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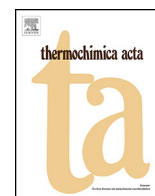


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Microstructural and CO₂ chemisorption analyses of Li₄SiO₄: Effect of surface modification by the ball milling process

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ABSTRACT

The ball milling process was used to modify microstructurally the Li₄SiO₄, and different structural and microstructural analyses were performed, followed by an analysis of the CO₂ chemisorption process. In comparison to previous reports, the Li₄SiO₄ modified sample exhibited very important differences and improvements during the dynamic CO₂ chemisorption process. Additionally, an analysis of the Li₄SiO₄–CO₂ chemisorption products showed that the Li₂CO₃–Li₂SiO₃ external shell exhibits a degree of mesoporosity at $T < 500^\circ\text{C}$, which is favorable for diffusion processes. Finally, the CO₂ chemisorption–desorption process was analyzed at 550°C during 10 cycles. The ball milled Li₄SiO₄ sample showed a stable performance during the CO₂ chemisorption–desorption test and presented better efficiencies than the solid-state sample. The mechanical milling technique proved to be an effective method for modifying the microstructural properties of the ceramic absorbent by enhancing the CO₂ chemisorption–desorption process without further sintering effects.

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1. Introduction

Currently, the general consensus is that global warming is directly related to the increased amount of anthropogenic greenhouse gases released to the atmosphere [1]. In fact, CO₂ has been identified as the main contributor to global warming due to the high amounts of CO₂ generated by the burning of fossil fuels [2]. To reduce CO₂ emissions, different options, such as improving the efficiency of energy utilization, increasing the use of low-carbon energy sources and capturing and sequestering CO₂, have been considered. Capture and sequestration has been identified as the most effective option for reducing emissions [2–8].

Among the possible CO₂ acceptors, alkaline ceramics such as Li₂ZrO₃, Li₄SiO₄, Li₂CuO₂, Li₅AlO₄, Li₂SiO₃, Na₂ZrO₃, and Li₆Zr₂O₇ have shown excellent CO₂ capture properties. These materials have the capability to chemisorb CO₂ over wide temperature and CO₂ partial pressure ranges and are useful for multicycle processes [9–34]. Additionally, recent studies have shown that the CO₂ capture capacity of lithium ceramics can be positively or negatively affected by the presence of other gases or vapors [9,13,31–34]. In that sense, the presence of water vapor seems to highly improve the CO₂ capture process due to a superficial hydroxylation process [9,31,32], while the presence of SO₂, even

at very low concentrations, results in an irreversible reaction with the absorbent and a decrease in CO₂ capacity [33].

Lithium orthosilicate (Li₄SiO₄) has displayed some of the best CO₂ chemisorption properties, as it is able to chemisorb up to 8.3 mmol of CO₂ per gram of ceramic and shows excellent thermal stability [13–16,23,24,29,33,35–37]. However, as it is common for the alkaline ceramics, Li₄SiO₄ presents a very low surface area, which limits the CO₂ chemisorption process [15]. Therefore, different types of syntheses have been proposed for Li₄SiO₄ and other alkaline ceramics in order to enhance its microstructural features, such as particle size and porosity. For example, some authors have proposed the synthesis of different alkaline ceramics by hydrothermal methods using different templates [12,26,34,38] to enhance microstructural characteristics, namely, particle size and porosity. Other authors have synthesized lithium ceramics by sol–gel [17,19,27,39–41], by combustion [41,42], via solid state reaction by using different oxide sources [14,23,24,43–45] and more recently by mechanical milling [46,47]. At laboratory scales, the microstructural modifications achieved on this kind of absorbents, usually are able to improve some CO₂ capture properties, although these may lead to important operation issues in industrial applications. Therefore, it is important have in mind the compromise between the proposed approaches and its feasibility. Currently, these materials are still far from practical applications. For any practical application of these solid CO₂-adsorbents, it must be taken into consideration their sorption capacity, selectivity and recyclability, but also other factors, e.g., their working temperatures, which should be compatible to that of the particular process.

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Thus, this will probably widen the application of these materials in catalysis. In light of the increasingly obvious global warming trends worldwide, capture, storage and utilization of CO₂ by means of solid CO₂-sorbents via a number of environmentally friendly processes is of increasing importance. However, one should keep in mind that a successful process is not only a scientific issue but also an engineering issue [8].

Among all of the issues aforementioned, mechanical milling is a relatively easy technique for increasing surface area, one of the most important issues of the CO₂ chemisorption process in alkaline ceramics. Therefore, the aim of the present paper was to analyze the microstructural characteristics and CO₂ chemisorption behavior of a Li₄SiO₄ surface mechanically modified via ball milling.

