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Surfactant-assisted hydrothermal crystallization of nanostructured lithium metasilicate (Li_2SiO_3) hollow spheres: II—Textural analysis and CO_2–H_2O sorption evaluation

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ABSTRACT

In a previous work, the synthesis and structural-microstructural characterization of different nanocrystalline lithium metasilicate (Li_2SiO_3) samples were performed. Then, in this work, initially, a textural analysis was performed over the same samples. Li_2SiO_3 samples prepared with a non-ionic surfactant (TRITON X-114) presented the best textural properties. Therefore, this sample was selected to evaluate its water vapor (H_2O) and carbon dioxide (CO_2) sorption properties. Sorption experiments were performed at low temperatures (30–80 °C) in presence of water vapor using N_2 or CO_2 as carrier gases. Results clearly evidenced that CO_2 sorption on these materials is highly improved by H_2O vapor, and of course, textural properties enhanced the H_2O–CO_2 sorption efficiency, in comparison with the solid-state reference sample.

1. Introduction

Lithium ceramics have been reported for several potential applications including the fabrication of ceramic breeders, ionic conductors, gas sensors and solid sorbents for CO_2 capture [1–13]. Such is the case of lithium metasilicate (Li_2SiO_3), which has been reported as promising tritium breeder material into the fusion reactors [14,15], as an ionic conductor [16,17] and as candidate for luminescent devices [18,19].

Usually, Li_2SiO_3 is synthesized by solid-state reaction, but also a few chemical routes have been studied [20–22]. These studies have shown the feasibility to fabricate Li_2SiO_3 for novel potential applications. Among these chemical routes, Khomane et al. [21] reported the synthesis of Li_2SiO_3 nanoparticles by coupling sol–gel method in reverse microemulsion. The obtained powders showed the ability to absorb CO_2 under certain conditions, where it was assumed that the synthesis route increased the reactivity of Li_2SiO_3 as a result of its small particle size and then, its high surface area.

In this context, different factors can limit the CO_2 capture process on lithium ceramics; for example, particle size and lithium diffusion [13]. Hence, several studies have been performed in order to elucidate the absorption mechanism as well as on possible microstructural, structural and/or chemical modifications of these alkaline ceramics sorbents, seeking to enhance efficiency and CO_2 absorption rates [11–13].

The chemical route used in this work was chosen to obtain particulate materials with microstructural and textural characteristics that could promote their performance for novel applications such as CO_2 sorption. In fact, in a previous work [23], we have described in detail the systematic hydrothermal synthesis and characterization of these nanostructured Li_2SiO_3 samples. Therefore, in the present work it is discussed, not only the effect of synthesis route on the characteristics of synthesized Li_2SiO_3 powders, but also their capability to absorb CO_2 at low temperature, giving a special emphasis to textural characteristics of solid sorbents and the effect of water vapor addition during CO_2 capture process.

2. Experimental procedure

Li_2SiO_3 samples were prepared by hydrothermal synthesis using three different surfactants (CTAB, TRITON X-114 and SDBS) at 100, 125 and 175 °C [23]. The obtained powders were washed, and calcined at 400 °C. Samples were labeled by a number, which correspond to hydrothermal synthesis temperature, followed by an abbreviation, indicating the surfactant used and the letter C indicating the calcination process. Samples prepared without

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surfactant were simply labeled by a number indicating the temperature used during synthesis. More details about the hydrothermal synthesis of the powders, as well as the corresponding structural and microstructural characteristics, had been already published [23]. Summarizing, it could be mentioned that Li_2SiO_3 powders were composed of uniform micrometric particles with a hollow sphere morphology and nanostructured walls. Finally, different thermal analyses showed that Li_2SiO_3 samples preserved their structure and microstructure even after different thermal treatments.

Textural properties of Li_2SiO_3 samples were evaluated by N_2 physisorption isotherms, which were measured using a BEL-Japan apparatus model Minisorp-II. Different mathematical models, such as BET and α_s methods, were utilized to analyze the isotherms.

