Textural, Structural, and CO_2 Chemisorption Effects Produced on the Lithium Orthosilicate by Its Doping with Sodium ($Li_{4-x}Na_xSiO_4$)

Victoria L. Mejía-Trejo, Esteban Fregoso-Israel, and Heriberto Pfeiffer*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n CU, Del. Coyoacán, CP 04510, México DF, Mexico

Received August 4, 2008. Revised Manuscript Received October 7, 2008

Solid solutions of lithium and sodium orthosilicate ($Li_{4-x}Na_xSiO_4$) were synthesized by coprecipitation. Samples were characterized by powder X-ray diffraction, scanning electron microscopy, N_2 adsorption, and thermogravimetric analyses (dynamic and isothermically). Results showed that the solubility limit of sodium into Li_4SiO_4 is 0.1, $Li_{3.9}Na_{0.1}SiO_4$. Sodium additions, higher than 0.1, produced the formation of secondary phases. Thermal analyses into a CO_2 flux showed that $Li_{4-x}Na_xSiO_4$ solid solutions present a much better CO_2 absorption than that observed for pure Li_4SiO_4. Isothermal analyses were performed to the samples in order to obtain kinetic information. These data were adjusted to double exponential model as there are two different processes taking place, the CO_2 absorption and diffusion processes. Nevertheless, in some cases, it was detected the presence of a third process, desorption. Those experiments were fitted to a triple exponential model. Finally the enthalpy activation energies for the different processes were calculated using the Eyring's model.

1. Introduction

Lithium ceramics are of research interest because of their technological applications. Among these ceramics, lithium silicates have been investigated as breeder materials for nuclear fusion reactors and as carbon dioxide absorbents, in addition to other more well-known applications such as in low thermal expansion glass-ceramics used in ceramic hobs.[1−5]

In the CO_2 capture field, so far, lithium orthosilicate (Li_4SiO_4) seems to be one of the best options to absorb CO_2. In this case, several authors have reported the CO_2 capture in this material through the following reaction.[6−11]

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3 \quad (1)$$

In addition, Li_4SiO_4 has a dense closed packed monoclinic crystalline structure with $a = 5.297$ Å, $b = 6.101$ Å, $c = 5.150$ Å, and $\beta = 90.251°$ cell parameters.[12] Li_4SiO_4 can be synthesized successfully from Li_2CO_3 and SiO_2 powder mixtures, as well as via crystallization of an amorphous powder produced by gelling tetraethyl orthosilicate (TEOS) and different lithium reagents.[5,13]

As this kind of ceramics has closed-packed structures, in general, the CO_2 absorption is usually limited because of the lithium diffusion process, which is activated after a lithium carbonate shell covers the surface of the lithium ceramic particles.[14] Therefore, as the limiting step is the diffusion process, different alternatives have been proposed to avoid or at least reduce this effect. For example, Venegas and co-workers[15] showed that particle size modifies the Li_4SiO_4 kinetic and efficiency of CO_2 capture. These results were explained in terms of reactivity for the chemisorption process. 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. Conversely, it has been published that some alkaline solid solutions, such as lithium−sodium zirconates ($Li_{2-x}Na_xZrO_3$)[16,17] and lithium−potassium zirconates ($Li_{2-x}K_xZrO_3$)[18] present better CO_2 properties than pure lithium or sodium zirconates. Moreover, it has been published that even small quantities of a doping component, such as potassium, enhances the CO_2 capture

---

* Corresponding author. Phone: 52 (55) 5622 4627. Fax: 52 (55) 5616 1371. E-mail: pfeiffer@iim.unam.mx.

