Sol-gel Synthesis of Li_4SiO_4 Nanoparticles for CO_2 Capture at High Temperature

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Removing carbon dioxide from industrial effluents (i.e. flue gas) via solid sorbents is a potential greenhouse gas mitigation strategy. Lithium orthosilicate (Li_4SiO_4) is one of the most promising materials for CO_2 capture at high temperature (500-700 °C).
In this study, the non-hydrolytic sol-gel technique was used to synthesized Li_4SiO_4 nanoparticles for improving lithium silicate features as solid sorbent for carbon dioxide. The CO_2 sorption properties of the obtained nanoparticles were investigated by using a thermal gravimetric analyzer (TGA) in a controlled gas flow environment at CO_2 partial pressure of 0.6 atm and at 700 °C. Li_4SiO_4 nanoparticles with average diameter less than 100 nm aggregated in clusters less than 500 nm were obtained. An amount of adsorbed carbon dioxide of 6.9 mmol of CO_2/g sorbent, corresponding to an 82.4 % conversion of lithium orthosilicate, was reached. The promising results could be related to high surface area of nano-size material synthesized by sol-gel process.

1. Introduction

The huge CO_2 emission induced by human activities, including the combustion of fossil fuels, have been recognized as one of main contributors to climate change, with the atmospheric CO_2 concentration increasing by 40 % since the industrial revolution (Yang et al., 2008). To address this global problem, carbon dioxide capture and storage (CCS) technologies including oxy-combustion, pre-combustion and post-combustion carbon capture have been developed (Pires et al., 2011). Post-combustion capture in particular, has shown significant potential for reducing CO_2 emissions through emerging technologies operating at high temperature (450-750 °C) by using regenerable solid sorbents based on lithium orthosilicate (Li_4SiO_4) (Puccini et al., 2016). The adsorption of CO_2 by Li_4SiO_4 proceeds by formation of lithium carbonate, Li_2CO_3, and lithium metasilicate, Li_2SiO_3, according to the reversible reaction r1:

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3 \tag{r1}$$

Li_4SiO_4 can be synthesized using different methods: the solid-state reaction, the precipitation method, the impregnation suspension method and the sol–gel method (Pfeiffer et al. 1998). In previous studies (Puccini et al., 2013), the authors synthesized Li_4SiO_4 powders by solid state reaction and precipitation method obtaining sorbents with high CO_2 sorption capacities.
The sol-gel process is a chemical technique for synthesizing high purity nanoparticles. The main advantage of this method is the precise control of nanoparticles size and size distribution since it usually takes place in solution and at low temperatures. The process is characterized by three steps: the formation of stable solutions of alkoxides or solvated metal precursors (sol), the creation of gel by polycondensation and polyesterification reactions which increase the viscosity of the solution and a thermal treatment that leads to the final desired material.

Sol-gel process could be hydrolytic (using water as medium) and non-hydrolytic (using an organic medium) (Cushing et al., 2004). The non-hydrolytic sol-gel method uses organic compounds in the reaction system (solvents, the binder of the precursor molecule, surfactants) that strongly determine the size and the shape of nanoparticles and the surface proprieties (Niederberger and Pinna, 2009). The process is based on the thermal decomposition of a sol-gel to synthesize small size monodisperse nanocrystals through the decomposition of organometallic compounds in organic solvents with high boiling point, in the presence of a stabilizing surfactant.

Recently, several studies are focused on the removal of pollutants in liquid and gas flows by using different types of nano-size materials. Chiavola et al. (2016) reports on new magnetite nanoparticles for arsenic removal from water. Muradova et al. (2016) investigate the effectiveness of nano Zero-Valent Iron and bimetallic nanoparticles of Fe/Cu in the remediation of nitrate-polluted groundwaters. González-Barriuso et al. (2016) develop amine-modified sorbents solid supports with highly developed porosity and active sites for CO_2 capture at low temperature.

