



## Solid state reaction of serpentinite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ with $\text{Li}^+$ to produce $\text{Li}_4\text{SiO}_4/\text{MgO}$ composites for the efficient capture of $\text{CO}_2$

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### ARTICLE INFO

#### Keywords:

Serpentinite

$\text{Li}_4\text{SiO}_4$

MgO

Carbonatation

### ABSTRACT

In this work, the reaction of serpentinite mineral ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), a low cost and available precursor, with LiOH was used to produce composites based on  $\text{Li}_4\text{SiO}_4/\text{MgO}$  with very high  $\text{CO}_2$  reaction capacities. Temperature Programmed Reaction with  $\text{CO}_2$  (TPRe- $\text{CO}_2$ ), X-ray diffraction (XRD), thermogravimetric coupled to mass spectrometry,  $\text{N}_2$  adsorption-desorption BET, scanning electron microscopy analyses showed that the impregnation of serpentinite with LiOH (5, 10, 20 wt%) and thermal treatment at 500, 700 and 900 °C produced a composite based on  $\text{Li}_4\text{SiO}_4$  and MgO. This process likely takes place by a  $\text{Li}^+$  diffusion into the interlayer serpentinite structure followed by the reaction with Si to form  $\text{Li}_4\text{SiO}_4$  18 nm crystallites and segregation of the MgO with crystallite sizes of 14 nm. TPRe- $\text{CO}_2$  experiments showed that the most efficient material was 20Li<sub>700</sub> (20% Li treated at 700 °C) with reaction capacity ca. 25 wt%  $\text{CO}_2$ . XRD data indicated that both phases react with  $\text{CO}_2$  in a new and complex equilibrium to form a mixture of  $\text{Li}_2\text{CO}_3/\text{Li}_2\text{MgSiO}_4$  and  $\text{MgCO}_3$ . The use of the Avrami–Erofeev model indicated a classical carbonation mechanism by a two steps process surface reaction combined with Li diffusion. This process is reversible and preliminary data suggests that at 700 °C the carbonates decompose and the material can be regenerated and reused.

### 1. Introduction

The separation (storage/recovery) of carbon dioxide mostly resulting from the combustion of fossil fuels and the generation of electricity, has attracted a great deal of interest in recent years [1]. Thus, the development of low-cost new materials for the efficiently reversible capture carbon dioxide has received a considerable attention. The most studied materials reported in the literature are zeolites [2–4], hydroxalites [5–7], MOFs [8,9], CaO [10–12], MgO [13–15] and ceramics [16–18]. Among these alternatives, lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) showed promising results such as high absorptive capacity (nominal ca. 37%) at relatively low temperature, 400–720 °C, and the possibility of reuse for several adsorption-desorption cycles [19–25].

Lithium orthosilicate has been produced from different materials, such as rice husk wastes as source of  $\text{SiO}_2$  [19,20,26], kaolin and aluminum silicate with a content of 46% of  $\text{SiO}_2$  and 38% of  $\text{Al}_2\text{O}_3$  [27], diatomite with a content of 75% of  $\text{SiO}_2$  [28], fly ashes from the energy industry [26,29] and by different routes of synthesis as: solid-state

reaction, precipitation method and sol-gel method [30]. All these Li orthosilicate materials showed high  $\text{CO}_2$  reaction capacity in the range of 15–30% with good recyclability.

Serpentinite with a general and simplified formula  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  is formed mainly by minerals of the serpentine group: antigorite, chrysotile and lizardite [31]. It contains 32–38% MgO, 35–40%  $\text{SiO}_2$  and 12–13%  $\text{H}_2\text{O}$ , in addition to small amounts of Fe, Al, Cr and Ni [32]. The serpentinite structure consists of octahedral sheets of  $\text{MgO}_2(\text{OH})_4$  bound to tetrahedral sheets of  $[\text{SiO}_4]$  [33] as a result of the hydration of ultramorphic rocks (dunite, peridotite and pyroxenite) in a temperature range between 100 and 700 °C [34].

Recent works have demonstrated that serpentinite is a versatile precursor to produce different silicates. For example, the thermal decomposition of serpentinite [35,36] at relatively low temperatures, e.g. 600 °C produces forsterite ( $\text{Mg}_2\text{SiO}_4$ ) and  $\text{SiO}_2$  [37]. The combination of serpentinite with the alkaline metals  $\text{K}^+$  [38] and  $\text{Na}^+$  [39] produced the  $\text{K}_2\text{MgSiO}_4$  and  $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$  silicates, active as basic catalysts.

