture unit showed that Ca-based SBA-15 samples were not efficient enough in CO_2 capture, due to the very low amount of Ca impregnated in the final materials, although they possessed an ordered mesoporous structure, being necessary to increase the amount of calcium to obtain satisfactory results in CO_2 capture processes. However, carbonation-calcination cycles performed in the TG unit were effective, showing that the Ca/SBA-15 sorbents are promising sorbents to be used for "calcium looping cycle" CO_2 capture if a high Ca loading in impregnated.

Concerning the synthetic non-supported sorbents, activated carbon was shown to be the best structurant, in terms of initial reactivity and reactivity decay. The calcination temperature was also shown to be crucial, as a lower temperature let a better initial reactivity.

Key words: Hexagonal SBA-15, mesoporous, microwave, CO_2 capture, calcium oxide, thermal stability.

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1. Introduction

Due to the large growth of the use of technology in the society, industries have been increasing the energy consumption with the consequent increase in the burning of fossil fuels for energy production. This has produced a greater emission of gases into the atmosphere, causing the greenhouse effect, mainly CO_2. Nowadays, the demand for mitigation of these emissions is widely accepted [1,2,3]. Carbon Capture and Storage (CCS) technologies aim to capture and provide suitable streams for appropriate storage, mitigating the CO_2 emissions [4,5]

For the sequestration step of CO_2, different sorbents are used: naturals or synthetics. Recently, calcium oxide is the most used due to its low price and widely availability. Ca-based sorbents are used in the "calcium looping cycles" and have a large adsorption capacity at high temperatures. The major challenge in these cycles is the deactivation suffered by the sorbents, for that reason many methods have been proposed for reducing that effect and improving the adsorption capacity [6,7,8]. Many researchers are studying the modification of the pore structure as a solution for enhancing the stability of sorbents[9,10].

The discovery of mesoporous silica materials, mainly SBA-15 in 1998, was a significant progress and has achieved considerable attention in recent years due to their high surface area, large pore volume and effectiveness as a sorbents. Synthesis of SBA-15 is composed by two principal steps: ripening and aging. Different routes have been developed in the synthesis in order to improve the hydrothermal stability of SBA-15 and to reduce of time, energy and cost without decrease the quality of the mesoporous material. The microwave-assisted synthesis in the hydrothermal step have resulted a successfully method, supplying a shorter crystallization time compared with the conventional method[9,11,12].

Therefore, this work is focused in the synthesis and stability study of SBA-15 at high temperatures under microwave conditions with the purpose of use the mesoporous material as support of CaO, improving the uptake capacity of synthetic sorbents in calcium-looping cycles processes.

2. Experimental

2.1. Support synthesis

For the mesoporous silica SBA-15 synthesized, the first method described by *Zhao et al.*[13] was followed. The triblock copolymer P123 used as a structure-directing agent is dissolved in distilled water, where HCl solution (37%) was previously added (acidic media). The mixture was stirred overnight. Next, the solution is heated during 4 hours at 40ºC and then, the required amount of TEOS (silica-source) is added dropwise to the solution with continuously stirring and at 40ºC during 2 additional hours, allowing the hydrolysis of TEOS and formation of an homogeneous reactive gel. The molar ratio used was: 1 SiO_2 : 0.02 P123 : 6.33 HCl : 178 H_2O.

Hydrolysis of TEOS and crystallization of SBA-15 are carried out by two different methods: conventional and under microwave-hydrothermal conditions.

In the conventional way, the gel product is transferred into a propylene bottle and is aged at 100ºC for another 48h without stirring.

In the microwave-assisted method, the resulting homogeneous mixture has to be divided into equal parts and transferred into the autoclaves that are placed in the microwave oven at desired temperature and time.

Both final products are filtered-off, washed with distilled water until a neutral pH is reached and dried at 100ºC overnight in an oven. SBA-15 is obtained after calcination at 550ºC for 10 hours with a heating rate of 2ºC/min.