Once all samples were characterized, some of these samples were subjected to different dynamic water vapor and CO_2 sorption tests. Experiments were carried out in a temperature-controlled thermobalance TA Instruments model Q5000SA, where experimental variables were temperature, relative humidity (RH) and the carrier gas (CO_2 or N_2, both provided by Praxair). First, water vapor sorption/desorption isotherms were generated at 30, 50 and 70 °C, varying the relative humidity from 0% to 85% to 0% under a N_2 flux. Additionally, in order to evaluate the capability of Li_2SiO_3 to absorb CO_2 at low temperature, different sorption curves were obtained maintaining the above experimental conditions, but in this case under a CO_2 flux. In order to identify the reaction products, humidity test products were characterized by thermogravimetry (TG) and infrared (FTIR) spectroscopy after sorption experiments. For TG analyses, experiments were performed under air atmosphere with a heating rate of 3 °C/min using a thermobalance TA Instruments model Q500HR. For FTIR analysis, samples were analyzed by diffuse reflectance using a FTIR Spectrometer NICOLET 6700 FT-IR.

3. Results and discussion

As it has been already shown in a previous paper [23], all the hydrothermal synthesis performed with or without surfactant produced nanostructured Li_2SiO_3 hollow spheres, independent of the temperature. Fig. 1 shows the adsorption–desorption isotherms of the same hydrothermal samples prepared at 100 °C and reported previously [23], using different surfactants and the one prepared by solid-state reaction. According to the IUPAC classification [24,25], all samples present isotherms type II, which are attributed not only to monolayer–multilayer adsorption on an open external surface of non-porous or macroporous adsorbents, but also, to a limited extend, microporous powder. On the other hand, applying the BET method, *C* values were obtained in the 120–190 range, which suggest a relatively strong adsorbent–adsorbate interaction, but since the point B is not as sharper as could be expected (Fig. 1), then high *C* values were attributed to the presence of certain heterogeneous adsorption.

In this case, the presence of certain microporosity can be ruled out because of both, the small gas volume that was adsorbed at low partial pressure values and the obtained *C* values (<200) [24]. Hysteresis loops are type H3, and non-stepwise is observed, that is usually interpreted as a result of presence of slit-like pores. In addition, it is noticeable that volume adsorbed decreases considerably for sample prepared by solid state reaction, which corroborates the formation of more dense particles due to a sintering process. Textural characteristics of the different samples after thermal treatment at 400 °C are presented in Table 1. It is evident that all hydrothermally samples exposed higher surfaces area values than the sample obtained by solid-state reaction. The highest surface area values correspond to samples, which were prepared using surfactant. Besides, the effect of hydrothermal