2. Experimental

Li₄SiO₄ was initially obtained via wet-mixing and the further solid-state reaction of the precursors first prepared by mixing lithium hydroxide (LiOH, Aldrich) and fumed silica (SiO₂, Sigma–Aldrich) in water in a Li/Si molar ratio of 4.1:1. The suspension was then stirred and heated at 70 °C to evaporate the water, and the final powder was calcined at 700 °C for 4 h [48]. After powder X-ray diffraction (XRD) characterization of the Li₄SiO₄ phase, a dry ball milling process was performed using a Spex Sample-Prep 8000 M with varying processing times (30, 45, 60 and 90 min).

The solid-state and ball milled modified samples were characterized by different techniques such as XRD, N₂ adsorption, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The XRD patterns were obtained with a BRUKER AXS Advance D8 Diffractometer coupled to a Cu anode X-ray tube. The $k_{\alpha 1}$ wavelength was selected with a diffracted beam monochromator, and the compounds were identified conventionally using the PDF database. Surface area analyses were performed on Minisorp II equipment from BEL Japan. The N₂ adsorption isotherms were determined at 77 K by volumetric adsorption. Before the N₂ adsorption process, all samples were outgassed at room temperature for 24 h under vacuum. Surface areas were calculated with the BET equation. The morphology of the samples was analyzed by SEM, using a JEOL JMS-7600F. Finally, different thermal analyses were performed using a Hi-Res TGA Q500HR thermogravimetric equipment from TA Instruments. A set of samples was heat-treated with a heating rate of 5 °C/min from room temperature to 800 °C. These analyses were carried out into a CO₂ atmosphere (Praxair, grade 3.0). Additionally, other samples were analyzed isothermally between 350 and 600 °C for 4 h in the same CO₂ atmosphere. Chemisorption–desorption (regenerability) tests were conducted at the following thermal conditions. While a CO₂ flow was used during the chemisorption process at 550 °C, the CO₂ desorption process was performed after switching the gas flow to N₂ (Praxair, grade 4.8) at the same temperature. The gas flow rate (CO₂ or N₂) in all of the thermogravimetric analyses was 60 mL/min, and the sample amount used in each thermal experiment was ~10 mg at 1 atm of pressure.

3. Results and discussion

Li₄SiO₄ was microstructurally modified by the ball milling process with varying amounts of time (30, 45, 60 and 90 min). Then, the samples were characterized by XRD. Fig. 1 shows the XRD patterns of the Li₄SiO₄ sample synthesized by the solid-state method before (Fig. 1A) and after (Fig. 1B) the ball milling modification process for 60 min. The Li₄SiO₄ structure was preserved, and it is evident that Li₄SiO₄ diffraction peaks in the ball milled sample became much broader than those observed in the solid-state sample. Also notable is that no secondary phases were detected in the Li₄SiO₄ sample.

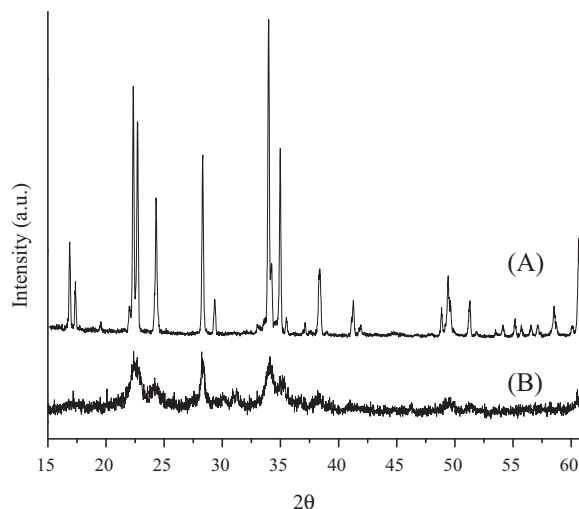


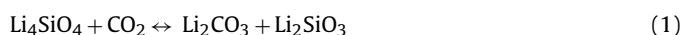
Fig. 1. XRD patterns of the Li₄SiO₄ sample (A) and after (B) 60 min of ball milling process.

Thus, the crystal sizes of the two samples were estimated using the Scherrer equation. The results indicated a significant decrease on the crystal size due to the ball milling process. While the Li₄SiO₄ sample before the ball milling process exhibited a crystal size larger than 500 Å (out of the detection limit), the Li₄SiO₄ crystal size decreased to 175 Å after 60 min of ball milling. These results indicate that the ball-milled sample displays a smaller crystal size. It is also important to note that the XRD profile suggests other microstructural features such as microstrain and residual stress may have changed.

