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Sodium metasilicate (Na_2SiO_3): A thermo-kinetic analysis of its CO_2 chemical sorption

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ABSTRACT

Sodium metasilicate (Na_2SiO_3) was prepared by two different methods, solid-state reaction and precipitation. Then, samples were characterized by powder X-ray diffraction, scanning electron microscopy, N_2 adsorption and thermogravimetric analysis. Thermal analyses showed that Na_2SiO_3 has the capacity to absorb small quantities of CO_2 between room temperature and 130 °C. Modeling the surface reaction and sodium diffusion, the activation energies for these two processes were estimated to be 17,482 J/mol and 23,968 J/mol, respectively. Finally, the effect of the particle size, on the CO_2 sorption, was found to be very important. The quantities of CO_2 absorbed increased three times, when the particle size decreased and consequently the surface area increased.

1. Introduction

One of the principal world concerns, is related to pollution gases, and especially carbon dioxide (CO_2) emissions [1,2]. In that way, in the last 10 years, several papers have shown that some alkaline ceramics, mainly lithium and sodium containing compounds, could be used as CO_2 absorbents [3–10]. In general, these ceramics present a double-step sorption mechanism: a chemical sorption of CO_2 over the ceramic surface, which produces an alkaline carbonate shell. Then, when the external shell is formed, the alkaline element diffuses throughout the carbonate external layer, to reach the surface and react with CO_2 [8–10]. Therefore, one of the most important features of these materials is related to the diffusion of the alkaline element.

So far, among these compounds, lithium silicates, specifically 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 through the following reaction [1,2,7,11–13].

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

Implicitly, these papers showed that Li_2SiO_3 does not react. In fact, Kato and Nakagawa [14] tested this material for the CO_2 capture. They did not observe any weight increment, and it was justified due to kinetic factors.

On the other hand, sodium ceramics have shown, in general, to be better CO_2 absorbents in comparison to lithium ceramics. For example Na_2ZrO_3 absorbs twice more CO_2 than Li_2ZrO_3, and its reaction rate is faster as well [9]. Therefore, although Li_2SiO_3 seems not to absorb CO_2, Na_2SiO_3 may have better reactivity. Then, the aim of this work was to study the thermal stability, CO_2 sorption reactivity and particle size effect of Na_2SiO_3, through thermal analyses to obtain information about the CO_2 sorption reactivity on Na_2SiO_3.

2. Experimental

Sodium metasilicate was synthesized by two different methods: solid-state reaction and precipitation. The solid-state reaction was performed with a mechanical mixture of silicon oxide (SiO_2, Aldrich) and sodium carbonate (Na_2CO_3, Aldrich) powders. Then, the mixture was calcined at 900 °C for 4 h. On the contrary, precipitation of Na_2SiO_3 was produced from an aqueous solution of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, Aldrich) and sodium hydroxide (NaOH, Baker). Here, NaOH was dissolved in water as a first step. TEOS was, then, slowly added, drop by drop, to the solution. The mixture obtained was stirred and heated at 70 °C until it dried. In this case, Na_2SiO_3 was obtained without any further thermal treatment. This synthesis was performed to obtain small particles, and analyze the effect of the particle size on the CO_2 absorption process. In both methods of synthesis the Na:Si molar ratio was equal to 2:1.

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The samples were characterized by different techniques such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption (BET) 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 Kα wavelength was selected with a diffracted beam monochromator, and compounds were identified conventionally using the JCPDS database. SEM (Stereoscan 440, Cambridge) was used to determine the particle size and morphology of the materials before and after the CO_2 capture. The samples were covered with gold to avoid a lack of electrical conductivity. Surface area analyses were performed on Micromeritics Gemini 2360 equipment. Before the N_2 adsorption process, the samples were out gassed in vacuum at 100 °C for 12 h. Surface areas were calculated with the BET equation. Finally, different thermal analyses were performed in Hi-Res TGA 2950 thermogravimetric analyzer equipment from TA Instruments. A set of samples was heat-treated, with a heating rate of 5 °C/min, from room temperature to 1000 °C. These analyses were carried out into a CO_2 flux (Praxair, grade 3.0), using 10 mg of sample in each analysis. Additionally, another set of samples was analyzed isothermically under the same CO_2 atmosphere at 80 °C, 100 °C and 120 °C for 5 h.

