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Improvements of Calcium Oxide Based Sorbents for multiple CO₂ Capture cycles

Laetitia Vieille*, Alexandre Govin, Philippe Grosseau

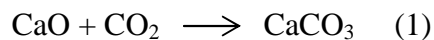
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Abstract

This study presents the development of a novel calcium-oxide sorbent for carbon dioxide capture. In this work, CaO sorbent was impregnated with different molar percentage of titanium ethoxide. The sorbent prepared with 50 % of titanium ethoxide resulted in the best uptake characteristics for CO₂. Compared to others, a higher BET surface area and a larger pore volume were observed. An excellent stability during extended carbonation-decarbonation cycles was also demonstrated. The high titanium content limits the sintering of particles and thus stabilizes the microstructure of CaO.

Introduction

Carbon dioxide emission into the atmosphere is widely known as to be an important contributor to global warming. In order to contain the greenhouse effect, the most viable solution is to find out cost-effective ways to capture and storage CO₂ before its releasing into the atmosphere. Currently, the most common commercial technology to capture CO₂ is amine-based absorption, but its application is limited to small scale, low temperature (40-150°C) and very high energy cost¹. Alternatively, these drawbacks can be overcome by using metal-oxide-based inorganic sorbents to capture CO₂ selectively from flue gas streams. Suitable sorbents should exhibit fast carbonation and regeneration within the temperature range of 200-800°C. Actually, CaO based sorbents have been the most promising candidates for CO₂ capture²⁻¹². Capture of CO₂ by CaO sorbents is based on the reversible reactions between CaO and CO₂, leading to the formation of CaCO₃ as follows:



During the carbonation cycle, CO₂ uptake increases, reaching the highest value at the end of the cycle. The carbonation is characterized by the reaction of gaseous CO₂ with solid CaO to yield CaCO₃, which can reciprocally be thermally regenerated to CaO and CO₂ by heating the carbonate beyond its decomposition temperature (about 850°C).

Some researchers reported¹³ that, for the carbonation reaction, after a rapid chemically controlled initial period, a slower product layer stage diffusion follows. The transition between the fast and slow reaction stages was attributed to the formation of a CaCO₃ product layer, which limits the carbonation conversions¹³. The curve in figure 1 confirms that the performance deteriorates with time (number of cycles). After the reaction of CaO with CO₂, the reaction product CaCO₃ must undergo a calcination process in order to regenerate CaO to be used repeatedly. In the process of calcination, some pores are produced inside the CaO

particle. At the same time, CaO sintering may occur during high-temperature calcination. The decline of CO₂ absorption capacity and cyclic stability with the increasing carbonation/calcination cycles can be attributed to changes in the particle structure during calcination. When small CaO particles are heated to certain temperatures high enough but below the melting point, CaO coalesces and sinters, and the surface area of nascent CaO decreases with the increase of residence time. Surface area and porosity are very important for the reaction of CaO with CO₂, but sintering reduces surface area and porosity sharply, which in turn affects the reaction rates and conversion of CaO with CO₂.^{14,15} Abanades et al.¹³ attributed the decay of CaO conversion to a certain loss of small pores and an increase of large pores. They carried out observations with SEM, which revealed that the pore distribution of the calcines was continuously changing with number of cycles; more and bigger macro-pores were being formed under the condition that micropores decreased.

Currently, many researches focus on the improvement of the performance of CaO-based sorbents by increasing porosity and improving stability. In the past, Gupta and Fan³ synthesized high-surface-area CaO sorbents from precipitated calcium carbonate (PCC). Recently, Smirniotis and his coworkers¹⁶ obtained high-performance CaO-based sorbents derived from different organometallic precursors. Some researchers¹⁷ promoted CaO sorbents by using additives, such as NaCl or Na₂CO₃. The addition of Na₂CO₃ increased the ions mobility but the capture of CO₂ is unchanged. On the other side, the presence of NaCl increased the surface area of the precursor material and enhanced its stability. Others⁵ have improved the sorbent capacity by doping with alkali metals. Their performance followed the order Li < Na < K < Rb < Cs, which revealed a strong relationship between the sorption characteristics and the increase of the atomic radii of the alkali metals. The same researchers employed a wide range of refractory dopants (Mn, Cu¹⁸, Si¹⁹, Ti, Cr, Co, Zr and Ce²⁰), and concluded that good results were obtained for manganese and cerium. In fact, these materials presented high surface areas and large porous volumes which facilitated the kinetic of carbonation and the absorption properties of CO₂. But the Zr-doped CaO (Zr/Ca 3:10 mol ratio) was found to exhibit the best CO₂-capture performance and the best stability during the multicyclic carbonation-decarbonation testing.

