Kinetic and Reaction Mechanism of CO_2 Sorption on Li_4SiO_4: Study of the Particle Size Effect

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Lithium orthosilicate (Li_4SiO_4) was synthesized by three different techniques: the solid-state reaction, precipitation, and sol−gel (using a microwave oven) methods. The better results were obtained by the two first methods. In the third case, pure Li_4SiO_4 could not be obtained, because the microwaves produced the lithium sublimation. The samples were characterized by X-ray diffraction, scanning electron microscopy, N_2 adsorption, and thermogravimetric analysis under a flux of CO_2. Different particles sizes were obtained as a function of the method of synthesis, and the CO_2 sorption analyses gave different results. The particle size modified the stability of the Li_4SiO_4 during the CO_2 sorption/desorption cycles, due to lithium sublimation, as Li_2O. Conversely, the isothermal study allowed measuring the kinetic parameters for the chemisorption and diffusion processes, as a function of the particle size. As could be expected, the activation energies obtained, for the small particles, were smaller than those obtained for the large particles. These results were explained in terms of reactivity, for the chemisorption process, and in terms of geometry, for the diffusion process.

Introduction

Growing concerns about the impact of pollution gases have led to a number of proposed works around the world.[1−4] Specifically, about carbon dioxide (CO_2) emissions, energy efficiency improvements, the use of renewable resources, and its capture and storage have been also recognized as necessities. In this way, different kinds of materials have been proposed as CO_2 captors, for example polymeric membranes, zeolites, hydrotalcitelike materials, and different oxides.[5−9] Nevertheless, all of these materials present one or more disadvantages. Hence, new materials for CO_2 capture must possess the following properties: high selectivity and sorption capacity for CO_2 at elevated temperatures, adequate absorption/desorption kinetics for CO_2, good cyclability for the absorption/desorption process, and good hydrothermal and mechanical properties.[10−11]

In the last nine years, several papers have reported the use of new materials for CO_2 sorption. Specifically, lithium and sodium ceramics seem to present adequate conditions as CO_2 captors.[12−18] Among all these ceramics, lithium orthosilicate (Li_4SiO_4) seems to have encouraging properties for CO_2 sorption.[19−23] For example, Li_4SiO_4 can absorb four or more times more CO_2 than other lithium ceramics such as lithium metazirconate (Li_2ZrO_3), during the first minutes.[16] Additionally, experimental results show that Li_4SiO_4 has excellent cyclability properties for CO_2 sorption/desorption.[18]

Li_4SiO_4, and in general all these ceramics, present a double sorption mechanism. First, there is a chemical sorption of CO_2 over the surface of the ceramics, breeding the particles with an external shield of alkaline carbonate. Later, once the external layer is completely formed, the alkaline element has to diffuse throughout the external layer, in order to reach the surface and continue reacting with the CO_2.[13,18,23] Therefore, one of the limiting steps is the diffusion process, which may be avoided or at least reduced by the synthesis of small particles, where most of the alkaline element is over the surface of the particles. There is only one published paper which has shown that the CO_2 sorption capacities of Li_2ZrO_3 increased when the particle size decreased.[24] Then, the aim of this work is to study the synthesis and CO_2 absorption capacities of Li_4SiO_4 with different particle sizes.

Experimental Section

Lithium orthosilicate was prepared by using solid-state reaction of a mechanical mixture of silica gel (SiO_2, analytical grade, Aldrich) and lithium carbonate (Li_2CO_3, 99+%, Aldrich); by precipitation using tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 98%, Aldrich) and lithium acetate ($LiO_2C_2H_3$, 99.99%, Aldrich); and by sol−gel synthesis using TEOS and lithium nitrate ($LiNO_3$, 99.99%, Aldrich). The sol−gel samples were calcined using a novel approach with a microwave furnace.[25] All the reactions were performed with a Li:Si molar ratio of 4.1:1. A lithium excess of 0.1 was added in all the preparations to prevent the sublimation of lithium produced at high temperatures.[14,26−29]

In the synthesis by solid-state reaction, the powders of SiO_2 and Li_2CO_3 were mixed mechanically and they were calcined at 800 °C for 4 h. For precipitation synthesis, lithium acetate was dissolved in water as a first step. TEOS was then slowly added, drop by drop, to the solution. The final solution was stirred and heated at 70 °C until it dried, and the powders were calcined at 800 °C for 4 h. A second sample was prepared using the same method, with only one variation. In this case, all the processes (lithium dissolution, TEOS addition, stirring, and drying) were performed in an ultrasonic bath at 70 °C, using a frequency equal to 25 kHz.