3. Results and discussion

Na_2SiO_3 was prepared by solid-state and precipitation methods. Initially, Na_2SiO_3 was prepared by solid-state reaction. The XRD pattern showed that the sample was pure Na_2SiO_3 (Fig. 1A). On the contrary, the sample prepared by precipitation was not totally pure (Fig. 1B), another secondary phase was detected in small quantities, $Na_6Si_2O_7$. The formation of $Na_6Si_2O_7$ is consistent with heterogeneities in the sample arising from areas locally richer in sodium, than the average. Nevertheless, this sample was not thermally treated to eliminate this secondary phase, in order to obtain smaller particles of Na_2SiO_3 in comparison to the solid-state sample.

Both samples were studied by SEM. The particle size was measured using standard procedures. Micrographs of Na_2SiO_3 obtained by the two methods showed morphological differences between them. The sample obtained by solid-state reaction showed large polyhedral particles with a particle size between 50 μm and 100 μm (Fig. 2A). Furthermore, the texture of these particles was highly dense. This kind of morphology corresponds very well with the solid-state reaction model.

On the contrary, the morphology of Na_2SiO_3 prepared by precipitation was totally different. In this case, Na_2SiO_3 seemed to

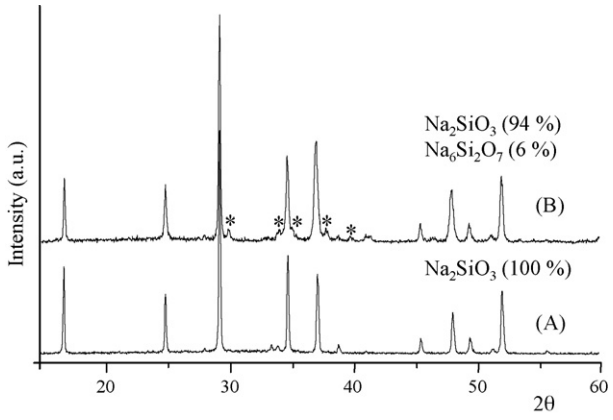

Fig. 1. XRD patterns of the Na_2SiO_3 samples prepared by solid-state reaction (A) and precipitation (B). Peaks labeled as (*) correspond to the $Na_6Si_2O_7$ phase and the percentage of each phase is indicated into parenthesis.

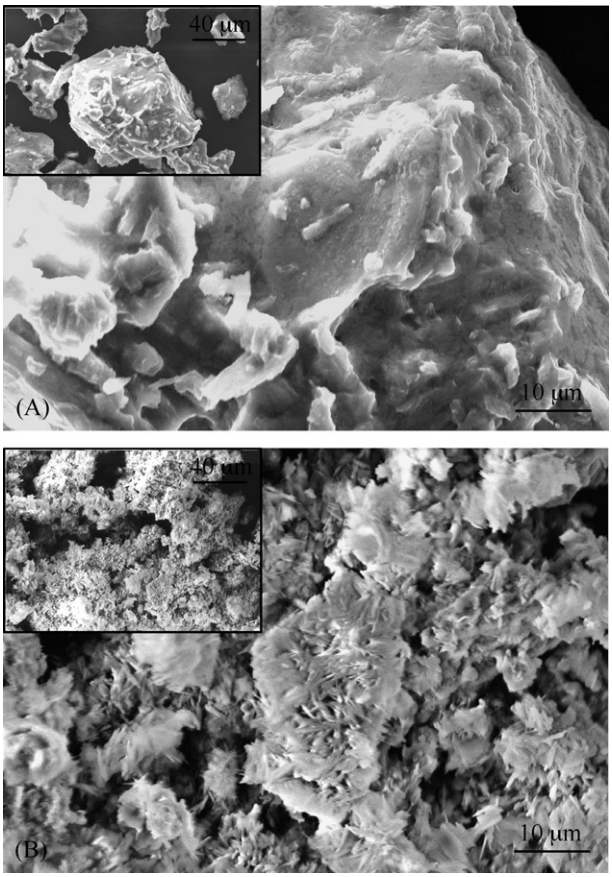

Fig. 2. SEM images of Na_2SiO_3 samples prepared by solid-state reaction at 900 °C for 4 h (A) and prepared by precipitation without nay thermal treatment (B).