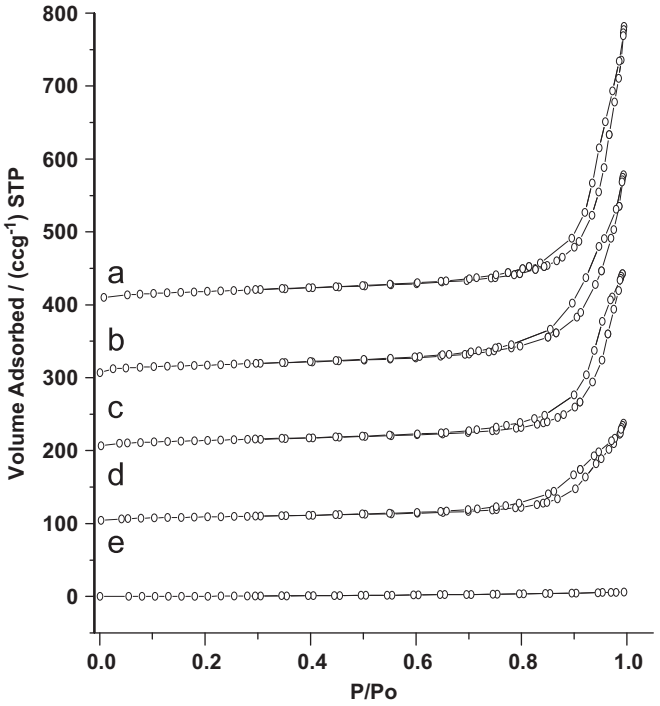

Fig. 1. N_2 physisorption isotherms of samples prepared with different surfactants: (a) 100TRITC, (b) 100SDBSC, (c) 100CTABC, (d) 100C and (e) solid-state reaction.

Table 1
Textural properties of different samples.

Sample	Textural properties		
	a_s, BET ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	Mean pore diameter (nm)
Solid-state	0.47	–	–
100C	31.9	0.199	26.02
125C	22.3	0.038	6.9
175C	13.4	0.02	4.9
100TRITC	66.9	0.529	33.7
125TRITC	56.9	0.501	35.9
175TRITC	24.2	0.263	43.9

temperature on textural properties of samples synthesized is also observed. It can be noticed a decrease on both, surface area and pore volume, at higher reaction temperatures, as it could be expected due to crystal growth.

In spite of the high *C* values suggest the validity of the standard BET procedure to calculate the surface area values, the α_s-method was also applied, in order to validate BET results. Fig. 2 shows the α_s plot of sample 100TRITC. The used standard isotherm was silica; this reference curve data was available at the equipment software data base. Specific surface area value was estimated as 68.2 $m^2\,g^{-1}$. This value agrees with that one calculated by BET method (see Table 1), which validates the obtained areas.

In general, all samples presented pore sizes in the mesoporosity range (Table 1). However, it is important to mention that based on the previous results, it would be infered that porous structure is composed of interparticle voids. Besides, since the obtained hysteresis loops are type H3; then, the estimated pore sizes are showed only for comparative purposes. The different obtained pore sizes are attributed to surfactant addition. Bigger pore sizes were obtained when TRITON-X114 surfactant was used. These textural characteristics are important for applications such as absorption where the reactivity plays an important role. Other advantages could be based on the fact that fast mass

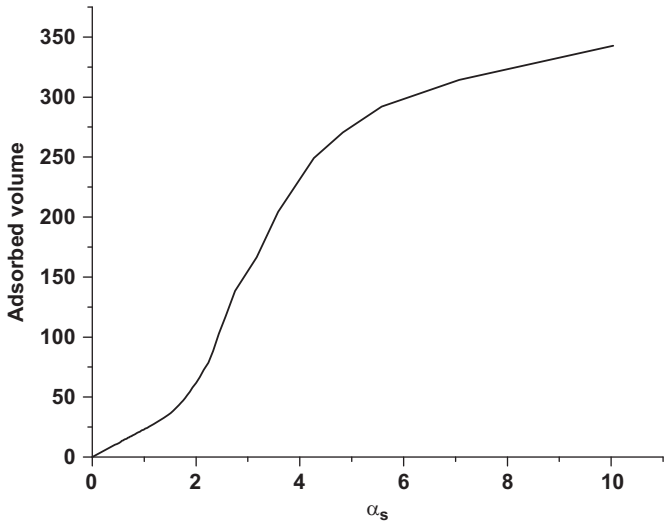

Fig. 2. α_s-Plot corresponding to sample 100TRITC.