2.2. CaO-based SBA-15 sorbents preparation

The CaO sorbents supported in SBA-15 were prepared by incipient wetness impregnation, mixing the support with a solution of the calcium source (calcium nitrate tetra-hydrate). First, a solution of the calculated amount of Ca precursor is prepared with distilled water and is added to the support. It is necessary to add the Ca precursor solution drop by drop, until the solid mixture turns into a malleable paste. Then, the paste formed is dried in an oven at 130 ºC overnight. Finally, the resulting sample is calcined in a muffle furnace at 550 ºC for 10 hours, with a heating rate of 2ºC/min.

2.3. Non-supported CaO sorbents

The CaO synthetic sorbents have been prepared following the sol-gel method. The calcium source used (calcium nitrate tetra-hydrate) was mixed with citric acid monohydrate (complexing agent) and distilled water as solvent. Different mesoporous-structuring agents were added: activated carbon (Norit GAC 1240 plus) and carbon BP2000. The solution is prepared with the predetermined amount of reagents. The mixture is continuously stirred and kept at 60ºC. After 3-4 hours, particles start precipitating and finally the gel is formed. The wet gel formed is dried into an oven, overnight at 130ºC. The sorbents were calcined in a muffle furnace at 750ºC for 5 hours, with a heating rate of 2ºC/min [7,14].

2.4. Characterization

After the preparation step, all sorbents were characterized by several techniques: thermogravimetric analysis (TGA-DSC), powder X-Ray diffraction (PXRD), and nitrogen sorption measurements.

Thermogravimetric analysis technique allowed determine the mass variation produced by the water absorbed loss and the template decomposition for the SBA-15 samples. The samples impregnated were analyzed in order to confirm the amount of CaO impregnated into the support. On the other hand, non-supported CaO-sorbents were analyzed under nitrogen atmosphere in order to know the mass loss produced during the first calcination. The equipment used for the analysis is SETERAM TGA92 model.

Powder X-Ray diffraction (XRD) was used with the purpose of identify the crystalline structure of the mesoporous samples, using small angle range (0.7-5º). In order to obtained about CaO-based samples, a higher angle range was used (15-70º). The XRD powder patterns were obtained in a Bruker Advance D8 diffractometer system, using a Cu Kα radiation and operating at 40 kV and 40 mA.

The surface area and the pore distribution were measured and performed at -196ºC on an Micrometrics ASAP 2010 apparatus. Samples were pretreated by degassing at 300ºC for 3 h previous the measurement. The surface area was calculated by BET method and the pore size distribution was obtained using the BJH model.

2.5. Reactivity testing

The cyclic carbonation-calcination reactions were carried out in a lab-scale CO_2 capture unit and by thermogravimetry (SETERAM TGA92 model).

In order to determine the carrying capacity of the CaO/SBA-15 samples and the non-supported CaO sorbents, several experiments with 10 cycles were carried out in the lab-scale CO_2 capture unit. First, the sample was heated to 800ºC under N_2 flow for a first calcination step, followed by carbonation during 5 minutes at 700ºC under a mixed flow composed by 15%CO_2 (v/v) (corresponding with 143.6 ml/min) and 850 ml/min of N_2. Then, the temperature was increased to 800ºC during 10 minutes under a pure flow of 850 ml/min of nitrogen. This process was repeated for 10 cycles [14].

For CaO/SBA-15 samples, the CO_2 capture tests were also performed by thermogravimetry. It was followed the same procedure above with the only difference of the step duration. Carbonation occurs during 48 min and calcination during 17 min.

In both processes the carrying capacity of the sorbents was calculated by the ratio between the mass of CO_2 adsorbed by the sorbent during the cycle *i* and the mass of the initial calcined sorbent. The carrying capacity is expressed in g CO_2 / g CaO [7].

3. Results and discussion

All samples synthesized are shown in table 1.

