Influence of the K-, Na- and K-Na-carbonate additions during the CO2 chemisorption on lithium oxosilicate (Li8SiO6)

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Influence of the K-, Na- and K-Na-carbonate additions during the CO$_2$ chemisorption on lithium oxosilicate (Li$_8$SiO$_6$)

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Abstract: Lithium oxosilicate (Li$_8$SiO$_6$) was synthesized and mechanically mixed with potassium carbonate, sodium carbonate, or a mixture of both. While the product sample composition was characterized using X-ray diffraction, the CO$_2$ chemisorption was evaluated using dynamic (30–800 °C), isothermal (350–650 °C) and cyclic thermogravimetric analyses. The presence of the K, Na, or K-Na-carbonates in Li$_8$SiO$_6$ changes the sorption properties in a wide temperature range. K-, Na-, K-Na-Li$_8$SiO$_6$ samples captured a maximum weight of 32 wt% at 400 °C, 42 wt% at 550 °C, and 38 wt% at 600 °C, respectively. The results revealed that the weight gained on Li$_8$SiO$_6$ mixed with K-, Na- and K-Na-carbonates was attributed to the formation of the eutectic phases. These materials would be suitable for CO$_2$ capture over a wide temperature range depending on the application process. Nevertheless, the cyclic experiments showed important variations in their respective efficiencies, depending on the temperature.

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Keywords: chemisorption; CO$_2$ capture; lithium silicate; thermal analysis.

Introduction

Nowadays, the burning of fossil fuels is the main energy source for the world economy. One consequence of the use of these carbon-based fuels is the emission of huge carbon dioxide (CO$_2$) quantities into the atmosphere, creating environmental problems such as global climate change.[1–6]

One approach to solving such environmental problems is to capture and store CO$_2$.[4–8] CO$_2$ capture and storage (CCS), from post-combustion flue gas, has been recognized as a promising approach to alleviating global warming, representing a possible contribution estimated between 15 and 55% of mitigation measures to reduce CO$_2$ emissions from fossil-fuel burning in the mid- to long-term (2030–2100).[7–10] The capture of CO$_2$ emissions, at stationary point sources (e.g. power stations, smelters, and refineries), is considered a key technology for achieving greenhouse gas (GHG) reductions. The selection of the best CO$_2$ sorbent is not a simple task, as the typical operating temperatures involved are 500–900 °C, which would rule out the majority of traditional CO$_2$ sorbents, for example polymer-based

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membrane materials and amine solution.[11] Therefore, CCS in solids has been considered to be the most practical option as an efficient and cheap alternative to reducing GHGs.

Various CO$_2$ sorption materials are alkali metal-promoted alumina and carbonates, alkaline ceramics, calcium oxides, layered double hydroxides, zeolites, porous (active) carbons and metal-organic frameworks (MOFs).[4,5,9,12–13] These materials are reported to be capable of CO$_2$ capture at moderate and/or high temperatures.[8]

Among these materials, lithium silicates have been reported as good solid candidates for CO$_2$ sorbents in terms of large CO$_2$ sorption capacity and high operating temperatures.[14–28] Recently, Durán-Muñoz *et al.*[22] published that lithium oxosilicate (Li$_8$SiO$_6$) is able to capture CO$_2$ over a wide temperature range with an experimental maximum capacity of 11.8 mmol CO$_2$ per gram of ceramic (theoretical 16.6 mmol/g). In addition, they reported that the Li$_8$SiO$_6$-CO$_2$ mechanism depends on the reaction temperature. Besides, it has been proposed that the CO$_2$ chemisorption, on the alkaline ceramics, can be significantly improved when a different alkaline carbonate is added.[29–32] The CO$_2$ chemisorption process on these mixed alkaline ceramics produces a molten carbonate phase, decreasing the partial fusion process and consequently increasing different diffusion processes involved on the CO$_2$ capture reaction mechanism.[33]

Therefore, in the present work, sodium and/or potassium carbonates were mixed with lithium oxosilicate to investigate their CO$_2$ chemisorption properties. The study was focused on the alkaline cations influence during the CO$_2$ carbonation process over a wide temperature range (350–650 °C). The mixture of these alkaline carbonates produces eutectic phases, which may promote the diffusion processes. Additionally, the reutilization of the solid ceramics was analyzed. It was found that the regeneration would be more difficult for sintered particles than for fresh particles. Also the CO$_2$ chemisorption of each carbonate-content material depends on the temperature.

Experimental section

Li$_8$SiO$_6$ was synthesized via a solid-state reaction using silicon dioxide (SiO$_2$, Aldrich) and lithium oxide (Li$_2$O, Aldrich) as reagents. Powders were mixed and then thermally treated at 800 °C for 8 h. A lithium excess of 15 wt% was used to prevent lithium sublimation.[22,32,34] After the Li$_8$SiO$_6$ synthesis, the powder was mechanically mixed with 10 wt% of sodium carbonate (Na$_2$CO$_3$, Aldrich), or potassium carbonate (K$_2$CO$_3$, Aldrich), or a 50:50 wt% mixture of both carbonates (20 wt% in total). The samples were labeled as follow: The Na$_2$CO$_3$-Li$_8$SiO$_6$ sample was labeled as Na-Li$_8$SiO$_6$, the K$_2$CO$_3$-Li$_8$SiO$_6$ sample was labeled as K-Li$_8$SiO$_6$ and the K$_2$CO$_3$-Na$_2$CO$_3$-Li$_8$SiO$_6$ sample was labeled as K-Na-Li$_8$SiO$_6$.