In this work, serpentinite was used as a low-cost precursor for the

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<https://doi.org/10.1016/j.jece.2018.06.026>

Received 19 March 2018; Received in revised form 7 June 2018; Accepted 8 June 2018  
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production of  $\text{Li}_4\text{SiO}_4/\text{MgO}$  composites for the efficient  $\text{CO}_2$  reaction. Hereon, it is described the effect of Li concentration (from 5 up to 30 wt %) and temperature (500–900 °C) on the different phases formation. It is also investigated the reaction of the composites with  $\text{CO}_2$ , the formed phases and preliminary regeneration studies.

## 2. Experimental

### 2.1. Synthesis and characterization of materials

The serpentinite used in this work was provided by Pedras Congonhas Ltda. The samples, retained in 200 mesh sieves, were impregnated with aqueous LiOH solutions in proportions of 5, 10 and 20% by weight of lithium ( $\text{Li}^+$ ). The impregnation was done in a beaker, on a heating plate and magnetic stirring, at 80 °C. The materials were oven dried for 24 h at 80 °C to ensure complete drying and calcined at a heating rate of 10 °C  $\text{min}^{-1}$  in a horizontal tubular oven at 500, 700 or 900 °C for 3 h under an atmosphere of air. To study the influence of the calcination temperature and metal content the impregnation of serpentinite was repeated according to the procedure described by Ballotín et al. [38]. These samples are named hereon according to the  $\text{Li}^+$  content and temperature treatment, for instance 20Li<sub>700</sub> contains 20 wt %  $\text{Li}^+$  treated at 700 °C.

The chemical composition of the materials was determined by fluorescence spectroscopy (FRX) on a Shimadzu EDX-720 vacuum spectrometer. The structural characterization was performed by X-ray powder diffraction (XRD) on a Shimadzu diffractometer, model XRD-7000 with  $\text{CuK}\alpha$  (1.5406 Å) and scanning speed of 4°  $\text{min}^{-1}$ . Scanning electron microscopy (SEM) measurements were obtained on a Quanta 200 - FEG 3D -FEI equipment. The specific surface areas (BET) of the samples were analyzed by adsorption of  $\text{N}_2$  at 77 K using the Autosorb1-MP Quantachrome equipment. Samples were degassed at 200 °C for 24 h prior to analysis.

### 2.2. $\text{CO}_2$ reaction carbonatation

The carbonatation performance of the materials was investigated by Temperature Programmed Reaction with  $\text{CO}_2$  (TPRe) experiments in a thermal-gravimetric analyzer, model NETZSCH STA 449 F3, coupled in a mass spectrometer NETZSCH Aeolos model QMS 403C. The samples were pretreated under the argon atmosphere (20 mL  $\text{min}^{-1}$ ) at 500, 700 or 900 °C (according to the temperature at which the material was prepared), remaining at this temperature for 3 h to eliminate possible impurities. The carbonatation capacity was evaluated in two ways, dynamic and isothermal.

In the dynamic process, the sample was heated to 1000 °C at a rate of 5 °C  $\text{min}^{-1}$  under  $\text{CO}_2$  (20 mL  $\text{min}^{-1}$ ). For the isothermal tests, the previously pretreated samples were heated at a rate of 5 °C  $\text{min}^{-1}$  in  $\text{CO}_2$  atmosphere (20 mL  $\text{min}^{-1}$ ) to the desired temperature (400–700 °C) remaining at this temperature for 3 h.

## 3. Results and discussion

The materials used in this work were prepared by the impregnation of serpentinite  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  with 5, 10 and 20 wt% LiOH followed by thermal treatment in the range of 500–900 °C. These samples are named hereon according to the amount of lithium impregnated and treatment temperature, i.e. 5Li<sub>700</sub> (5% Li treated at 700 °C). The serpentinite used in this work shows an approximate composition of 40%  $\text{SiO}_2$  and 30% MgO, 10%  $\text{Fe}_2\text{O}_3$  and small concentrations of Al, Ca, Ni and Mn.

It can be observed by structural characterization performed by X-ray powder diffraction (XRD) for pure serpentinite ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) treated at 700 °C the mainly presence of the phase forsterite ( $\text{Mg}_2\text{SiO}_4$  JCDPS 4-769) (Fig. 1) [39].