In this work, nanoparticles of Li_4SiO_4 were obtained by using the non-hydrolytic sol-gel method. Two different sorbents were produced, varying calcination conditions of the obtained gel. Their CO_2 adsorption properties were investigated by thermal gravimetric analysis (TGA) at 700 °C and at CO_2 partial pressure of 0.6 atm. X-ray diffraction analysis (XRD) and transmission electron microscope (TEM) were used to characterize the prepared sorbents and to understand the relationship between the sorbent microstructure and CO_2 sorption properties.

2. Experimental

2.1 Sorbents preparation and characterization

Li_4SiO_4 nanoparticles were synthesized by the non-hydrolytic sol-gel method. Starting reagents (all from Sigma Aldrich) were lithium hydroxide (LiOH), silicon tetraacetate ($Si(OCOCH_3)_4$), 1,2-tetradecanediol ($C_{14}H_{30}O_2$) as promoting agent and benzyl-ether ($(C_6H_5CH_2)_2O$) as solvent. The equipment necessary for non-hydrolytic sol-gel synthesis was composed by a three-neck round bottom flask and a reflux round bottom flask, with a stirring/heating mantles and a temperature control. The system was taken under nitrogen flow and the outlet gas was purifying by flushing through silicon oil. The core of the system is the three-neck round bottom flask, which is the reactor that contains the reagents have to react together.

The basic reactions of the non-hydrolytic sol-gel synthesis process are an alcoholysis reaction and an ester's elimination, according to Joo et al. (2005) that report the synthesis of ZnO nanocrystals. The reaction is composed by two steps, as shown in Figure 1. The first stage takes place at 200 °C and has the purpose to create the precursor of lithium orthosilicate, the orthosilicic acid (H_4SiO_4). The orthosilicic acid reacts with lithium hydroxide with an alcoholysis reaction to form the network which is the gel's precursor. The gel is formed during the second stage by a condensation reaction which takes place thanks to the high electronegativity of Si that weakens the bond (Cushing et al., 2004). This step is made at 300 °C to allow the reaction of esters elimination. After the gel formation, as third step a thermal treatment (dry-out process and calcination) is applied to the samples. The calcination is particularly required to redistribute the bonds in order to create lithium orthosilicate, to eliminate the residual organic material and to define the crystallized structure. This step can be defined as densification and gel decomposition because the residual bonds are destroyed, the gel's structure collapses and the desired ceramic material is created (Cushing et al., 2004).

The reacting solution was prepared inside the three-neck round bottom flask with 2.5 mmol of $Si(OCOCH_3)_4$, 18 mmol of LiOH, 35 mmol of 1,2-tetradecanediol and 25 mL of benzyl-ether. Under nitrogen flow, the solution was mixed vigorously and the temperature was increased until 200 °C and kept constant for 2 h. Next, the temperature was increased again until 300 °C and maintained constant for 1 h. At this temperature, the solvent starts to evaporate and the reflux round bottom flask works as condenser permitting the recycle of the solvent. After cooling at room temperature, the obtained solution was washed in three steps. First, each 20 mL of solution was mixed with 20 mL of methanol, sonicated until complete dissolution of the solid and centrifuged to separate solid and liquid phases (9800 rpm, 10 min). Next, the remained solid was mixed with 20 mL of hexane and sonicate until complete dissolution. Finally, the solution was mixed with 25 mL of ethanol, sonicated until homogenous status and centrifuged to separate the two phases (9800 rpm, 10 min). The remaining solid was dry-out in air at room temperature, overnight. After that it was crushed, mixed and calcined in air at 700 °C for 2 h. Two Li_4SiO_4 samples were prepared using two different heating rates: 3 °C/min (sample I) and 10 °C/min (sample II).