The pure and carbonated Li$_8$SiO$_6$ samples preparation were characterized by X-ray diffraction using a diffractometer (Bruker AXS, D8 Advance) coupled to a copper anode X-ray tube (data not shown). Different CO$_2$ chemisorption experiments (dynamic, isothermal and cyclic) were performed using a Q500HR instrument from TA Instruments. Initially, the samples were dynamically heated from room temperature to 800 °C under a CO$_2$ atmosphere at 5 °C/min. Then, different isothermal experiments were acquired for each sample. Each isotherm was performed using fresh sample, where samples were heated up to the isothermal experiment (varying the temperature range) into an N$_2$ (Praxair, grade 4.0) atmosphere. Then, once the experimental temperature conditions were reached, the gas was switched from N$_2$ to CO$_2$. Thermal experiments were performed using a CO$_2$ gas flow rate of 60 ml/min (Praxair, grade 3.0). Finally, some of the Li$_8$SiO$_6$-CO$_2$ isothermal products were re-characterized using XRD. In addition, the cyclic experiments were performed at different temperatures, using N$_2$ as secondary gas for the desorption processes. Desorption processes were performed at 800 °C to guarantee the CO$_2$ desorption.

Finally, differential scanning calorimetry (DSC) experiments were performed using DSC equipment from Instruments Specialists Incorporated. Different Li-K, Li-Na and Li-K-Na carbonate mixtures were heated from room temperature to 600 °C at the rate of 10 °C/min, into a N$_2$ atmosphere, to elucidate the fusion temperature of each mixture.

Results and discussion

Samples were thermally treated under a CO$_2$ flow to determine the temperature range in which these materials were able to capture CO$_2$. Figure 1 shows the dynamic thermograms of the Na-, K- and K-Na-Li$_8$SiO$_6$ samples in comparison to the Li$_8$SiO$_6$ sample. Initially, all samples decrease in weight ($\leq$ 4.5 wt%)
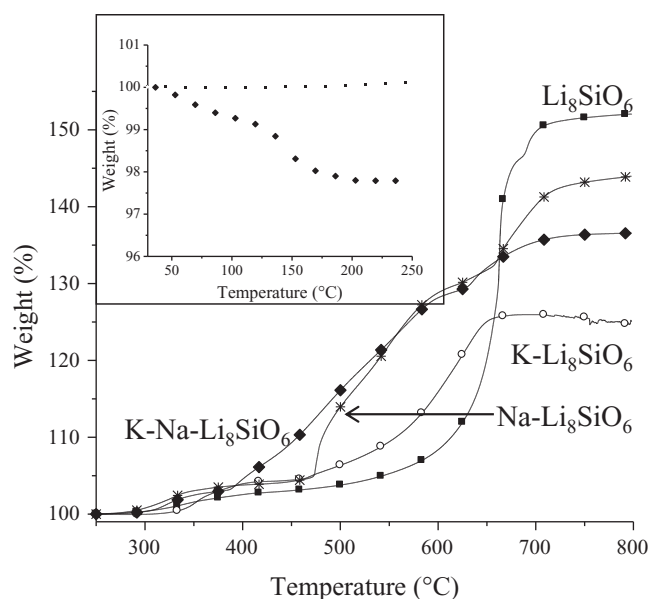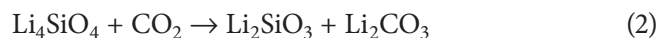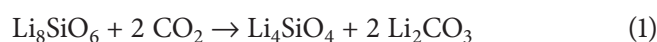
Figure 1. Dynamic thermogravimetric analysis in a CO$_2$ flux between 30 and 800 °C. The inset amplifies the gain weight (wt%) in the temperature range between 30 and 165 °C.

between 30 and 165 °C, where the amount of weight decreased as follows: K-Li$_8$SiO$_6$ > K-Na-Li$_8$SiO$_6$ > Na-Li$_8$SiO$_6$ (see inset in Fig. 1). This weight loss must be associated to the dehydration and dehydroxylation processes, induced by the sodium and/or potassium carbonates presence. After that, samples presented an initial weight increase of about 4.0 wt% between 265 and 420 °C, associated to a superficial CO$_2$ reaction, where an external lithium carbonate shell is formed over the surface of the lithium ceramic particles.[22,33] Then, each curve presented different weight increases, depending on the Na and/or K content. While the Na- and K- containing Li$_8$SiO$_6$ samples started to increase their weight between 400 and 450 °C, the Li$_8$SiO$_6$ sample began to increase its weight up to temperatures higher than 570 °C. Thus, the CO$_2$ chemisorption process continues through the bulk of the material.[33] However, in the Na-, K- or K-Na-samples the diffusion processes presented variations depending on the carbonate addition. The K-Li$_8$SiO$_6$ and Na-Li$_8$SiO$_6$ samples began to increase its weight at 465 °C, but in these cases the weight trend did not seem to be so different from the Li$_8$SiO$_6$ sample. In fact, the K-Li$_8$SiO$_6$ final weight was considerably low. In the Na-Li$_8$SiO$_6$ case, the weight increase occurred between 400 and 620 °C (up to ~30 wt%) and it was

considerably higher than that observed in the Li$_8$SiO$_6$ sample. Finally, the dynamic thermogram, which corresponds to the K-Na-Li$_8$SiO$_6$ sample, seems to present a synergetic weight increase attributed to the independent K and Na carbonates increments. However, at the highest temperatures (T ≥ 700 °C) none of the carbonated samples presented higher CO$_2$ capture than that observed in the pure Li$_8$SiO$_6$.