The XRD of the material after impregnation with 5% Li (molar ratio Li/Si of 1/1) and treatment at 700 °C showed the presence of a new

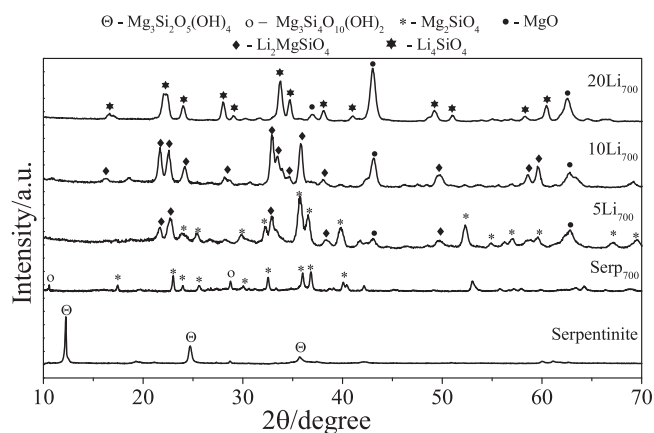


Fig. 1. XRD patterns for the samples Serpentine, Serp<sub>700</sub>, 5Li<sub>700</sub>, 10Li<sub>700</sub> and 20Li<sub>700</sub>.

phase  $\text{Li}_2\text{MgSiO}_4$  (JCDPS 24-633) besides forsterite ( $\text{Mg}_2\text{SiO}_4$ ) suggesting the following reaction:



When serpentinite was impregnated with 10% Li (molar ratio Li/Si = 2) the main phases observed were  $\text{Li}_2\text{MgSiO}_4$  (JCDPS 24-633) and MgO (JCDPS 45-946) which suggests the following simplified reaction (Eq. (2)).



For 20% Li the Mg was completely segregated as MgO and the main silicate phase was  $\text{Li}_4\text{SiO}_4$  (JCDPS 37-1472). In this case, the high Li/Si molar ratio of 4 favors the formation of the  $\text{Li}_4\text{SiO}_4$  phase.



It is interesting to observe for the sample 20Li<sub>700</sub> average crystallite sizes estimated by the Scherrer's equation of 18 and 14 nm for  $\text{Li}_4\text{SiO}_4$  and MgO, respectively.

SEM images of the materials Serp<sub>700</sub>, 5Li<sub>700</sub>, 10Li<sub>700</sub> and 20Li<sub>700</sub>, are shown in Fig. 2. The samples Serp<sub>700</sub> and 5Li<sub>700</sub> showed the similar morphology of irregular particles 5–50 μm in size.

As the  $\text{Li}^+$  content increased to 10 and 20% the particles apparently sintered and new structures similar to hollow cylinders on the surface were formed. As a result of this sintering process, the surface decreased from 12 m<sup>2</sup> g<sup>-1</sup> (Serp<sub>700</sub>) to 10, 7 and 5 m<sup>2</sup> g<sup>-1</sup> for 5Li<sub>700</sub>, 10Li<sub>700</sub> and 20Li<sub>700</sub>, respectively.

Although this solid state reaction mechanism is not clear, it likely involves the diffusion and intercalation of  $\text{Li}^+$  ions in the interlayer space of the serpentinite structure. Upon thermal treatment, the small  $\text{Li}^+$  ions (0.60 Å [40]) likely diffuse through the solid to combine with Si-O bonds and expel the Mg from the crystalline structure. A simplified representation of this process is shown in Fig. 3. The  $\text{Li}_4\text{SiO}_4$  structure shows  $[\text{SiO}_4]$  tetrahedral interacting with the small  $\text{Li}^+$  ions coordinated by oxygen.

The  $\text{CO}_2$  reaction capacity of the obtained materials was investigated using temperature programmed reaction (TPRe) experiments (Fig. 4). It can be observed that the serpentinite (without lithium) treated at 700 °C (Serp<sub>700</sub>) showed a gradual  $\text{CO}_2$  reaction of ca. 5–6% from ca. 80 up to 250 °C. Most of the experiments were carried out in duplicate to ensure reproducibility of the results.

This  $\text{CO}_2$  uptake is likely related to the formation of  $\text{MgCO}_3$  by reaction with available MgO in the sample Serp<sub>700</sub>. It is interesting to observe that the presence of  $\text{Li}^+$  at 5 and 10% (5Li<sub>700</sub> and 10Li<sub>700</sub>) did not cause a significant change in  $\text{CO}_2$  reaction. This result suggests that the main phase produced in these samples, i.e.  $\text{Li}_2\text{MgSiO}_4$  and  $\text{Mg}_2\text{SiO}_4$ , are not able to capture  $\text{CO}_2$ .

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