(1) Kudo, H.; Okuno, K.; O'hira, S. *J. Nucl. Mater.* **1988**, *155−157*, 524–528.
(2) Wen, G.; Zheng, X.; Song, L. *Acta Mater.* **2007**, *55*, 3583–3591.
(3) Yamaguchi, T.; Niitsuma, T.; Nair, B. N.; Nakagawa, K. *J. Membr. Sci.* **2007**, *294*, 16–21.
(4) Essaki, K.; Kato, M.; Nakagawa, K. *J. Ceram. Soc. Japan* **2006**, *114*, 739–742.
(5) Pfeiffer, H.; Bosch, P.; Bulbulian, S. *J. Nucl. Mater.* **1998**, *257*, 309–317.
(6) Kato, M.; Nakagawa, K.; Essaki, K.; Maezawa, Y.; Takeda, Sh.; Kogo, R.; Hagiwara, Y *Int. J. Appl. Ceram. Technol.* **2005**, *2*, 467–475.
(7) Gauer, C.; Heschel, W. *J. Mater. Sci.* **2006**, *41*, 2405–2409.
(8) Essaki, K.; Nakagawa, K.; Kato, M.; Uemoto, H. *J. Chem. Eng. Jpn.* **2004**, *37*, 772–777.
(9) Kato, M.; Yoshikawa, S.; Nakagawa, K. *J. Mater. Sci. Lett.* **2002**, *21*, 485–487.
(10) Essaki, K.; Kato, M.; Uemoto, H. *J. Mater. Sci.* **2005**, *21*, 5017–5019.
(11) Escobedo-Bretado, M.; Guzmán-Velderrain; V.; Lardizábal-Gutiérrez, D.; Collins-Martínez, V.; Lopez-Ortiz, A. *Catal. Today* **2005**, *107−108*, 863–867.
(12) McMurdie, H. F. *Powder Diffr.* **1986**, *1*, 334–339.
(13) Khomane, R. B.; Sharma, B. K.; Saha, S.; Kulkarni, D. *Chem. Eng. Sci.* **2006**, *61*, 3415–3418.
(14) Mosqueda, H. A.; Vazquez, C.; Bosch, P.; Pfeiffer, H. *Chem. Mater.* **2006**, *18*, 2307–2310.
(15) Venegas, M. J.; Fregoso-Israel, E.; Escamilla, R.; Pfeiffer, H. *Ind. Eng. Chem. Res.* **2007**, *46*, 2407–2412.
(16) Pfeiffer, H.; Lima, E.; Bosch, P. *Chem. Mater.* **2006**, *18*, 2642–2647.
(17) Pfeiffer, H.; Vazquez, C.; Lara, V. H.; Bosch, P. *Chem. Mater.* **2007**, *19*, 922–926.
(18) Veliz-Enriquez, M. Y.; Gonzalez, G.; Pfeiffer, H. *J. Solid State Chem.* **2007**, *180*, 2485–2492.

10.1021/cm802132t CCC: $40.75

capacity of lithium ceramics.[19] Hence, mixed compounds Na doped Li_4SiO_4 ceramics could present similar behaviors in CO_2 sorption than those observed for other materials. Therefore, the aim of this paper was to study the synthesis of $Li_{4-x}Na_xSiO_4$ solid solutions, characterize them systematically, and then analyze, kinetically, the CO_2 absorption capacity on the $Li_{4-x}Na_xSiO_4$ solid solutions.

2. Experimental Section

Lithium orthosilicate (Li_4SiO_4) and different solid solutions ($Li_{4-x}Na_xSiO_4$) were synthesized by the coprecipitation method. Actually, these nominal values were used to label the samples, for example $Li_{3.8}Na_{0.2}SiO_4$. The materials were produced from an aqueous solution of tetraethyl-orthosilicate (TEOS, Si-$(OCH_2CH_3)_4$, Aldrich), lithium carbonate (Li_2CO_3, Aldrich) and sodium carbonate (Na_2CO_3, Aldrich). Reactions were performed using alkaline:Si molar ratios of 4:1, to obtain $Li_{4-x}Na_xSiO_4$. First, alkaline carbonates, Na_2CO_3 and Li_2CO_3, were dissolved in water. TEOS was, then, slowly added drop by drop to the solutions. The mixture obtained was stirred and heated at 70 °C until it dried. Finally, the different powders were heat-treated at 900 °C for 6 h.

The samples were characterized by different techniques such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption, 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 compounds were identified conventionally using the JCPDS database. SEM (Stereoscan 440, Leica-Cambridge) was used to determine the particle size and morphology of the materials. The samples were covered with gold to avoid a lack of electrical conductivity. Surface area analyses were performed on an ASAP 2020 Analyzer (Accelerated Surface Area and Porosimetry) from Micromeritics. As these materials usually present very poor surface areas, the filler rod accessory was used to reduce the experimental error. The N_2 adsorption isotherms were determined at 77 K by volumetric adsorption. Before the N_2 adsorption process, all the samples (~150 mg) were outgassed at 200 °C for 12 h. Surface areas were calculated with the BET equation. Finally, different thermal analyses were performed in a Hi-Res TGA 2950 thermogravimetric analizer equipment from TA Instruments. A set of samples was heat-treated, with a heating rate of 5 °C min^{-1}, from room temperature to 1000 °C. These analyses were carried out into a CO_2 flux (Praxair, grade 3.0). Additionally, other samples were analyzed isothermically under an atmosphere of CO_2, at 500, 550, 575, 600, and 650 °C for 5 h into the same CO_2 flux.

