Lithium-based sorbents for high temperature CO$_2$ capture: effect of precursor materials and synthesis method

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Abstract

The aim of this work was to study the effect of the silica source (pure reagent or fly ash, FA) and preparation method (solid state reaction and precipitation method) using a Li-pure reagents on the CO_2 uptake at high temperature of the prepared sorbents. CO_2 uptake of sorbents prepared from pure reagents or FA was compared. A relationship between surface area, pore volume and particle size with CO_2 uptake of the prepared samples was not found. X-ray diffraction (XRD) characterization revealed different Li_4SiO_4 contents in the produced samples. Sample prepared from Li_2CO_3 and SiO_2 pure reagents by solid state method had a high Li_4SiO_4 content (91.5 wt%), but in the presence of FA the main compound was Li_2CaSiO_4, which has a low theoretical CO_2 uptake capacity. There is a negligible effect of the preparation method on samples prepared from LiOH with either pure silica or FA. However, for pure reagents (LiOH and SiO_2), the Li_4SiO_4 content was lower than that found when Li_2CO_3 was used as starting material, probably due to a lower synthesis temperature. For LiOH-FA derived samples, XRD patterns showed that CaO was the main crystal phase and the Li content was low, indicating that this element was probably present in the amorphous phase. Except for the Li_4SiO_4 rich sample, a linear relationship was found between the experimentally measured CO_2 uptake and the theoretically calculated one based on the stoichiometry of carbonation reactions exhibited by active phases contained within each sorbent, and normalised to crystal phase contents. Despite the high CaO content in some of the FA-derived samples, the carbonation reaction does not proceed via $CaCO_3$ formation and Li_2CaSiO_4 and $Ca_5(SiO_4)_2CO_3$ crystal phases are present in the carbonated samples, limiting the CO_2 capture of CaO present in the fly ash.

1. INTRODUCTION

Carbon capture and storage (CCS) is one of the technological options to reduce anthropogenic CO_2 emissions. In CCS, CO_2 is captured at large point sources such as coal-fired power plants or industrial plants, compressed to supercritical conditions and, then, sent for storage.

The costs of CCS can be divided into three components: capture (including separation and compression), transport and storage (including measurement, monitoring and verification). The cost of capture dominates the cost of CCS systems [1].

Solid sorbents have become a promising option to capture CO_2, although liquid solvents are still considered as the most mature CO_2 capture technology. However, the commonly used amine-type solvents are prone to degradation and oxidation (performance stability) resulting in products that are corrosive and may require hazardous material handling procedures [2].

In this context, the use of solid sorbents represents an alternative that could reduce the energy required to move liquid solvents and their regeneration by more than 30% if high CO_2 uptake capacity of the sorbent is achieved [3].

Lithium ceramics represent a group of high-temperature CO_2 sorbents that have attracted interest mainly because their superior stability compared to CaO [4]: they can work under a wide temperature range, between 25 °C and 700 °C [5], and they can maintain the CO_2 capture efficiency upon cycling [5, 6].

Among lithium ceramics, lithium orthosilicate, Li_4SiO_4, is one of the most promising materials due to its high CO_2 uptake capacity and sorption kinetics, especially at high temperatures [5]. Li_4SiO_4 chemisorbs CO_2 according to the following reaction:

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

The theoretical maximum uptake of Li_4SiO_4 is 735 g CO_2/kg sorbent, but previous works claimed that Li_2SiO_3 was not able to absorb CO_2 [7, 8]. Recent papers proposed that CO_2 absorption on Li_2SiO_3 does occur, but it is not kinetically favoured [9, 10]. Furthermore, practically, this reaction product restricts the sorption process, limiting the CO_2 theoretical maximum uptake of Li_4SiO_4 to 367 g CO_2/kg sorbent.

A process simulation study for integration of a Li_4SiO_4/Li_2CO_3 looping of a post-combustion CO_2 capture plant into a natural gas combined (NGCC) plant was carried out to compare energy penalty, and thus costs, with amine-CO_2 based capture (conventional MEA and second generation solvent CESAR-1) and calcium looping into the same power plant [11]. The authors showed lower energy penalty for Li_4SiO_4/Li_2CO_3 looping system compared to the best performing (CESAR-1) and they also found a significant efficiency improvement compared to calcium looping.

It has been reported that doping Li_4SiO_4 with sodium [12], potassium [13] aluminium and iron [14] could improve ion mobility. Since the reaction of Li_4SiO_4 with CO_2 is assumed to occur at the outer surface of the crystal grain, it is related to ion diffusion of Li^+ and O^{2-}, which react with CO_2 to form lithium carbonate [15]. Thus, inserting defects into Li_4SiO_4 crystal lattice could improve its reactivity.

