The effects of high-pressure on the chemisorption process of CO_2 on lithium oxosilicate (Li_8SiO_6)

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HIGHLIGHTS

- CO_2 capture was evaluated on Li_8SiO_6 at high-pressure.
- CO_2 is trapped chemical and physically on Li_8SiO_6.
- High-pressure enhances the CO_2 capture between 30 and 350 °C.

ARTICLE INFO

ABSTRACT

High-pressure CO_2 capture was evaluated on Li_8SiO_6. Several different high-pressure experiments were performed using CO_2, and the sample products were analyzed using XRD, N_2 adsorption, SEM and DSC. The results clearly showed that CO_2 is chemically and physically trapped and that the CO_2 chemisorption improved as a function of temperature. Depending on the temperature, Li_8SiO_6 reacted with 2 mol or less of CO_2 to produce an external shell composed of Li_4SiO_4, Li_2CO_3 and Li_2O in a non-stoichiometric reaction. Independently of the external shell composition, the final surface area and pore volume increased independent of the external shell composition and favored the second sorption process: CO_2 adsorption. Therefore, high pressures enhance CO_2 capture between 30 and 350 °C, promoting the chemisorption and adsorption processes.

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1. Introduction

Recently, the concentration of atmospheric carbon dioxide (CO_2) reached 400 ppm, which has never been observed in recent centuries. Consequently, the so-called greenhouse effect and global warming have increased as well [1–4]. Therefore, several strategies have been proposed to reduce or control CO_2 emissions [2].

Among the possible solutions, different materials have been studied as CO_2 captors at low (30–100 °C), moderate (100–400 °C) or high ($T \geqslant 400$ °C) temperatures [5–7]. At low temperatures, different activated carbons, zeolites, and other organic/inorganic cage structures have been tested as possible CO_2 captors, presenting some advantages and disadvantages [7]. Other materials have been analyzed as possible CO_2 captors at high temperatures, such as calcium oxide and some lithium or sodium ceramics [8–26]. Thermodynamically, several of these lithium and sodium materials are able to trap CO_2 at moderate temperatures (100–400 °C), although the reaction processes are kinetically
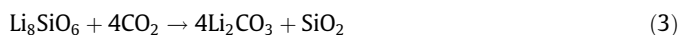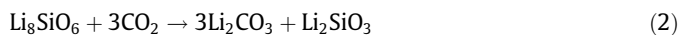
limited [15,17]. Nevertheless, several papers have shown that CO_2 capture kinetics and efficiencies depend on several different factors, such as the chemical and structural compositions, and several microstructural factors, among others [15,17,23–24].

Among the alkaline ceramics, lithium silicates present good CO_2 capture properties at moderate and high temperatures [8–17]. There are several studies showing that lithium orthosilicate (Li_4SiO_4) [8–12,15–19] and lithium oxosilicate (Li_8SiO_6) are able to chemisorb CO_2 between 400 and 650 °C [13–15], although the theoretical data say that CO_2 chemisorption would occur at lower temperatures [15]. Recently, it has been shown that Li_8SiO_6 is capable of trapping significant quantities of CO_2 at temperatures equal to or higher than 600 °C (11.9 mmol of CO_2 per gram of ceramic at 650 °C). Additionally, this temperature range can be modified via sodium (9.3 mmol/g at 550 °C) and/or potassium (7.5 mmol/g at 400 °C) carbonate additions [13,14]. However, substantial CO_2 chemisorption values on this ceramic are only produced at temperatures higher than 400 °C. In addition, CO_2 chemisorption on Li_8SiO_6 is dependent on the temperature as follows:

$$Li_8SiO_6 + 2CO_2 \rightarrow 2Li_2CO_3 + Li_4SiO_4 \tag{1}$$

$$Li_8SiO_6 + 3CO_2 \rightarrow 3Li_2CO_3 + Li_2SiO_3 \tag{2}$$

$$Li_8SiO_6 + 4CO_2 \rightarrow 4Li_2CO_3 + SiO_2 \tag{3}$$

These reactions show that Li_8SiO_6 would be able to react with different quantities of CO_2, producing Li_2CO_3 and different lithium secondary phases: Li_4SiO_4, Li_2SiO_3 and SiO_2. Moreover, at temperatures between 400 and 580 °C, Li_4SiO_4 reacts with CO_2, [8–12, 15–19] while Li_2SiO_3 is able to chemisorb CO_2 at temperatures below 250 °C [25]. Therefore, the formation of these two phases may improve the total CO_2 chemisorption capacity.