It should be mentioned that crystal size decreased as a function of the ball milling time between 30 and 60 min. However, at longer times (90 min), the formation of other phases such as Li₂SiO₃ was detected (data not shown). Thus, the sample prepared by 60 min of milling presented the smallest crystal size without the presence of any secondary phases.

For the microstructural analysis, SEM and N₂ adsorption–desorption experiments were performed to determine the microstructural characteristics of the Li₄SiO₄ ball milled sample. As shown in Fig. 2, the morphology of the Li₄SiO₄ sample varied notably after the ball milling process. Although the Li₄SiO₄ sample presented dense, large micrometric particles (>60 μm, Fig. 2A), the sample after the ball milling process (Fig. 2B) had decreased particle sizes of 1–3 μm, on average. From these results it can be established that the Li₄SiO₄ particles are polycrystalline (see crystal size at the XRD results). In fact, these morphological features were corroborated by the N₂ adsorption–desorption results (Fig. 2C). In this case, both samples presented isotherms type II with very narrow H3 hysteresis loops, according to the IUPAC classification [49,50]. While this isotherm corresponds to non-porous or macroporous materials, the hysteresis is associated with non-rigid aggregates [49]. The initial Li₄SiO₄ sample, synthesized by solid-state reaction, presented a BET surface area of 0.4 m²/g, while the BET surface area of the Li₄SiO₄ modified by ball milling was equal to 4.9 m²/g. This result means that the Li₄SiO₄ modified by ball milling had a 10 times larger surface area after only 60 min of milling.

These microstructural variations must induce an important improvement in the CO₂ chemisorption process observed on the sample, as it has been reported in previous papers [15], where the CO₂ chemisorption on the Li₄SiO₄ has been described as follows:



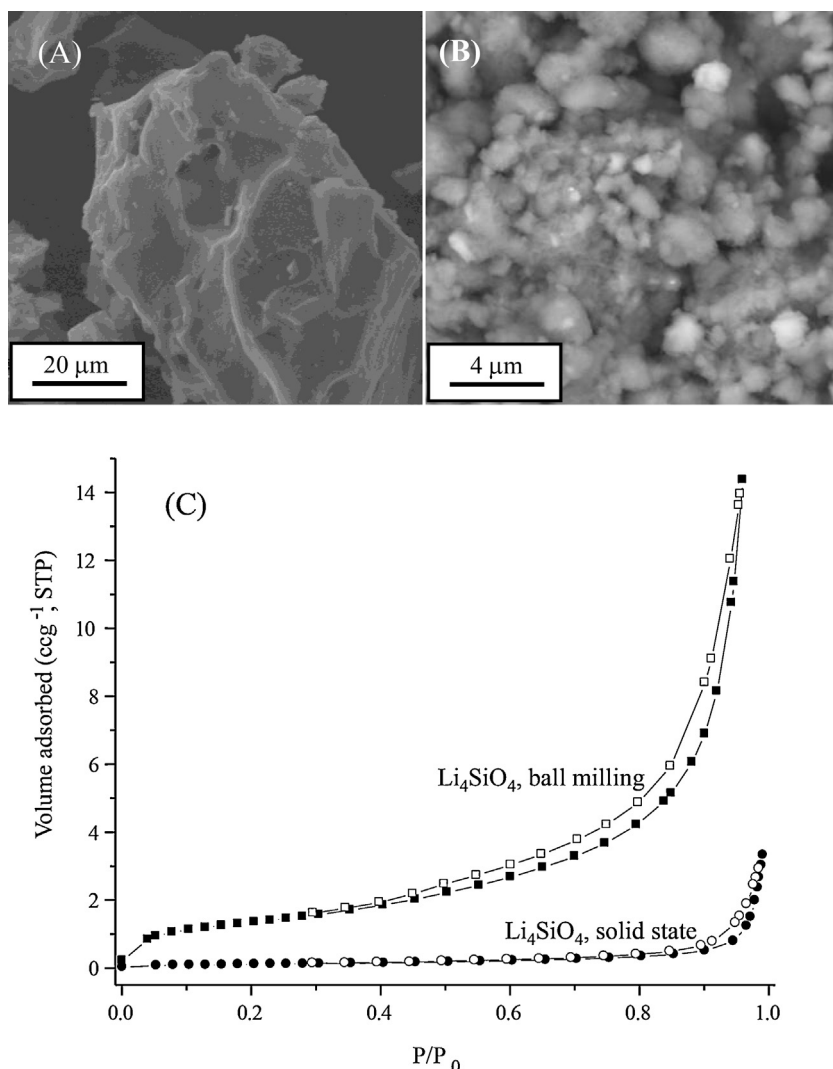


Fig. 2. SEM images of the Li_4SiO_4 synthesized by solid-state reaction (A) and after 60 min of ball milling process (B), as well as the N_2 adsorption–desorption isotherms of these two Li_4SiO_4 samples (C).