Li_4SiO_4 sol−gel samples were synthesized by dissolving in isopropyl or ethylic alcohol the required amounts of $LiNO_3$. Latter, TEOS was added to the solution, drop by drop (taking 5 s between drops). The alcohol:alkoxide molar ratio was 20, and the mixture was stirred under continuous agitation. The metallic complex solution was hydrolyzed by the slow addition of a commercial nitric acid solution (HNO_3, 70%, Aldrich). The stirring was continued until gelation was completed. The

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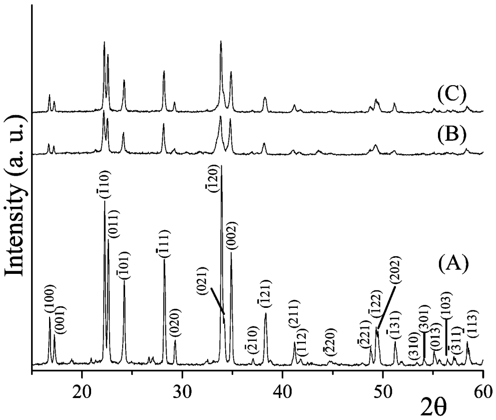

Figure 1. XRD patterns of the Li_4SiO_4 prepared by solid-state reaction (A), precipitation (B), and precipitation with an ultrasonic treatment (C).

obtained gel was dried at 70 °C in air. The powders were then calcined in a microwave furnace (Model CEM Technology MAS-700) with a microwave frequency of 2450 MHz. Samples were heat-treated using different times (5, 10, and 15 min) and temperatures (400, 600, 700, 800, 900, and 1000 °C).

The samples were characterized by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and nitrogen adsorption (BET). 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 compounds were identified conventionally using the JCPDS database. The percentages of the different compounds were estimated from the total area under the most intense peak for each phase, with an experimental error equal to ±3%. SEM (Stereoscan 440, Cambridge) was used to determine the particle size and morphology of the materials prepared by the different methods. As Li_4SiO_4 is not a conductor material, the samples were covered with gold to avoid a lack of electrical conductivity.

Two different kinds of thermal analyses were performed in Hi-Res TGA 2950 thermogravimetric analizer equipment from TA Instruments. First, a set of samples was heat-treated from room temperature to 1000 °C, with a heating rate of 5 °C/min, using a 100% CO_2 flux. These analyses were carried out to identify if there were differences on the CO_2 sorption due to the size of the particles. Later, another set of samples was analyzed isothermically under an atmosphere of 100% CO_2, at 500, 550, 575, and 600 °C for 5 h. The sorption analyses were double checked in most of the cases, in order to be certain about the experimental data. Finally, surface area analyses were performed on Micromeritics Gemini 2360 equipment. Before the N_2 adsorption process, all the samples were out gassed in a vacuum at 400 °C for 12 h. Surface areas were calculated with the BET equation.

Results and Discussion

Synthesis and Characterization. Figure 1 shows the X-ray diffraction patterns for the synthesized samples of Li_4SiO_4 by solid-state reaction and precipitation (with and without ultrasonic treatment). In the three cases, the XRD patterns clearly show that Li_4SiO_4 was obtained pure, as it may be expected. However, the crystallinity of the samples seems to be significantly different among them, according to the intensities obtained in each case. Moreover, the crystal size varied as well. While the solid-state sample presented crystals of ≈400 Å, the samples prepared by precipitation (with or without ultrasonic effect) had smaller crystals, around 300 Å.