In contrast, in the temperature range between 100 and 400 °C, there are not many viable CO_2 capturing materials. In fact, layered double hydroxides (LDH) are one of the few types of materials evaluated in this temperature range [7,27]. In addition, there are few studies related to high-pressure CO_2 capture, and these works were performed using LDH structures, where the CO_2 capture efficiencies are usually improved several times in comparison to CO_2 capture at atmospheric pressure [28–30]. Therefore, the aim of the present paper is to study the CO_2 capture process on lithium oxosilicate (Li_8SiO_6) at varying pressures and moderate temperatures, which may increase the CO_2 capture efficiency.

2. Experimental section

Li_8SiO_6 was synthesized via a solid-state reaction using silica gel (SiO_2, Merck) and lithium oxide (Li_2O, Aldrich) as reagents; excess lithium oxide (15 wt%) was used to prevent lithium sublimation. The powders were mechanically mixed and thermally treated at 800 °C for 8 h as previously reported [13,14]. Additionally, Li_4SiO_4 was synthesized for comparative purposes. In the present work, Li_4SiO_4 was also prepared via solid-state reaction using fumed silica (SiO_2, Aldrich) and the same lithium source described previously in the Li_8SiO_6 synthesis. In this case, the Li/Si molar ratio was equal to 4.1/1. The Li_4SiO_4 powders were mechanically mixed and thermally treated at 700 °C for 4 h [11].

The Li_8SiO_6 samples, before and after CO_2 sorption experiments, were characterized using X-ray diffraction (XRD), N_2 adsorption–desorption and scanning electron microscopy (SEM). The XRD patterns were obtained using a D5000 diffractometer from Siemens with a Co $K_{\alpha 1}$ radiation source at 34 kV and 30 mA. The diffraction patterns were recorded over the 2-theta range of 10–80° with a step size of 0.02° and were correlated with the different JCPDS files.

The microstructural characteristics of the initial sample and high-pressure CO_2 products were determined using scanning electron microscopy (SEM) and N_2 adsorption. The particle size and morphology were determined using SEM in a JEOL JMS-7600F microscope. Additionally, the textural characteristics (BET surface area, pore size and pore volume) were determined via N_2 adsorption–desorption experiments at 77 K using a Minisorp II instrument from Bel-Japan and a multipoint technique. All samples were outgassed at room temperature under high vacuum for 24 h before the N_2 adsorption–desorption tests.

The CO_2 capture capacity at elevated pressure on the Li_8SiO_6 was determined using a volumetric Belsorp-HP instrument from Bel-Japan. This equipment has the capacity of degassing the sample by vacuum and measure the dead volume using Helium. Then, CO_2 capture capacity was determined at different temperatures (between 30 and 350 °C), using a thermal electric chamber, while the CO_2 was dosed by a manifold thermalized at 30.5 °C. The experiments were performed between atmospheric and 1 MPa of pressure. The non-ideal behavior of the CO_2 gas was corrected by applying virial equations using four virial coefficients. The virial coefficients were calculated from the National Institute of Standards and Technologies (NIST) web page. Data were calculated at the respective temperature in the heater at a maximum pressure of 1.0 MPa. It must be mentioned that the virial equation of state of gases has additional terms beyond that for ideal gases, which account for the interactions between the molecules. Pressure can be expressed in terms of the molar volume $V_m = V/n$ (where n is the number of moles of gas molecules in a volume V), the absolute temperature T, and the universal gas constant, $R = 8.3145$ J K^{-1} mol^{-1} (Eq. (4)). In this equation the virial coefficients $B_n(T)$ are functions only of the temperature and depend on the nature of the gas, CO_2 in this case.

$$\frac{V_m}{RT} = 1 + \frac{B_2(T)}{V_m} + \frac{B_3(T)}{V_m} + \frac{B_4(T)}{V_m^3} + \dots \tag{4}$$

The powders were initially activated before the CO_2 sorption tests. First, the sample was introduced in the adsorption cell and outgassed at 60 °C for 4 h before testing because the materials are sensitive to the presence of moisture and environmental CO_2. The adsorption experiments were performed at temperatures between 30 and 350 °C. At each temperature, the pressure was increased to 1000 kPa, establishing equilibrium times between 1 and 50 min.