Powder X-ray diffraction (XRD) characterization of Li_4SiO_4 samples was conducted using a PANalytical X'Pert PRO XRPD X-ray diffractometer with 1.8 kW sealed X-ray tube source, using a Cu target, and a vertical circle theta: theta goniometer with a radius of 240mm. The XRD patterns were recorded over a 2θ range between

15° and 70°. Phase identification was verified by comparison against the standard diffractograms contained in the International Centre for Diffraction Data (ICDD).

Transmission electron microscope (TEM) was used to analyze the internal structure of the sample. The TEM model used was a FEI Tecnai Multipurpose TEM (G2 Spirit TWIN). It is a high quality 120 kV multipurpose TEM, providing high resolution and good contrast.
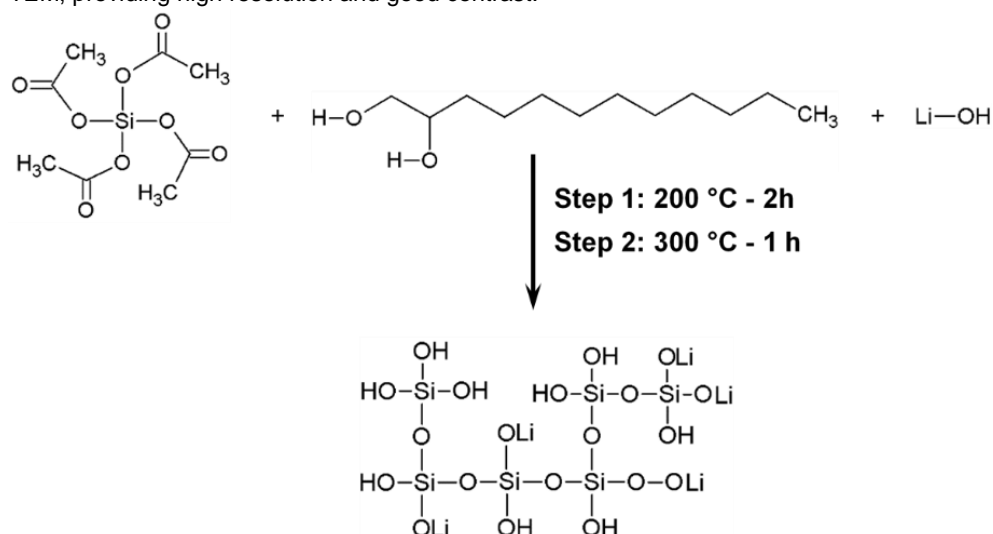

Figure 1: Schematic representation of non-hydrolytic sol-gel method.