From the reaction (1), it has been established that only 1 mole of CO_2 can be chemisorbed by each mole of Li_4SiO_4 between 400 and 600 $^\circ\text{C}$, as thermodynamically Li_2SiO_3 is only able to react with CO_2 in a different temperature range ($T < 250^\circ\text{C}$) at atmospheric pressure [34]. In the present study, TGA showed important differences in the CO_2 chemisorption of Li_4SiO_4 , as a result of the surface modification via ball milling (Fig. 3). Li_4SiO_4 , prepared by solid-state synthesis, presented a typical CO_2 chemisorption. This sample increased its mass by $\sim 4\%$, which is in good agreement with previous dynamic thermogravimetric reports [15,37]. The chemisorption process began at approximately 460 $^\circ\text{C}$, and the maximum chemisorption was obtained and stabilized at 585 $^\circ\text{C}$. At higher temperatures, the sample desorbed the CO_2 . On the other hand, the Li_4SiO_4 modified sample showed significant improvements in its CO_2 chemisorption. The maximum increase in mass was equal to 8.2%, which corresponds to twice the amount of CO_2 chemisorbed in the solid-state sample. Additionally, in this sample, the CO_2 chemisorption range changed. The CO_2 chemisorption process began at $\sim 50^\circ\text{C}$, and the maximum chemisorption temperature did not shift. From 50 to 320 $^\circ\text{C}$, the sample chemisorbed 3.4%; then, between 320 and 470 $^\circ\text{C}$, part of this mass was lost (1.2%). Between 490 and 585 $^\circ\text{C}$, the sample chemisorbed up to 8.2% in total. Finally, at $T > 600^\circ\text{C}$, this sample lost 13.2%.

Similar CO_2 chemisorption behaviors on alkaline ceramics have been reported elsewhere in the literature [13,15,18,20,22,25,28,37]. In those cases, the CO_2 chemisorption has been divided into two different steps. Initially, the CO_2

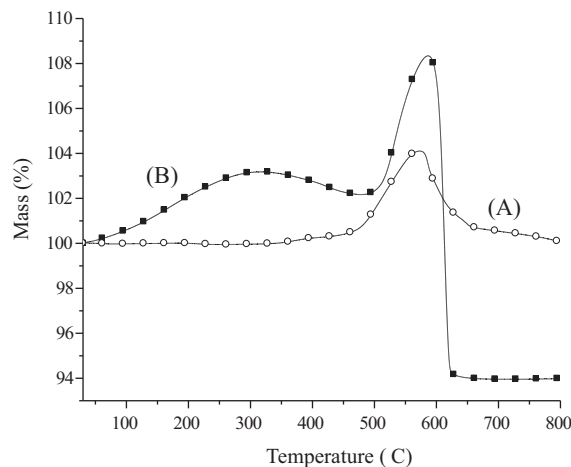


Fig. 3. Dynamic thermograms of the Li_4SiO_4 sample before (A) and after (B) 60 min of ball milling process, into a CO_2 flux.

Table 1CO₂ chemisorption kinetic parameters obtained for the Li₄SiO₄ microstructurally modified by ball milling.

T (°C)	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	A	B	C	R ²
350	0.00134	0.00015	-1.212	-2.083	3.457	0.9995
400	0.00103	0.00011	-1.242	-2.580	4.001	0.9973
450	0.00429	0.00013	-1.571	-10.580	12.273	0.9999
500	0.00409	0.00029	-11.388	-7.620	18.242	0.9978
550	0.00517	0.0003	-13.129	-10.225	23.484	0.9948
600	0.00737	0.00033	-15.894	-11.644	26.326	0.9933

chemisorption is produced on the particle surfaces. Then, once the diffusion processes are thermally activated, the CO₂ chemisorption continues through the ceramic bulk. Li₄SiO₄ must present the same micrometric reaction mechanism, but these steps are not generally distinguishable. The Li₄SiO₄ sample prepared by ball milling has different microstructural properties than those obtained usually by solid-state synthesis, for example, smaller crystal sizes and a larger surface area. Then, the CO₂ chemisorption produced on the ceramic surface must be increased as well, producing the initial mass increment between 50 and 320 °C. Then, between 320 and 470 °C, a CO₂ chemisorption–desorption equilibrium must be reached at the particle surfaces, as the diffusion processes have not yet been activated. At 480 °C, once the diffusion processes are thermally activated, the CO₂ chemisorption takes place in the ceramic bulk. Finally, at temperatures higher than 600 °C, the sample lost more mass (5%) than that previously chemisorbed. This finding can be attributed to a previous carbonation of the sample, which must take place during the sample handling.