3. Results and discussion

Fig. 1 shows the CO_2 sorption isotherms on Li_8SiO_6 at different temperatures (30–350 °C) and high pressures (5–1000 kPa). At 30 °C, the CO_2 sorption was low (0.2 mmol/g). However, at 100 °C the CO_2 sorption increased exponentially up to 2.45 mmol/g, when pressure reached 1 MPa of pressure. The CO_2 captured under these temperature and pressure conditions are substantially higher than those observed in previous works for the Li_8SiO_6–CO_2 system at atmospheric pressure [13,14]. In fact, in those previous cases, where all the experiment were at atmospheric pressure, only varying temperature, the CO_2 chemical capture began only at temperatures higher than 300 °C, even in the presence of K_2CO_3 and Na_2CO_3, where were used as additives. Thus, these initial results strongly suggest that pressure seems to improve both the physical and chemical CO_2 capture. It must be related to different CO_2 sorption–desorption equilibriums at atmospheric and high pressure conditions.

At temperatures between 150 and 250 °C, the CO_2 sorption decreased as a function of temperature from 1.9 to 1.1 mmol/g. This behavior suggest a dominant CO_2 adsorption process, where the CO_2 adsorption–desorption equilibrium is altered by the temperature. These isotherms trapped CO_2 in two different steps. Initially, at pressures close to atmospheric pressure, Li_8SiO_6
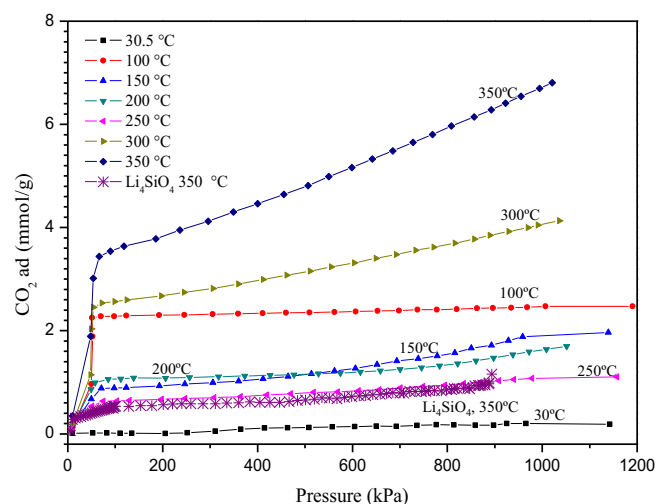

Fig. 1. High-pressure CO_2 sorption curves at different temperatures.

trapped the most CO_2. This CO_2 sorption process must be associated with a CO_2 chemisorption process on the Li_8SiO_6 particle surfaces, where Li_2CO_3 and different lithium secondary phases are produced (see reactions 1–3). Then, at higher pressures, these isotherms present slight increments, which may be attributed to some types of CO_2 adsorption over the external shell, which is induced by the pressure increase.

The isotherms did not follow the same trend at temperatures above 250 °C. At 300 and 350 °C, the CO_2 sorption increased to 4.1 and 6.8 mmol/g, respectively. These CO_2 sorption increments do not match an adsorption process but a combination of CO_2 chemisorption and physisorption processes. Additionally, these isotherms present a different shape than the isotherms performed at lower temperatures. At higher temperatures, the isotherms did not reach a plateau. Although half of the CO_2 sorption was produced at pressures lower than 100 kPa, the other half extended up to 1000 kPa. Furthermore, at atmospheric pressure, the pristine and K- and Na-doped Li_8SiO_6 samples only chemisorbed ~1 mmol/g [14] over the same temperature range. At atmospheric pressure, Li_8SiO_6 only can chemisorb more than 6 mmol/g of CO_2 at $T \geqslant 500$ °C.