3. Results and Discussion

3.1. Characterization. After the synthesis of the different solid solutions ($Li_{4-x}Na_xSiO_4$), the samples were characterized by XRD. The results are presented on the figure 1. Li_4SiO_4 diffraction pattern fitted very well to the JCPDS file 37−1472, which corresponds to the same compound. Once the sodium addition started, the sample with $x = 0.1$ showed only the presence of Li_4SiO_4. However, when the x value was increased to 0.15 or higher quantities (0.2 and 0.3), different phases were detected: Li_3NaSiO_4 and Li_2SiO_3. Therefore, the solubility limit of sodium into Li_4SiO_4 seems to be 0.1, $Li_{3.9}Na_{0.1}SiO_4$. Such result may be attributed to the difference in atomic radii of lithium and sodium, 2.05 and 2.23 Å, respectively and the closed packed structure of the silicate.[20,21] Consequently, sodium atoms are not expected to diffuse so much into the Li_4SiO_4 network. Actually, in a previous work it was reported that sodium was not able to produce a solid solution with lithium metazirconate (Li_2ZrO_3), this work probed the formation of a different phase (Na_2ZrO_3) occluded in the Li_2ZrO_3.[16] Hence, a different option could be that sodium would not have reacted producing a solid solution, instead very small particles of a different phase could be produced, such as Li_3NaSiO_4, and they were not identified in the first samples because its abundance is beyond the XRD resolution. If that were the case, this secondary phase may be located on the surface and/or occluded into the Li_4SiO_4 particles.

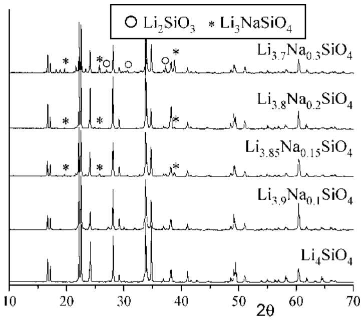

Figure 1. XRD patterns of different $Li_{4-x}Na_xSiO_4$ samples. Only the peaks corresponding to phases different than Li_4SiO_4 were labeled.

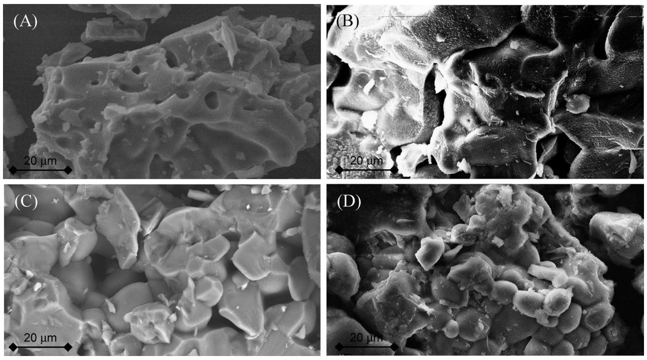

Figure 2. SEM images of different $Li_{4-x}Na_xSiO_4$ samples: (A) Li_4SiO_4, (B) $Li_{3.9}Na_{0.1}SiO_4$, (C) $Li_{3.8}Na_{0.2}SiO_4$, and (D) $Li_{3.7}Na_{0.3}SiO_4$.

SEM analysis showed some interesting results (Figure 2). Li_4SiO_4 sample presented large and dense particles, with a particle size of around 96 μm, having a polyhedral shape. However, this morphology was changing as a function of the sodium content. It seemed that sodium inhibited the growing of the particles. As the sodium content was increased, the particles seemed to become smaller, up to 25 μm for the $Li_{3.7}Na_{0.3}SiO_4$ sample, forming agglomerates among them. As a consequence of this effect, the material seemed to have a higher surface area. SEM observations were, in fact, corroborated by the N_2 adsorption analyses. All the samples presented isotherms of type III, exhibiting a very narrow H3 type hysteresis loops, according to the

---

(19) Ida, J. I.; Xiong, R.; Lin, Y. S. *Sep. Purif. Technol.* **2004**, *36*, 41–51.