The use of waste materials as a source of silica for lithium orthosilicate synthesis has been previously investigated [16]; it could help not only to reduce the cost of the sorbent but also to introduce foreign elements into the Li_4SiO_4 crystal lattice that could avoid the kinetic restrictions due to the formation of

Li_2SiO_3 layer [14, 17]. However, there are other elements present in this type of silica-containing wastes that could not participate in the reaction, which could limit the sorbent performance; so as a general guide, the CO_2 uptake capacity of waste-derived high temperature solid sorbents should be to at least similar to the commercially available solvents, which has been reported around 180 g CO_2/kg solvent for 30% MEA (in water) at 40 ºC and an inlet CO_2 concentration 4% [18].

In this work, the effect of silica source (pure reagent or fly ash) and the preparation method (solid state reaction and precipitation method) on CO_2 uptake at high temperature of derived Li_4SiO_4 sorbents have been evaluated. The main goal is to assess the role of foreign elements present in the fly ash as potential promoters of CO_2 capture by the derived sorbent materials. Lastly, a comparison between the aforementioned sorbents and those prepared from pure reagents under the same synthesis conditions will be also established.

2. EXPERIMENTAL

2.1. Preparation of samples

Lithium sources used were Li_2CO_3 (Across Organics, purity 99.0%) and $LiOH.H_2O$ (Across Organics, purity 98.0%). Silica sources used were SiO_2 (Aldrich, purity 99.5) and a fly ash from an Estonian oil shale power plant (composition in Table 1).

To obtain lithium orthosilicate according to reactions (2) and (3) the Li source with a 10% of excess of the stoichiometric amount was added to prevent the sublimation of lithium at high temperature [19]. When the fly ash (FA) was used as silica source, the amount added to the synthesis was that equivalent to the

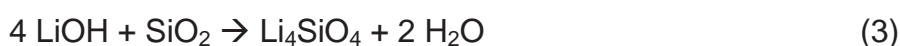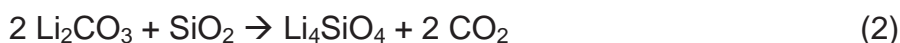required stoichiometric molar SiO_2 content.

$$2 Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2 CO_2 \qquad (2)$$

$$4 LiOH + SiO_2 \rightarrow Li_4SiO_4 + 2 H_2O \qquad (3)$$

Table 1. Fly ash composition

Component	%
SiO_2	33.97
Al_2O_3	8.77
Fe_2O_3	4.36
MgO	4.51
CaO	34.84
Na_2O	0.01
K_2O	4.94
TiO_2	0.51
MnO	0.06
P_2O_5	0.19
LOI	7.5

Two different methods for Li_4SiO_4 preparation have been used: solid state reaction (SS) and precipitation method (P).

The conventional SS method is the dominating pathway for ceramic synthesis due to its simplicity. The appropriate amount of Li- and Si- sources were mixed in a planetary ball mill (Pulverissete 6, Fritsch). After that, the resulting powder was submitted to calcination in a muffle furnace, at 600 ºC when using LiOH and at 800ºC when using Li_2CO_3.

The precipitation method was only used with LiOH because its higher solubility compared to Li_2CO_3. LiOH was dissolved into deionized water, using a water ratio previously used by Chang et al. [20]: 1 mol $LiOH.H_2O$/375 ml H_2O. Once the clear solution is prepared, the Si source is added to maintain a molar ratio 4.4 $LiOH.H_2O$/1 SiO_2. The total amount of solid added depends on Si-source: pure reagent or fly ash, as it has been explained above. The solution is stirred

during 20 min at room temperature. After that, it is subjected to evaporation.
Two different procedures were applied to evaporate water from the solution: (i)
a simple evaporation (E) at 70 ºC until constant weight; (ii) evaporation using a
rotary evaporation (R) at 55 ºC under vacuum. After the evaporation step, the
resulting powder was submitted to calcination at 600 ºC in a muffle furnace. The
synthesis temperature was lower in this case based on the studies of Chang et
al. [20].

The calcined material was ground by a mechanical mortar and pestle to break
down agglomerated particles before characterization and analysis.

A summary of the preparation conditions as well as sample labelling of the
prepared sorbents is depicted in Table 2.

Table 2. Synthesis conditions and nomenclature for prepared samples.

Label	Li-source	Si-source	Synthesis method	Evaporation method	Calcination
LiC_Si/SS	Li_2CO_3	SiO_2	Solid state	-	800 ºC, 7 h
LiOH_Si/SS	LiOH	SiO_2	Solid state	-	600 ºC, 7 h
LiC_FA/SS	Li_2CO_3	Fly ash	Solid state	-	800 ºC, 7 h
LiOH_FA/SS	LiOH	Fly ash	Solid state	-	600 ºC, 7 h
LiOH_Si/P_E	LiOH	SiO_2	Precipitation	70 ºC	600 ºC, 7 h
LiOH_Si/P_R	LiOH	SiO_2	Precipitation	Rotary, 55 ºC	600 ºC, 7 h
LiOH_FA/P_E	LiOH	Fly ash	Precipitation	70 ºC	600 ºC, 7 h
LiOH_FA/P_R	LiOH	Fly ash	Precipitation	Rotary, 55 ºC	600 ºC, 7 h