An other approach²¹ presented the integration of CaO inside a mineral material of mayenite (Ca₁₂Al₁₄O₃₃). For 35 wt % of CaO, a significantly improved CO₂ absorption capacity was observed and the cyclic carbonation reactivity of the new absorbent remains constant after 11 cycles.

The objective of the present investigation is the development of a high-performance CaO-based sorbents. This study describes the incorporation of titanium as additive into CaO-based sorbents and its implication on the cyclic carbonation reactivity.

Material and methods

Sorbent preparation

Natural limestone provided by Tamuin quarries (Mexico) was used. CaO was prepared by calcination of natural limestone at 850°C under nitrogen for 3 hours. Then, CaO powder was impregnated with predefined quantities of titanium ethoxide (Aldrich), corresponding to molar percentage of 0.1, 1, 10, 20, 30, 40 or 50. After the impregnation, the material was dried at 100°C overnight then calcinated at 300°C under air for 12 hours. In fact, the additive

is decomposed under 250°C ²². The final product will be noted CaTi-x with x corresponding to the doping level of titanium ethoxide.

The calculated conversion rate corresponds to the molar number of absorbed CO_2 divided by the molar number of theoretical CaO.

Characterizations

X-ray diffraction (XRD) measurements were employed for the identification of phases of the synthesized CaO-based sorbents. The XRD analyses were conducted on a Siemens D500 powder X-ray diffractometer with a Cu $K\alpha$ radiation source (wavelength = 1.5406 \AA).

BET surface area measurements were performed using nitrogen adsorption and desorption isotherms at -196°C on a Micromeritics ASAP 2000 volumetric adsorption analyzer. The CaO sorbents were degassed at 150°C for a night in the degassing port of the apparatus before the measurements. The adsorption isotherms of nitrogen for BET measurements were collected at -196°C by using ten values of pressure ranging from about 40 to 240 mmHg.

The porosity was measured by mercury intrusion porosimeter Autopore IV (Micromeritics) which allows the determination of the pore size distribution.

Scanning electron microscopy (SEM) measurements were performed on selected sorbents to obtain information on morphology using a JEOL 6500F field-emission scanning electron microscope. The samples were prepared by placing CaO sorbents on double-sided carbon tape mounted on the sample holder. Then a gold metallization was realized to improve image quality.

Volume-weighted particle size distributions of CaO-based sorbents powders were determined by laser scattering using a Scirocco cell (Mastersizer 2000, Malvern).

Decarbonation-Carbonation. Decarbonation/Carbonation experiments were conducted with a Setaram 92 thermogravimetric analyzer (TGA). All steps of the carbonation and decarbonation experiments, heating of the sample, cooling of the sample, and shifting gases between CO_2 (99.995 %) and nitrogen (99.999 %) were programmable. A small amount of sorbent was placed in an alumina crucible and heated to the decarbonation temperature (850°C) at a ramp rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen. When the decarbonation process had been completed, the temperature was decreased to 650°C at a ramp rate of $10^{\circ}\text{C}/\text{min}$, a mixed of 2/3 of CO_2 and 1/3 of nitrogen was automatically switched into the system to replace nitrogen. When the carbonation process finished, the temperature was increased at $10^{\circ}\text{C}/\text{min}$ to the decarbonation temperature. A new decarbonation/carbonation cycle began when the decarbonation temperature was achieved. In this work, the typical carbonation time was set at 120 min to achieve a relatively high uptake capacity of CO_2 , and the decarbonation time was set at 60 min to allow the sorbent to be decarbonated completely. During the entire process, the sorbent weight and the temperature were continuously recorded.