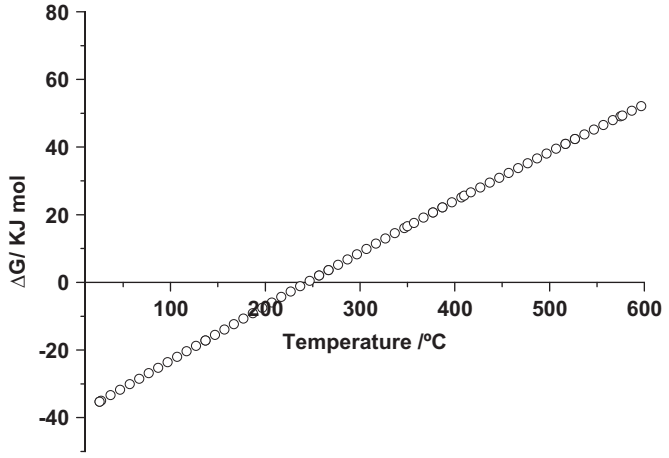

Fig. 3. Gibbs free energy change as a function of the temperature for reaction (1).

transference inside the agglomerate-particles could be improved by this kind of textures [26].

To further analyze and test these materials, CO_2 sorption in presence of water vapor was studied. Based on theoretical thermodynamic data calculated by FACTSage software [27], a reversible reaction between Li_2SiO_3 and CO_2 can take place at temperatures lower than 250 °C (Fig. 3).

$$Li_2SiO_3 + CO_2 \leftrightarrow Li_2CO_3 + SiO_2 \quad (1)$$

In fact, Khomane et al. [21] reported that CO_2 capture on Li_2SiO_3 occurs in spite of its low reactivity and kinetic factors. Of course, reaction was carried out at temperature up to 600 °C and under specific conditions of pressure and small particle size with relatively high surface areas values (7 $m^2 g^{-1}$). On the other hand, some researchers have reported water vapor addition effects on CO_2 capture of lithium ceramics. They observed that water addition enhances kinetic properties even at low temperatures [28–31]. So, with these antecedents, and taking into consideration the novel textural properties observed in the synthesized materials, studies of low temperature CO_2 absorption on Li_2SiO_3 in presence of water were carried out. The selected samples were 100C and 100TRITC, but also sample prepared by solid state reaction was tested as a reference.

First, selected samples were exposed to water vapor at 30, 50 and 70 °C, using N_2 as carrier gas. These experiments were performed to

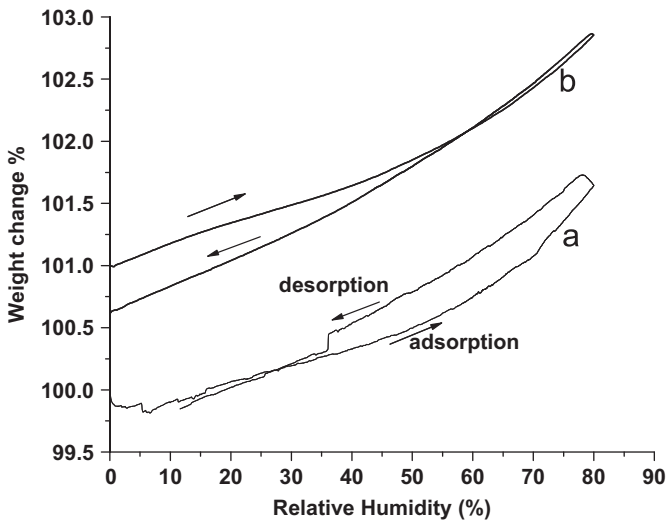

Fig. 4. Isotherms of water adsorption/desorption in the sample 100TRITC at different relative humidity (RH) conditions, under N_2 flux and temperature of (a) 30 °C and (b) 70 °C.

seek for any possible reaction between lithium metasilicate and water vapor. Fig. 4 shows water vapor adsorption/desorption isotherms, which were generated for sample 100TRITC at temperatures of 30 and 70 °C. These water vapor adsorption isotherms belong to type III, according to the IUPAC, which indicates a relative weak adsorbate–adsorbent interaction. In the adsorption stage, weight increments, of about 1.82% and 1.86 wt%, were registered for samples treated at 30 and 70 °C, respectively (Fig. 4). After that, during desorption stage, sorption hysteresis is observed. However, hysteresis loops tend to close indicating that a reversible process took place, and weight increments were due to physisorbed water.