(20) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 9th ed.; Limusa Noriega: Mexico City, Mexico, 2001.

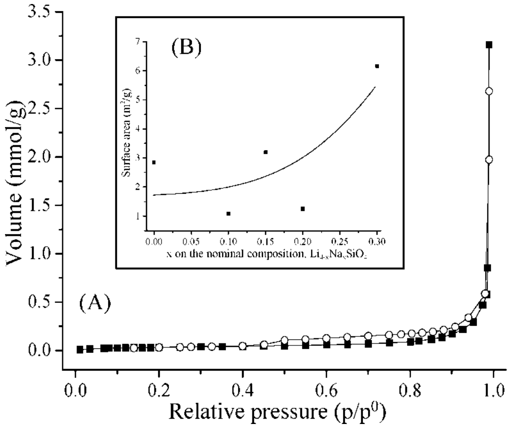

Figure 3. Nitrogen isotherm for Li_4SiO_4 sample (A) and BET surface area trend observed as a function of the x value on $Li_{4-x}Na_xSiO_4$ (B).

IUPAC classification (Figure 3A). This behavior corresponds to aggregates of nonporous materials, as it could be expected. Although the BET surface areas presented a high dispersion (which can be attributed to the low surface areas obtained, which of course increase considerably the experimental errors), they showed an increasing trend, as a function of the sodium addition. The surface areas were double, increased from about 3 to 6 g/m^2 for Li_4SiO_4 and $Li_{3.7}Na_{0.3}SiO_4$, respectively (Figure 3B). The surface area increased twice, which is in good agreement with the formation of smaller particles as a function of the sodium addition observed by SEM. Therefore, sodium addition, into the Li_4SiO_4 system, acted as a growing controller of the particle size. These results strongly suggest that although some sodium atoms may be into the Li_4SiO_4 crystalline structure, most of these atoms are mainly located over the surface of the particles, inhibiting the growing of the particles.

3.2. CO_2 Absorption. As was previously mentioned, Li_4SiO_4 is a good CO_2 absorbent material. Conversely, it has been probed, for other ceramics, that addition of sodium enhances CO_2 absorption on lithium ceramics.[6−11,17,18] Then, if $Li_{4-x}Na_xSiO_4$ ceramics present a synergetic effect, they should capture CO_2 more efficiently than Li_4SiO_4 pure, and the reaction should be

$$Li_{4-x}Na_xSiO_4+CO_2 \leftrightarrow Li_{2-x}Na_{x/2}CO_3+Li_{2-x}Na_{x/2}SiO_3$$

where $Li_{2-x}Na_{x/2}CO_3$ represents only a mixture of Li_2CO_3 and Na_2CO_3.

In Figure 4, it can be seen that all samples absorbed CO_2. First, Li_4SiO_4 presented a standard CO_2 absorption, as previously reported.[15] 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 12 wt %. Later, at temperatures higher than 680 °C, the sample presented a desorption process. The second sample analyzed was $Li_{3.9}Na_{0.1}SiO_4$, which did not show any change in comparison with the Li_4SiO_4. However, the $Li_{3.85}Na_{0.15}SiO_4$ sample showed a significant improvement on the CO_2 absorption. It increased on 7.3 wt %, getting a total CO_2 absorption equal to 19.3 wt %. Besides, the absorption seemed to be faster in this sample, due to the higher slope observed on the sorption temperature range, in comparison to the two first samples. In addition, this sample presented a second important difference, which took place on desorption temperature range. Desorption proceeds in a straightforward manner initially, but it suddenly stops. Then, a second small weight increase was detected. This effect has been reported for other lithium ceramics.[22] Apparently, there is lithium sublimation as Li_2O. This decomposition effect was not observed on the previous samples. Actually, it has been reported that Li_4SiO_4 can be recycled several times without any kind of degradation.[7] Therefore, the presence of sodium may be producing a faster decomposition of the Li_4SiO_4, or sodium atoms are the element that is sublimating by itself, perhaps as Na_2O. Finally, $Li_{3.8}Na_{0.2}SiO_4$ and $Li_{3.7}Na_{0.3}SiO_4$ presented similar behaviors. Nevertheless, the quantity of CO_2 absorbed decreased as a function of the sodium addition. It should be pointed out that although these results (Figure 4) are just qualitative, small quantities of sodium seem to act as a promoter of the CO_2 absorption. If sodium atoms are located at surface, according with the XRD and SEM analyses, they may be acting as active reactive sites for the CO_2 capture.