To explain the CO_2 sorption behavior, the isothermal products were structurally and microstructurally characterized using XRD, N_2 adsorption–desorption, and SEM. Initially, the isothermal products were analyzed using XRD to determine any compositional and structural change (Fig. 2). The first isothermal product ($T = 30$ °C) did not present structural changes when compared with the pristine Li_8SiO_6. At this temperature, it appears that only a recrystallization process was produced because all of the phase diffraction peaks presented higher intensities, which is in good agreement with the low CO_2 sorption previously described. At higher temperatures, the recrystallization process continued, but at the same time, other crystalline phases were detected. Between 100 and 250 °C, new phases were elucidated, lithium carbonate (Li_2CO_3), lithium orthosilicate (Li_4SiO_4) and lithium oxide (Li_2O). Li_2O may be presented in the initial XRD pattern, but it was much more obvious in these isothermal products. Therefore, it was produced during the CO_2 capture process. The presence of Li_2CO_3 and Li_4SiO_4 confirmed that Li_8SiO_6 is reacting chemically with CO_2 according to reaction (1) described above.

In contrast, the Li_2O increase may be associated with an incomplete or non-stoichiometric reaction process as follows (reaction (5)):

$$Li_8SiO_6 + 2 - xCO_2 \rightarrow Li_4SiO_4 + 2 - xLi_2CO_3 + xLi_2O \qquad (5)$$
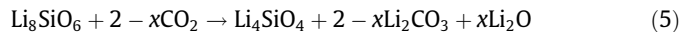
It seems that the pressure produces a partial CO_2 capture process between 100 and 250 °C. If some of the lithium atoms ($2x$) are released from the Li_8SiO_6 crystalline structure ($0 < 2x < 2$) and react with CO_2, Li_2CO_3 and Li_4SiO_4 are produced. However, the rest of the lithium atoms are not stabilized in any of these new crystalline phases, producing Li_2O. In a previous paper, the CO_2 chemisorption on Li_2O was described [31], experimentally showing that, at atmospheric pressure, Li_2O chemisorbs CO_2 superficially at temperatures above 200 °C; however, bulk CO_2 chemisorption is produced at approximately 650 °C, once different diffusion processes are activated. Therefore, the Li_2O formation and stabilization are in good agreement with the results presented here.

Returning to the XRD patterns, the samples treated at 300 and 350 °C presented the following compositions: Li_8SiO_6, Li_2CO_3 and Li_4SiO_4. In these cases, Li_2O was no longer detected. Thus, in this temperature range, the reaction reached total conversion as described in reaction (1). In fact, it has been previously reported that Li_8SiO_6 reacts with CO_2 as a function of the temperature (see reactions (6) and (7) [13]):

$$Li_8SiO_6 + 2CO_2 \xrightarrow{(300-700\ °C)} Li_4SiO_4 + 2Li_2CO_3 \qquad (6)$$

$$Li_8SiO_6 + 3CO_2 \xrightarrow{(400-580\ °C)} Li_2SiO_3 + 3Li_2CO_3 \qquad (7)$$

Based on this reaction mechanism, it was described that Li_8SiO_6 reacts with 2 or 4 mol of CO_2 depending on the temperature. In this case (30–350 °C), it may be assumed that Li_8SiO_6 only reacts with 2 mol of CO_2. Li_4SiO_4 reacts with CO_2 at temperatures higher than 400 °C (see reaction (8)), although the pressure may affect the reactivity.

$$Li_4SiO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \qquad (8)$$
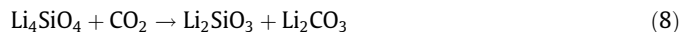
Therefore, the CO_2 chemisorption at high pressure was evaluated on Li_4SiO_4 at 350 °C (see Fig. 1). Li_4SiO_4 only chemisorbed 1.0 mmol/g at 350 °C, which strongly suggests that Li_4SiO_4 reacts with CO_2 only at a superficial level. Therefore, only reactions (1) and (4) must be considered for the Li_8SiO_6–CO_2 system at these temperatures and pressures.