Results and Discussion

In figure 1, the performance results of the natural limestone Tamuin was presented. The curve confirms that the performance deteriorates with time (number of cycles). After the reaction of CaO with CO_2 , the reaction product CaCO_3 must undergo a calcination process in order to regenerate CaO to be used repeatedly. In the process of calcination, some pores are produced inside the CaO particle. At the same time, CaO sintering may occur during high-temperature calcination. The decline of CO_2 absorption capacity and cyclic stability with the increasing carbonation/calcination cycles can be attributed to changes in the particle structure during calcination. When small CaO particles are heated to certain temperatures high enough but

below the melting point, CaO coalesces and sinters, and the surface area of nascent CaO decreases with the increase of residence time. Surface area and porosity are very important for the reaction of CaO with CO₂, but sintering reduces surface area and porosity sharply, which in turn affects the reaction rates and conversion of CaO with CO₂.^{14,15} In our study, the surface area of CaO decreases to 7.2 m²g⁻¹ before calcination to 0.4 m²g⁻¹ after five cycles of calcination-carbonation. The porosity is closed and it is difficult to CO₂ to diffuse inside the material, its reactivity towards CO₂ decreases.

In order to find an appropriate high-temperature CO₂ absorbent, we doped pristine CaO with titanium ethoxide. Different ratios of additive were added. Their cyclic reaction characteristics are observed and recorded as shown in Figure 2. The calculated conversion rate corresponds to the molar number of absorbed CO₂ divided by the molar number of theoretical CaO. The conversion rate increases with the molar percentage of additive. It can be seen from figure 2 that at weak doping level (0.1 and 1 %), the additive does not impact the absorption of CO₂ by the material. The shape of the curve changes when the rate of titanium is higher than 20 %. The cyclic reaction capacity of CaTi-40 and CaTi-50 with CO₂ are almost the same and very stable. It decreases slowly with the increase of cycles. Particularly, no significant changes with number of cycles suggests that these samples are promising CO₂ absorbents. No molar fraction of titanium ethoxide higher than 0.5 was tested because the reactivity toward CO₂ is the same for CaTi-40 and CaTi-50, a maximum conversion rate seems to be attained. CO₂ should interact chemically with CaO rather than with TiO₂ because CO₂ and TiO₂ are acidic oxides. Some studies show that only CO is adsorbed at the surface of TiO₂²³ or CO₂ is converted to CO when it is adsorbed at the TiO₂ surface^{24,25}.

The BET surface specific area values of titanium ethoxide doped sorbents are presented in table 1. All measurements were made twice.

Sorbents	Surface specific area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)
CaCO ₃	1.2	0.80
CaO (obtained after calcination of CaCO ₃)	7.2	1.75
CaTi-0.1	8.0	1.83
CaTi-1	8.2	1.88
CaTi-10	9.4	2.15
CaTi-20	8.4	1.93
CaTi-30	9.6	2.20
CaTi-40	11.7	2.69
CaTi-50	13.8	3.30

Table 1 : BET SSA and Pore volume of various sorbents

All of the surface areas are higher than for pristine CaO. CaTi-40 and CaTi-50 exhibit the highest surface areas and porosities among the various sorbents investigated in this study. Sorption capacity depends on the degree of microporosity development, high surface area and high pore volume facilitate the diffusion of CO₂ inside these materials.

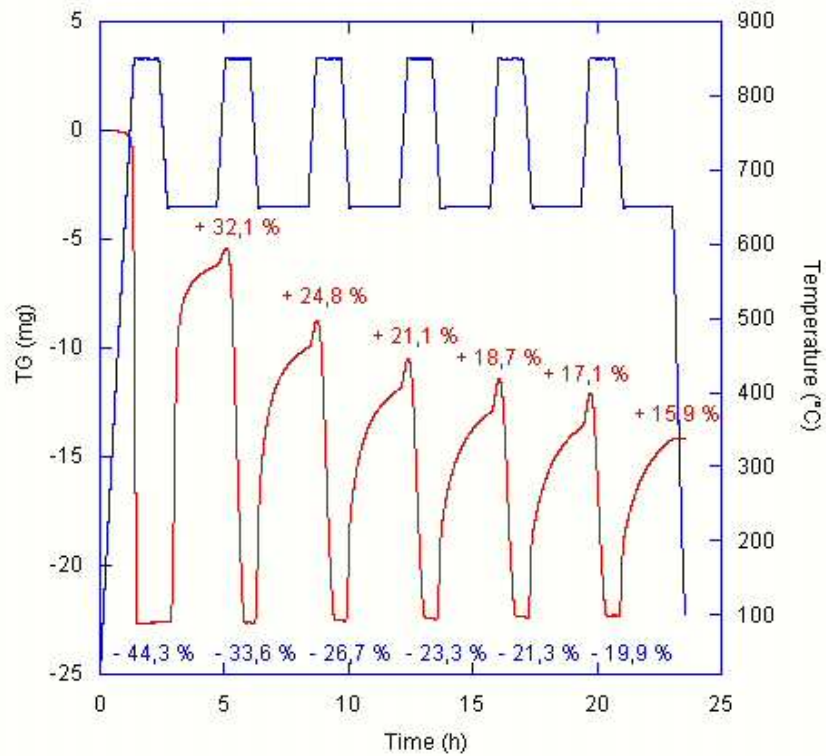


Figure 1 : Carbonation of the limestone in 66 vol % CO₂ gas stream and completely regenerated in nitrogen