3.1. Influence of synthesis method

Two samples were synthesized under the same conditions but with different crystallization treatment: conventional (S_CL) and microwave (S_MW) method. Fig. 1 shows the XRD patterns, where the three well-defined peaks were detected in both samples, corresponding to (100), (110) and (200) reflections characteristics of highly ordered hexagonal structure of SBA-15.

Nitrogen sorption isotherms (Fig. 2) correspond with isotherms type IV and hysteresis loop H1, typical of well-ordered mesoporous materials. The isotherm inflection point of S_CL is slightly moved to lower relative pressures, indicating a smaller pore size in the material. This sample presented a higher pore volume and surface area than S_MW, due to the higher silica condensation under MW conditions. The textural parameters are presented in table 2.

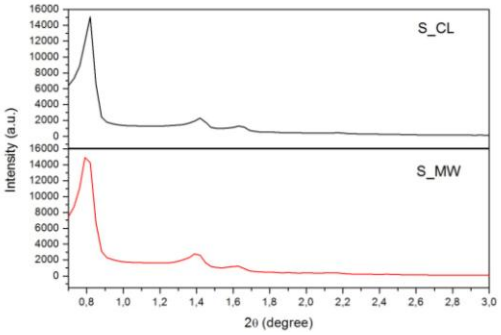


Fig. 1: XRD for SBA-15 samples synthesized by conventional and microwave-assisted method. Black: S_CL; red: S_MW

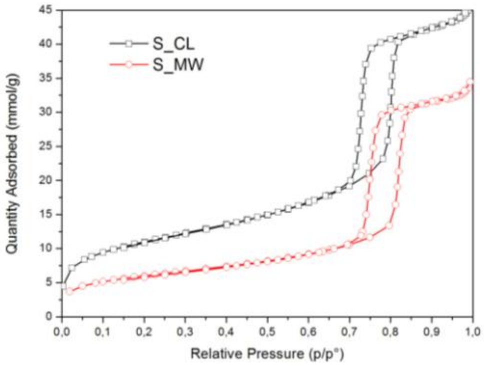


Fig. 2: : N2 sorption isotherms of SBA-15 samples synthesized by conventional and MW method. Black: S_CL; red: S_MW

3.2. Influence of experimental parameters in hydrothermal treatment

Several samples were synthesized under MW heating but with different temperatures (140-170ºC) and times (1-2h) in the crystallization process. The time of pre - hydrolysis step was also modified at 4h. All samples presented the hexagonal ordered structure and isotherms of type IV with a H1 hysteresis loop. The inflection point shifts gradually to higher relative pressures when temperature is increased, in the same way that the height of the capillary condensation range. SBA-15 with uniform pores was obtained when crystallization temperature and time are increased, conforming XRD results. Results showed that 170ºC and 2h were the most optimal conditions.

3.3. Influence of time in pre-hydrolysis step

Both samples with similar MW conditions (170ºC and 2h) but with different duration of pre-hydrolysis step were compared: S_MW (2h) and S_MW_170_2 (4h).

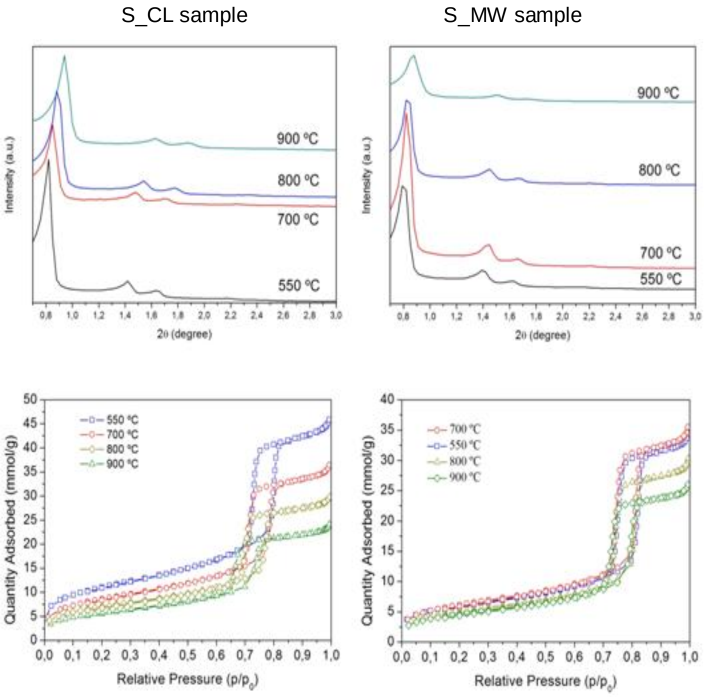
Table 1: Synhtesis conditions of SBA-15 samples