When samples were treated under a mixture of CO_2 and water vapor, a totally different sorption behavior was observed. Fig. 5 shows the water vapor isotherms of these samples synthesized at 100 °C without surfactant addition (Fig. 5a) and using TRITON X-114 (Fig. 5b). In both cases, during sorption stage, important increments in the weight change were registered as a function of temperature. Even during desorption, weight increments continued and hysteresis loops did not close. In fact, at the end of sorption–desorption cycles important final weight increments were registered, suggesting a chemical process. It is important to mention that, in spite of thermodynamic data indicate that reaction between Li_2SiO_3 and CO_2 could occur spontaneously at low temperatures ($\Delta G < 0$ at $T < 250$ °C), CO_2 is not absorbed in absence of water vapor. This fact must be due to kinetic factors associated to surface area and textural properties, as it is shown below when solid-state sample is compared.

Additionally, it is noticeable that not only water vapor but also surface area has a crucial effect on Li_2SiO_3 reaction with CO_2. In Fig. 6, the sorption isotherms of solid-state, 100C and 100TRITC samples are shown. While solid-state sample does not absorb CO_2, samples with higher surface areas absorbed up to 37.5 wt% under the same experimental conditions (Table 2). Based on reaction (1), theoretically, lithium metasilicate could absorb a maximum of CO_2 equal to 48.9 wt%. The maximum weight increment registered after sorption corresponded to 37.5 wt% for the 100TRITC sample thermally treated at 70 °C. However, it is important to have in mind that the presence of water vapor could promote the formation of hydrated and/or hydroxylated products. Then, in order to analyze the reaction products, they were characterized by FTIR and TGA.

Fig. 7 shows FTIR spectra of the 100TRITC sample before and after the humidity treatments at 30 and 70 °C, using N_2 as carrier gas, respectively. All these spectra do not present any significant

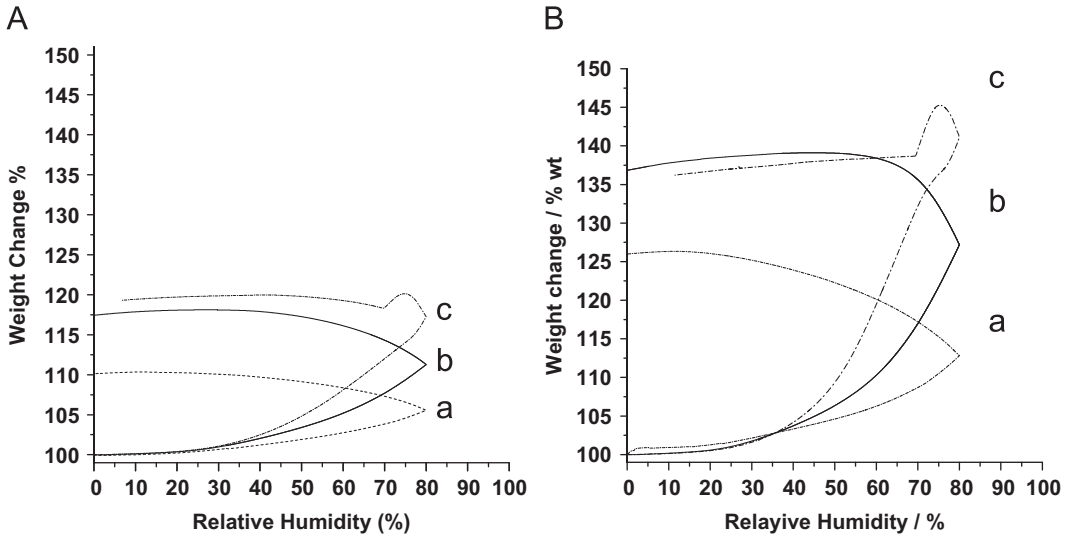

Fig. 5. CO_2 and water vapor sorption on Li_2SiO_3 particles in a dynamic process at different relative humid (RH) conditions (0–85–0%RH), and temperatures: Panel (A) corresponds to the sample 100C at (a) 30 °C, (b) 50 °C and (c) 70 °C and panel (B) corresponds to the sample 100TRITC at (a) 30 °C, (b) 50 °C and (c) 70 °C.