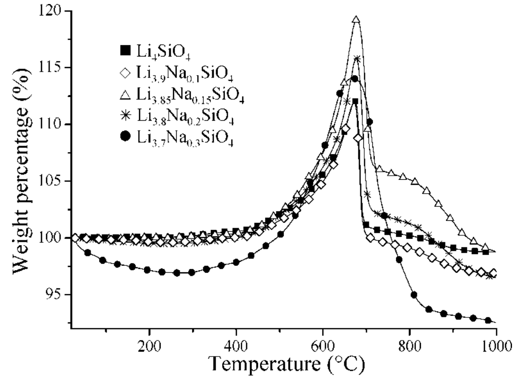

Figure 4. Thermogravimetric analyses of different $Li_{4-x}Na_xSiO_4$ samples into a CO_2 flux.

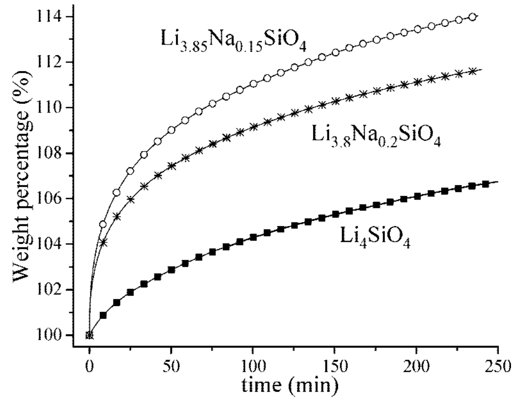

Figure 5. Isothermal analyses of $Li_{4-x}Na_xSiO_4$ samples heat-treated at 500 °C into a flux of CO_2.

To further understand the CO_2 absorption on these ceramics, we performed some extra experiments. Figure 5 shows the isothermal graphs of Li_4SiO_4, $Li_{3.85}Na_{0.15}SiO_4$, and $Li_{3.8}Na_{0.2}SiO_4$ at 500 °C. As in the dynamic TGA, samples containing sodium, $Li_{3.85}Na_{0.15}SiO_4$, and $Li_{3.8}Na_{0.2}SiO_4$, absorbed more CO_2 than Li_4SiO_4. In fact, Li_4SiO_4 is the sample

---

(22) Pfeiffer, H.; Bosch, P. *Chem. Mater.* **2005**, *17*, 1704–1710.
(23) Zhao, T.; Rønning, M.; Chen, D. *Chem. Mater.* **2007**, *19*, 3294–3301.

Table 1. Kinetic Parameters Obtained from the Isotherms of Lithium−Sodium Silicates Fitted to a Double Exponential Model

sample	k_1 (s^{-1})	k_2 (s^{-1})	A	B	C^a	R
Li_4SiO_4	3.3×10^{-4}	2.0×10^{-5}	−12.158	−2.744	115.190	0.9994
$Li_{3.85}Na_{0.15}SiO_4$	2.23×10^{-3}	1.3×10^{-4}	−5.542	−9.715	115.071	0.9985
$Li_{3.8}Na_{0.2}SiO_4$	1.76×10^{-3}	1.2×10^{-4}	−3.455	−8.073	113.063	0.9991

[a] C values varied from 100 as a consequence of the initial dead times and variation of mass (dehydration) presented in each isothermal experiment.

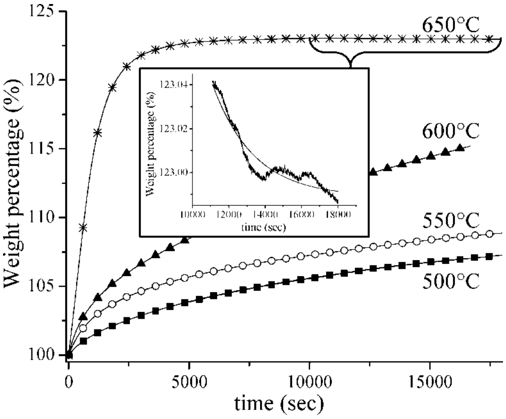

Figure 6. CO_2 absorption isothermal analyses of Li_4SiO_4 sample at different temperatures into a flux of CO_2.