SAMPLE	TEOS PRE-HYDROLYSIS TEMPERATURE / DURATION	HYDROTHERMAL TREATMENT SYNTHESIS METHOD
S_CL	40 ºC / 2h	Conventional 100ºC / 48h
S_MW	40 ºC / 2h	Microwave 170ºC / 2h
S_MW_140_1	40ºC / 4h	Microwave 140ºC / 1h
S_MW_140_2	40ºC / 4h	Microwave 140ºC / 2h
S_MW_170_1	40ºC / 4h	Microwave 170ºC / 1h
S_MW_170_2	40ºC / 4h	Microwave 170ºC / 2h
S_MW2	40 ºC / 2h	Microwave 170ºC / 2h

XRD and N_2 isotherms resulted with the typical shape, and the textural parameters for each samples are rather similar (table 2).

3.4. Thermal stability of SBA-15 materials

The thermal stability of samples calcined at different temperatures was also studied. Samples synthesized by conventional and MW method (S_CL and S_MW) were calcined at different temperatures: 700, 800 and 900ºC, and compared with the samples calcined at 550ºC.


S_CL sample

S_MW sample

Fig. 3: XRD and N_2 isotherms of SBA-15 synthesized by conventional (left) and microwave (right) method. Black: 550ºC; red: 700ºC; blue: 800ºC: green: 900ºC

The XRD patterns (Fig. 3) show that the 2-D hexagonal ordered structure is maintained even after the calcination at 900ºC for both samples. The peaks are softly shifted to higher values of 2θ angles when the temperature of calcination increases, indicating that the mesoporous network suffers a small shrank when samples are calcined at high temperatures.

All isotherms (Fig. 3) are a type IV with a hysteresis loop H1. For both synthesis methods, the isotherms are moved to lower relative pressures and lower amount of N_2 absorbed when the temperature of calcination is increased, meaning that there is a reduction in the pore width and in the pore volume. These changes are stronger for samples synthesized under conventional conditions, while under MW conditions only the decrease of N_2 adsorbed is more pronounced. The textural parameters are shown in table 2.

3.5. Stability study of Ca/SBA-15 samples

A new SBA-15 was synthesized using MW conditions in the hydrothermal treatment and optimized experimental conditions (S_MW2). The conditions were: 2h for TEOS adding and 170ºC and 2h for MW crystallization. The sample was subsequently impregnated with calcium nitrate solution in order to obtain two CaO supported sorbents with 10 and 20 wt.-% Ca (S_MW_10Ca and S_MW_20Ca, respectively). After impregnation and subsequent calcination, Ca/SBA-15 samples were characterized with the purpose of evaluating the physicochemical properties. Fig. 4 shows the thermogravimetric analysis performed for both samples impregnated, before calcination at 550ºC.

For both samples, two main weight loss processes can be identified: the first one can be attributed to the loss of water physically absorbed (endothermic peak around 100ºC); the second one corresponds to the decomposition of $Ca(NO_3)_2$. The second process presents two peaks between 400 and 600ºC. It can be seen that the heat peaks in S_MW_20Ca sample are higher, when comparing with S_MW_10Ca and occur at slightly higher temperatures. This is normal because the sample requires more energy for the decompositions due to the higher amount of calcium nitrate.