2.2. Characterization of samples

Sorbents were characterized by different techniques. N_2 physisorption analysis
at -196 ºC was performed in a Micromeritics Gemini VII to obtain BET surface
area and pore volume. XRD diffractograms were collected by a Bruker D8

Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector. Identification and quantification of crystalline phases were carried out by DIFFRAC.EVA and TOPAS software. DIFFRAC.EVA software supports a reference pattern database derived from Crystallography Open Database (COD) and The Powder Diffraction File (PDF) for phase identification. Quantitative XRD analysis of the crystal phase was performed by Rietveld refinement [21] using TOPAS software. Inorganic Crystal Structure Database (ICSD) was used to obtain crystal structures of the considered phases. S-Q method was used in complex diffractograms; this method is based on the comparison of peak intensities between the considered samples. Particle size distribution (PSD) was obtained using a Mastersizer 3000 with a Hydro SM to disperse the sample in the solvent. The solvent used was ethanol in order to avoid FA dissolution.

2.3. CO_2 capture tests

The CO_2 uptake capacity of the prepared sorbents was evaluated using a thermobalance Q500 from TA Instruments. The performance of the sorbents was tested under 50 ml/min flow containing 92% CO_2. The sample was in-situ pre-treated during 60 min at 110ºC under N_2, followed by 30 min at 600 ºC, heating rate of 25ºC/min, under N_2 atmosphere. After this pre-treatment, the atmosphere was changed to the CO_2 atmosphere (92 %, N_2 as balance) and it was kept under isothermal conditions at 600 ºC during 120 min. Blank tests were performed for those running conditions.

3. RESULTS AND DISCUSSION

3.1. Sample characteristics and CO_2 uptake

The fly ash used has a silica content of 33.97 %, which was lower than that used in other works [22, 23], and thus a higher amount of fly ash had to be added to the synthesis in order to obtain the desired Li_2CO_3-SiO_2 stoichiometry that yields Li_4SiO_4 (reaction 2). The presence of Na in the fly ash is almost negligible (0.01% Na_2O); despite Na_2SiO_3 is able to capture CO_2, the quantity is limited to values around 1% under dry conditions [24]. The presence of Ca in the fly ash is however noteworthy (34.84% CaO). This FA was selected because its high calcium content and it is representative of fly ash resulting from combustion of lignite and sub-bituminous coal with CaO up to 15-35% [25]. Thus, other fly ash with high CaO content coming from combustion of lignite and sub-bituminous coal could be used for this approach.

It has been well established that CaO-based sorbents have high sorption capacity (stoichiometric uptake value of 78 wt%) and fast kinetics under a wide range of temperatures, but regeneration has to be conducted at temperatures higher than 900 ºC [26], which implies rapid loss of sorbent activity during capture looping leading to the need to add fresh sorbent during the process [27].

Other elements also present in the fly ash such as K, Fe and Al are reported to enhance Li-containing sorbents performance by Li_4SiO_4 doping [14, 28, 29]. Hence, the influence of the abovementioned fly ash containing elements in the resultant synthesised sorbents was evaluated. Towards that aim, sorbents prepared from pure reagents were also evaluated for CO_2 uptake under the same experimental conditions.

The strong effect of the carbonation temperature was already observed for pure Li_4SiO_4 and alkali promoted Li-sorbents [20, 23, 30, 31] and accordingly the carbonation temperature selected for this study was 600 °C.

Figure 1 depicts the CO_2 uptake at 600 °C obtained in thermogravimetric experiments for the samples prepared (notation in Table 2).
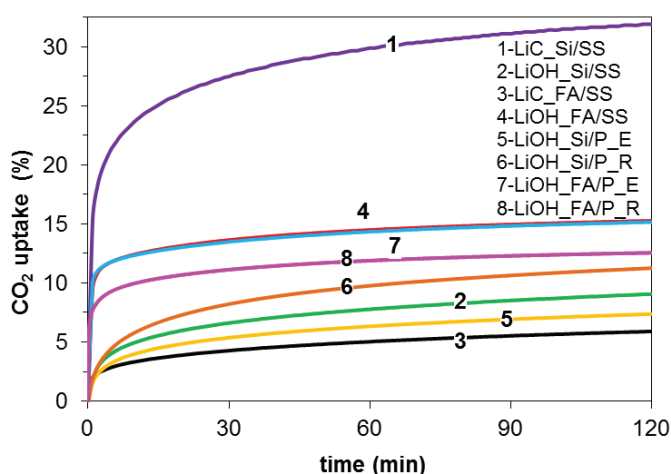

Figure 1. TG curves of CO_2 uptake isothermal experiments for the prepared samples.