From these thermogravimetric experiments, other features must be mentioned. Previously, in the Li$_8$SiO$_6$ case, it was reported a two step reaction mechanism as follows:[22]

$$Li_8SiO_6 + 2\,CO_2 \rightarrow Li_4SiO_4 + 2\,Li_2CO_3 \qquad (1)$$

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

where, the beginning of the second reaction is indicated by an additional weight increase observed between 680 and 705 °C (Fig. 1). In the same way, the Na-Li$_8$SiO$_6$ and K-Na-Li$_8$SiO$_6$ samples presented a similar double weight increase, but the second process was initiated at lower temperatures (600–650 °C). Thus, the Li$_4$SiO$_4$ carbonation (reaction (2)) temperature is shifted to lower temperatures in the presence of Na or K-Na carbonate mixtures, but it may not be produced when potassium carbonate was added. Additionally, between 650 and 800 °C, the Na, K-Na and K-carbonate containing samples presented smaller final increases than pure Li$_8$SiO$_6$. All these features may be associated to different sintering processes, as the Li-K, Li-Na and Li-K-Na carbonate eutectic phases formation must favor faster sintering processes.[35]

To better understand the K-, Na- and K-Na-carbonate influence in the Li$_8$SiO$_6$-CO$_2$ reaction system, different isothermal experiments were performed. Figure 2(a) shows the isothermal experiments performed on the K-Li$_8$SiO$_6$ sample. The K-Li$_8$SiO$_6$ isotherm performed at 350 °C presented the typical exponential behavior, at which the final weight increased by 3.6 wt%. When this sample was isothermally treated at 400 °C a dramatic weight gain was observed, in comparison to the previous temperature. At this thermal condition, the sample chemisorbed 10 times more CO$_2$ (32.4 wt%). Additionally, the total weight increase was produced in two different steps. In the first 10 min, the sample gained 15.3 wt%, and immediately a second weight gain began up to the end of the weight increase. A similar behavior was observed in the isotherms performed between 450 and
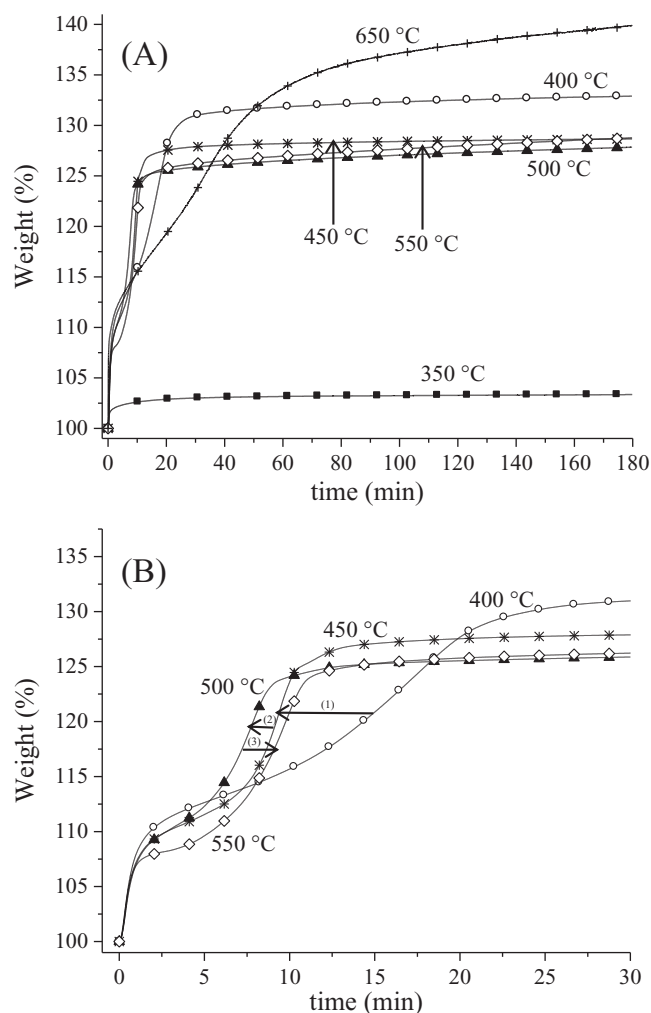
Figure 2. CO$_2$ chemisorption isotherms of K-carbonate addition in the Li$_8$SiO$_6$-CO$_2$ system at different temperatures (a) and CO$_2$ chemisorption isotherms at the first 30 min of the thermal processes (b).

550 °C. The sample treated at 650 °C presented a slightly different behavior as the second process seemed to be slower. Figure 2(b) shows the first 30 min of these isotherms. In the second reaction step, the curve at 500 °C was faster than the 450 and 400 °C isotherms, but at 550 °C this reaction is carried out slower. Finally, the isothermal CO$_2$ chemisorption was performed at 650 °C (Fig. 2(a)) and the weight increase was considerably improved. In this case, the diffusion process (second weight increment) was slower than those obtained at any other temperature. Thus, the high CO$_2$ capture must be produced through a different diffusion process, the intercrystalline one.