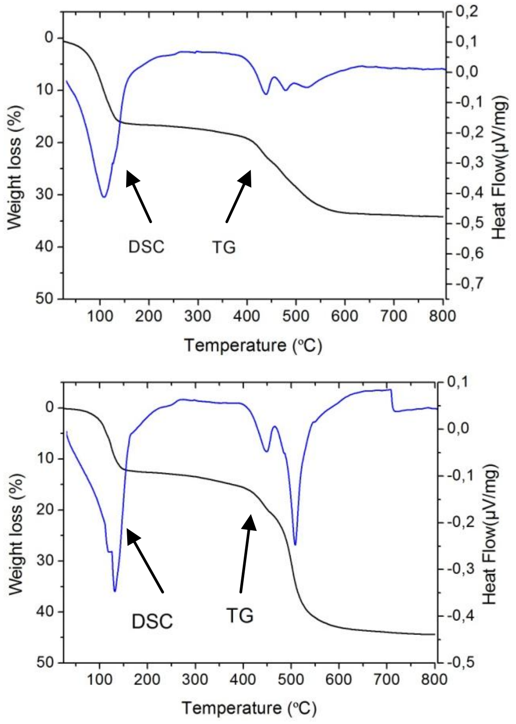


Fig. 4: TG and DSC curves of S_MW_10Ca (top) and S_MW_20Ca (down).

XRD patterns (Fig. 5) show an intense peak, characteristic of large pores present in the materials. However, only raw material and S_MW_10Ca sample show the two additional peaks, maintaining the 2D-hexagonal structure. Probably S_MW_20Ca lost this 2D-hexagonal organization because of the important amount of Ca nitrate during the impregnation preparation. The intensity of the peaks decreases with the increase of Ca amount.

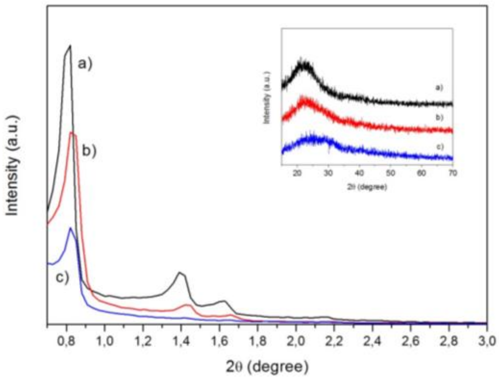


Fig. 5: : Small and high-angles XRD patterns of Ca/SBA-15 samples: a) raw; b) 10 wt-% Ca; c) 20 wt-% Ca

High angles patterns are also shown in Fig. 5. No extra peak characteristic of CaO phase was found. It can be concluded that: a) CaO particles are too small so they do not produce any diffraction peak (CaO phase is well dispersed in the SBA-15 material); b) Ca reacted with support silica, producing an amorphous phase, not detectable by XRD technique.

The S_MW_10Ca isotherm has also the same aspect as the S_MW2, maintaining the ordered mesoporous structure, although with a shift for lower amount of N_2 adsorbed, which means that Ca species are covering the surface of the mesopores. In S_MW_20Ca sample, the capillary condensation step is moved to higher pressures, occurring some structural transformation (Fig. 6). Textural properties of these three samples are also collected in table 2.

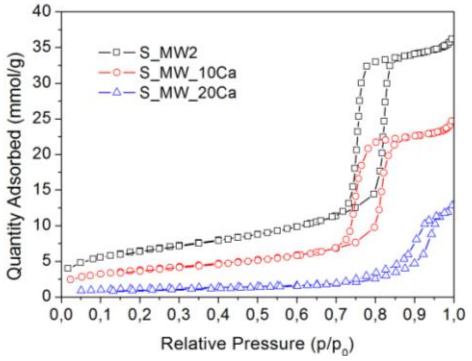


Figure 6: N_2 sorption isotherms of Ca/SBA-15 Black: raw SBA-15; red: S_MW_10Ca; blue: S_MW_20Ca

With the objective of using the Ca/SBA-15 synthesized samples in the CO_2 capture experiments (repeated cycles at high temperatures: 700 and 800ºC). Both Ca/SBA-15 samples were subjected to a blank test with 10 cycles under an inert atmosphere (only nitrogen, without carbon dioxide), in order to know if the mesoporous structure can thermally tolerate the process. Both samples maintain the typical 2-D hexagonal ordered structure. S_MW_10Ca isotherm after blank test is substantially different, indicating the apparition of non-uniform pore distribution. S_MW_20Ca isotherm does not present any change.