In a previous paper [15], the dependence of the Li₄SiO₄–CO₂ chemisorption as a function of the CO₂ flow rate was shown and correlated to the state of the gas–solid film interface. Therefore, according to Fig. 3, the gas–film interface must be saturated in the Li₄SiO₄ solid-state sample, while in the Li₄SiO₄ ball milled sample the gas–film interface was not saturated, in agreement with the chemisorption–desorption equilibrium observed at low temperatures. Thus, as the CO₂ flow rate was not varied, the changes observed in the gas–film regime must be associated with the increase in surface area.

To further analyze the CO₂ chemisorption in the Li₄SiO₄ sample modified by ball milling, a kinetic analysis was performed. As expected, all of the isothermal experiments followed a typical behavior (Fig. 4), wherein the CO₂ chemisorption increased as a function of temperature in an exponential trend. While the samples heat-treated at 350 and 400 °C chemisorbed only 3.0 and 3.4% of CO₂, respectively, after 4 h, the total mass increment observed at

600 °C was 21.1% for the same period of time. This means that when heat-treated at 600 °C, the Li₄SiO₄ sample had a final efficiency of 57.6% of the theoretical uptake capacity, displaying significantly increased CO₂ chemisorption in comparison to samples treated at lower temperatures. However, none of the isotherms reached a plateau after 4 h, indicating that the chemisorption–desorption equilibrium had not been reached. In previous works [15,37,48], the CO₂ chemisorption isotherms obtained in Li₄SiO₄ samples, at the same temperature range, presented efficiencies equal to or lower than 35.5%. Therefore, the increment observed in the present study must be attributed to the enhanced microstructural properties obtained in the Li₄SiO₄ milled sample, where the surface area is notably larger than those reported in previous papers.

In previous papers different models have been used to determine some kinetic parameters of the CO₂ capture process in lithium ceramics [12–15,18,24,28,37,51,52]. In the present case, the isotherms were fitted to a double exponential model (Eq. (2)), assuming that there are two global processes taking place during CO₂ capture on Li₄SiO₄: the CO₂ chemisorption occurred directly over the Li₄SiO₄ surface (k_1), and the CO₂ chemisorption kinetically controlled by diffusion processes (k_2). The second process occurs once the carbonate–oxide external shell is totally formed, Li₂CO₃–Li₂SiO₃ in the present case. This model has been successfully used in Li₄SiO₄ [13–15,24,37,52]. Then, the double exponential model is:

$$y = A \cdot \exp^{-k_1 t} + B \cdot \exp^{-k_2 t} + C \quad (2)$$

where y represents the mass of CO₂ chemisorbed, t is the time, and k_1 and k_2 are the exponential constants for the CO₂ chemisorption produced directly over the particles and the CO₂ chemisorption kinetically controlled by diffusion processes, respectively. Additionally, the pre-exponential factors A and B indicate the intervals at which each process controls the whole CO₂ capture process, and C indicates the y -intercept.

Table 1 shows the constant values obtained for the CO₂ direct chemisorption (k_1) and the chemisorption kinetically controlled by diffusion processes (k_2), including the pre-exponential constants and R^2 values. The k_1 values obtained are at least one order of magnitude higher than those obtained for the k_2 constants, over the entire temperature range. These values are in good agreement with previous reports [15], where the CO₂ chemisorption controlled by diffusion processes is the limiting step of the whole reaction process. It should be noticed that the A and B pre-exponential values do not follow a common trend. The A values are smaller than B values, at low temperatures (between 350 and 500 °C). However, at high temperatures ($T > 500$ °C), this trend is reversed. In other words, the B values became smaller than A values. To explain this behavior, it should be mentioned that the alkaline external shell produced during the CO₂ chemisorption may present different microstructural characteristics depending on the temperature. Specifically, Martínez-díCruz and Pfeiffer [53] showed that the Na₂CO₃–ZrO₂ external shell produced during the CO₂ capture on Na₂ZrO₃ at low temperatures is mesoporous. Therefore, under these thermal conditions, the CO₂ chemisorption process was not limited to bulk diffusion processes. To analyze whether the Li₄SiO₄ sample modified by ball milling presents a similar