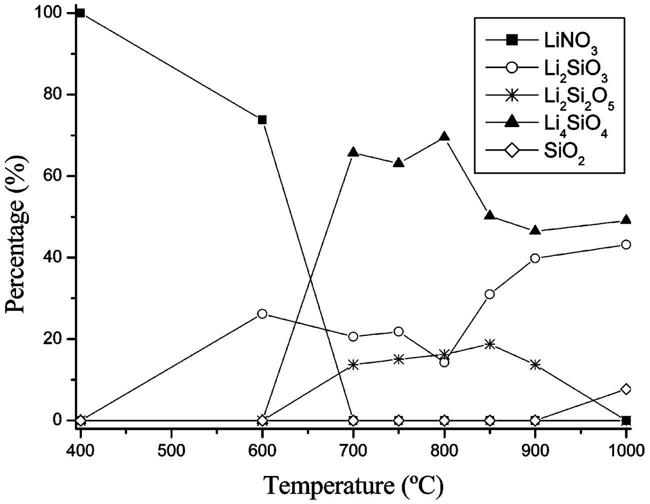

Figure 2. Percentage of $LiNO_3$, Li_2SiO_3, $Li_2Si_2O_5$, Li_4SiO_4, and SiO_2, as a function of the temperature. The samples were prepared by the sol−gel method, using a microwave oven.

On the contrary, the sol−gel synthesis was not as successful as the two previous methods. Figure 2 summarizes the different compositions obtained when the samples were calcined at different temperatures for 5 min in the microwave furnace, using ethanol as solvent (samples heat-treated for longer times or using isopropyl alcohol presented similar results). At 400 °C, only $LiNO_3$ was found. This clearly means that the reaction was not carried out under these conditions. Silicon was not quantified because only the crystalline compounds were identified. In the sample heat-treated at 600 °C, $LiNO_3$ was the main phase again (74%), but a second phase was presented, Li_2SiO_3 (26%). Although the formation of this lithium silicate indicates that some reactions are taking place, these conditions were not adequate to produce Li_4SiO_4. Afterward, the composition of the sample changed significantly at 700 °C. In this case, $LiNO_3$ was not present any more and the sample was composed by three different lithium silicates: Li_2SiO_3 (20%), $Li_2Si_2O_5$ (14%), and Li_4SiO_4 (66%). Similar results were obtained when the sample was heat-treated at 750 and 800 °C, getting the highest percentage of Li_4SiO_4 at 800 °C, 70%. Nevertheless, at 850 °C, the Li_4SiO_4 composition decreased significantly from 70% to 50%. Furthermore, this decrement was combined with the increment of Li_2SiO_3, which increased its composition from 17% to 31%. Finally, $Li_2Si_2O_5$ remained without any significant change. This result strongly suggests that Li_4SiO_4 decomposes on Li_2SiO_3 through the lithium sublimation as Li_2O, according to the following reaction (1):

$$Li_4SiO_4 \rightarrow Li_2SiO_3 + Li_2O \qquad (1)$$

Lithium sublimation has been observed on several lithium ceramics at high temperatures, when the ceramics are heated for a few hours.[14,26−29] However, in this case, sublimation occurred in just 5 min. Then, it should be associated to the microwaves, which must accelerate the lithium sublimation. Actually, this effect was corroborated with the samples heat-treated at 900 and 1000 °C. In these cases, higher lithium sublimations were observed through the disappearance of the lithium silicates and the appearance of silicon oxide at 1000 °C.

As a summary, Li_4SiO_4 could not be obtained in pure form by the sol−gel route. This result is in agreement with previous

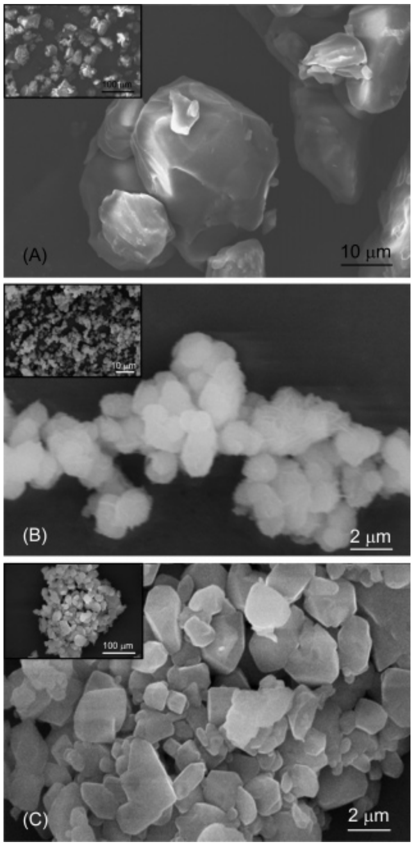

Figure 3. SEM images of Li_4SiO_4 samples prepared by solid-state reaction (A), by precipitation (B), and by sol−gel with microwaves (C).