It must be noticed that even in the first reaction steps, the CO$_2$ capture produced more important

weight increases than those observed at 350 °C and in the pure Li$_8$SiO$_6$ sample treated at T ≤ 500 °C (6.7 wt%).[22] Therefore, to explain this behavior, three different factors must be taken into account. (i) Pure Li$_8$SiO$_6$ isotherms did not present the double step behavior.[22] (ii) It has been shown that K addition significantly increases the CO$_2$ chemisorption in the same temperature range ~400 °C.[20,27,29,32] (iii) The external shell produced during the CO$_2$ chemisorption of lithium and sodium ceramics may present some mesoporosity, when the reaction process is performed at T ≤ 550 °C.[22,36]

Based on the previous results, the following explanation may be proposed. At low temperatures, the CO$_2$ chemisorption must be mainly limited to the Li$_8$SiO$_6$ surface, as the diffusion processes have not been activated. Then, between 400 and 550 °C, the Li$_2$CO$_3$ surface product and the K$_2$CO$_3$ presence must produce an eutectic phase which partially fused. This liquid phase in addition to the mesoporous external shell microstructure[22] must improve the CO$_2$ diffusion, which is indicated in the isotherms through the second weight increase step. At temperatures higher than 550 °C, the mesoporosity disappears due to sintering effects and the CO$_2$ chemisorption process continues through out intercrystalline diffusion processes.[36] Figure 3 schematizes the thermal evolution involved in this reaction mechanism. First, between 300 and 465 °C, the sample gained ~4.5 wt%, attributed to the superficial reaction. The reaction between CO$_2$ and Li$_8$SiO$_6$ produced the external shell, which contains lithium carbonate (Li$_2$CO$_3$), potassium carbonate (K$_2$CO$_3$) and other lithium secondary phases (Li$_4$SiO$_4$ and Li$_2$SiO$_3$). The CO$_2$ sorption rate on Li$_8$SiO$_6$ is controlled by the CO$_2$ diffusion in the external shell. Between 400 and 550 °C, the CO$_2$ capture tended to increase. This weight increase suggests the subsequent activation of diffusive processes due to the liquid eutectic Li-K carbonate phase formation, which carries the CO$_2$ through the external shell mesoporosity,[20,27,29,32] up to the Li$_8$SiO$_6$ core shell. On the contrary, at T > 550 °C the CO$_2$ capture is reduced. It may be attributed to a sintering process, as on the Li$_8$SiO$_6$ phase. However, in the pure phase the sintering process was only observed at T > 650 °C. Thus, the sintering temperature may have been reduced by the fused eutectic phase.

Figure 4 shows the Na-Li$_8$SiO$_6$ isotherms. At 400 °C, there is an initial weight increase of 8.5 wt% during the first 5 min. After that, there is a lag time of
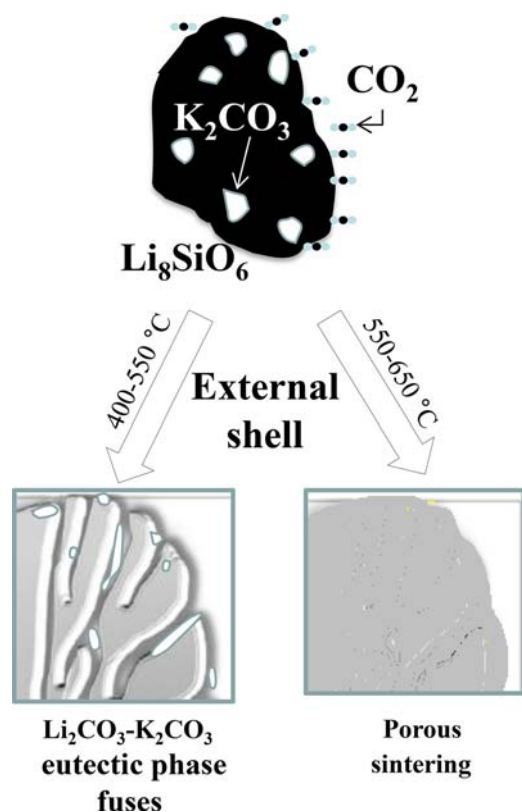
Figure 3. Schematic representation of the plausible K$_2$CO$_3$-Li$_8$SiO$_6$ CO$_2$ chemisorption mechanism.

approximately 85 min at which the weight increase could be considered negligible. Finally, the Na-Li$_8$SiO$_6$ sample presented the second reaction step, producing

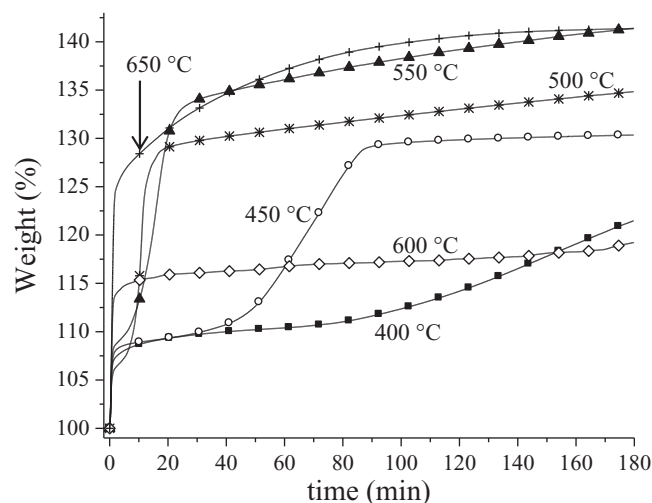a final increase of 21.6 wt%. In this case, the equilibrium was not reached. Once the Na-Li$_8$SiO$_6$ sample was treated at 450 °C, the sample isothermal trend was identical for the first isothermal part, although the second reaction-step was activated at shorter times (40 min). In addition, the weight increase did not vary during the first weight gain, but the final weight increment did increase up to 30.6 wt%. Samples treated at 500 and 550 °C presented similar behaviors (the final weight increases were 34 and 40 wt%, respectively), at which the second reaction steps were faster. Nevertheless, Na-Li$_8$SiO$_6$ samples treated between 600 and 650 °C presented a totally different trend. At these temperatures, simple growing exponential behaviors were observed with similar trends to the pure Li$_8$SiO$_6$ sample.[22] However, in this temperature range, the sodium addition decreased significantly the final weight increases (between 18 and 42 wt%) in comparison to the Li$_8$SiO$_6$ sample (between 31 and 52.2 wt%).