For sample LiC_Si/SS, a CO_2 uptake of 31.9 % was obtained, which is close to the theoretical sorption capacity of Li_4SiO_4 of 36.7 % and comparable to that found by other authors using a similar synthesis procedure [14, 26, 31, 32]. Except for LiC_Si/SS and LiC_FA/SS samples, for which the use of pure reagents has a very positive impact on CO_2 uptake, 31.9% and 5.9% respectively, for the rest of the samples the use of FA has enhanced the CO_2 uptake performance. This is somehow unexpected due to the amount of inert material that would be present in FA-derived samples, which would accordingly lower the capture capacity of the sorbents. Therefore, in order to compare

performance of the samples, capture capacity values of those sorbents obtained using FA as Si source were normalized to the SiO_2 content of the raw FA. So, if reactions (2) and (3) are complete, Li_4SiO_4 content of samples prepared with pure reagents would be 100% and Li_4SiO_4 content of samples prepared with FA would be 50.6%.

Figure 2 shows normalised CO_2 uptake values, i.e. corrected for the theoretical active mass of each sample. As can be seen, normalized CO_2 uptake values are around 30%, near to the theoretical sorption capacity of Li_4SiO_4 of 36.7% for samples LiOH-FA/SS and LiOH-FA/P-E.
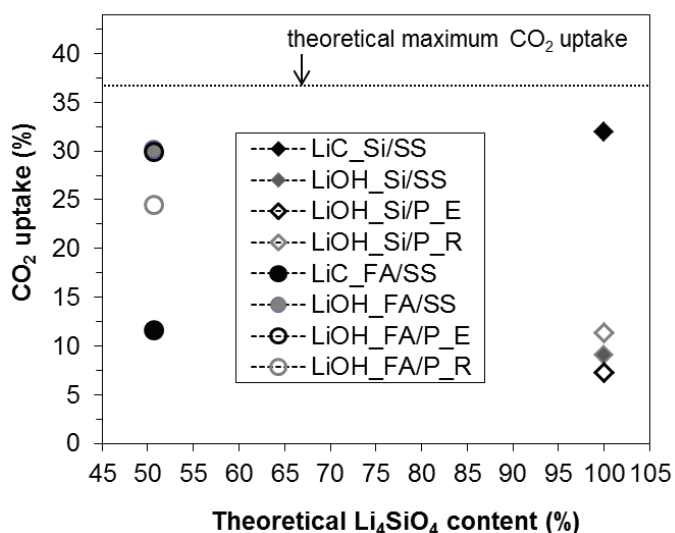

Figure 2. CO_2 uptake from TG isothermal experiments at 600 °C (for samples synthetized with FA CO_2 uptake values have been normalized to theoretical active mass).

Surface area, pore volume, average particle size and CO_2 uptake values of the samples are reported in Table 3. It can be observed that there is not a relationship between surface area, pore volume or particle size and CO_2

uptake. Kanki et al. [33] reported the dependence of the CO_2 absorption reaction on the Li_4SiO_4 surface properties, which were modified by ball milling processing; they observed a change of CO_2 uptake from c.a. 10% to 30% for as-prepared Li_4SiO_4 and 120 min milled Li_4SiO_4, respectively, and they found surface areas five times larger after 120 min ball milling. In the same way, Venegas et al. [10] reported an increased reactivity when using very small particles, < 3 μm, and they attributed this result to the presence of more Li atoms over the surface of those small particles.

In this work, similar CO_2 uptake is obtained with samples exhibiting quite different particle size, as can be deduced from Table 3. On the contrary, samples exhibiting simultaneously similar particle size and surface area, for instance LiC_FA/SS and LiOH_FA/SS samples, exhibited a quite different CO_2 uptake capacity, 11.6% and 30.2% (see Figure 2), respectively. Thus, surface area, pore volume and average particle size values cannot explain the different CO_2 uptake values.

Table 3. Characterization of prepared sorbents

Label	BET surface area m^2/g	Pore volume* cm^3/g	Particle size μm	CO_2 uptake** %
LiC_Si/SS	4.3	0.005	39	31.9
LiOH_Si/SS	4.0	0.007	83	9.0
LiC_FA/SS	1.7	0.003	136	7.3
LiOH_FA/SS	2.3	0.004	124	11.3
LiOH_Si/P_E	5.1	0.005	163	5.9
LiOH_Si/P_R	5.2	0.006	140	15.3
LiOH_FA/P_E	4.9	0.006	91	15.2
LiOH_FA/P_R	4.2	0.005	93	12.4

*(p/p$_0$=0.95)

**raw values from Figure 1.

3.2. Evaluation of CO_2 capture uptake from different sorbents active phases

When the synthesis was carried out in presence of FA other reaction products rather than Li_4SiO_4 could be present in the prepared sorbent due to other reaction paths apart from reaction (2) and (3). The CO_2 uptake capacity of the sorbent would be influenced by the ability to absorb CO_2 of those compounds. In addition, the presence of other elements could act as dopants for the Li_4SiO_4 structure. An increased reactivity for CO_2 absorption has been reported when Li_4SiO_4 is doped with heteroatoms that help ions diffusion [14, 22, 28]. Despite some authors [5] found that doping enhanced the carbonation reaction kinetics due to ions diffusion enhancement through the carbonate shell, these authors also found a decrease of CO_2 uptake because the reduction of the active mass. This fact was also observed in this work and it was particularly relevant because the SiO_2 content of the FA is lower than that used in other studies [22, 23]; this was the reason to normalise CO_2 capture to Li_4SiO_4 content on the whole sorbent assuming complete reaction (2) and (3).