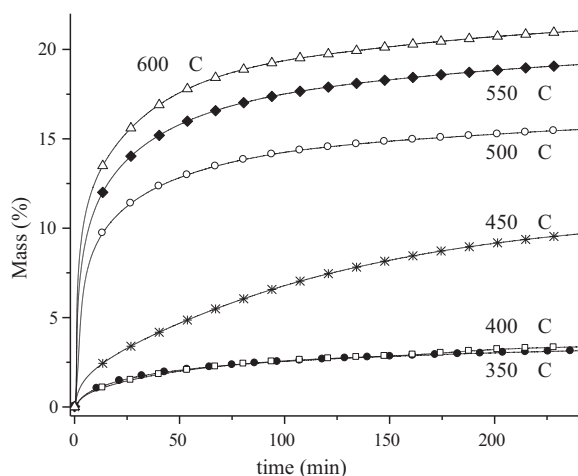


Fig. 4. CO₂ chemisorption isothermal analyses of the Li₄SiO₄ microstructurally modified by ball milling at different temperatures for 60 min.

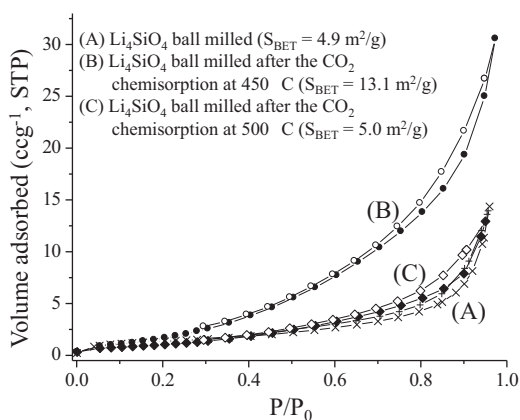


Fig. 5. N₂ adsorption–desorption isotherm of the fresh Li₄SiO₄ microstructurally modified sample by ball milling for 60 min (A), and isotherms of the Li₄SiO₄–CO₂ sample products obtained from chemisorption isothermal experiments performed at 450 (B) and 500 °C (C).

behavior, which would be explained by *A* and *B* pre-exponential values, part of this sample was isothermally treated at 450 and 500 °C (temperatures where the *A* and *B* values tended to be reversed) into a CO₂ atmosphere. The textural properties were determined by N₂ adsorption. The isotherms obtained presented a higher hysteresis process, which strongly suggests the formation of mesoporous external shell (Fig. 5), as formed in the Na₂ZrO₃ case reported previously [53]. Furthermore, higher surface areas were observed for these samples (13.1 and 5.0 m²/g

at 450 and 500 °C, respectively) than in the initial sample, and the pore size distribution obtained from the BJH model indicated the presence of some mesoporosity in the Li₄SiO₄–CO₂ sample products, with an average pore radius of 1.9 nm. At temperatures above 500 °C, the porosity disappeared due to a sintering effect. Therefore, the mesoporosity observed between 450 and 500 °C must be produced in the Li₂CO₃–Li₂SiO₃ external shell, and this mesoporosity must increase the CO₂ direct chemisorption, as the CO₂ molecules can diffuse through these pores to reach the Li₄SiO₄ core. In previous works, this effect may have not been detected, as the CO₂ chemisorption was limited to higher temperatures due to the surface area, producing the sintering of all phases present in the corresponding system (Li₄SiO₄, Li₂CO₃ and Li₂SiO₃).

Returning to Table 1, Eyring's model (Eq. (3)), relevant in solid–gas systems, was used to quantitatively analyze the temperature dependence of different processes:

$$\ln \left(\frac{k_i}{T} \right) = - \left(\frac{\Delta H^\ddagger}{RT} \right) + \ln E + \frac{\Delta S^\ddagger}{R} \quad (3)$$

where k_i is the rate constant value of the process i ; E represents a pre-exponential factor, which in Eyring's formulation is equal to the ratio of Boltzmann's constant to Planck's constant; R is the ideal gas constant and ΔH^\ddagger and ΔS^\ddagger are the activation enthalpy and entropy, respectively. Although both constant values (k_1) and (k_2) were fitted to Eyring's model, only CO₂ direct chemisorption (k_1) could be fitted to obtain a linear trend. The activation enthalpy (ΔH^\ddagger) measured for CO₂ direct chemisorption was 28.5 kJ/mol. This result confirmed that CO₂ direct chemisorption becomes less dependent on temperature after the ball milling process, as the ΔH^\ddagger values