2.2 CO$_2$ sorption test

Carbon dioxide adsorption on Li$_4$SiO$_4$ samples prepared with non-hydrolytic sol-gel method was studied using a thermogravimetric analyzer (TGA Q500 TA Instrument). The sample was placed in a platinum sample pan and first was pre-conditioned and dried in a nitrogen flow (100 mL/min) elevating the temperature to 600 °C and maintaining constant for 1 h. This pre-treatment was required to remove the residual water and organic compounds from the sample and stabilize the sample's weight. Then, the adsorption step was carried out at 700°C switching the N$_2$ flow to a mixture CO$_2$/N$_2$ containing 60 vol% of CO$_2$. The total feed gas flow rate was maintained at 100 mL/min at atmospheric pressure. The weight increase due to CO$_2$ sorption was recorded as a function of time during the adsorption process lasted 60 min. Afterwards, the desorption process was carried out just by switching the gas flow to 100 vol% of N$_2$, maintaining the temperature at 700°C until the sample was completely regenerated.
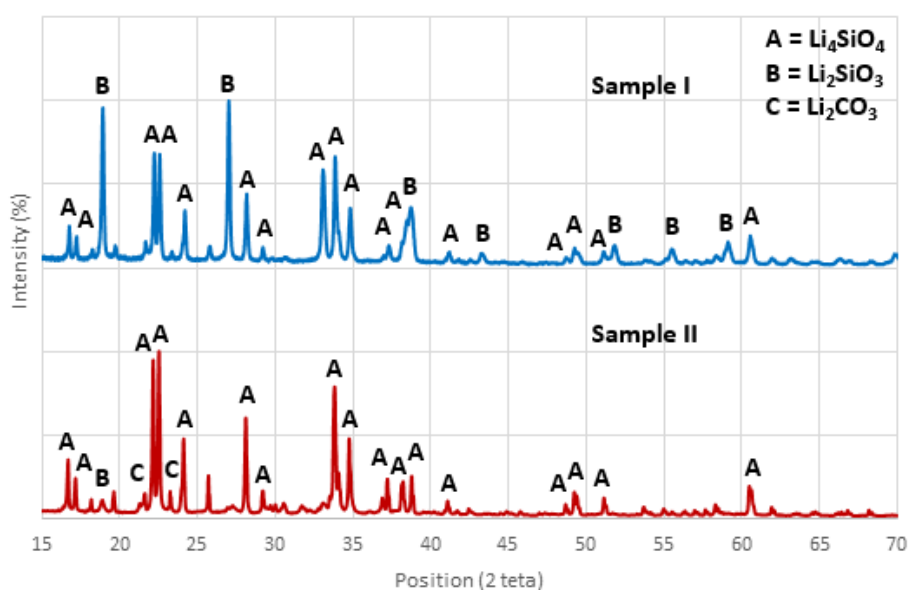

Figure 2: XRD patterns of Li4SiO4 (samples I and II) sorbents synthesized by non-hydrolytic sol-gel method.

3. Results and discussion

The XRD analysis was conducted on both Li_4SiO_4 samples obtained by non-hydrolytic sol-gel synthesis (I and II). The results are shown in Figure 2. The XRD patterns of both samples confirm the formation of Li_4SiO_4, showing the characteristic peaks of lithium orthosilicate with inclusion of lithium metasilicate (Li_2SiO_3) and lithium carbonate (Li_2CO_3). Sample II, obtained using a heating rate of 10 °C/min for calcination step, presents a reduction of the intensity of peaks associated to Li_2SiO_3.

By a comparison between the TEM analysis of sample I (Figure 3) and sample II (Figure 4), it can be seen that the average size of sample II is smaller than sample I. In particular, sample I is characterized by nanoparticles of average diameter less than 100 nm aggregated in clusters with an average size of about 1 μm. Whereas, by increasing the heating ramp during the calcination step (from 3 to 10 °C/min) the resulting product still presents nanoparticles with average diameter less than 100 nm aggregated in clusters with an average size less than 500 nm.

In order to evaluate the CO_2 sorption behavior of obtained Li_4SiO_4 nanoparticles, sorption runs were performed on samples I and II. Figure 5 shows the weight increase of Li_4SiO_4 samples as a result of CO_2 sorption from a 60 vol% CO_2 stream at 700 °C. As can be seen, the CO_2 sorption capacity increases up to 6.9 mmol of CO_2/g sorbent for sample II, whereas sample I reaches 5.7 mmol of CO_2/g sorbent. However, both samples display a high adsorption rate reaching the maximum CO_2 sorption capacity just after 3 minutes of adsorption at 700 °C. The difference in the amount of CO_2 adsorbed by samples I and II can be attributed to the differences in purity and surface area. Sample II, which is made by a calcination heating rate of 10°C/min instead of 3°C/min, present a more defined XRD pattern (Figure 2) and a less aggregated material (Figure 3 and 4). Indeed, a more purity of the sample leads to a higher content of Li_4SiO_4 which means a higher amount of reacting reagent. At the same time, a higher surface area promotes the contact between the solid sorbent (Li_4SiO_4) and the gas phase (CO_2) and their reaction.