Based on the previously described mechanism (Fig. 3), it must be established that Na-Li$_8$SiO$_6$ presented the same general mechanism, but the sodium presence highly decrease the whole CO$_2$ chemisorption due to the sintering at T ≥ 600 °C. Hence, the weight increase differences, observed between 600 and 650 °C, must be attributed to the intercrystalline diffusion.

K-Na-Li$_8$SiO$_6$ isotherms are presented in Fig. 5. In this case, the double reaction step was not indicated. Here, weight increases were directly proportional to

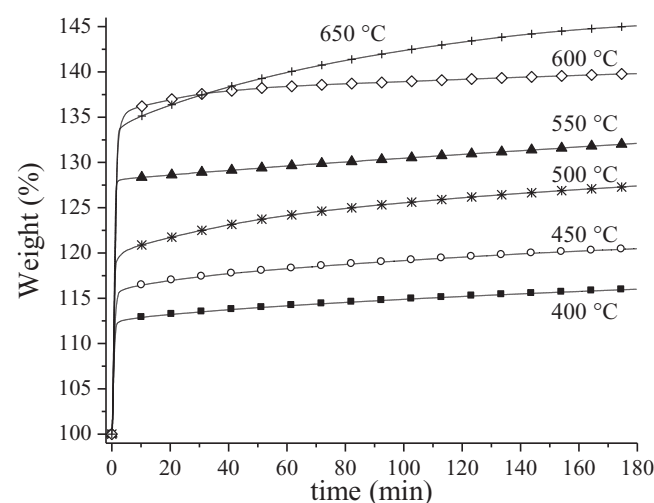**Figure 4.** CO$_2$ chemisorption isotherms of Na-carbonate addition in the Li$_8$SiO$_6$-CO$_2$ system at different temperatures.

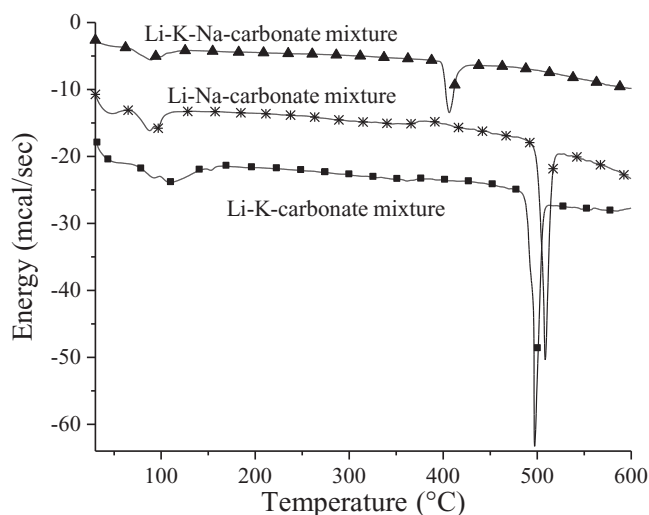**Figure 5.** CO$_2$ chemisorption isotherms of K-Na-carbonate addition in the Li$_8$SiO$_6$-CO$_2$ system at different temperatures.

Figure 6. DSC experiments of different alkaline carbonate mixtures.

Figure 7. CO$_2$ chemisorption isotherms of K-, Na-, K-Na-Li$_8$SiO$_6$ and pure Li$_8$SiO$_6$ at 400 °C.

the temperature; from 16.1 wt% at 400 °C to 45 wt% at 650 °C. Thus, two different options could be established: (i) the external shell did not present the same microstructural properties as the previous cases; or (ii) the Li-K-Na carbonate eutectic phase fuse faster than in the previous cases, producing indistinguishable weight increases. In fact, it has been published that Li-K-Na carbonate phase can partially fuse at temperatures as low as 397 °C, which is a lower temperature than those reported for the Li-K and Li-Na carbonate eutectic phases, 491 and 510 °C, respectively.[35]

Figure 6 shows the DSC experiments of different equimolar Li-K, Li-Na and Li-K-Na carbonate mixtures, as ideal eutectic models. Initially, at temperatures lower than 150 °C, there were different endothermic peaks associated to dehydration process of the alkaline carbonates. At higher temperatures, each carbonate mixture presents a well-defined endothermic peak at different temperatures, being the Li-K-Na carbonate mixture the one with the lowest fusion temperature, as it could be expected. Therefore, these results confirmed that Li-K-Na carbonate significantly decreased the partial fusion of the mixture, improving the CO$_2$ diffusion at temperatures as low as 400 °C.