Accordingly, XRD analysis was carried out in order to gain insight on the reasons for the different CO_2 uptake performance of the samples.

XRD patterns of the samples as well as main crystal phase assignation are presented in Figure 3. As shown, Li_4SiO_4 is the main crystalline phase present in the samples synthesised from pure reagents. However, this is not the case for samples synthesised from FA in which other crystalline phases were found as a result of the reaction of Li_2CO_3 or LiOH with other elements present in the FA. Moreover, Li_4SiO_4 was not the main phase in none of the samples prepared from FA. It can be seen that the main crystal phase present in sample LiC-

FA/SS is Li_2CaSiO_4, but this compound is a minority phase in the rest of FA-based samples. According to the low CO_2 uptake of the LiC-FA/SS sample (5.9%), that crystal phase seems to be low efficiency for CO_2 absorption. Li_2CO_3 is found in all samples, including in those ones prepared from LiOH. For samples prepared from LiOH and FA, this fact could be explained in terms of unburned carbon present in the FA (LOI value of 7.5%). Moreover, the presence of Li_2CO_3 has been observed during the synthesis of Li_4SiO_4 from LiOH at temperatures lower than 600 ºC [20] and it was described as a result of a formation mechanism of Li_4SiO_4. Accordingly, despite Li_2CO_3 was not the raw material used for the synthesis of those samples, its presence is not unexpected, according the above description.

For the three samples prepared from LiOH and FA, the main crystal phase is CaO. These samples exhibited relatively high CO_2 uptake capacity, despite the different synthesis method and despite Li_4SiO_4 is not the main phase present. It is well-known the high theoretical CO_2 uptake capacity of CaO (78%), so CO_2 capture uptakes for samples LiOH_FA/SS, LiOH_FA/P-E and LiOH_FA/P-R could be related to the CaO content of the samples as well as the presence of Li_4SiO_4. For these samples, the Li_2CaSiO_4 content, which was shown to have low potential for CO_2 capture in the case of sample LiC-FA/SS, seems to be low based on the peak intensity in the XRD patterns. The interaction of CaO present in the FA with the rest of the compounds present in the FA during synthesis at high temperature is not different to that found during calcination at high temperature in the Ca-looping process in presence of coal ash [34], except in the case of sample LiC_FA/SS in which the main calcium phase is Li_2CaSiO_4. This is probably due to the higher temperature used in the synthesis with Li_2CO_3

when compared with that with LiOH (800ºC and 600 ºC, respectively) and the same SS synthesis method.

For the samples prepared from LiOH and SiO_2, the CO_2 uptake was very low compared with that prepared from Li_2CO_3 and SiO_2, regardless of the synthesis method used. This fact could be understood in terms of the low Li_4SiO_4 content because no other elements are present.
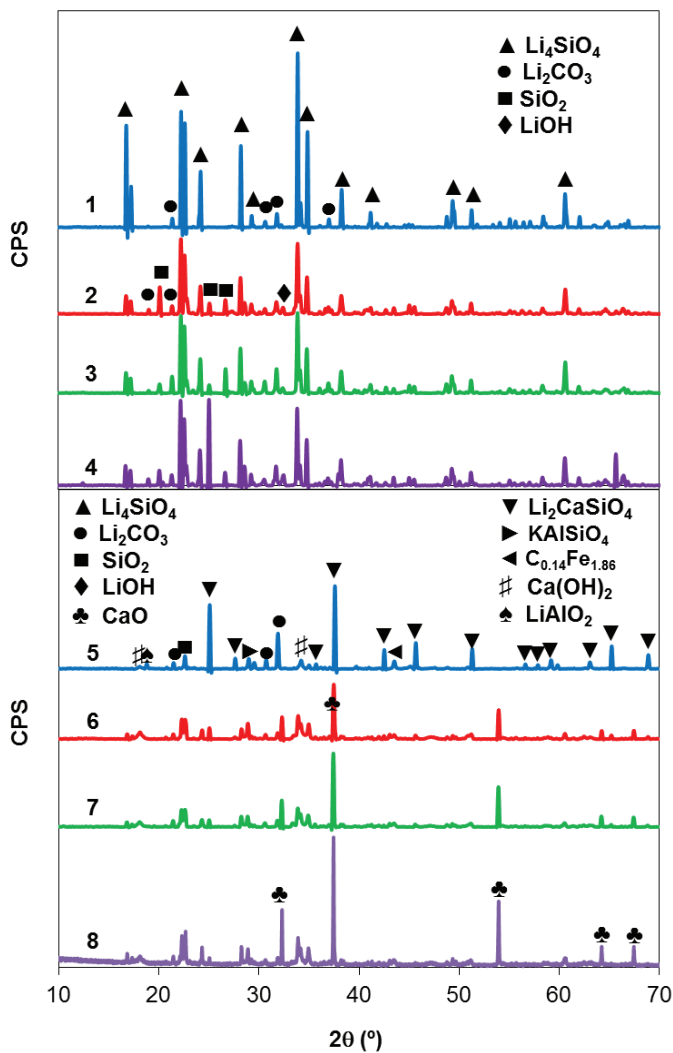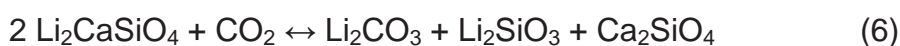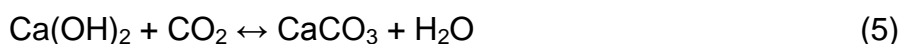