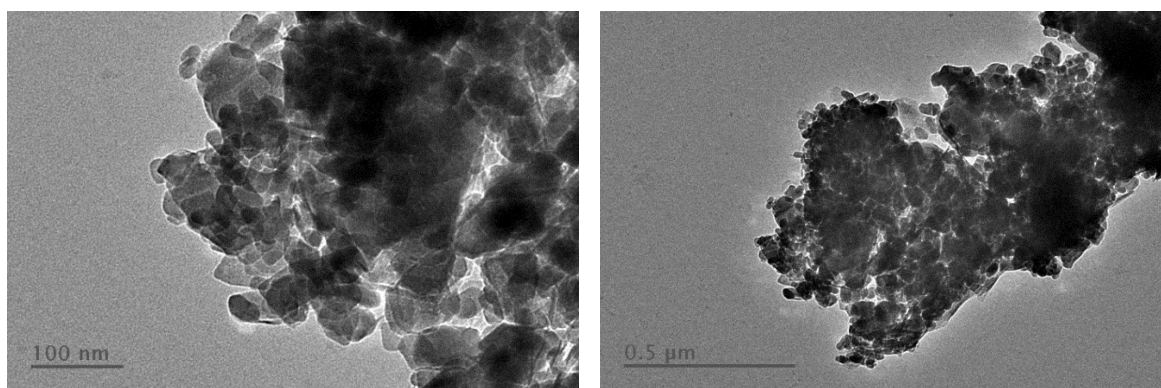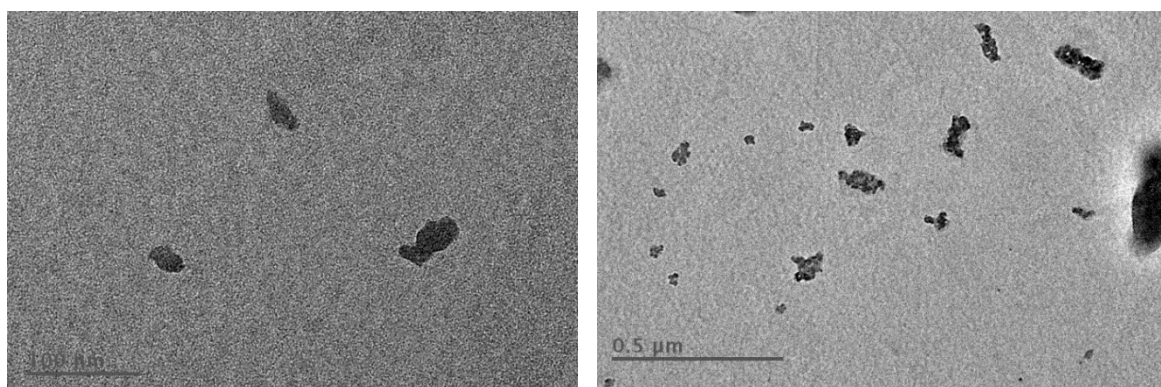*Figure 3: TEM images of Li_4SiO_4 obtained by non-hydrolytic sol-gel synthesis, with calcination step at 700 °C and a heating rate of 3 °C/min (sample I).*

Figure 4: TEM images of Li_4SiO_4 obtained by non-hydrolytic sol-gel synthesis, with calcination step at 700 °C and a heating rate of 10 °C/min (sample II).

The percentage conversion of Li_4SiO_4, $X_{Li_4SiO_4}$, was calculated following the equation Eq(1):