Table 2: Textural properties of all synthesized samples

SAMPLE	S_{BET} (m^2/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	D_{BJH} (Å)
S_CL	884	0.11	1.19	78
S_MW	484	0.05	0.92	85
S_MW_140_1	662	0.05	0.58	72
S_MW_140_2	605	0.04	0.58	74
S_MW_170_1	522	0.03	0.84	78
S_MW_170_2	450	0.03	0.84	80
S_CL 700ºC	698	0,05	0,98	73
S_CL 800ºC	573	0.03	0.81	70
S_CL 900ºC	472	0,02	0,63	63
S_MW 700ºC	501	0,05	0,95	80
S_MW 800ºC	418	0,03	0,80	82
S_MW 900ºC	377	0,03	0,70	79
S_MW2	522	0.05	1.03	88
S_MW_10Ca	307	0.03	0.67	85
S_MW_20Ca	92	0.014	0.08	88/200
S_MW_10Ca after blank test	247	0.017	0.45	82
S_MW_20Ca after blank test	88	0.009	0.16	91/203

3.6. Ca-based SBA-15 sorbents in carbonation-calcination cycles

The next step was the evaluation of the capacity of Ca/SBA-15 sorbents to be used in CO_2 capture (conditions are explained in section 2.5). Unfortunately, in the tests carried out in the lab-scale unit no amount of CO_2 adsorbed in the CaO supported sorbents could be detected by the CO_2 detector.

In the tests performed in the TG unit, both sorbents (S_MW_20Ca and S_MW_10Ca) were effective, although the carrying capacities obtained were not high due to the low amount of Ca impregnated in the support (Table 3).

Table 3: Carrying capacity of S_MW_10Ca and S_MW_20Ca in the TG unit

N cycles	S_MW_10Ca (g CO_2 / g CaO)	S_MW_20Ca (g CO_2 / g CaO)
1	0.08	0.11
2	0.08	0.13
3	0.09	0.07

3.7. Non-supported CaO sorbents

Following the results obtained by Joana Hipólito [14], three synthetic non-supported CaO sorbents (table 4) were prepared and studied for a better understanding of the influence of the calcination temperature at the end of the preparation step, and for comparing their CO_2 capture activity with the Ca/SBA-15 supported sorbents.

Table 4: Synthesis conditions of non-supported CaO sorbents

SAMPLE	STRUCTURANT	CALCINATION TEMPERATURE
CA_250_2	Activated Carbon (250 mg)	750ºC at 2ºC/min
CA_BP_250_2	Carbon BP2000 (250 mg)	750ºC at 2ºC/min
SG_2	-	750ºC at 2ºC/min

Experiments of 10 carbonation/calcination cycles were performed. Fig. 7 shows the results obtained. The sorbent CA_250_2 750ºC presents a higher initial activity (0.67 $gCO_2/gCaO$) compared with the sample calcined at 850ºC (0.51 $gCO_2/gCaO$). However, this sorbent CA_250_2 850ºC shows a constant activity and good stability and does not deactivate along the 10 cycles, while the sorbent calcined at 750ºC shows an activity decrease until achieving the same carrying capacity of the calcined sorbent at 850ºC on the 10th carbonation cycle. The heat released during the calcination at the end of the sorbent preparation causes an initial sintering effect in the solid sorbent, being stronger in the case of the higher calcination temperature (850ºC). Granular activated carbon resulted better than carbon BP2000. Both sorbents (CA_250_2 750ºC and CA_BP_250_2 750ºC) were calcined at 750 ºC. The sorbent prepared with activated carbon shows a higher initial activity than the sorbent with carbon BP2000, but both have the same deactivating tendency along the 10 cycles. Comparing sorbent SG_2 750ºC (without structurant and calcined at 750 ºC) with CA_250_2 750ºC, it is possible to see that sorbent CA_250_2 750ºC has a slightly higher initial activity and a smaller rate of deactivation along the cycles.