agglomerate in particles of 5–20 μm, where the agglomerates were formed by some kind of laminar or filament particles (Fig. 2B). Therefore, the agglomerates are highly porous. It seems that the precipitation process is promoting the union of several Na_2SiO_3 chains, resulting in the formation of this kind of structures. Na_2SiO_3 is a chain of many $(SiO_3)^{2-}$ molecules, produced by the conjugation of a large number of $(SiO_4)^{4-}$ tetrahedrons linked by two oxygen atoms among them [15]. Thus, several of this Na_2SiO_3 chains must be linked, producing filament-like structures. The SEM results were supported by a surface area analyses. While the solid-state sample had a surface area of 1.35 m^2/g, the precipitation sample had a larger area, 6.25 m^2/g. Although none of the samples presented significant surface areas, the samples prepared by precipitation have up to four times more area than the sample prepared by solid state.

Once, the samples were characterized, the thermal behavior of Na_2SiO_3, into a flux of CO_2, was studied. Initially, the sample prepared by solid-state reaction was chosen in order to have similar geometry and particle size than those characteristics presented by other materials in similar studies [6–11]. Thermogravimetric analysis of Na_2SiO_3 into a flux of carbon dioxide (CO_2) is shown in Fig. 3. The thermogram only showed an small weight increment between room temperature and 130 °C, which was attributed to a CO_2 sorption process. After that, the sample started losing weight in two different processes, one between 130 °C and 700 °C, and another one between 700 °C and 920 °C. The total weight lost was equal to 9 wt%. These processes were associated to dehydroxylation and decarbonation of the sample, as usually sodium ceramic are highly hygroscopic. The CO_2 chemisorption at low temperatures was confirmed by XRD, as follows: Na_2SiO_3 powder was heat treated up to 130 °C into a flux of CO_2, and then, the heating process was

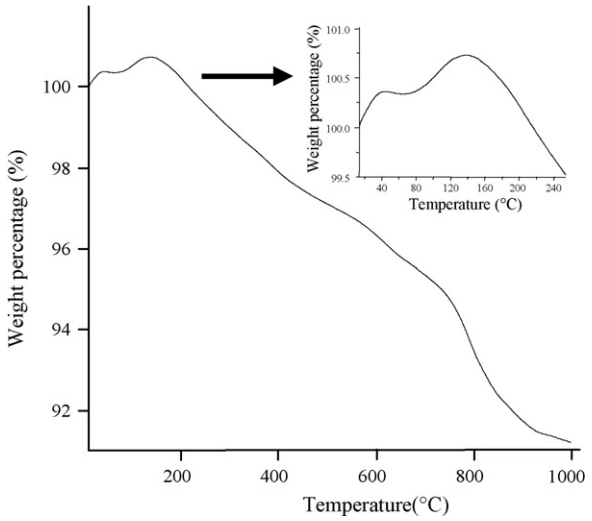

Fig. 3. Thermogravimetric analysis of the Na_2SiO_3 into a flux of CO_2.

stopped. The XRD pattern showed the formation of small quantities of Na_2CO_3, 5% (data not shown).

Na_2SiO_3, under a flux of CO_2, presented a totally different behavior than that observed on other alkaline ceramics such as Li_4SiO_4, Li_2ZrO_3, Na_2ZrO_3 and Li_2O [1,2,7,11–13]. All these materials absorb CO_2 at different ranges of temperatures, and they can retain high quantities of CO_2. On the contrary, Na_2SiO_3 only absorbed ≈1–2 wt%, and the absorption was produced at low temperatures. Nevertheless, this result is coherent with the results reported for Li_2SiO_3, which apparently is not able to absorb CO_2 either [14]. In this case, Na_2SiO_3 absorbed small quantities of CO_2, in the agreement with the reports that indicates that in general sodium ceramics are more reactive than lithium ceramics [9].