papers where Li_4SiO_4 synthesis by sol−gel was not possible either.[30] Apparently, TEOS may be polymerizing by itself, and this reaction does not allow a complete saturation of $(SiO_4)^{4-}$ with lithium to produce Li_4SiO_4. Instead, some molecules of $(SiO_4)^{4-}$ polymerize producing different chains such as $(SiO_3)^{2-}$ or $(Si_2O_5)^{2-}$. Conversely, Yang and co-workers produced magnesium silicate in pure form (Mg_2SiO_4),[25] using similar conditions. The unique difference was the use of lithium instead of magnesium. Both elements are highly reactive, and their atomic radii are very similar. Therefore, the unique difference is that magnesium is almost 4 times heavier than lithium. Hence, microwaves must provide lots of energy to the lithium atoms, which, due to their weight, react either to produce lithium silicates or sublime as Li_2O.

Li_4SiO_4 samples synthesized by solid-state, precipitation, and sol−gel were studied by SEM. Micrographs of the lithium orthosilicate, obtained by the three methods, showed morphological differences among the preparation methods. The sample obtained by solid-state reaction showed homogeneous polygonal particles (Figure 3A). These particles were very dense and presented an average particle size equal to 36 μm. However, Li_4SiO_4 prepared by the precipitation method presented a totally different morphology. The particles were spherical, and they seemed to be corrugated. Furthermore, the particle size decreased down to 3 μm (Figure 3B). This is 10 times less than the particle size obtained by the solid-state method. Finally, although the sol−gel sample was not pure, it was analysed by SEM. The morphology of this sample (calcined at 800 °C for 5 min) was approximately polygonal particles that seemed to be dense. Additionally, the size of the particles varied between 3 and 0.5 μm (Figure 3C). The microwaves were supposed to generate a nanoparticle size. Nevertheless, it was not obtained. Lithium seems to be very reactive under these conditions, because it sublimes very quickly (see the XRD results). Perhaps, this high reactivity induces some kind of sintering or other process, which inhibits the formation of nanoparticles. This result is in agreement with the results obtained by XRD.

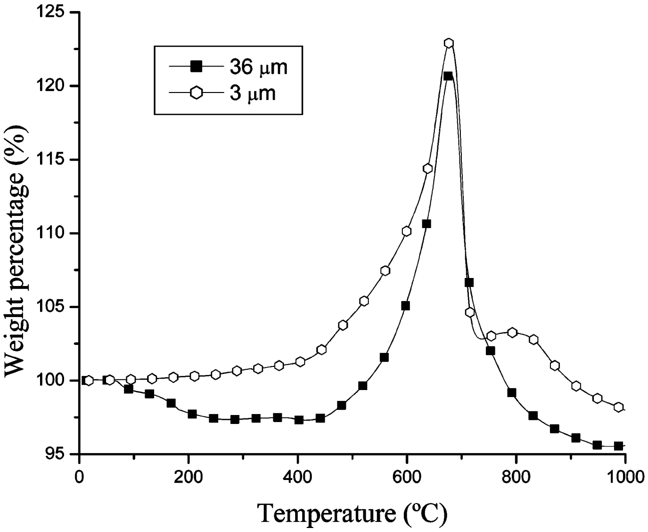

Figure 4. Thermogravimetric analyses of Li_4SiO_4, with different particle sizes, into a flux of CO_2.

CO_2 Sorption Process. As the two Li_4SiO_4 samples in pure form presented a considerable difference in their particle sizes, of 1 order of magnitude (36 and 3 μm), CO_2 absorption was analyzed on these samples. Figure 4 shows the thermograms of both samples, under a flux of 100% CO_2, which only gives a qualitative scheme of the CO_2 absorption behavior. First, the thermogram of the large particles presented a small loss of weight (≈2 wt %), between 80 and 200 °C. It was attributed to a dehydration process. In this case, water might be adsorbed by the Li_4SiO_4 during the air cooling of the powders. Then, the sample began to absorb CO_2 at around 450 °C, finishing this process at 680 °C. In this case, the maximum absorption was equal to 21 wt %. This value corresponds to 57.22% efficiency, in comparison with the maximum theoretical capacity of 36.7 wt %, assuming the following reaction:

$$Li_4SiO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \qquad (2)$$

Later, at temperatures higher than 680 °C, the sample presented a desorption process. These results are in good agreement with previous reports for this material.[19,22] On the other hand, the thermogram of the small particles presented two important differences. First, the CO_2 absorption process began at 350 °C. This is 100 °C lower than in the case of Li_4SiO_4 large particles. The only explanation of this effect would be associated with a higher reactivity due to the formation of small particles, which is associated with the presence of more lithium atoms over the surface of the particles, and consequently the generation of higher steam pressures on the grain boundaries and triple points produced among the Li_4SiO_4 particles.

The second difference takes place during the desorption process. In this case, desorption occurs through two steps. Initially, desorption proceeds in a straightforward manner, but it suddenly stops. Then, the sample presented a second small weight increase between 720 and 830 °C. This effect has been already reported for other lithium ceramics,[14] and it has been associated with a second absorption of CO_2. Apparently, the lithium ceramic decomposes and produces Li_2O. If Li_2O is produced, it reacts with CO_2 producing Li_2CO_3 that disappears later by thermal decomposition. This decomposition effect was

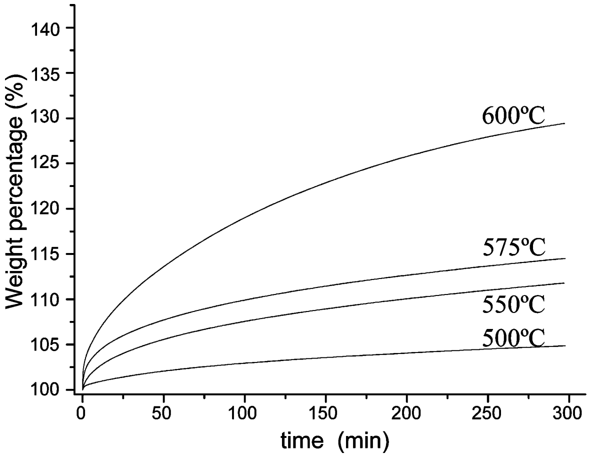

Figure 5. Isotherms of the CO_2 sorption on Li_4SiO_4 (large particles), into a flux of CO_2.

Table 1. Kinetic Parameters Obtained from the Isotherms of Li_4SiO_4 with Large Particles Fitted to a Double Exponential Model

temperature (°C)	k_1 (1/s)	k_2 (1/s)	R
500	2.0622	0.1884	0.99977
550	3.5568	0.2532	0.99968
575	4.8030	0.2946	0.99939
600	6.1698	0.3690	0.99988

not observed on the previous sample. Actually, it has been reported that Li_4SiO_4 can be recycled several times without any kind of degradation.[19] Therefore, the small particle size may be producing a faster decomposition, as most of the lithium is available to react or sublime over the surface of the particles. In fact, the final composition of this sample, determined by XRD, showed the presence of small quantities of Li_2SiO_3, which confirmed the loss of lithium. This result is in agreement with the high reactivity of lithium to capture CO_2, at lower temperatures, observed on the same sample. Finally, this sample absorbed 23 wt %, which corresponds to 62.67 wt % of the theoretical capacity.

Figure 5 shows the isothermal graphs of Li_4SiO_4 (large particles) at different temperatures. As it was expected, the sorption capacity increased as a function of the temperature. While at 500 °C the ceramic only absorbed 5 wt %, at 600 °C the absorption was equal to 30 wt %, after 5 h. Moreover, the four isotherms fitted to a double exponential model:

$$y = A \exp^{-k_1 x} + B \exp^{-k_2 x} + C \tag{3}$$

where y represents the weight percentage of CO_2 absorbed, x is the time, k_1 and k_2 are the exponential constants, and A, B, and C are the pre-exponential factors. The exponential constant values obtained at each temperature are presented in Table 1. As can be seen, k_1 (chemisorption) values are 10 times higher than those of k_2, which means that the limiting step of the total process is the lithium diffusion.