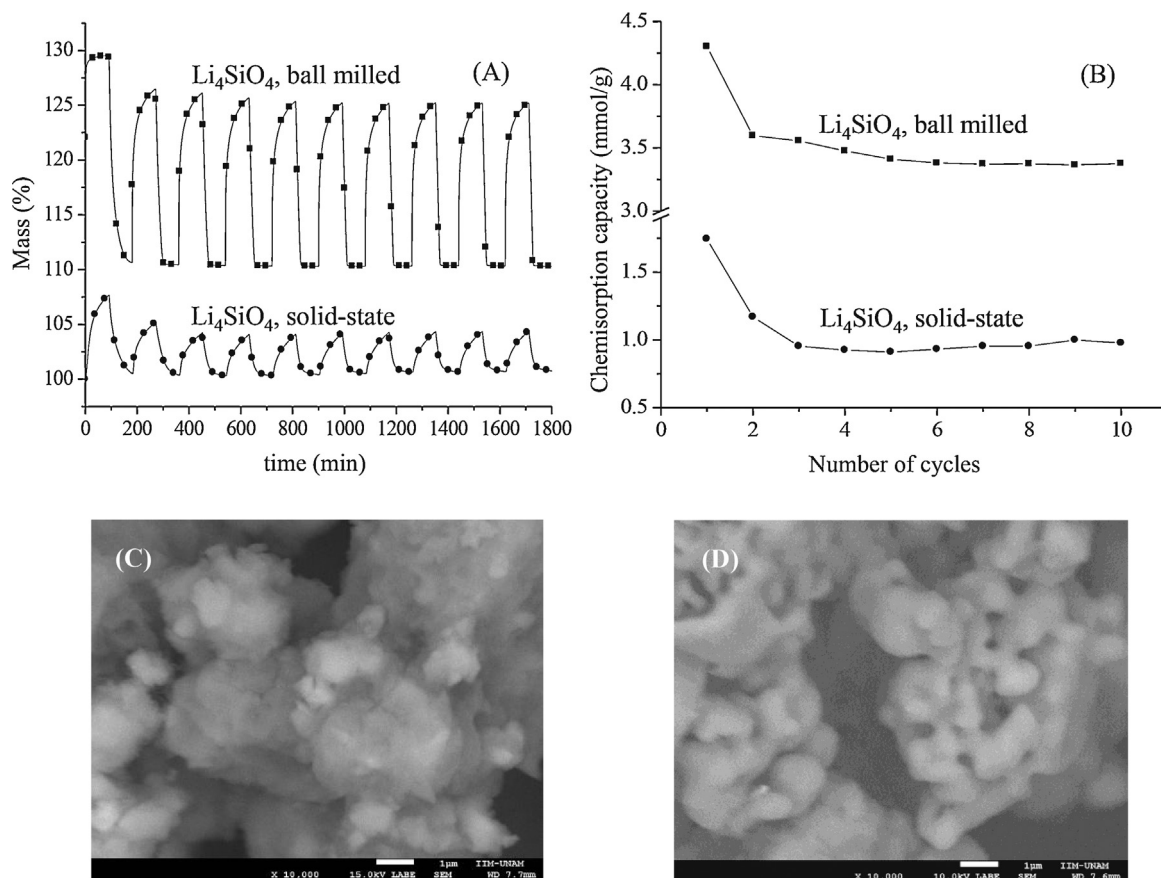


Fig. 6. Multicycle performance of CO₂ chemisorption/desorption on Li₄SiO₄ sample before and after ball milling process (A). Both, CO₂ chemisorption and desorption processes were performed at 550 °C for 90 min each one. Cyclic stability of the two samples in millimols of CO₂ per gram of Li₄SiO₄ (B). SEM images of the Li₄SiO₄ microstructurally modified by ball milling (C) and after ten CO₂ chemisorption/desorption cycles (D).

reported previously are over 60 kJ/mol [15,37]. In the second case (k_2), the presence of several diffusion processes did not allow the use of this model. Qualitatively, a more complex behavior should occur, as there are different secondary phases and porosity, which, depending on the temperature, may inhibit or allow diffusion.