After the compositional and structural characterizations, the microstructures of the isotherm products were analyzed using N_2 adsorption–desorption and scanning electron microscopy. Fig. 3 shows the N_2 adsorption–desorption curves of all of the isothermal
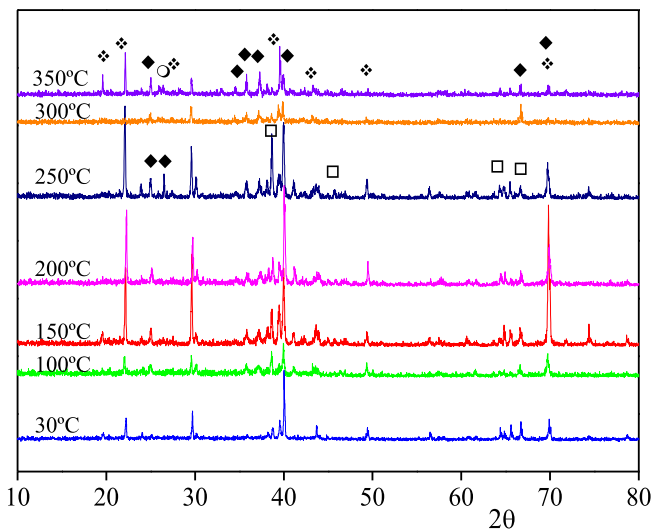

Fig. 2. XRD patterns of the CO_2 high-pressure sorption products obtained at different temperatures. The crystalline phases were labeled as follows: ❖Li_8SiO_6, ○Li_4SiO_4, □Li_2O and ◆Li_2CO_3.
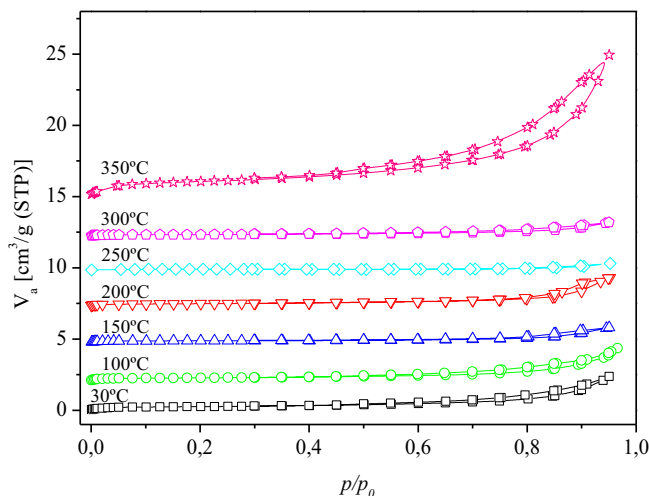

Fig. 3. N_2 adsorption–desorption isotherms of the CO_2 high-pressure sorption products obtained at different temperatures.

products. All of these curves presented type-II isotherms, according to the IUPAC classification [32,33], although the hysteresis loops tended to slightly increase as a function of the CO_2 capture temperature. The surface area decreased on Li_8SiO_6 after the CO_2 isothermal process was performed between 30 and 250 °C, from 0.8 to 0.2 m^2/g. In fact, all of these areas are smaller than that determined for the pristine Li_8SiO_6 (1.2 m^2/g). However, the surface area increased again up to 3.5 m^2/g, when the CO_2 isotherm was performed at 350 °C. These results strongly suggest changes in the microstructures of the Li_8SiO_6–CO_2 products. The XRD results showed partial CO_2 chemisorption at temperatures lower than 300 °C, which is in agreement with the surface area tendency. Conversely, at the highest temperatures (300–350 °C), the surface area increased significantly, and these results are in agreement with a complete CO_2 chemisorption process (reaction (1)) previously determined using XRD. Additionally, the pore volume increased one order of magnitude at 350 °C, in comparison with the pristine sample and the other products. The pore volume increased from 0.0042 to 0.0152 cm^3/g in the pristine and the product treated at 350 °C, respectively. The same trend was observed with the pore diameter. It increased from 14.2 nm in the initial Li_8SiO_6 sample to 17.5 nm in the product treated at 350 °C. In previous papers [17], it has been determined that different lithium and sodium ceramics produce mesoporous external shells through which CO_2 can diffuse and continue reacting with the initial ceramic, Li_8SiO_6 in this case. Moreover, the presence of mesopores is also shown by the CO_2 isothermal curves because these isotherms (300 and 350 °C) did not reach the plateau, but a continuous adsorption increment was observed. This idea is corroborated by the CO_2 desorption process shown in Fig. 4, where all of the CO_2 adsorbed after 100 kPa was lost as the CO_2 pressure decreased. Based on this analysis, CO_2 capture occurs both chemically and physically. Specifically, at 350 °C, CO_2 is initially chemisorbed (~3.5 mmol/g) producing an external shell composed of Li_2CO_3 and Li_4SiO_4. This external shell contains mesopores, where CO_2 adsorption is produced as a function of pressure and temperature (3.3 mmol/g).