In order to obtain some kinetic information about the CO_2 sorption, additional isothermal analyses were performed. Fig. 4 shows the isothermal graphs of Na_2SiO_3 heat-treated at different temperatures into a flux of CO_2. The sorption rates presented similar behaviors at the three different temperatures, and data fitted to a double exponential model: $y = A\exp(-k_1 t) + B\exp(-k_2 t) + C$, where, y represents the percentage of weight increased due to CO_2 absorption, t is the time, k_1 and k_2 are the rate constants and A, B and C are the pre-exponential factors. This model has been used in other alkaline ceramics to describe the CO_2 chemisorption and alkaline diffusion process simultaneously, obtaining two different rate constants values; k_1 for the chemisorption process and k_2 for the diffusion process [7,9]. The values obtained at each temperature are presented in Table 1. As the data adjusted to a double exponential model, it means that there are two different processes associated, as in some other alkaline ceramics, a chemisorption and diffusion processes [7,9]. Then, Na_2SiO_3 reacts with CO_2, producing an external layer of Na_2CO_3, and after that, sodium must have to diffuse throughout the carbonate layer to be able to react with the CO_2. In this case, k_1 (chemisorption process) is one order of magnitude larger than k_2 (diffusion process). Therefore, kinetically the limiting step of the whole process is the diffusion. Then, the poor CO_2 sorption results may be attributed the structural or packing factors of the Na_2SiO_3 crystal structure, which should inhibit sodium diffusion. For a model of these characteristics, if the kinetic constant values (k_1 and k_2) are linear dependent with temperature, the gradients of these best-fit lines should follow an Arrhenius-type behavior. Fig. 5 shows the plots of $\ln k$ versus $1/T$, where linear trends are observed for both processes. The fitting observed for both graphs varied significantly. While the chemisorption process fitted excellent ($\ln k_1$ vs. $1/T$), it was not the case on the diffusion process ($\ln k_2$ vs. $1/T$). It may be explained due to interference produced by the chemisorption process, which occurs firstly. Another explanation would be that the diffusion process does not follow the Arrhenius-type behavior. Anyway, the activation energies for the CO_2 absorption (chemisorption) on Na_2SiO_3 and sodium diffusion were estimated to be 17,482 J/mol and 23,968 J/mol, respectively.

The CO_2 capture capacity of this sample was extremely poor, in comparison with other ceramics. For example, Na_2ZrO_3, which is

Table 1
Kinetic parameters obtained from the experimental data fitted to a double exponential model

Parameter	Temperature (°C)		
	80	100	120
k_1 (1/s)	1.2786	2.0589	2.3304
k_2 (1/s)	0.0894	0.2108	0.2022
A	−1.1194	−1.5088	−1.1031
B	−0.2506	−0.2361	−0.5841
C	101.3	101.7	101.6
R^2	0.99972	0.99997	0.99933

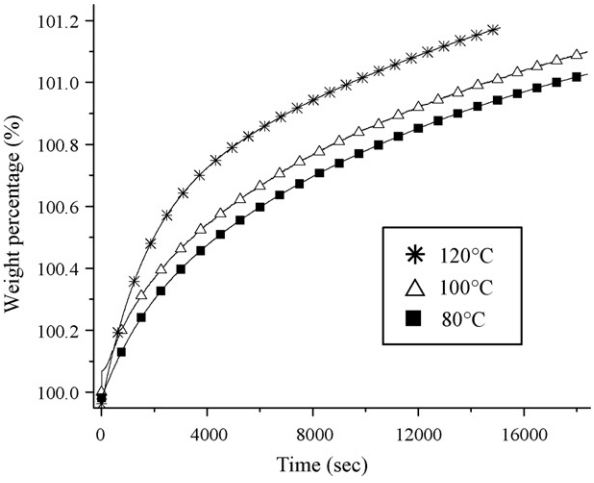

Fig. 4. Isotherms of CO_2 sorption on Na_2SiO_3 heat-treated at 80 °C, 100 °C and 120 °C into a flux of CO_2. The symbols correspond to the experimental data, and the lines correspond to the double exponential fit.

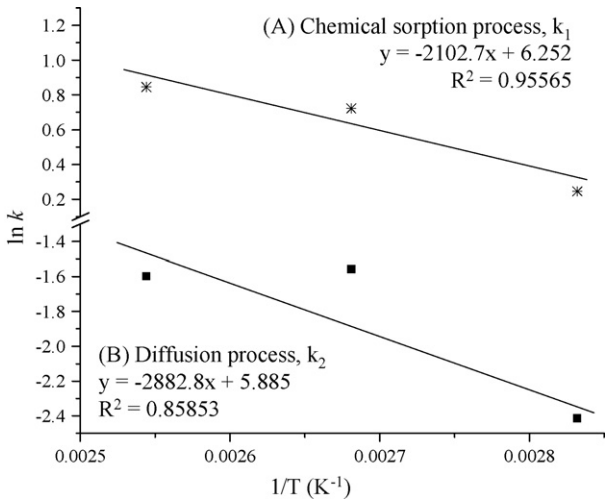

Fig. 5. Plots of $\ln k$ vs. $1/T$, for the two different processes observed on the CO_2 sorption on Na_2SiO_3.