Figure 3. Diffractograms, with identification of main crystal phases, for samples synthetized from pure reagents (top): 1) LiC-Si/SS; 2) LiOH_Si/SS; 3) LiOH_Si/P_E; 4) LiOH_Si/P_R; and from FA (bottom): 5) LiC_FA/SS; 6) LiOH_FA/SS; 7) LiOH_FA/P_E; 8) LiOH_FA/P_R.

For those samples prepared from FA, it seems obvious that some of the crystal phases present in the samples could capture CO_2. In addition to the CO_2 capture uptake exhibited by Li_4SiO_4 through reaction (1), CaO, $Ca(OH)_2$ and Li_2CaSiO_4 can also react with CO_2 through reactions (4), (5) and (6):

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad\qquad\qquad (4)$$

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O \qquad\qquad\qquad (5)$$

$$2\,Li_2CaSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3 + Ca_2SiO_4 \qquad\qquad (6)$$

The stoichiometric CO_2 uptake is 78%, 59% and 15% for reactions (4), (5) and (6), respectively. Therefore, in order to evaluate the CO_2 uptake of the samples when considering the presence of different active compounds for CO_2 capture, quantification of the crystal phases was carried out. For samples synthesised from pure reagents, quantification has been carried out by Rietveld refinement. For samples synthesised from FA, values reported come from S-Q (semi-quantitative) procedure. The patterns were very complex and it was not possible to model the diffractograms by Rietveld refinement. Despite these S-Q values are not as accurate as those obtained by refinement, they can provide knowledge on the abundance of each crystalline phase on the sample.

Table 4 shows XRD quantification analysis of the crystalline phases.

As qualitatively predicted before, the Li_4SiO_4 content is very limited for samples prepared from FA, despite the amount of FA added was equivalent to the SiO_2 molar ratio needed for reactions (2) or (3). This fact could be understood for sample LiC_FA/SS, because the main crystalline phase obtained was Li_2CaSiO_4; however, the amount of elemental Li considering the contribution of the species reported in Table 4 (9.4% Li), is far from the Li amount added for the synthesis, 23.2% Li. This suggests that an important part of this element is

in the amorphous phase. For samples LiOH_FA/SS, LiOH_FA/P_E and

LiOH_FA/P_R the main compound was CaO, and small amounts of Li_4SiO_4 can

be found despite free LiOH is still available in the crystal phase. Again, the Li

content of the crystalline phases reported in Table 4 was lower than 6%,

indicating that some Li compounds would be in the amorphous phase.

Table 4. Main crystal phases of prepared samples from XRD analysis

Label	Crystaline phases, wt%								
	Li_4SiO_4	Li_2CO_3	LiOH	SiO_2	Li_2CaSiO_4	$Ca(OH)_2$	CaO	$LiAlO_2$	$KAlSiO_4$
LiC_Si/SS	91.5	6.3	-	2.2	-	-	-	0.0	0.0
LiOH_Si/SS	52.3	9.9	19.8	15.7	-	-	-	0.0	0.0
LiC_FA/SS	-	17.0	-	2.9	62.0	6.1	-	3.0	3.0
LiOH_FA/SS	8.4	2.9	6.4	-	1.9	10.5	65.0	2.9	2.0
LiOH_Si/P_E	52.1	10.5	21.3	16.1	-		-	0.0	0.0
LiOH_Si/P_R	63.0	9.3	14.5	13.2	-		-	0.0	0.0
LiOH_FA/P_E	9.0	3.0	4	-	2.0	6.0	70.9	3.0	2.0
LiOH_FA/P_R	8.5	3.5	7.5	-	3.2	3.2	66.8	2.5	2.5

As can be seen, the synthesis method does not affect the composition of the

crystal phase when comparing LiOH and FA starting materials; however, for

Li_2CO_3 and FA starting materials, the synthesis temperature played an

important role on the final composition of the prepared material.