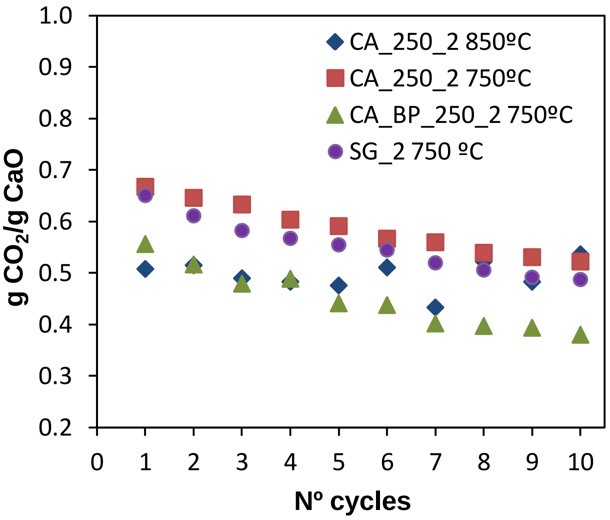


Figure 7: Influence of calcination temperature and type of structurant in non-supported CaO-sorbents

4. Conclusions

The goal of this work was the synthesis of a stable SBA-15 mesoporous material with the purpose of being used as a support material for Ca-based sorbents used in the calcium-looping cycle CO_2 capture. Microwave-assisted (MW) method was used during the synthesis, in order to study the different advantages compared to the conventional method.

Several samples of SBA-15 were synthesized by conventional and MW method and calcined at different temperatures, analyzing the thermal stability by different characterization techniques: thermogravimetric analysis (TGA-DSC), X-Ray diffraction (XRD) and nitrogen sorption measurement. Using optimized MW synthesis conditions, a SBA-15 sample was synthesized and used to impregnate calcium nitrate in order to obtain suitable sorbents for CO_2 capture evaluation.

The most important difference between conventional and MW synthesis methods is the possibility of later allowing to program and control easily temperature and time during synthesis so reducing the hydrothermal treatment duration from days to hours, without sacrificing the quality of the final porous materials. MW-assisted method allowed to obtain a SBA-15 material with higher thermal stability than the one prepared under conventional method, even calcined at 900ºC maintaining the ordered mesoporous structure, thus being suitable as support of CaO particles. High temperatures (170ºC) and 2 hours of crystallization under MW were determined as optimal conditions to synthesis a SBA-15 material presenting a high hexagonal ordered.

10 and 20 wt.-%Ca impregnated samples were tested in the lab-scale CO_2 capture unit but due to the very small amount of Ca impregnated the consequent amount of CO_2 captured was not detected by the CO_2 detector. However, the ordered mesoporous structure was maintained after Ca impregnation and even after the Ca/SBA-15 mesoporous sorbents were tested in the lab-scale CO_2 capture unit. The tests performed in the TG unit were effective, showing that Ca/SBA-15 sorbents can be used for "calcium looping cycle"

CO2 capture, but low reactivity values for both sorbents, thus confirming the need to use Ca/SBA-15 sorbents with high Ca loading.

Three synthetic non-supported CaO sorbents were also synthesized and studied in this work for a better understanding of the influence of using a structurant in the sol-gel preparation step (granular activated carbon AC and carbon BP2000), of the influence of the calcination temperature at the end of the sol-gel preparation step, and also for comparing their CO_2 capture activity with that of the prepared Ca/SBA-15 supported sorbents.