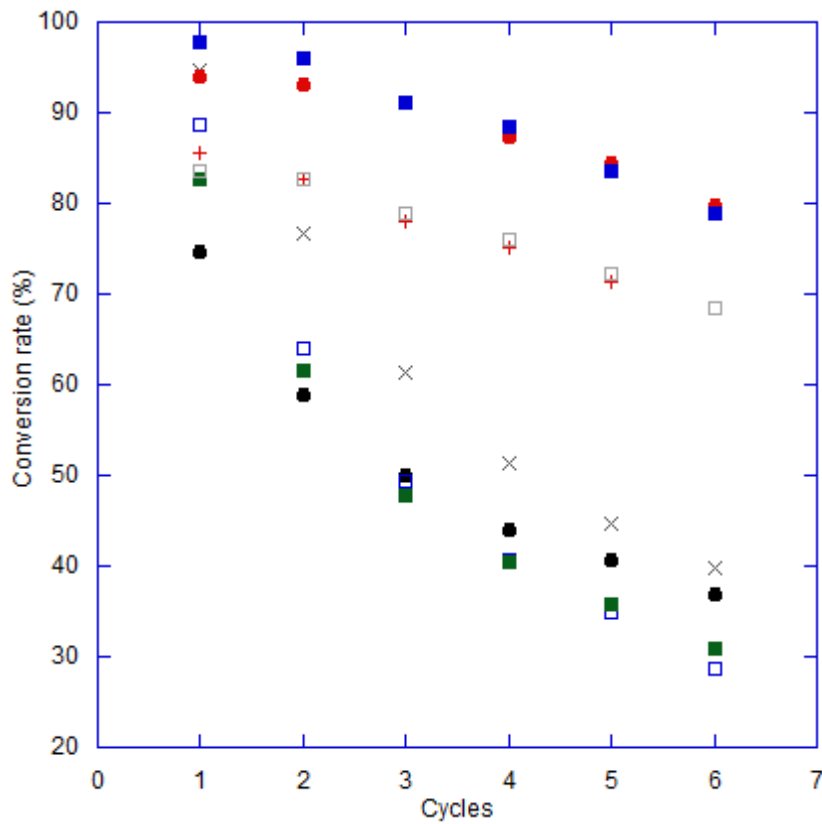


Figure 2 : Carbonation/decarbonation cycles (rate of titanium ethoxide : 0.1 % ■, 1 % □, 10 % ×, 20% +, 30 % □, 40 % ●, and 50 % ■) and limestone Tamuin : ●

The XRD patterns of the various rate of incorporated titanium ethoxide are presented in figure 3. From figure 3, the formation of crystalline CaCO_3 , CaO , Ca(OH)_2 and TiO_2 were noted in all of the materials. CaCO_3 and Ca(OH)_2 are formed during the impregnation process, after the calcination at 850°C under nitrogen, they are decomposed to CaO , only CaO and TiO_2 are present for the first carbonation cycle. The content of TiO_2 increases with the percentage of titanium ethoxide. However, TiO_2 peaks were visible only from 20% molar. No mixed oxide such as CaTiO_3 was observed during the thermal treatment. The low temperatures could be responsible for such behavior.

If we put on a graph, the content of titanium according to TiO_2 , we obtain a straight line with a correlation coefficient $R^2 = 0.98$ and the intercept is 4.81. So, nearly 5% of titanium is introduced inside the CaO lattice.

In order to study surface morphology and explore the structural features at the grain level, SEM studies were performed on various CaO sorbents with different ratios of titanium ethoxide. The corresponding SEM images obtained are presented in figure 4. The limestone Tamuin is dense and compact, some small particles of nearly $2\ \mu\text{m}$ are observed. After calcination, the departure of CO_2 creates some cavities and the material becomes very porous.