Figures 7, 8, and 9 show comparative isotherms analysis at three different temperatures (400, 500, and 550 °C). Figure 7 shows the K-, Na-, K-Na- and pure Li$_8$SiO$_6$ isotherms performed at 400 °C. At this specific temperature, K and/or Na addition dramatically
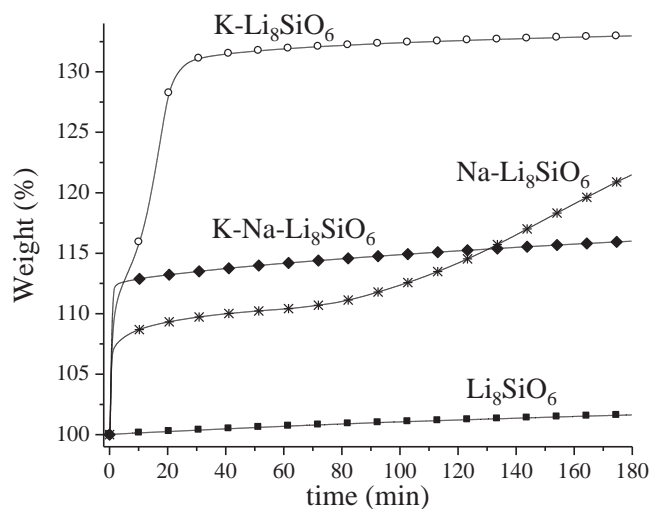
improves the CO$_2$ capture in Li$_8$SiO$_6$. Li$_8$SiO$_6$ only chemisorbed 1.6 wt%, while the K-, Na- and K-Na-Li$_8$SiO$_6$ samples chemisorbed 32.9, 21.5 and 15.9 wt%, respectively. In other words, the presence of these carbonates can improve the CO$_2$ capture ten times or more. Additionally, from this image it is possible to elucidate how the different eutectic carbonate phases fuse and consequently modify the CO$_2$ chemisorption behavior. The K-Li$_8$SiO$_6$ sample presented a better partial fusion than Na-Li$_8$SiO$_6$. However, when both alkaline elements (K-Na) were added, the CO$_2$
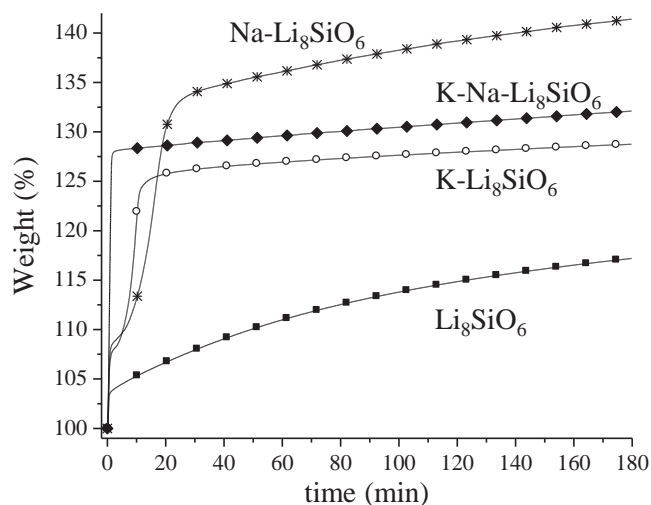

Figure 8. CO$_2$ chemisorption isotherms of K-, Na-, K-Na-Li$_8$SiO$_6$ and pure Li$_8$SiO$_6$ at 550 °C.
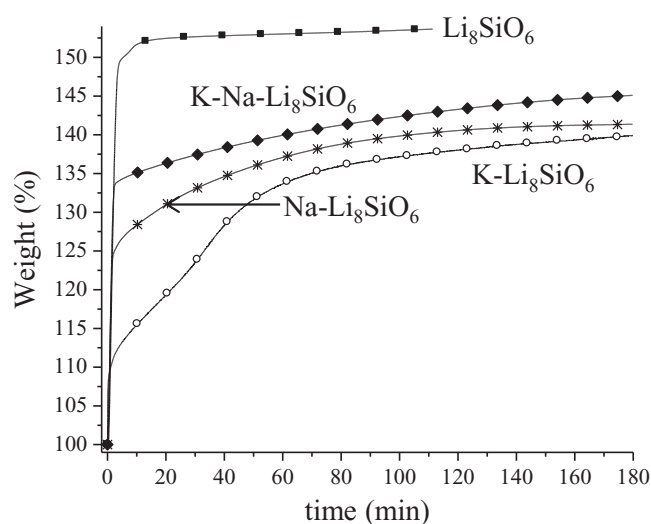
Figure 9. CO_2 chemisorption isotherms of K-, Na-, K-Na-Li_8SiO_6 and pure Li_8SiO_6 at 650 °C.

chemisorption was initially as fast as in the other samples, but at long period of time the CO_2 chemisorption reached the equilibrium. Here, the sintering process of the external shell must be enhanced due to the Li-Na-K carbonate fusion, which is produced at lower temperatures than the other possible mixtures. Thus, in the K-Na-Li_8SiO_6 sample the sintering process may have limited the CO_2 chemisorption process.

At 400 °C, the K-Li_8SiO_6 sample presented the highest CO_2 capture and the XRD pattern of the K-Li_8SiO_6 isothermal product (data not shown) indicated the presence of Li_8SiO_6, Li_4SiO_4 and Li_2CO_3 phases. This analysis suggests that reaction (1) has been partially produced. The presence of Li_8SiO_6 indicates an incomplete reaction. This assumption agrees with the fact that the final weight increase was 32.9 wt%, and considering that reaction (1) was completed the weight increase must be 49.0 wt%. Additionally, reaction (2) did not seem to take place as Li_2SiO_3 was not detected in the XRD pattern. These results are in agreement with the dynamic TG results, where the curve inflection was attributed to the Li_4SiO_4 carbonation, which was not detected (Fig. 1).