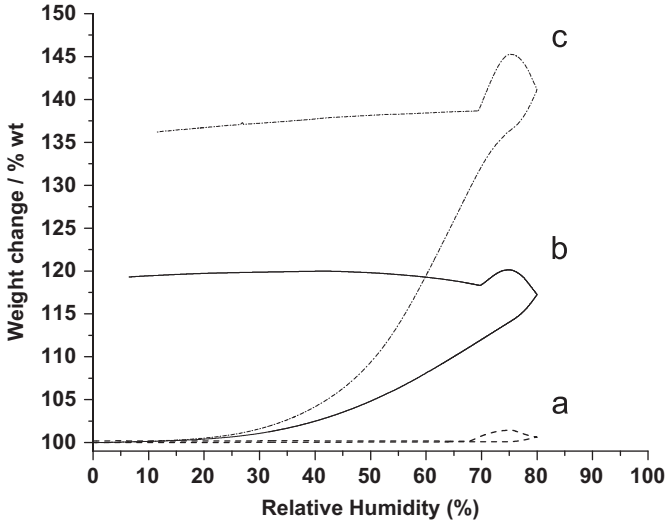

Fig. 6. CO_2 and water vapor sorption on Li_2SiO_3 particles in a dynamic process at different relative humid (RH) conditions (0–85–0%RH), and temperature of 70 °C. Isotherms correspond to different samples: (a) solid-state reaction, (b) 100C, (c) 100TRITC.

Table 2
Weight changes during CO_2–H_2O sorption for the different samples.

Temp. (°C)	Weight increments observed during sorption processes (wt%)					
	Solid-state		100C		100TRITC	
	Sorpion	After desorp.	Sorption	After desorp.	Sorption	After desorp.
30	0.19	0.20	5.55	10.2	12.87	26.4
50	0.09	0.10	11.29	17.6	27.50	38.3
70	0.63	0.20	17.28	19.5	41.42	37.5

variation among them. Vibration bands at 411 and 491 cm^{-1} are due to vibrations of the terminal Si–O and Li–O bonds [20], respectively. The bands located at 615, 736, 981 and 1050 cm^{-1} correspond to Si–O–Si bonds. The bands at 857 and 938 cm^{-1} were assigned to O–Si–O^- and O–Si–O bonds vibration, respectively. Besides the band at 1436 cm^{-1} was attributed to presence

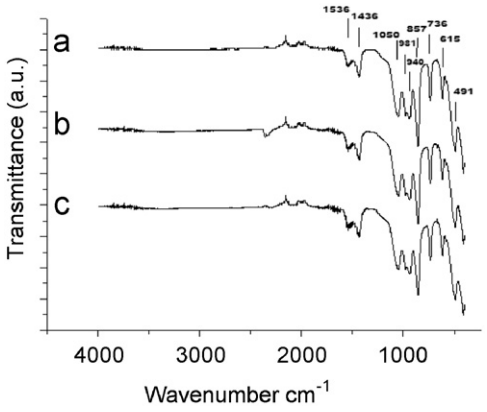

Fig. 7. Infrared spectra of the Li_2SiO_3 samples recorded after humidity treatment under N_2 flux: (a) sample 100TRITC without any treatment, (b) sample treated at 30 °C, and (c) sample treated at 70 °C.

of Li_2CO_3 on lithium metasilicate particle surface. These results suggest that lithium metasilicate seems not to react with water vapor under the studied conditions.