The SEM images of doped- CaO show fine particles of CaO dispersed into dense block of TiO_2 . The size and crystallinity of blocks increase with the titanium content. The presence of TiO_2 limits the sintering of CaO particles.

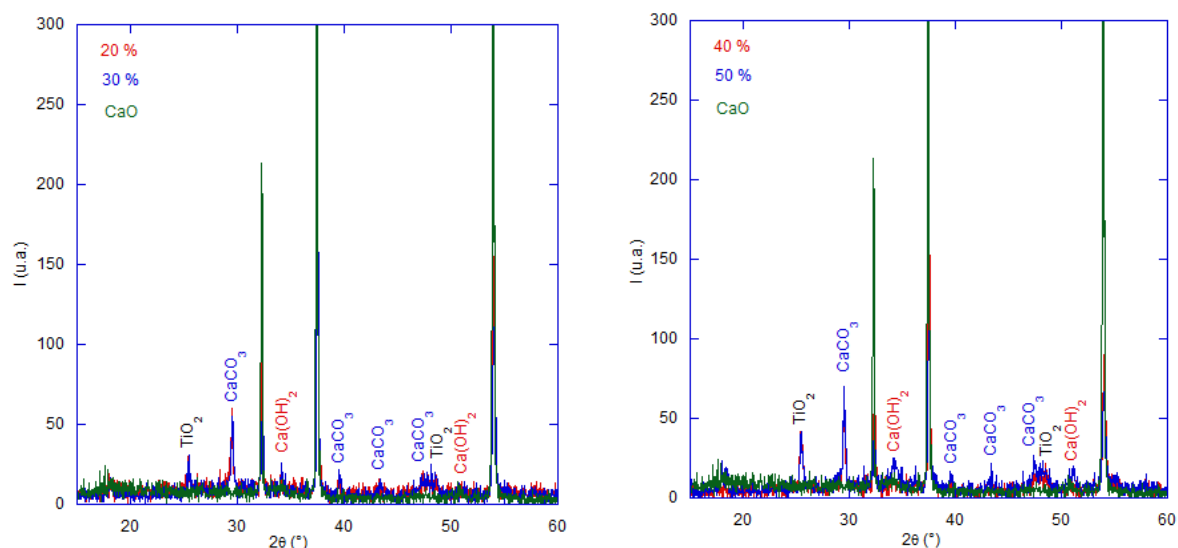
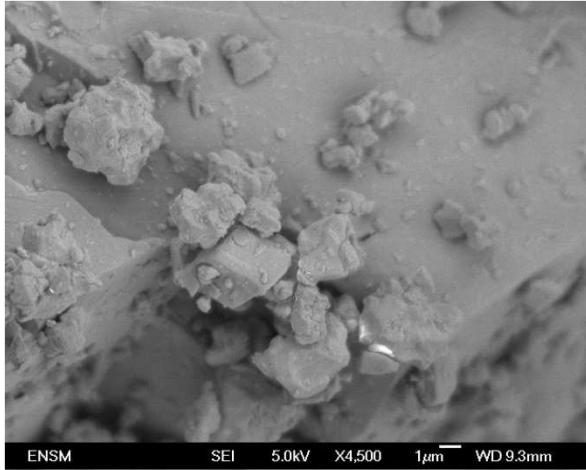
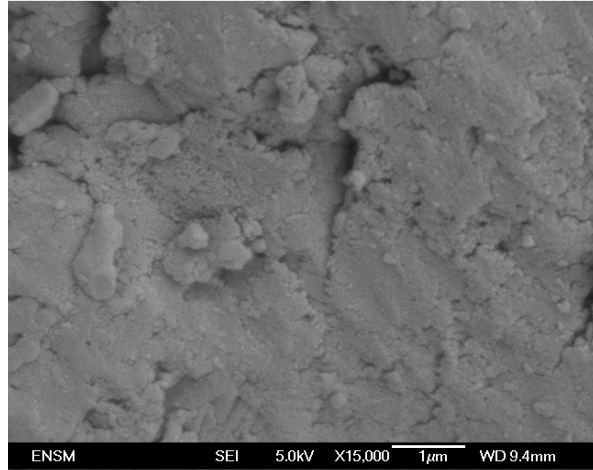


