



The effects of high-pressure on the chemisorption process of CO₂ on lithium oxosilicate (Li₈SiO₆)



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HIGHLIGHTS

- CO₂ capture was evaluated on Li₈SiO₆ at high-pressure.
- CO₂ is trapped chemical and physically on Li₈SiO₆.
- High-pressure enhances the CO₂ capture between 30 and 350 °C.

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ABSTRACT

High-pressure CO₂ capture was evaluated on Li₈SiO₆. Several different high-pressure experiments were performed using CO₂, and the sample products were analyzed using XRD, N₂ adsorption, SEM and DSC. The results clearly showed that CO₂ is chemically and physically trapped and that the CO₂ chemisorption improved as a function of temperature. Depending on the temperature, Li₈SiO₆ reacted with 2 mol or less of CO₂ to produce an external shell composed of Li₄SiO₄, Li₂CO₃ and Li₂O in a non-stoichiometric reaction. Independently of the external shell composition, the final surface area and pore volume increased independent of the external shell composition and favored the second sorption process: CO₂ adsorption. Therefore, high pressures enhance CO₂ capture between 30 and 350 °C, promoting the chemisorption and adsorption processes.

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1. Introduction

Recently, the concentration of atmospheric carbon dioxide (CO₂) reached 400 ppm, which has never been observed in recent centuries. Consequently, the so-called greenhouse effect and global warming have increased as well [1–4]. Therefore, several strategies have been proposed to reduce or control CO₂ emissions [2].

Among the possible solutions, different materials have been studied as CO₂ captors at low (30–100 °C), moderate (100–400 °C) or high ($T \geq 400$ °C) temperatures [5–7]. At low temperatures, different activated carbons, zeolites, and other organic/inorganic cage structures have been tested as possible CO₂ captors, presenting some advantages and disadvantages [7]. Other materials have been analyzed as possible CO₂ captors at high temperatures, such as calcium oxide and some lithium or sodium ceramics [8–26]. Thermodynamically, several of these lithium and sodium materials are able to trap CO₂ at moderate temperatures (100–400 °C), although the reaction processes are kinetically

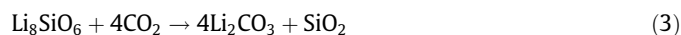
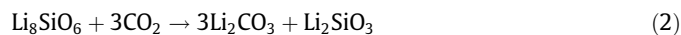
limited [15,17]. Nevertheless, several papers have shown that CO₂ capture kinetics and efficiencies depend on several different factors, such as the chemical and structural compositions, and several microstructural factors, among others [15,17,23–24].

Among the alkaline ceramics, lithium silicates present good CO₂ capture properties at moderate and high temperatures [8–17]. There are several studies showing that lithium orthosilicate (Li₄SiO₄) [8–12,15–19] and lithium oxosilicate (Li₈SiO₆) are able to chemisorb CO₂ between 400 and 650 °C [13–15], although the theoretical data say that CO₂ chemisorption would occur at lower temperatures [15]. Recently, it has been shown that Li₈SiO₆ is capable of trapping significant quantities of CO₂ at temperatures equal to or higher than 600 °C (11.9 mmol of CO₂ per gram of ceramic at 650 °C). Additionally, this temperature range can be modified via sodium (9.3 mmol/g at 550 °C) and/or potassium (7.5 mmol/g at 400 °C) carbonate additions [13,14]. However, substantial CO₂ chemisorption values on this ceramic are only produced at temperatures higher than 400 °C. In addition, CO₂ chemisorption on Li₈SiO₆ is dependent on the temperature as follows:



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These reactions show that Li_8SiO_6 would be able to react with different quantities of CO_2 , producing Li_2CO_3 and different lithium secondary phases: Li_4SiO_4 , Li_2SiO_3 and SiO_2 . Moreover, at temperatures between 400 and 580 °C, Li_4SiO_4 reacts with CO_2 , [8–12, 15–19] while Li_2SiO_3 is able to chemisorb CO_2 at temperatures below 250 °C [25]. Therefore, the formation of these two phases may improve the total CO_2 chemisorption capacity.

In contrast, in the temperature range between 100 and 400 °C, there are not many viable CO_2 capturing materials. In fact, layered double hydroxides (LDH) are one of the few types of materials evaluated in this temperature range [7,27]. In addition, there are few studies related to high-pressure CO_2 capture, and these works were performed using LDH structures, where the CO_2 capture efficiencies are usually improved several times in comparison to CO_2 capture at atmospheric pressure [28–30]. Therefore, the aim of the present paper is to study the CO_2 capture process on lithium oxosilicate (Li_8SiO_6) at varying pressures and moderate temperatures, which may increase the CO_2 capture efficiency.

2. Experimental section

Li_8SiO_6 was synthesized via a solid-state reaction using silica gel (SiO_2 , Merck) and lithium oxide (Li_2O , Aldrich) as reagents; excess lithium oxide (15 wt%) was used to prevent lithium sublimation. The powders were mechanically mixed and thermally treated at 800 °C for 8 h as previously reported [13,14]. Additionally, Li_4SiO_4 was synthesized for comparative purposes. In the present work, Li_4SiO_4 was also prepared via solid-state reaction using fumed silica (SiO_2 , Aldrich) and the same lithium source described previously in the Li_8SiO_6 synthesis. In this case, the Li/Si molar ratio was equal to 4.1/1. The Li_4SiO_4 powders were mechanically mixed and thermally treated at 700 °C for 4 h [11].