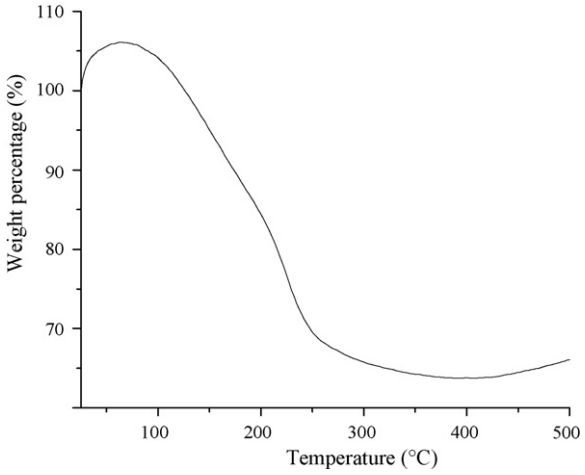

Fig. 6. Thermogravimetric analysis of the Na_2SiO_3 prepared by the precipitation method, into a flux of CO_2.

an isostructural ceramic, do absorb CO_2 [9,16]. In this case, Na_2ZrO_3 begins the CO_2 absorption at low temperatures as well. Nevertheless, in this case, the absorption continues through the bulk of the ceramic. In other words, the CO_2 absorption is not limited to the surface or by sodium diffusion. On the other hand, it has been proved, for other materials, that the particle size and surface area play very important roles on the CO_2 capture [7,17]. Therefore, it could be interesting to analyze this material with different particle size and surface area. Therefore, although the Na_2SiO_3 sample prepared by the precipitation method was not pure (see XRD results), it was used to analyze its CO_2 capture capacity, because it has a smaller particle size and the larger surface area. The thermogram of this sample, into a flux of CO_2, showed a similar behavior than that observed for the sample with solid-state reaction (Fig. 6). The thermogram presented a similar trend, where the only significant difference was the quantity of CO_2 trapped. In this case, the amount of CO_2 absorbed was 6 wt%. It means three times more CO_2 than that absorbed on the solid-state sample. The increment observed on this analysis could be explained as a function of the particle size and surface area of the samples. As the sample prepared by precipitation has a larger surface area, there must be more sodium atoms at the surface of the particles, enabling the Na_2CO_3 formation. Furthermore, as particles are smaller and there is the presence of porosity, these factors may increase the vapor pressures into the porous, grain boundaries and triple points produced by the junction of several particles, increasing the reactivity. Conversely, the thermal stability of this sample was highly modified. After the CO_2 sorption 30 wt% was lost, which may be partially attributed to decarbonation and sodium sublimation processes. In this case, perhaps as there is more sodium atoms present at the surface, it may be presented some sodium sublimation at high temperatures, which contributed to the loss of weight as well.

4. Conclusion

The CO_2 chemisorption kinetics, of Na_2SiO_3, was analyzed in this work. Later the particle size effect was investigated as well. CO_2 sorption analyses showed that Na_2SiO_3 has the capacity to absorb CO_2 between room temperature and 130 °C. The quantity of CO_2 absorbed is not high enough to utilize this ceramic as CO_2 captor. Nevertheless, it was performed the kinetic analysis of the CO_2 sorption. The results indicate that sorption mechanism occurs through a double-step process; superficial chemical sorption and sodium diffusion processes, where the diffusion process is the limiting step. The activation energies for the CO_2 chemical sorption and the diffusion of sodium were estimated to be 17,482 J/mol and 23,968 J/mol, respectively. Finally, it was observed that particle size and surface area play very important roles during the CO_2 capture.

It has to be pointed out that, although the CO_2 absorption observed in Na_2SiO_3 is considerably small, this material absorbed more CO_2 than its lithium isostructural ceramic, Li_2SiO_3. Again, sodium ceramics show to be better CO_2 absorbents, in comparison to lithium ceramics, as the zirconates case (Li_2ZrO_3 and Na_2ZrO_3).

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