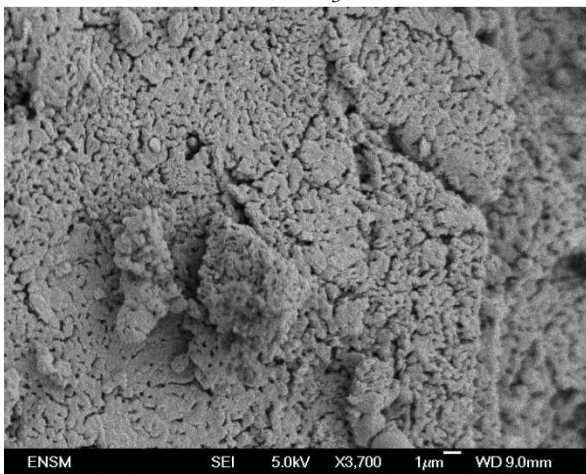
Figure 3 : XRD patterns of CaTi-20, CaTi-30, CaO (starting material) (on left) and CaTi-40, CaTi-50, CaO (starting material) (on right) (CaCO_3 : jcpds number, 00-047-1743; Ca(OH)_2 : jcpds number, 00-044-1481; TiO_2 , jcpds number, 00-004-0477)



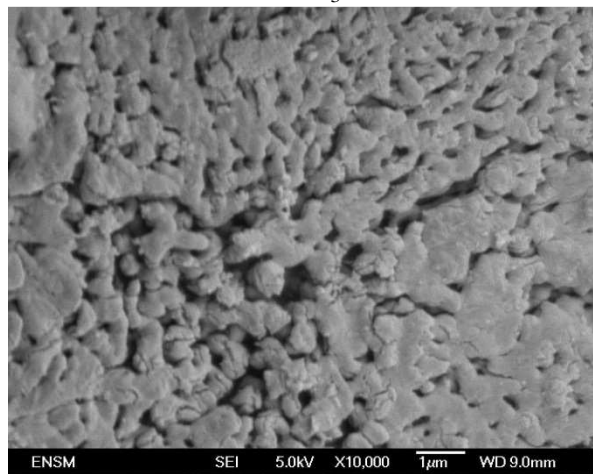
CaCO₃



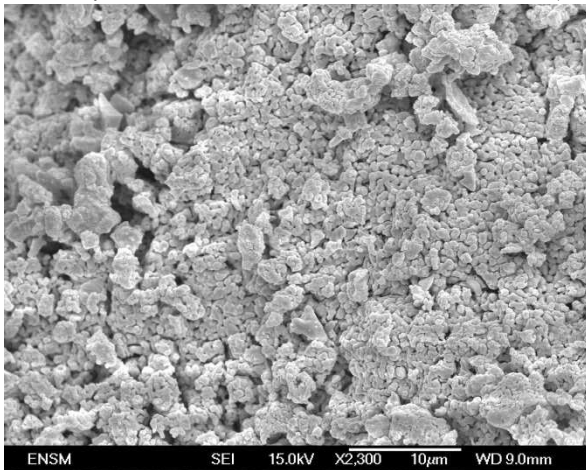
CaCO₃



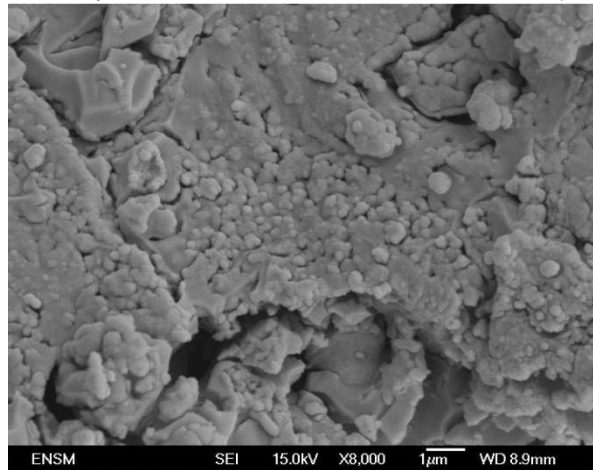
CaO (obtained after calcination of CaCO₃)