To complement the CO_2 sorption analysis on Li_8SiO_6 at high pressures, some high-pressure DSC experiments were performed. Fig. 5 shows the DSC experiments performed in Li_8SiO_6 under different atmospheres and pressures. When the DSC experiments were performed with N_2 or CO_2 (at atmospheric pressures) typical endothermic peaks were found, associated to a superficial
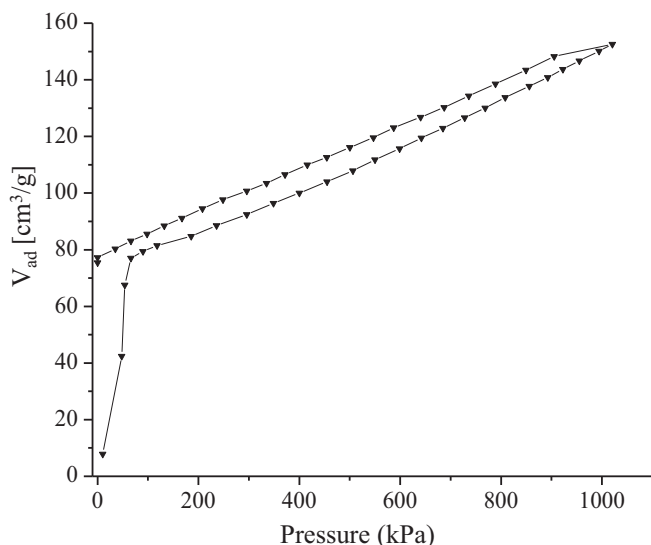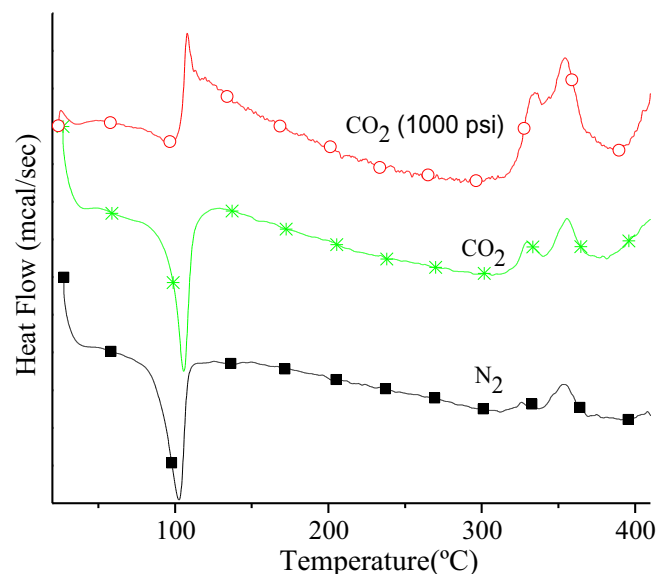

Fig. 5. Li_8SiO_6 differential scanning calorimetry curves under different atmospheres and pressures.

dehydration processes ($T \leqslant 100$ °C). Then, between 100 and 333 °C, the samples treated with CO_2 presented a continuous endothermic process, in comparison to the sample treated with N_2. In fact, when the DSC was performed with pressurized CO_2 (1000 psi), the same continuous endothermic process increased significantly. Therefore, this effect must be associated with CO_2 chemisorption, which is increased by pressure. At higher temperatures, all of the samples presented two endothermic peaks at 357 and 389 °C. These peaks may be related to superficial Li_8SiO_6 dehydroxylation processes because lithium ceramics tend to be highly hygroscopic.