$$X_{Li_4SiO_4}(\%) = \frac{\Delta W}{F_{Li_4SiO_4} \cdot r_s} \tag{1}$$

where ΔW is the percentage weight change of the sorbent during the adsorption, $F_{Li_4SiO_4}$ is the weight fraction of Li_4SiO_4 in the sorbent and r_s is the stoichiometric uptake of CO_2 by Li_4SiO_4, which is about 0.367 g of CO_2/g of Li_4SiO_4 (corresponding to 8.34 mmol of CO_2/g sorbent). In Table 1 are reported the conversion of Li_4SiO_4 reached for both samples I and II, compared with results obtained in previous works (Puccini et al. 2013) with lithium orthosilicate produced by solid state method doped with 20 wt% of K_2CO_3 (LiK). As can be seen, the sample II reaches a conversion of lithium orthosilicate of 82.4 %, similar to the value reached by sample LiK. Indeed, the conversion of pure-Li_4SiO_4 (Li) produced by solid-state method shows a conversion of 13.8 % (see Table 1). Since the CO_2 diffusion is the main limitation during carbon dioxide adsorption, the results could be related to the lower average size of the sample synthesized by sol-gel methods (nano-size) compared to the other ones (micron-size). Therefore, similar Li_4SiO_4 reactivity can be reached by reducing the particles size of material, or by mixing with dopants.
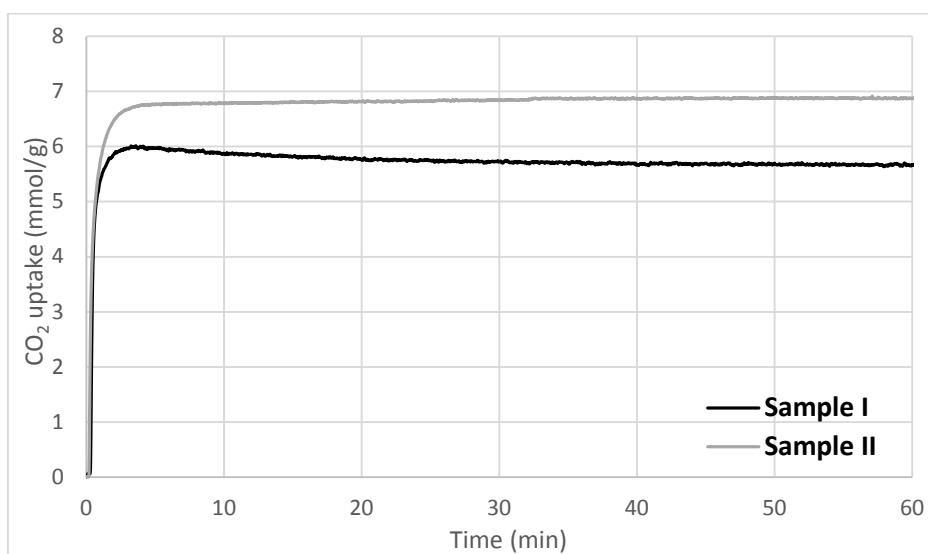

Figure 5: CO_2 sorption profiles on samples I and II in 60 vol% CO_2 at 700 °C.

Table 1: Percentage conversion of Li_4SiO_4 after adsorption in 60 vol% CO_2 at 700 °C.

Sample	$X_{Li4SiO4}$ (%)
I	68.0
II	82.4
Li	13.8
LiK	92.5

4. Conclusions

The present work had the purpose to investigate the behaviour of lithium orthosilicate as solid sorbent for CO_2 capture at high temperature (600-700 °C). Since the adsorption process is a surface controlled mechanism, to increase the carbon dioxide uptake a high surface area of the solid is required. In this study, nanoparticle sized Li_4SiO_4 was synthesized using a non-hydrolytic sol-gel method followed by a calcination step at 700 °C for 2 h. The results showed that by increasing the heating ramp during the calcination step (from 3°C/min to 10°C) the resulting Li_4SiO_4 presented higher purity and showed a smaller average size. Nanoparticles with average diameter less than 100 nm aggregated in clusters with an average size less than 500 nm were obtained. CO_2 sorption capacity was investigated by TGA at 700 °C and at 0.6 atm CO_2 partial pressure. Nanoparticle sized Li_4SiO_4 showed high adsorption rate and reached a CO_2 sorption capacity of 6.9 mmol of CO_2/g sorbent corresponding to 82.4 % conversion of lithium orthosilicate.

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