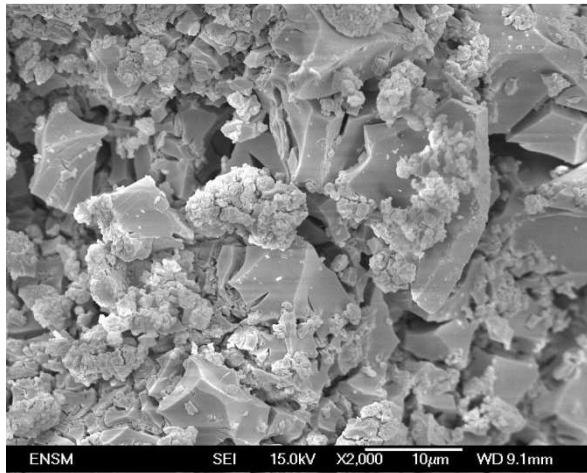
CaO (obtained after calcination of CaCO₃)



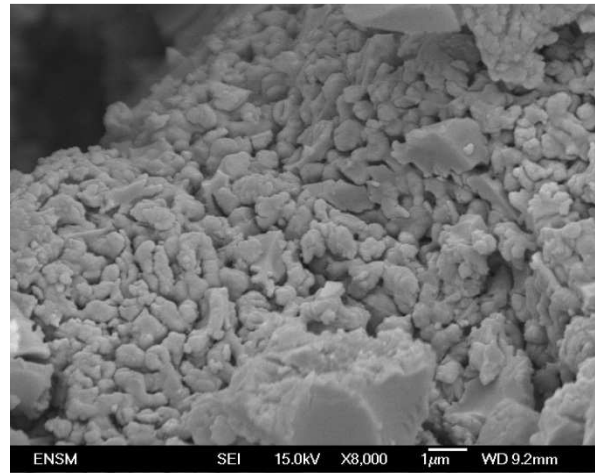
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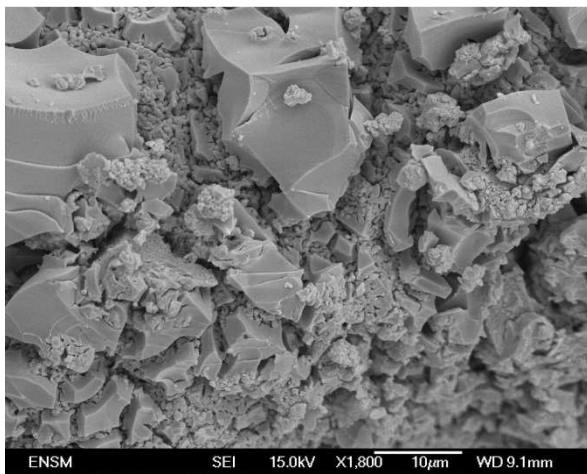
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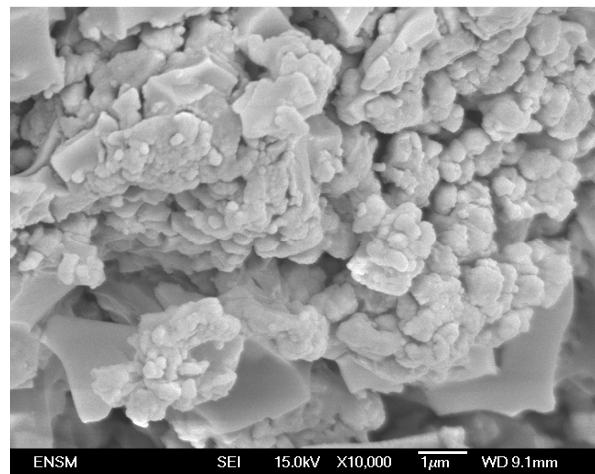
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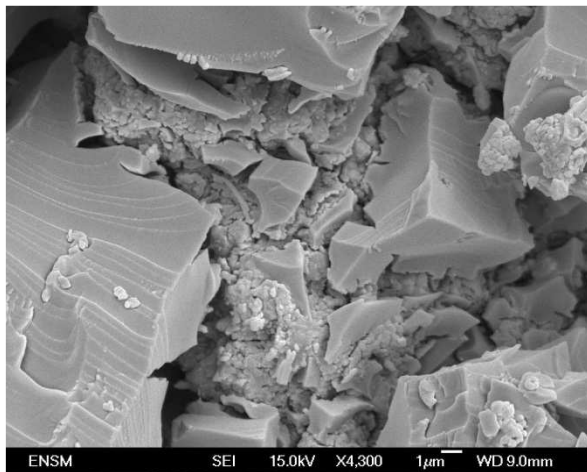
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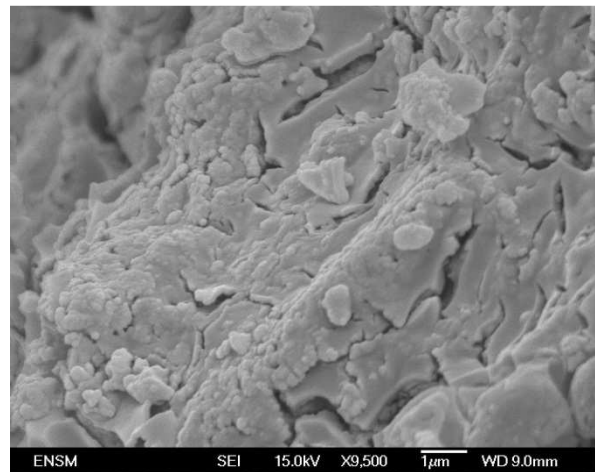
40 %