Finally, to analyze the CO₂ chemisorption/desorption properties and the thermal stability of the Li₄SiO₄ modified by ball milling, this sample was tested using a multicycle method. The Li₄SiO₄ regeneration process has been previously analyzed at $T \geq 600^\circ\text{C}$ [13,28,54–56] because this temperature range is where Li₄SiO₄ presents higher CO₂ chemisorption. However, in this case, the ball milling process produced an important CO₂ chemisorption at a slightly lower temperatures; therefore, the cyclic behavior was analyzed at 550°C , to identify a larger temperature range for possible Li₄SiO₄ applications. Fig. 6A presents the cyclic chemisorption/desorption performance of the Li₄SiO₄ sample, before and after the ball milling modification process. From this image, it is clear that the milling process considerably improved several factors of the CO₂ chemisorption, although both ceramics exhibited good stability after 10 cycles. Initially, the CO₂ chemisorption was improved more than three times in the Li₄SiO₄ ball milled sample (12.6% in average) compared to the solid-state Li₄SiO₄ sample (3.7% in average). Additionally, after the third cycle, the chemisorption–desorption was highly stabilized up to 10 cycles, which may suggest very low aggregation through the following cycles. The desorption process is faster in the Li₄SiO₄ ball milled sample than in the original sample. In fact, while the Li₄SiO₄ ball milled sample desorbed the CO₂ in only 30 min, the untreated Li₄SiO₄ needed 90 min for the same process. These results must be associated to the larger surface area obtained which produced a higher CO₂ direct chemisorption and the formation of a Li₂CO₃–Li₂SiO₃ porous microstructure, where the CO₂ can be easily chemisorbed and desorbed.

Despite the CO₂ cyclic chemisorption performed at 550°C , the Li₄SiO₄ ball milled sample chemisorbed more than 3.5 mmol of CO₂ per gram of Li₄SiO₄ (Fig. 6B), that means a higher chemisorption than the values reported previously, which were between 1.9 and 2.5 mmol/g [28]. In fact, Li₄SiO₄ is only able to chemisorb more CO₂ in cyclic experiments, if K₂CO₃ is added to the system [23,28]. K₂CO₃–Li₄SiO₄ has been able to trap up to 4.5 mmol/g at higher temperatures ($T \geq 600^\circ\text{C}$). The addition of K₂CO₃ in the Li₄SiO₄ ball milled sample would be the following step toward a better CO₂ chemisorption–desorption behavior. Additionally, because cyclic experiments (chemisorption and desorption processes) were successfully performed at 550°C , the materials did not experience any important sintering.

Fig. 6C and D presents the morphologies of the fresh Li₄SiO₄ ball milled sample (Fig. 6C) and the same sample after ten CO₂ chemisorption–desorption cycles (Fig. 6D). From these images, it can be noted that the Li₄SiO₄ presented only an incipient sintering process after the cyclic procedure, where particle surfaces seemed to become smooth, but particle size did not increase. Finally, it is important to point out that ball milling is an easy processing method that does not require the use of reagents or templates, which are usually expensive and contaminating.

4. Conclusions

Li₄SiO₄ was initially synthesized by a solid-state reaction, and then this sample was microstructurally modified by ball milling. The structural analysis showed that the Li₄SiO₄ phase was preserved after the ball milling process, although the microstructural properties changed. The surface area was increased 10 times, from 0.4 to 4.9 m²/g, and the crystal size was reduced from >500 Å to 175 Å.

The microstructural features of Li₄SiO₄ obtained by ball milling substantially modified and improved the CO₂ chemisorption process. The initial dynamic TGA experiment showed that both the CO₂ chemisorption temperature range and the chemisorption efficiency were significantly increased in the microstructurally modified Li₄SiO₄, in comparison to the solid-state sample. The results were confirmed by different isothermal analysis. Additionally, it was shown that the formation of a Li₂CO₃–Li₂SiO₃ mesoporous external shell at $T < 500^\circ\text{C}$ enhances the CO₂ direct chemisorption. At higher temperatures, the mesoporosity disappeared, limiting diffusion processes. Finally, the CO₂ chemisorption–desorption process was analyzed at a lower temperature (550°C) than those usually used in this ceramic ($T \geq 600^\circ\text{C}$). At this temperature, the ceramic did not present significant sintering or melting effects. The results confirmed an important and stable CO₂ chemisorption–desorption performance. Therefore, the ball milling process seems to be an interesting process for the preparation of absorbents with enhanced microstructural features and consequently improved CO₂ chemisorption properties such as better efficiencies, different temperature CO₂ capture ranges and kinetic parameters. Of course, the whole CO₂ capture capacity depends of several other factors such as diffusion processes, lithium secondary phases and the ceramic quantity. Moreover, this process would be considered as a viable alternative to the current industrial procedures due to its high volume processing capability and lack of expensive and contaminating precursors.

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