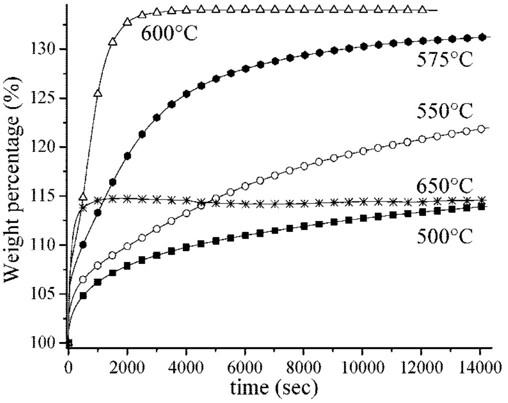

Figure 7. CO_2 absorption isothermal analyses of $Li_{3.85}Na_{0.15}SiO_4$ sample at different temperatures into a flux of CO_2.

that absorbed CO_2 at slower rate in comparison to the two solid solutions, as the slopes of these curves (at short times, 0−10 min) are 0.09, 0.43, and 0.52 wt % min^{-1} for Li_4SiO_4, $Li_{3.85}Na_{0.15}SiO_4$, and $Li_{3.8}Na_{0.2}SiO_4$, respectively. These results confirm that sodium addition does enhance the CO_2 absorption up to 5 times, at short times, acting as reactive active sites. The decrement, of CO_2 absorption observed for sample $Li_{3.8}Na_{0.2}SiO_4$ in comparison to the $Li_{3.85}Na_{0.15}SiO_4$ sample, should be attributed to the presence of secondary phases (Li_3NaSiO_4 and Li_2SiO_3) which do not absorb CO_2 and may inhibit the absorption.

It has been reported that CO_2 chemisorption on Li_4SiO_4 fits to a double exponential model ($y = A\exp^{-k_1t} + B\exp^{-k_2t} + C$), as there are two different processes taking place, the chemisorption and the lithium diffusion.[15] Table 1 shows the kinetics parameters obtained from the isotherms of the three samples, Li_4SiO_4 and both solid solutions, fitted to the same double exponential model. Some interesting results come out from this table. First, the chemisorption constant (k_1) increased 1 order of magnitude with the sodium addition. In other words, it confirms that CO_2 absorption reactivity is higher due to the sodium presence. Again, the difference observed between $Li_{3.85}Na_{0.15}SiO_4$ and $Li_{3.8}Na_{0.2}SiO_4$ should be attributed to the presence of secondary phases. A similar situation occurs for the diffusion constant (k_2). $Li_{3.85}Na_{0.15}SiO_4$ and $Li_{3.8}Na_{0.2}SiO_4$ diffusion constants (k_2) are again 1 order of magnitude faster than that of Li_4SiO_4, but it does not change between them. Apparently, the diffusion process is not longer enhanced by the addition of some extra sodium, from $Li_{3.85}Na_{0.15}SiO_4$ to $Li_{3.8}Na_{0.2}SiO_4$.

On the basis of the previous results, Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$ were further analyzed at different temperatures. Isotherms of these two samples are shown in Figures 6 and 7, which were fitted to double or triple exponential models. Figure 6 shows the isothermal graphs of Li_4SiO_4 at different temperatures. As was expected, qualitatively, CO_2 absorption increased as a function of the temperature. Although after 5 h at 500 °C, the ceramic absorbed only 7.2 wt %, at 650 °C, the absorption was increased up to 23 wt % in the same period of time. For this sample, only the isotherms performed at 500, 550, and 600 °C could be fitted to a double exponential model. On the contrary, the isotherm performed at 650 °C was fitted to a triple exponential model, because it was evidenced desorption process at long times (Figure 6, inset). The exponential constant values obtained at each temperature are presented in Table 2. As can be seen, k_1 (chemisorption) values are at least 1 order of magnitude higher than those of k_2, which means that the limiting step of the total process is the lithium diffusion. These results are in total agreement to previous reports.[15,24] Furthermore, desorption constant value (k_3), observed at 650 °C, is smaller than k_1. Therefore, the absorption is 10 times favored over the desorption process.