40 %



50 %



50 %

Figure 4 : SEM images of CaCO₃, CaO and CaO doped with titanium ethoxide

A study of aging was done on the best absorbent (CaTi-50), under 30 cycles of carbonation-calcination. After 30 cycles, its reactivity towards CO₂ is clearly superior to that of pure limestone Tamuin (see figure 5).

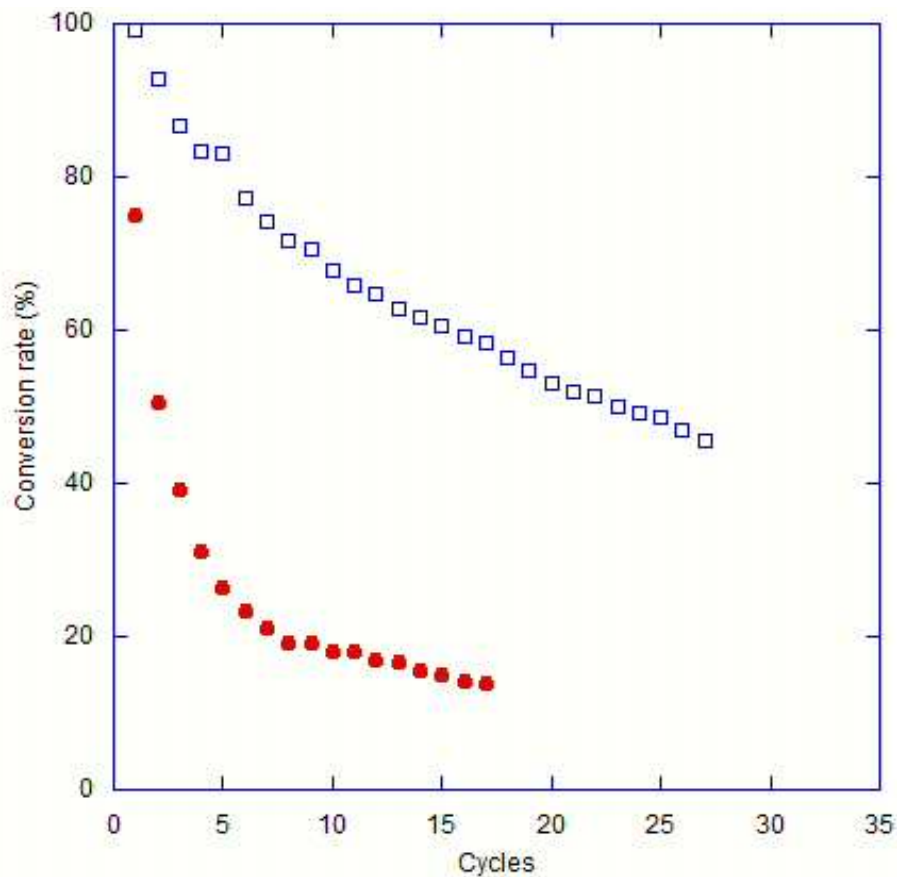


Figure 5 : Carbonation-decarbonation cycles of CaTi-50 : \square and limestone Tamuin : \bullet

Conclusion

CaTi-40 and CaTi-50 were identified as promising sorbents for CO₂ capture, they exhibit very high CO₂-capture capacity and a strong stability during the course of multicyclic carbonation-decarbonation testing. The high titanium content limits the sintering of particles and stabilizes the microstructure of CaO.

Acknowledgment

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