For sorbents prepared with pure reagents, Li content obtained from XRD

quantification is close to the amount of Li added for the synthesis, in particular

for sample prepared from Li_2CO_3 (22.4% versus the added 23.2%); in those

samples prepared with LiOH the Li content was about 20%. This lower value

cannot be attributed to Li volatilization during synthesis, because the

temperature used was lower (600°C) than that used when Li_2CO_3 was the

starting material. This would entail that either the precursor or the lower

synthesis temperature promotes the movement of Li-containing compounds to the amorphous phase and this fact is independent of the synthesis method used, SS or precipitation. Despite some authors have attributed an enhanced CO_2 uptake capacity to the amorphousness of finely grinded Li_4SiO_4 [33], in this work those samples with a lower content of crystalline Li compounds (mainly due to Li_4SiO_4), i.e. higher amorphous Li content, exhibited different CO_2 uptake capacities.

In order to take into account the contribution of relevant crystalline phases to CO_2 capture, the maximum theoretical CO_2 uptake of the synthesized materials was calculated and normalised based on the content of each of the active crystalline phases (Table 4) and according to reactions (1), (4), (5) and (6). This normalised theoretical value was then compared with the experimentally measured CO_2 uptake in Figure 4.
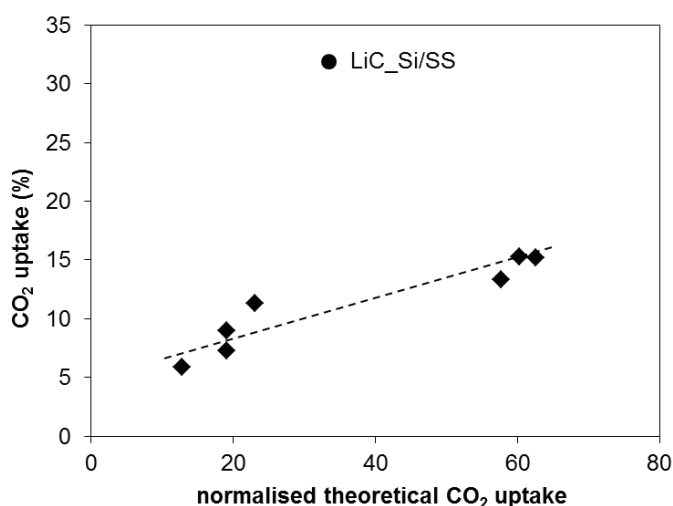

Figure 4. Experimentally measured CO_2 uptake versus normalised theoretical CO_2 uptake calculated from identified active crystalline phases according to reactions (1), (4), (5) and (6).

If the point corresponding to sample LiC_Si/SS is disregarded, it would be a direct relationship between the experimentally measured CO_2 uptake and the theoretically calculated one (based on stoichiometric CO_2 uptake values for reactions (1), (4), (5) and (6) and normalized to its crystal phase content). In other words, it seems that the only factor affecting the CO_2 uptake performance of the prepared samples is the presence of active phases for CO_2 capture.

However, the data point corresponding to sample LiC_Si/SS is far from the trend line depicted in Figure 4. The Li_4SiO_4 content of this sample is the highest among all the studied samples and there is no other compound present that could capture CO_2. The CO_2 uptake was 31.9%, but normalizing to the Li_4SiO_4 content, i.e. to the active mass, the CO_2 uptake is 33.4%, which is close to the theoretical stoichiometric uptake. Despite CaO has a much higher theoretical CO_2 uptake capacity than that of Li_4SiO_4 and the content of CaO of samples prepared with LiOH and FA is high, the experimental CO_2 uptake for sample LiOH_FA/SS was only 15.3% respect to the calculated one of 60.3%. In order to explain this behaviour, XRD patterns of some samples after carbonation at 600 ºC were obtained.