On the other hand, FTIR spectra of samples treated under a water vapor and CO_2 flux (Fig. 8), corroborate the CO_2 absorption on lithium metasilicate by the formation of Li_2CO_3 according to reaction (1). In this case, the band located at 491 cm^{-1} disappears when the treatment temperature increased. Since this band is attributed to terminal bonds surface reaction occurs on these surface active sites, as expected. There is another group of bands, which decrease in intensity after reaction; this group includes the bands located at 615, 736 and 981 cm^{-1}. All these signals correspond to Si–O–Si vibration bonds on silicate. On the contrary, it is clear that 1436 and 1050 cm^{-1} bands increased in intensity. Then, if it is kept in mind that CO_2 absorption products are Li_2CO_3 and, SiO_2 then it can be assumed that these last two bands correspond to lithium carbonate and Si–O–Si (asymmetric stretch) on formed silica, respectively. This claim is also supported by the fact that the presence of small bands at 470 and 798 cm^{-1} are a consequence of Si–O–Si bend and symmetric stretch of silica [32,33].

Finally, a thermal analysis of reaction products was carried out. The TG curves exhibit important weight-losses (Fig. 9). Initially, between room temperature and 150 °C, samples lost adsorbed water from hydration. However, it was not higher than

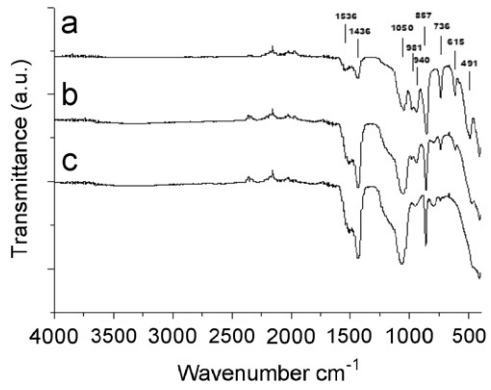

Fig. 8. Infrared spectra of the Li_2SiO_3 samples recorded after humidity treatment under CO_2 flux: (a) 100TRITC sample without any treatment, (b) 100TRITC sample treated at 30 °C, and (c) 100TRITC sample at 70 °C.

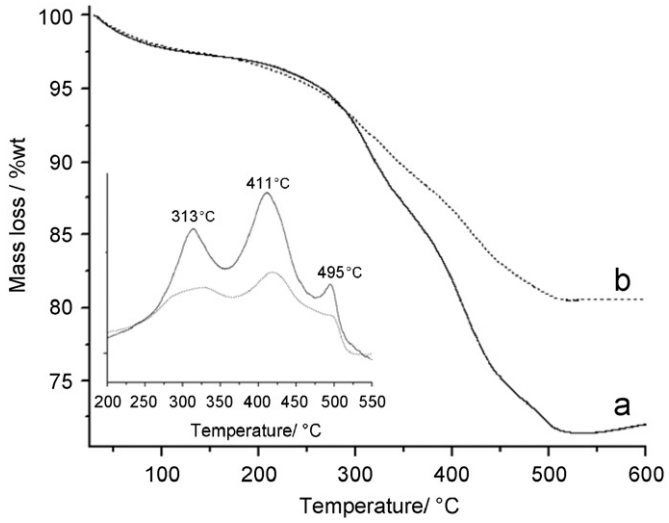

Fig. 9. TGA curves for different Li_2SiO_3 samples after humidity treatment under CO_2 flux: (a) 100TRITC sample without any treatment and (b) 100TRITC sample treated at 70 °C. The inset shows the derivative curve of thermogravimetric data.

3 wt%. The second weight loss began at about 313 °C, and it is more likely due to decomposition of carbonates [31].