At 550 °C, the isotherms correlation slightly changed (Fig. 8) in comparison to the behavior observed at 400 °C. Li_8SiO_6 isotherm was, again, the sample that chemisorbed less CO_2 (17.1 wt%). However, the K-Li_8SiO_6 sample did not present the highest CO_2 chemisorption. In fact, it presented the lowest CO_2 chemisorption among the carbonated samples. Here, the K-, Na- and K-Na-Li_8SiO_6 samples

chemisorbed 28.7, 41.3, and 32.1 wt%, respectively. Therefore, the potassium carbonate addition decreased the CO_2 captured in comparison to the sodium case, although the CO_2 capture was favored with potassium over short times. As it was described previously, it may be associated to a faster sintering produced in the K-Li_8SiO_6 sample in comparison to the Na-Li_8SiO_6, which tends to close the external mesoporosity reducing the diffusion processes. In the K-Na-Li_8SiO_6 case, the CO_2 chemisorption was the fastest during the first minutes, but after the initial CO_2 chemisorption it was practically stabilized. It was a similar behavior than that observed at 400 °C.

At 550 °C, Na-Li_8SiO_6 was analyzed by XRD, as it was the sample that presented the highest weight increase (41.3 wt%). The crystalline phases detected were: Li_8SiO_6, Li_4SiO_4, Li_2SiO_3, Na_2CO_3 and Li_2CO_3. The presence of Li_4SiO_4 and Li_2SiO_3 confirms that reactions (1) and (2) have contributed in the CO_2 chemisorption. However, none of these reactions went to completion as Li_8SiO_6 and Li_4SiO_4 were detected. Reaction (2) was evidenced at this temperature and it is in good agreement with other reports showing that Li_4SiO_4 is able to chemisorb CO_2 between 460 and 580 °C.[16,23–28,34]

The last isothermal comparison was performed at 650 °C (Fig. 9). Potassium and/or sodium carbonate additions did not enhance the CO_2 chemisorption on Li_8SiO_6, as it had been described at lower temperatures. Initially, samples presented a very fast weight increase, followed by exponential growth curves, in which the initial and final weight increments followed this trend: K < Na < K-Na < Li_8SiO_6. As in the previous cases, the K- and/or Na-carbonate additions significantly increased the sintering process of the external shell, limiting the CO_2 capture through diffusion processes.

Figure 10 summarizes the maximum weight increase obtained in the isotherms, in which different factors must be pointed out. K- and Na-Li_8SiO_6 samples presented similar behaviors. The K-Li_8SiO_6 sample increases the CO_2 captured between 350 and 400 °C, being 400 °C the highest chemisorptions temperature. The increase observed between these temperatures may be associated to the Li-K carbonate partial fusion, which considerably increases the CO_2 diffusion through the porous external shell. At higher temperatures (450–550 °C), the K-Li_8SiO_6 presented smaller weight increases, which is associated to the porous sintering process. This process limits the CO_2
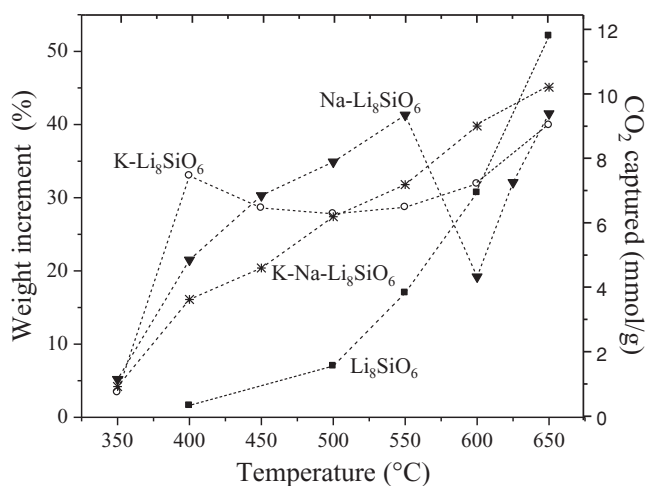
Figure 10. Comparative graph of K-, Na-, K-Na-Li$_8$SiO$_6$ and pure Li$_8$SiO$_6$ as function of CO$_2$ weight gained and millimoles chemisorbed on Li$_8$SiO$_6$, between 350 and 650 °C.

diffusion. Finally, at 600 and 650 °C the CO$_2$ capture was increased again. At these temperatures the external shell does not have a porous microstructure, so the weight increase must be related to the inter-crystalline diffusion processes.

Na-Li$_8$SiO$_6$ presented a similar behavior, but in this sample the phenomena were shifted to higher temperatures. Between 350 and 550 °C, the CO$_2$ capture tends to increase and the maximum CO$_2$ capture was shifted 150 °C in comparison to the K-Li$_8$SiO$_6$ case. Then, at higher temperatures, the sintering process decreases the CO$_2$ capture between 550 and 600 °C. Finally, as in the previous case, at T > 600 °C the CO$_2$ capture was increased due to the intercrystalline diffusion processes. In contrast, K-Na-Li$_8$SiO$_6$ and Li$_8$SiO$_6$ do not present the same trend. In these cases, both samples presented a continuous weight increase as a function of temperature. The K-Na-Li$_8$SiO$_6$ sample presented the Li-K-Na carbonate fusion at the lowest temperature, thus it may activate the sintering process faster, limiting the CO$_2$ porous diffusion. Consequently, the CO$_2$ capture must be highly controlled by the intercrys-talline diffusion processes.

The Li$_8$SiO$_6$ pure sample presented a constant weight increase between 400 and 650 °C, but only at 650 °C it presented a CO$_2$ capture higher than the carbonated samples. In this case, there is not formation of eutectic phases and CO$_2$ porous diffusion is not promoted at T ≤ 600 °C. The main CO$_2$ capture is produced at

high temperatures, once the intercrystalline diffusion processes are activated.