The Li_8SiO_6 samples, before and after CO_2 sorption experiments, were characterized using X-ray diffraction (XRD), N_2 adsorption-desorption and scanning electron microscopy (SEM). The XRD patterns were obtained using a D5000 diffractometer from Siemens with a $\text{Co K}_{\alpha 1}$ radiation source at 34 kV and 30 mA. The diffraction patterns were recorded over the 2-theta range of 10–80° with a step size of 0.02° and were correlated with the different JCPDS files.

The microstructural characteristics of the initial sample and high-pressure CO_2 products were determined using scanning electron microscopy (SEM) and N_2 adsorption. The particle size and morphology were determined using SEM in a JEOL JMS-7600F microscope. Additionally, the textural characteristics (BET surface area, pore size and pore volume) were determined via N_2 adsorption-desorption experiments at 77 K using a Minisorp II instrument from Bel-Japan and a multipoint technique. All samples were outgassed at room temperature under high vacuum for 24 h before the N_2 adsorption-desorption tests.

The CO_2 capture capacity at elevated pressure on the Li_8SiO_6 was determined using a volumetric Belsorp-HP instrument from Bel-Japan. This equipment has the capacity of degassing the sample by vacuum and measure the dead volume using Helium. Then, CO_2 capture capacity was determined at different temperatures (between 30 and 350 °C), using a thermal electric chamber, while the CO_2 was dosed by a manifold thermalized at 30.5 °C. The experiments were performed between atmospheric and 1 MPa of pressure. The non-ideal behavior of the CO_2 gas was corrected by applying virial equations using four virial coefficients. The virial coefficients were calculated from the National Institute of Standards and Technologies (NIST) web page. Data were calculated at the respective temperature in the heater at a maximum pressure

of 1.0 MPa. It must be mentioned that the virial equation of state of gases has additional terms beyond that for ideal gases, which account for the interactions between the molecules. Pressure can be expressed in terms of the molar volume $V_m = V/n$ (where n is the number of moles of gas molecules in a volume V), the absolute temperature T , and the universal gas constant, $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ (Eq. (4)). In this equation the virial coefficients $B_n(T)$ are functions only of the temperature and depend on the nature of the gas, CO_2 in this case.

$$\frac{V_m}{RT} = 1 + \frac{B_2(T)}{V_m} + \frac{B_3(T)}{V_m} + \frac{B_4(T)}{V_m^3} + \dots \quad (4)$$

The powders were initially activated before the CO_2 sorption tests. First, the sample was introduced in the adsorption cell and outgassed at 60 °C for 4 h before testing because the materials are sensitive to the presence of moisture and environmental CO_2 . The adsorption experiments were performed at temperatures between 30 and 350 °C. At each temperature, the pressure was increased to 1000 kPa, establishing equilibrium times between 1 and 50 min.

3. Results and discussion

Fig. 1 shows the CO_2 sorption isotherms on Li_8SiO_6 at different temperatures (30–350 °C) and high pressures (5–1000 kPa). At 30 °C, the CO_2 sorption was low (0.2 mmol/g). However, at 100 °C the CO_2 sorption increased exponentially up to 2.45 mmol/g, when pressure reached 1 MPa of pressure. The CO_2 captured under these temperature and pressure conditions are substantially higher than those observed in previous works for the Li_8SiO_6 - CO_2 system at atmospheric pressure [13,14]. In fact, in those previous cases, where all the experiment were at atmospheric pressure, only varying temperature, the CO_2 chemical capture began only at temperatures higher than 300 °C, even in the presence of K_2CO_3 and Na_2CO_3 , where were used as additives. Thus, these initial results strongly suggest that pressure seems to improve both the physical and chemical CO_2 capture. It must be related to different CO_2 sorption-desorption equilibria at atmospheric and high pressure conditions.

At temperatures between 150 and 250 °C, the CO_2 sorption decreased as a function of temperature from 1.9 to 1.1 mmol/g. This behavior suggest a dominant CO_2 adsorption process, where the CO_2 adsorption-desorption equilibrium is altered by the temperature. These isotherms trapped CO_2 in two different steps. Initially, at pressures close to atmospheric pressure, Li_8SiO_6

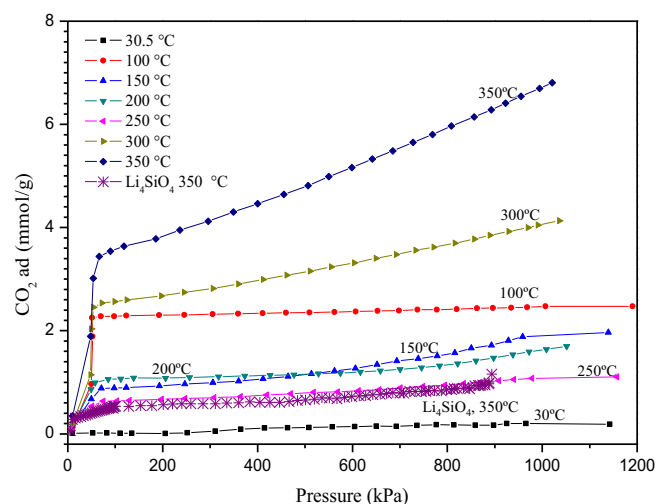


Fig. 1. High-pressure CO_2 sorption curves at different temperatures.

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