Furthermore, as the data adjusted to a double exponential, this means that there are two different processes taking place. Actually, it is already known that Li_4SiO_4 has the following CO_2 sorption mechanism. First, CO_2 reacts with the lithium present on the surface of the Li_4SiO_4 particles producing a Li_2CO_3 external shield. Later, once the external layer of lithium carbonate is totally produced, a diffusion process begins, where lithium has to diffuse throughout the carbonate layer in order to reach the surface and react with the CO_2.[23] Additionally, similar results have been obtained for other lithium ceramics.[13,16] For a model of these characteristics, the gradients of these best-fit lines usually follow an Arrhenius-type behavior, so that

$$D = D_0 \exp^{-E_a/RT} \tag{4}$$

where, D_0 is the reaction rate constant, E_a is the activation energy of the surface reaction or the diffusion process, R is the gas constant, and T is absolute temperature. Figure 6 shows the plots of ln D versus $1/T$. The curves clearly show a linear trend for both processes. Hence, the activation energies for the CO_2 absorption on Li_4SiO_4 and lithium diffusion throughout Li_2CO_3 were estimated to be 61 444 ± 1060 and 36 472 ± 740 J/mol, respectively. As can be seen, the activation energy of the chemisorption process is more dependent on the temperature, in comparison with the energy required for the lithium diffusion, in this range of temperatures.

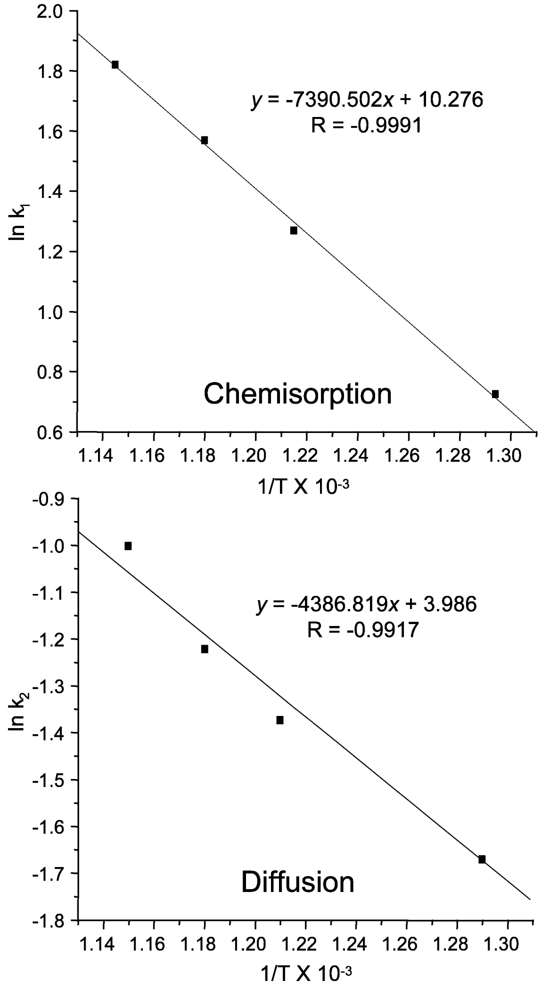

Figure 6. Plots of ln k versus $1/T$, for the two different processes, chemisorption (k_1) and diffusion (k_2), observed on the sample of Li_4SiO_4 with large particles.

In order to analyze the effect of the particle size on the kinetic reaction, the Li_4SiO_4 with small particle size (3 μm) was studied under the same conditions. Figure 7 shows the isothermal graphs of this sample at different temperatures. The behavior was similar to the results obtained in the previous sample. The only significant difference observed on the isotherms is the maximum absorption of CO_2 at 600 °C, which in this case was equal to 37.4 wt %, after 5 h. The efficiency exceeds, in this case, by almost 1 wt % the maximum theoretical capacity of CO_2 sorption on Li_4SiO_4 (36.7 wt %). Actually, the experimental data, of both samples heat-treated isothermally at 600 °C, were fitted to the double exponential model, and then, simulated

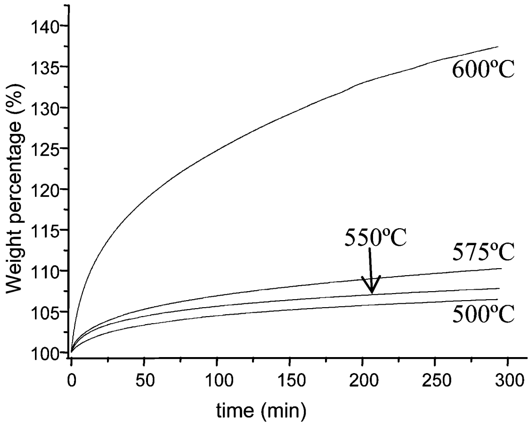

Figure 7. Isotherms of CO_2 sorption on Li_4SiO_4 (small particles), into a flux of CO_2.