Overall, in this temperature range (350–650 °C) the maximum CO$_2$ capture is obtained by different samples according to the eutectic phases produced. While K-Li$_8$SiO$_6$ presented its better CO$_2$ capture conditions at 400 °C, Na-Li$_8$SiO$_6$ is the best CO$_2$ captor between 450 and 550 °C. The K-Na-Li$_8$SiO$_6$ sample presented the better CO$_2$ capture conditions at 600 °C and Li$_8$SiO$_6$ at T > 600 °C. As a result of this analysis, the Na and/or K carbonate addition on Li$_8$SiO$_6$ significantly improves the CO$_2$ capture, if this process is going to be performed at T < 600 °C. On the contrary Li$_8$SiO$_6$ does not need any carbonate addition at T > 600 °C.

To analyze the possible regeneration of these samples, different chemisorption-desorption cyclic experiments were performed. Figure 11 shows the maximum weight increases observed in each cyclic experiment performed on the different samples at different temperatures. According to the best CO$_2$ chemisorptions (Fig. 10), the cyclic experiments were performed at 400 and 550 °C for K-Li$_8$SiO$_6$ and Na-Li$_8$SiO$_6$, respectively. As it can be seen, both samples presented high weight increases (>30 wt%, ~3 mmol CO$_2$ per gram ceramic) during the first cycle. However, in subsequent cycles the CO$_2$ chemisorption decreased significantly. The decrease

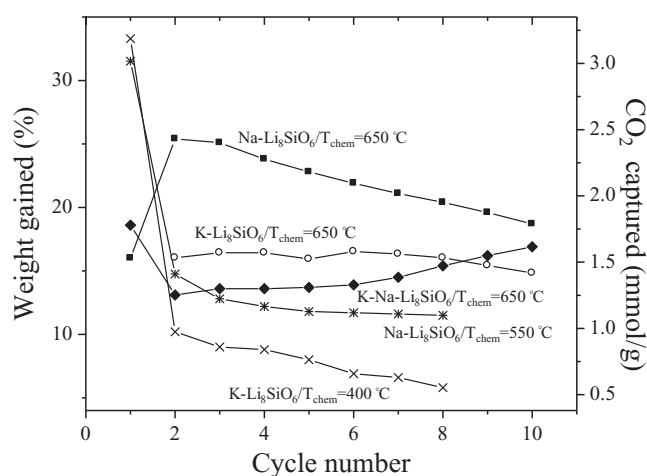**Figure 11.** Maximum experimental weight increments determined after each CO$_2$ chemisorption in the Li$_8$SiO$_6$, K-Li$_8$SiO$_6$, Na-Li$_8$SiO$_6$ and K-Na-Li$_8$SiO$_6$ samples. Desorption processes were performed into a N$_2$ flow at 800 °C, while the CO$_2$ chemisorptions were performed at different temperatures (labeled in the figure as T$_{chem}$).

observed on both samples must be associated to the desorption temperature (800 °C), which must induce the particles sintering, inhibiting the CO_2 chemisorption in the subsequent cycles. Although the CO_2 chemisorption decreased considerably with the number of cycles, it was always higher than that observed on the Li$_8$SiO$_6$ isotherm at the corresponding temperature.

Hence, the cyclic experiments were repeated at a higher temperature, 650 °C, once the intercrystalline diffusion processes are already active. At these new thermal conditions (CO_2 chemisorption 650 °C and desorption 800 °C) the K-, Na- and K-Na-Li$_8$SiO$_6$ samples were reevaluated. As it could be expected the first CO_2 chemisorption was not as high as in the previous case. However, the following cycles presented a more stable CO_2 chemisorption, due to the already activated intercrystalline diffusion processes. The samples chemisorbed between 1.5 and 2.5 mmol CO_2 per ceramic gram, which represents good values in comparison to other lithium ceramics.[37]

Conclusions

Li$_8$SiO$_6$ was synthesized via a solid-state reaction, and it was mixed mechanically with potassium, sodium, or potassium-sodium carbonates. Then, different CO_2 chemisorption experiments were performed (dynamic, isothermal and cyclic) using a thermogravimetric equipment. The presence of the K-, Na- and K-Na- carbonates into Li$_8$SiO$_6$ change the sorption properties in a wide temperature range, due to the eutectic phase's formation. The formation of eutectic phases improved the CO_2 diffusion between 400 and 550 °C, but once the chemisorption temperature was higher than 550 °C, the external shell sintered, producing the mesoporosity loss. Thus, at T > 550 °C the CO_2 chemisorption was controlled by intercrystalline diffusion processes.

The results revealed that potassium and/or sodium carbonate additions improved the total CO_2 chemisorption on Li$_8$SiO$_6$ at different temperature ranges. While the K-Li$_8$SiO$_6$ sample captures a maximum weight of 32.4 wt% at 400 °C, the Na-Li$_8$SiO$_6$ sample has a maximum weight increase of 42 wt% at 550 °C; and the K-Na-Li$_8$SiO$_6$ sample presented the maximum weight increase at 600 °C (38 wt%). In all cases, the CO_2 chemisorption was higher than that observed on Li$_8$SiO$_6$. However, when the CO_2 capture process was performed at 650 °C or higher temperatures, none of the carbonated samples chemisorbed more CO_2 than Li$_8$SiO$_6$.

Acknowledgments

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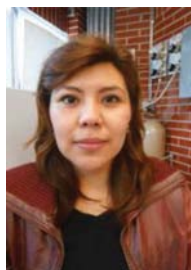
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