The results showed a higher initial CO_2 adsorption capacity of the sorbent prepared with AC and calcined at 750 ºC, being also higher than the initial CO_2 adsorption capacity obtained with structurant carbon BP2000, probably due to the larger size of the granular activated carbon particles which create larger pores during carbon burning. However, both have the same deactivating tendency for the rate of activity decay along the 10 cycles. When comparing the results obtained for the non-supported sorbent prepared without structurant and calcined at 750 ºC, with the sorbent prepared with AC and calcined at the same, it is possible to conclude that sorbent prepared with AC has a slightly higher initial CO_2 capture activity and that this sorbent has a smaller rate of deactivation along the 10 cycles although this deactivation rate is not very different from the case of the sorbent prepared without structurant.

The results obtained for the CO_2 capture activity with the sorbents prepared with AC and calcined at 750 and 850ºC, showed that the calcination temperature at the end of the sol-gel preparation step is an important parameter. Since AC calcination is a highly exothermic process, the heat released during the calcination will cause a local temperature increase producing a sintering effect in the solid sorbent, which will be stronger at 850 ºC. For this reason, for lower calcination temperatures the initial sorbent activity for CO_2 capture is higher as for the case of the sorbent prepared with AC and calcined at 750ºC.

Comparisons with the reactivity of Ca/SBA-15 sorbents could not be made due to the experimental limitations explained earlier.

5. References

[1] **United States Environmental Protection Agency (EPA)**.

[2] **European Environmental Agency (EEA)**

[3] Blamey, J.; Anthony, E.J.; Wang, J.; Fennell, P.S. **The calcium looping cycle for large-scale CO2 capture.** Elsevier, 2009

[4] D'Alessandro, Deanna M.; Smith, Berend; Long, Jefrrey R. **Carbon Dioxide Capture: Prospects for New Materials.** Angewandte Chemie International Edition, 2010

[5] Markusson, N.; Kern, F.; Watson, J.; Arapostathis, S.; Chalmers, H.; Ghaleigh, N.; Heptonstall, P.; Pearson, P.; Rossati, D.; Russell, S. **A socio-technical framework for assessing the viability of carbon capture and storage technology.** Elsevier, 2011.

[6] Dean, C.C.; Blamey, J.; Florin, N.H.; Al-Jeboori, M.J.; Fennell, P.S. **The calcium looping cycle for CO2 capture from power generation, cement manufacture and hydrogen production**. Elsevier, 2011.

[7] Santos, E.T.; Alfonsín, C.; Chambel, A.J.S.; Fernandes, A.; Soares Dias, A.P.; Pinheiro, C.I.C, Ribeiro, M.F. **Investigation of a stable synthetic sol–gel CaO sorbent for CO2 capture.** Elsevier, 2011.

[8] Nicholas H., F.; Blamey, J.; Fennell, Paul S. ***Synthetic CaO-based sorbent for CO_2 capture from large-point sources.*** Energy&fuels, 2010

[9] Huang, C.H.; Chang, K.P.; Yu, C.T.; Chiang, P.C.; Wang, C.F. **Development of high-temperature CO2 sorbents made of CaO-based mesoporous silica.** Elsevier, 2010.

[10] Abanades, J.C. **Calcium looping for CO2 capture in combustion systems.** Spanish Research Council (CSIC), 2013.

[11] Norhasyimi, R.; Abdullah, A.Z.; Mohamed, A.R. ***A review: mesoporous Santa Barbara Amorphous-15, types, synthesis and its applications towards biorefinery production.*** *American Journal for Applied Sciences* 2010.

[12] Celer, E.; Jaroniec, M. ***Temperature-Programmed Microwave-Assisted Synthesis of SBA-15 Ordered Mesoporous Silica.*** 2006

[13] Zhao, D.; Fenq, J.; Huo, Q.; Melosh, N.; Fredrickson, G.H.; Chmelka, B.F.; Stucky, G.D. ***Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores.*** SCIENCE, 1998.

[14] Fernandes Hipólito, Joana. ***Influência das condições operatórias na síntese de adsorventes à base de CaO com carvão ativado na Captura de*** CO_2. Universidade Nova de Lisboa, 2014.