Finally, the microstructural characterization was completed using SEM. Fig. 6 shows secondary electron images of the pristine Li_8SiO_6 sample and those samples treated with CO_2 at high pressures and different temperatures. Fig. 6A shows some of the morphological characteristics of the pristine Li_8SiO_6 sample. The size of the particles did not exceed 10–20 μm (inset of Fig. 6A), which is consistent with the synthetic method: solid-state reaction. Additionally, the particle surface is corrugated, showing some type of superficial sintered flakes. In fact, this morphology is in good agreement with a previous report [13]. The high-pressure isothermal CO_2 products had varied morphologies, in comparison with the pristine sample. Although the particle size did not seem to vary importantly, the texture varied as follows. The initial sintered flakes disappeared as soon as the sample was exposed to CO_2 at high pressures, independently of temperature. Between 30 and 300 °C (Figs. 6B–E), the particle surfaces became more corrugated, showing a texture of very tiny particles agglomerated and sintered. As shown previously, these changes must be attributed to the CO_2 chemisorption process, where different phases are produced (Li_4SiO_4, Li_2O and Li_2CO_3). However, at 350 °C (Fig. 6F), the surface morphology changed. In this case, the surface seemed to be smoother and denser than in the previous cases. It must correspond with a shell formation thermal effect, where the densification process is more active. This sample showed the formation of some macropores, which, together with the mesopores, may be correlated with the previously described adsorption processes.

Fig. 7 shows an illustrative image, where the Li_4SiO_4–Li_2CO_3 external shell and the Li_8SiO_6 core are depicted. The Li_8SiO_6 core particle seems to present a smother and denser surface than the pristine sample (see Fig. 6A). This result may be associated with

Fig. 4. CO_2 high-pressure sorption–desorption curve performed at 350 °C.
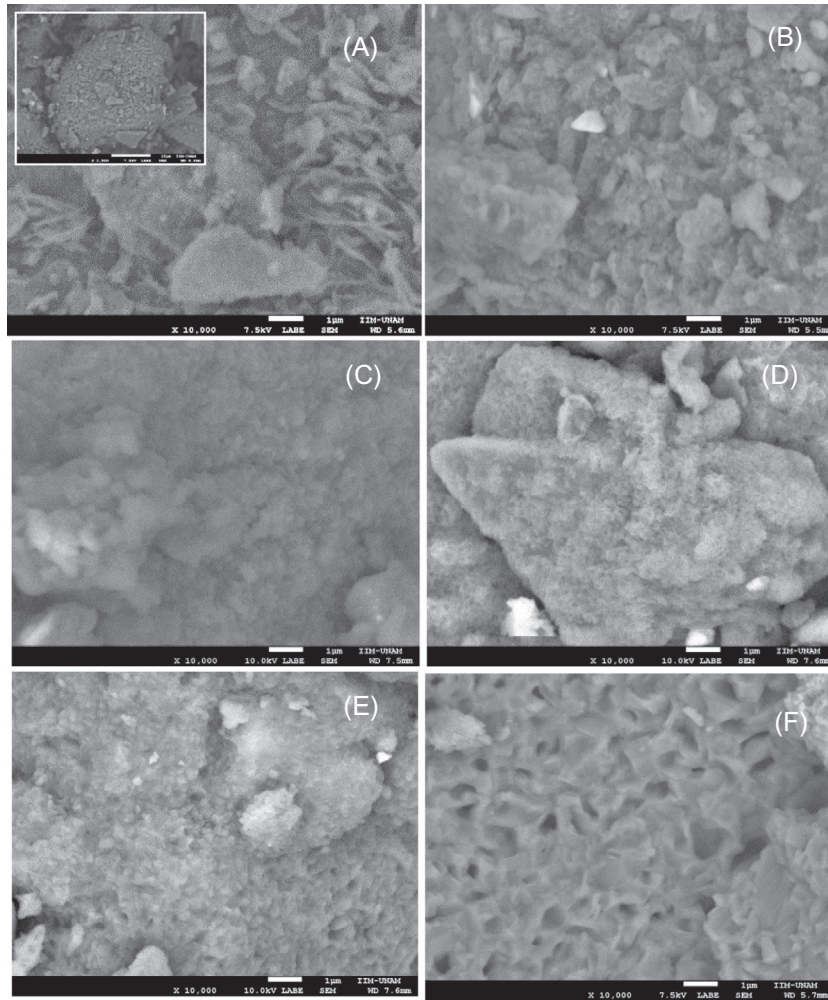
Fig. 6. SEM images of the pristine Li_8SiO_6 and their corresponding CO_2 high pressure sorption products at the following temperatures. (A) Initial Li_8SiO_6 pristine sample, (B) 30 °C, (C) 100 °C, (D) 200 °C, (E) 300 °C and (F) 350 °C.
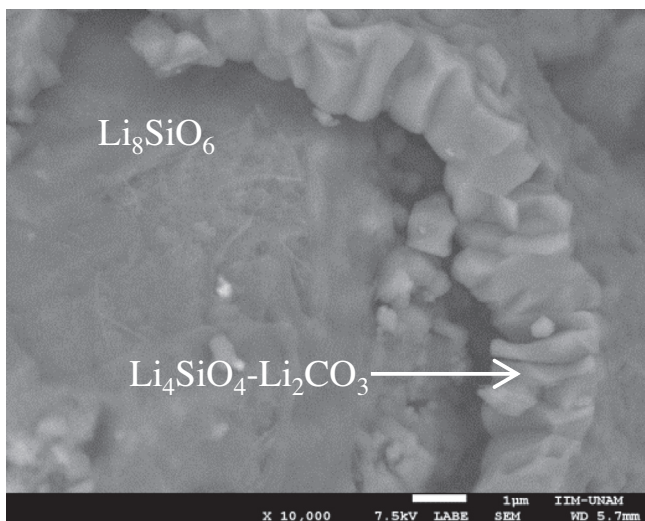
Fig. 7. SEM image of the Li_8SiO_6 sample treated with CO_2 at high-pressure (1 MPa) and 350 °C. The image show a particle cross section, where the Li_8SiO_6 core and Li_4SiO_4–Li_2CO_3 external shell are evidenced.