Table 2. Li_4SiO_4 Kinetic Parameters Obtained at Different Temperatures, Using a Double or Triple Exponential Model

T (°C)	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	R
500	3.3×10^{-4}	2×10^{-5}		0.9994
550	6.9×10^{-4}	4×10^{-5}		0.9995
600	1.27×10^{-3}	7×10^{-5}		0.9997
650	3.71×10^{-3}	1.9×10^{-4}	5.1×10^{-4}	0.9984

A similar, but more drastic, behavior was observed on the isotherms of the $Li_{3.85}Na_{0.15}SiO_4$ sample (Figure 7). In this case, desorption process was detected at 600 °C, which is a decrement of 50 °C, in comparison to Li_4SiO_4. Moreover, the isotherm performed at 650 °C evidenced dramatically the presence of desorption process. Actually, CO_2 desorption got some equilibrium with the absorption process before the material could reacted totally. For this reason, only 14 wt % increment was obtained. Therefore, it is clearly evident that $Li_{3.85}Na_{0.15}SiO_4$ cannot be used as CO_2 absorbent at temperatures higher than 575 °C, otherwise, the desorption process is activated.

---

(24) Alcérreca-Corte, I.; Fregoso-Israel, E.; Pfeiffer, H. *J. Phys. Chem. C* **2008**, *112*, 6520–6525.

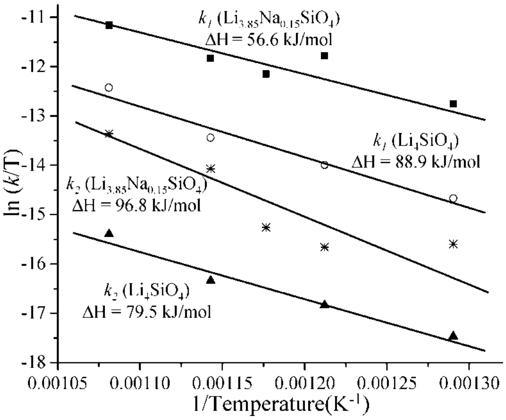

Figure 8. Eyring's plots for the rate constants chemisorption (k_1) and diffusion (k_2) processes for Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$.

Table 3. $Li_{3.85}Na_{0.15}SiO_4$ Kinetic Parameters Obtained at Different Temperatures, Using a Double or Triple Exponential Model

T (°C)	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	R
500	2.23×10^{-3}	1.3×10^{-4}		0.9991
550	6.33×10^{-3}	1.3×10^{-4}		0.9989
575	4.50×10^{-3}	2.0×10^{-4}		0.9982
600	6.38×10^{-3}	6.7×10^{-4}	1.1×10^{-5}	0.9536
650	1.32×10^{-2}	1.46×10^{-3}	9.4×10^{-4}	0.9832

Although desorption process was activated at 600 °C or higher temperatures, the kinetic constant values were higher than those obtained for the Li_4SiO_4 sample (Table 3). As it can be observed, both chemisorption and diffusion constant values were enhanced by the sodium addition. While, the chemisorption process was improved 1 order of magnitude, the diffusion process was improved four times. In addition, desorption constant value increased in 2 orders of magnitude, raising only 50 °C the temperature of analysis. Therefore, CO_2 absorption kinetics and lithium diffusion were highly improved by the sodium addition, although the thermal stability of these materials seem not to be as good as Li_4SiO_4.

To analyze the temperature dependence of the different processes, the Eyring's model was used, as it can be used on solid−gas system reactions. The effect of temperature on the rate constants of the chemisorption and diffusion processes, for Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$, are illustrated in Figure 8. It is clear that plots of $\ln(k/T)$ versus $1/T$ describe linear trends, fitting Eyring's model. Therefore, fitting the data to linear plots gave the activation enthalpies ($\Delta H^{\ddagger}$) for the different processes. Some interesting results come out from these data. First, $\Delta H^{\ddagger}$ values for the chemisorption process decreased by the sodium addition. The $\Delta H^{\ddagger}$ values obtained were 88.9 and 56.6 kJ/mol for Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$, respectively. The $\Delta H^{\ddagger}$ decreased 36.3% because of the presence of sodium. This result clearly shows that CO_2 chemisorption on Li_4SiO_4 is more dependently to temperature. On the other hand, $\Delta H^{\ddagger}$ obtained for the diffusion processes presented an inverse behavior. Although Li_4SiO_4 gave a $\Delta H^{\ddagger}$ of 79.5 kJ/mol, $\Delta H^{\ddagger}$ of $Li_{3.85}Na_{0.15}SiO_4$ increased up to 96.8 kJ/mol. In means that diffusion process on $Li_{3.85}Na_{0.15}SiO_4$ is more dependent on temperature than Li_4SiO_4. It could be produced by the sodium atoms in terms of mass and size, which should compromise the diffusion process as a function of energy obtained from temperature. Summarizing, it could be said that sodium atoms located on the surface favor the chemisorption process, decreasing the energy necessary for the reaction. However, sodium atoms do not seem to help with the whole diffusion process; as the $\Delta H^{\ddagger}$ is increased, this process becomes more dependent on temperature. Again, these results suggest that most of the sodium atoms should be located over the surface of the particles, importantly increasing the CO_2 absorption, but inhibiting the lithium diffusion.