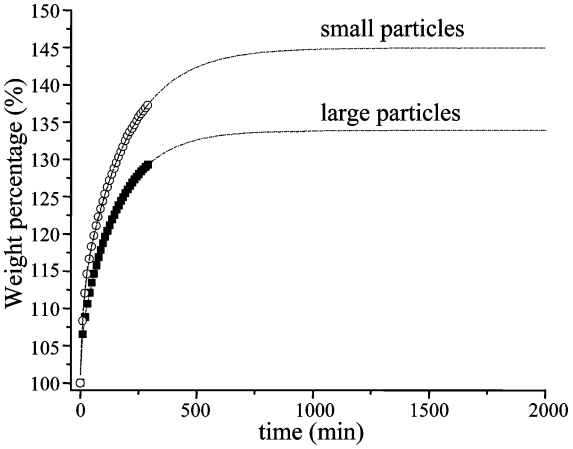

Figure 8. CO_2 sorption isotherms on large and small particles of Li_4SiO_4 at 600 °C, with the simulated extrapolated curves.

Table 2. Kinetic Parameters Obtained from the Isotherms of Li_4SiO_4 with Small Particles Fitted to a Double Exponential Model

temperature (°C)	k_1 (1/s)	k_2 (1/s)	R
500	3.3930	0.2616	0.99961
550	3.4002	0.3294	0.99976
575	4.5744	0.3582	0.99950
600	4.8126	0.3084	0.99986

graphs were extrapolated for longer times (Figure 8). In the large particles, according to the simulated graph, Li_4SiO_4 can absorb 33.7 wt %, which is very close the maximum theoretical capacity. On the contrary, the small particles can absorb up to 44.94 wt %, which is 8.24 wt % more than the increase of weight expected. Therefore, some CO_2 is been trapped by a different mechanism. Perhaps Li_2SiO_3 is reacting with CO_2 according to the following reaction:

$$Li_2SiO_3 + CO_2 \rightarrow Li_2CO_3 + SiO_2 \qquad (5)$$

This result was confirmed by XRD, where some SiO_2 was detected, as quartz and an amorphous phase.

This sample seems to have a more complex sorption mechanism, involving three different processes at least. For that reason, the experimental data was fitted to double and triple exponential models. The results clearly indicate that the double exponential model is the best one, because when the triple exponential model was analyzed, the results converged to a double exponential system. Therefore, assuming a double exponential model, the results are shown on Table 2. Again, the k_1 values are higher than k_2 values, indicating that chemisorption is faster than lithium diffusion. Following the same procedure, these data were fitted to the Arrhenius theory (Figure 9), but the results were not as good as those of the first data, as could be expected. This can be explained by the oversorption present in the samples, which implies some kind of interference on the data. Anyway, supposing that these results present linear trends, the activation energies for the CO_2 absorption on the small Li_4SiO_4 particles and its respective lithium diffusion throughout Li_2CO_3 were estimated to be 20 923 ± 1663 and 12 208 ± 1741 J/mol, respectively. Once more, temperature modifies chemisorption more evidently than lithium diffusion.