CO_2 chemisorption and Li_4SiO_4–Li_2CO_3 external shell production, which is devastating to the Li_8SiO_6 particle. In contrast, the Li_4SiO_4–Li_2CO_3 external shell presents the textural characteristics described above. However, in this case, it is possible to observe its thickness: 1–1.5 μm. Similar textures are found on Li_8SiO_6 particles when they are exposed to CO_2 at high temperatures and atmospheric pressure. This morphological finding is in good agreement with the fact that the pressure does not modify the CO_2 capture mechanism on Li_8SiO_6 but its kinetics.

4. Conclusions

High-pressure CO_2 capture on Li_8SiO_6 was evaluated by associating the kinetic results with different structural and microstructural parameters. The results clearly showed that CO_2 is chemically and physically trapped. The CO_2 chemisorption at lower temperatures than previously studied was significantly improved as a function of the temperature and pressure. Between 30 and 250 °C, Li_8SiO_6 chemisorbed less than two moles of CO_2 per mole of ceramic. This non-stoichiometric reaction was shown by the formation of Li_2O in addition to Li_2CO_3 and Li_4SiO_4. At temperatures above 250 °C, the same reaction went to completion because only Li_2CO_3 and Li_4SiO_4 were produced. The external shell presented different textural properties (surface area and pore volume) at higher temperatures independently of the external shell composition obtained from the CO_2 chemisorption. In fact, these characteristics favored CO_2 adsorption.

All of these results were obtained from the high-pressure CO_2 sorption experiments and from the analysis of the sample

products. All of the high-pressure sample products were analyzed using different techniques, such as XRD, N_2 adsorption–desorption, SEM and DSC.

Finally, it must be mentioned that high pressures significantly enhance the CO_2 capture between 30 and 350 °C. For example, Li_8SiO_6, at 350 °C and high pressure sorbed 6.8 mmol/g, while the same ceramic trapped less than 1 mmol/g at atmospheric pressure and the same temperature. At atmospheric pressure, Li_8SiO_6 can only chemisorb approximately 6 mmol/g of CO_2 at temperatures higher than 500 °C.

Acknowledgements

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