Conclusions

Li_4SiO_4 doped with sodium was prepared by the precipitation method and the limit of solubility, determined by XRD for the $Li_{4-x}Na_xSiO_4$ solid solutions, was obtained. In this case, the limit for the solid solution was $Li_{3.9}Na_{0.1}SiO_4$. As lithium is a smaller and lighter atom than sodium, the quantity of sodium that could be added into the Li_4SiO_4 structure was not high, only the 2.5% of the whole alkaline atoms could be interchanged. Additionally, the sodium addition to the Li_4SiO_4 system produced important changes in the textural properties of the ceramics. The particle size of the ceramic decreased as a function of the sodium addition, and therefore its surface area increased. Another explanation proposed for this behavior is that most of the sodium atoms are located over the surface of the Li_4SiO_4 particles and not in its crystalline structure. In any case, sodium atoms were stabilized.

The addition of sodium to the Li_4SiO_4 produced an important increase in the kinetic reaction of the CO_2 absorption, it compared to pure lithium silicate. All the samples presented a similar behavior on the dynamic absorption process. Nevertheless, the isothermal experiments probed an important increase in CO_2 absorbed as a function of the sodium added. It seems that sodium atoms are acting as reactive active sites for the CO_2 capture, on the basis of the fact that most of these atoms are located over the surface of the particles (XRD and SEM analyses).

The sample that presented the best CO_2 absorption properties was the sample $Li_{3.85}Na_{0.15}SiO_4$. Something else has to be pointed out; the addition of sodium diminished the maximum absorption temperature, as an equilibrium absorption/desorption was activated at lower temperatures than that for pure Li_4SiO_4. The experimental isotherms obtained for the samples Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$ were fitted to a double or triple exponential models, to perform a kinetic analysis. The triple exponential model used in those cases where desorption process was evidenced, as there were three processes taking place: CO_2 absorption, alkaline (lithium−sodium) diffusion, and CO_2 desorption. In both ceramics, Li_4SiO_4 and $Li_{3.85}Na_{0.15}SiO_4$, the diffusion processes turned out to be the limiting step of the total process, according to the kinetic constants obtained. Additionally, when the Eyring model was used to fit these constant values, it was found linear trends for all the cases. Therefore, the activation enthalpies ($\Delta H^{\ddagger}$) for the absorption reactions and diffusion processes were calculated. In the case of Li_4SiO_4, the energy values obtained were 88.9 and 79.5 kJ/mol, for the CO_2 absorption and diffusion processes, respectively. On the other hand, $\Delta H^{\ddagger}$ obtained for the $Li_{3.85}Na_{0.15}SiO_4$ were

56.6 and 96.8 kJ/mol, for the CO_2 absorption and diffusion processes, respectively. It can be seen that the $\Delta H^{\ddagger}$ of the CO_2 absorption decreased significantly with the sodium addition, which means that CO_2 absorption is less dependent on the temperature by the addition of sodium. On the contrary, the same addition of sodium increased the diffusion enthalpy activation energy. In this case, the diffusion becomes more dependent on the temperature. Perhaps, as sodium atoms are bigger and heavier than lithium ones, the whole diffusion process is limited. Finally, all these results agree with the hypothesis suggesting that sodium atoms are located on the surface, and therefore, they act as active sites for the CO_2 capture.

Acknowledgment. This work was performed in the frame of the Project IMPULSA-PUNTA, UNAM. Additionally, this work was financially supported by CONACYT (23418-SE-MARNAT-CONACYT) and UNAM-PAIIT. V.L.M.-T. thanks CONACYT for financial support (46522Q-SEP-CONACYT).

CM802132T