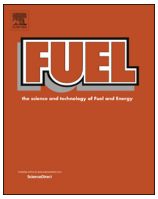
Fuel 230 (2018) 45–51

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Lithium-based sorbents for high temperature CO_2 capture: Effect of precursor materials and synthesis method

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ARTICLE INFO

Keywords:
CO_2 capture
Li-based sorbents
Fly ash
Rietveld refinement

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 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:

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

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.

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https://doi.org/10.1016/j.fuel.2018.05.041
Received 13 March 2018; Received in revised form 3 May 2018; Accepted 8 May 2018

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 °C 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 $LiOH{\cdot}H_2O$ (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.

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

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

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

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 °C when using LiOH and at 800 °C 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 $LiOH{\cdot}H_2O$/375 ml H_2O. Once the clear solution is prepared, the Si source is added to maintain a molar ratio 4.4 $LiOH{\cdot}H_2O$/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 °C until constant weight; (ii) evaporation using a rotary evaporation (R) at 55 °C under vacuum. After the evaporation step, the resulting powder was submitted to calcination at 600 °C 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.

2.2. Characterization of samples

Sorbents were characterized by different techniques. N_2 physisorption analysis at −196 °C 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 110 °C under N_2, followed by 30 min at 600 °C, heating rate of 25 °C/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 °C during 120 min. Blank tests were performed for those running conditions.