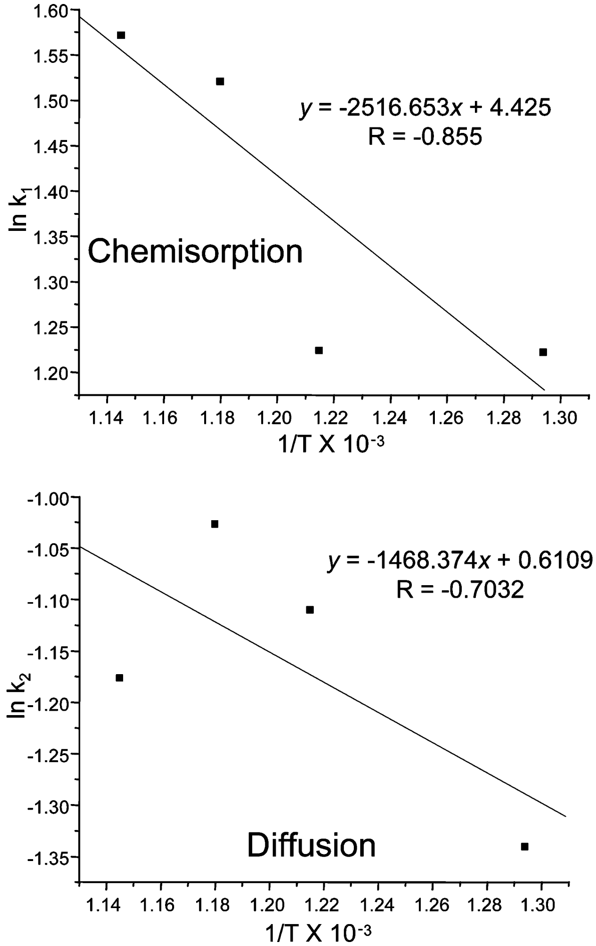

Figure 9. Plots of ln k versus $1/T$, for the two different processes, chemisorption (k_1) and diffusion (k_2), observed on the sample of Li_4SiO_4 with small particles.

When the activation energies of both materials are compared, some interesting results come out. The lithium diffusion activation energy, which is less dependent on temperature, diminishes when the particle size decreases as well, from 36 472 ± 740 to 12 208 ± 1741 J/mol. Actually, the value decreases three times. This effect can be simply explained by the differences between the diameters of the particles, which imply that lithium, on the small particles, does not have to diffuse at such long distances as on the large particles.

On the other hand, the activation energy of the chemisorption process decreases, as well, as a function of the particle size. In these cases, the energies varied from 61 444 ± 1060 to 20 923 ± 1663 J/mol. As it was already suggested for the thermogravimetric analysis, this sample may have a higher reactivity due to the formation of small particles, which is associated with the presence of more lithium atoms over the surface of the particles and the generation of different steam pressures on the grain boundaries and triple points.

Finally, in order to support these results, surface area analyses were performed on the samples. The results confirmed the differences between the samples. While the large particles had a surface area equal to 0.3421 m^2/g, the surface area of the small particles was 1.6683 m^2/g. Although none of the samples present significant surface areas, the small particles have almost 5 times more area. This result and the observation of tiny particles by SEM confirm the theory of the greater reactivity of the small Li_4SiO_4 particles.

Conclusions

Li_4SiO_4 was prepared by different techniques, and it was obtained in pure form when the samples were prepared by the solid-state and precipitation methods. However, all the samples prepared by sol−gel, using a microwave oven, provided a mixture of lithium silicates and quartz. According to the results, there are two different factors that inhibit the production of Li_4SiO_4 under these conditions. (1) TEOS polymerizes partially reducing its capability to react with the lithium present in the solution. (2) The use of microwaves seems to induce an earlier sublimation of lithium as Li_2O.

The particle size effect on the CO_2 sorption process was analyzed. Li_4SiO_4 synthesized with two different sizes (3 and 36 μm) was analyzed isothermically under a flux of CO_2. The results showed that the particle size may have modified the stability of the Li_4SiO_4 particles during the CO_2 sorption/desorption cycles. It seems that lithium sublimation, as Li_2O, is induced on the small particles.

Finally, both materials seem to adjust to the same CO_2 sorption mechanism: a chemical sorption process followed by a lithium diffusion process. However, the energies obtained in each material varied significantly. While the activation energies calculated for the large particles were 61 444 ± 1060 (chemisorption) and 36 472 ± 740 J/mol (diffusion), the same energies for the small particles were 20 923 ± 1663 and 12 208 ± 1741 J/mol. This means that the activation energies obtained for the large particles are roughly twice the values obtained for the small particles. The differences in the diffusion energies were explained simply by the geometrical differences between the diameters of the particles. On the contrary, the energy differences of the chemisorption processes were explained in terms of reactivity. The small particles should have a higher reactivity due to the presence of more lithium atoms over the surface of the particles and the generation of different steam pressures on the grain boundaries and triple points.

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