Figure 5 shows the main crystal phases of samples LiC_Si/SS, LiC_FA/SS and LiOH_FA/SS before (as prepared samples) and after carbonation. As can be seen, after carbonation the main crystalline phases in sample LiC_Si/SS are Li_2CO_3 and Li_2SiO_3, as expected according to reaction (1); however, it can be observed the presence of c.a. 3.5 % of unreacted Li_4SiO_4. This value can explain the disagreement between the experimental and calculated CO_2 uptake of sample LiC_Si/SS (31.9% and 33.4%, respectively).
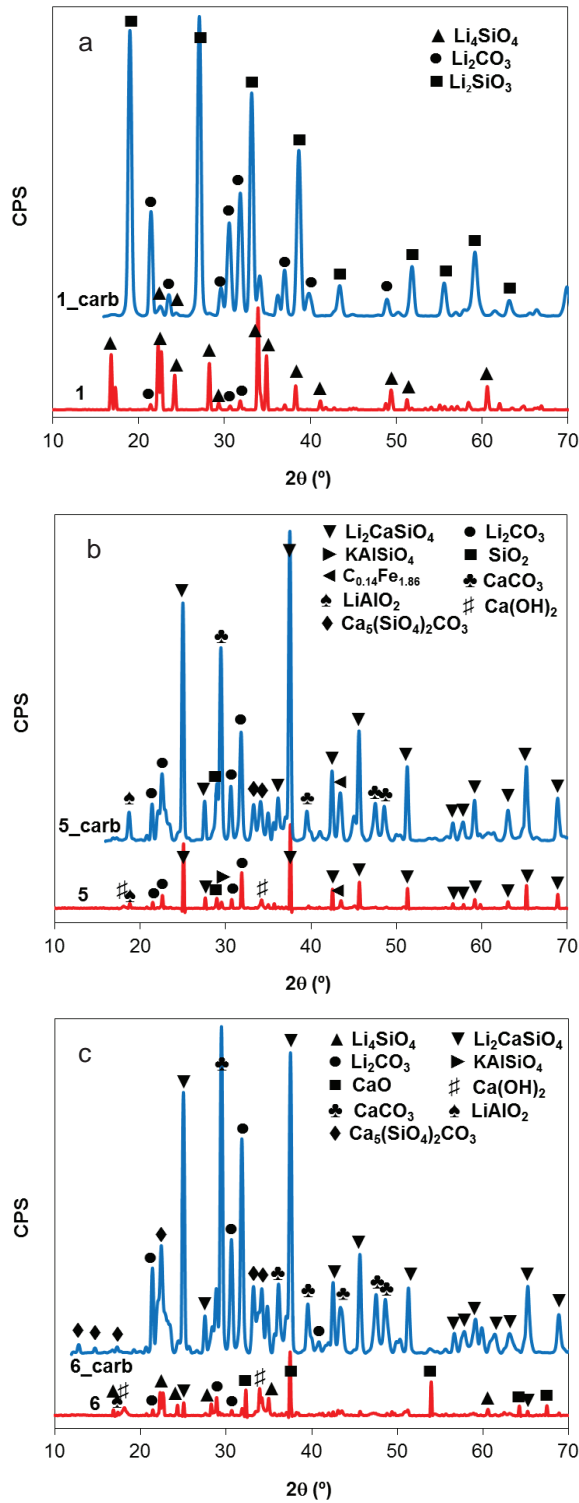
Figure 5. Main crystal phases from XRD for as prepared samples (only as reference: more detailed in Figure 3) and after carbonation at 600 ºC: Samples (a) 1-LiC-Si/SS; (b); 5-LiC-FA/SS; (c) 6-LiOH-FA/SS

After carbonation of sample LiC_FA/SS, it can be observed the presence of unconverted Li_2CaSiO_4 according to reaction (6), which was the main crystal phase in the prepared sample. $CaCO_3$ is present after carbonation, according to reaction (5), because CaO was not present in the prepared sample.

Moreover, a new crystal phase is present, $Ca_5(SiO_4)_2CO_3$, which could come from the reaction between Li_2CaSiO_4 and CO_2 following a different path than that of reaction (6) including also connected reaction paths with reaction (5). The difference among experimental and calculated CO_2 uptake of sample LiC_FA/SS, 5.9% and 12.8%, respectively, could be explained in terms of the unreacted Li_2CaSiO_4 crystal phase.

After carbonation of sample LiOH_FA/SS it cannot be observed the presence of CaO, which was the main crystal phase in the raw sample; this means that CaO reacted with CO_2 according to reaction (4). The new crystal phase, $Ca_5(SiO_4)_2CO_3$, is also present and again it can be observed the presence of unconverted Li_2CaSiO_4 according to reaction (6). The presence of $CaCO_3$ in the carbonated LiOH_FA/SS sample is lower than in sample LiC_FA/SS despite the high amount of CaO present in the former sample. However, the content of Li_2CaSiO_4 and $Ca_5(SiO_4)_2CO_3$ is higher. This fact could explain the difference among experimental and calculated CO_2 uptake of sample LiC_FA/SS, 15.3% and 60.3%, respectively.

4. CONCLUSIONS

Li-based sorbents have been synthesised from either pure reagents or using a fly ash as a silica source by two different methods: solid state and precipitation. Measured CO_2 uptake of the samples did not show to have a linear relationship

with either surface area, pore volume or particle size of the samples.

The CO_2 uptake for samples prepared from LiOH and SiO_2 was very low compared with that for samples synthesised from Li_2CO_3 and SiO_2, independently of the synthesis method used, SS or precipitation. This fact could be attributed to the Li_4SiO_4 content, as the only compound present in those samples that could absorb CO_2.

Samples prepared with FA exhibited higher CO_2 uptake values than the samples prepared with pure reagents (except that prepared with Li_2CO_3 and solid state synthesis method), which cannot be explained because the reduced active mass due to the FA dilution addition. This fact could be explained in terms of the presence of high CaO content.

Except for the sample containing almost pure Li_4SiO_4, a direct relationship between experimentally measured CO_2 uptake values and theoretically calculated values considering crystal phase contents and theoretical CO_2 uptake of each phase has been found. For the sample containing almost pure Li_4SiO_4 it seems that this compound is completely available for reaction with CO_2, reaching a CO_2 uptake of 31.9%. Despite the high CaO content in some of the synthesized samples, the carbonation reaction does not proceed via $CaCO_3$ formation and Li_2CaSiO_4 and $Ca_5(SiO_4)_2CO_3$ crystal phases are present in the carbonated samples, limiting the CO_2 capture of CaO present in the fly ash.

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