Once CO_2 absorption on Li_2SiO_3 was corroborated, it is necessary to understand how the capture process take place. Although some authors have suggested that water exposure can inhibit CO_2 absorption on some lithium ceramics [11], in general, there is an agreement that the presence of water vapor promotes CO_2 absorption on alkaline ceramics as well as in some other ceramic compounds such as hydrotalcites [34]. In fact, different mechanisms of CO_2 capture in presence of water vapor have been proposed [28–31]. Essaki et al. [29] found that humidity increases CO_2 absorption on lithium orthosilicate Li_4SiO_4 at room temperature. Authors proposed a capture mechanism where acid-base reactions with hydrolysis of CO_2 and Li_2O are involved. They also suggested that carbonate layer formed on the ceramic surface during absorption, might be dissolved in water thus, in this way, absorption is promoted. Siausinuas et al. [30] studied the carbonation of Tobermorite powders stressing the effect of both textural properties of the sorbent and the presence of water vapor during the process. In this case (similarly to Essaki et al. conclusions), authors suggested an intermediate hydrolysis reaction but additionally they consider the formation of more reactive species into the Tobermorite structure as a result of its textural properties. Ochoa-Fernandez et al. [28] studied the effect of water vapor addition on the CO_2 capture at elevated temperatures by lithium zirconates (Li_2ZrO_3, K-doped Li_2ZrO_3 and Na_2ZrO_3) and Li_4SiO_4 ceramics. Ceramics presented improvements on the CO_2 absorption and desorption processes due to the presence of water vapor. They concluded that water vapor promotes alkaline ions mobility and therefore the reaction rate. In a more recent work Martinez-dlCruz and Pfeiffer [31] reported the effect of water sorption on Li_2ZrO_3 and K-doped Li_2ZrO_3 during their carbonation at low temperatures. They found that CO_2 absorption on these ceramic is proportional to its reactivity with water vapor. They concluded that during CO_2 capture on alkaline ceramics (specially on lithium zirconate which has the capacity to react with water) the formation of intermediate species like M–OH is involved, since these species are more prone to react with CO_2 than the adsorbent itself, leading to a general increase in the kinetic of capture. In fact, Li_4SiO_4 chemisorbs water vapor at a similar thermal conditions than the present work, forming Si–OH and Li–OH species [35].

Based on the above results, more than one mechanism might be taking place in this system. However, thermodynamic data show that the following reaction (2) do not occur spontaneously:

$$Li_2SiO_3 + H_2O = 2LiOH + SiO_2, \quad \Delta G = 62.84\ \text{KJ/mol} \tag{2}$$

In fact, this claim is supported by the experimental results since the reaction was not observed (Figs. 6a and 7). Then, in the Li_2SiO_3–CO_2–H_2O system the formation of intermediate species must be promoted by the porous microstructures, large surface areas and aqueous environment. All these factors must induce the beginning of CO_2 reaction in active sites such as terminal bonds and, perhaps, enriched lithium zones on the solid.

4. Conclusions

Pure and nanocrystalline Li_2SiO_3 samples with high surface area values (as high as 66.9 $m^2\ g^{-1}$) were previously synthesized by hydrothermal method. Li_2SiO_3 samples prepared with TRITON X-114, a surfactant, presented the best textural properties. In general, surfactant addition and hydrothermal temperatures played crucial roles to control morphology and microstructure, resulting in the formation of spherical hollow aggregates which present novel microstructural and textural characteristics. Despite, the water vapor does not seem to modify substantially the Li_2SiO_3 surface, the combination of CO_2 and water vapor enhances importantly the CO_2 capture on Li_2SiO_3 at low temperatures. CO_2 capture occurred chemically and this reaction was enhanced by the porous microstructure and large surface areas.

According with the literature, Li_2SiO_3 practically does not react with CO_2 in this temperature range under dry conditions, due to kinetic factors. Nevertheless, the results presented here showed that water addition improves the CO_2 capture on this ceramic. From this point of view, these results suggest that water vapor addition may improve the CO_2 capture on other lithium ceramics.

Acknowledgments

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