CHEMICAL ENGINEERING TRANSACTIONS

VOL. 47, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Angelo Chianese, Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN 978-88-95608-38-9; **ISSN** 2283-9216

DOI: 10.3303/CET1647024

Removal of CO_2 from Flue Gas at High Temperature Using Novel Porous Solids

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Since the CO2 separation is the first and most energy intensive step of carbon capture and storage (CCS) technology, many research have targeted at improving the current technologies or developing new approaches of CO2 separation and capture. In this study, lithium orthosilicate-based pellets were developed and characterized as potential regenarable high-temperature CO_2 sorbents. A mechanical method was used for pelletization of the powdered materials, namely K_2CO_3-doped lithium silicate (Li_4SiO_4). For increasing the performance of the pellets over multiple cycles an activation strategy was applied: the powdered sorbents were pelletized with a binder for enhancing their porosity by applying a thermal activation before adsorption process. Different amounts of binders (layered graphite and carbon nanotubes) were added to powered doped-sorbent in order to identify the optimal amount to ensure an adequate porosity into the pellets. The CO_2 sorption properties of the obtained pellets were investigated by using a thermal gravimetric analyzer (TGA) in a controlled gas flow environment at low CO_2 partial pressure (0.04 atm). Compared to the pure K_2CO_3-doped lithium silicate pellets, the sorbents prepared using layered graphite showed greater CO_2 capture capabilities, which were ascribed to the higher porosity developed as a result of the activation. At 580 °C and a CO_2 partial pressure of 0.04 atm, the uptake of CO_2 in pellets prepared with 20 % of graphite reached about 200 mg CO_2/g sorbent within 120 minutes corresponding to a Li_4SiO_4-conversion of 72.1 %. During multiple sorption/desorption cycles, a decay of the sorption capacity of the pellets was observed due to a partial sintering of the materials.

1. Introduction

The emission of carbon dioxide (CO_2), one of the major greenhouse gases, has raised great concerns about the relationship between anthropogenic CO_2 and global warming: CO_2 emissions may have contributed to urban smog, acid rain, and health problems. As a consequence, carbon capture and storage (CCS) technology is attracting increasing interest to reduce the ever-increasing amount of CO_2 released into the atmosphere. CCS involves capturing the carbon dioxide emitted by power plant and other industrial operations and permanently storing it deep underground. On average, implementing a CCS process will increase the capital cost of a power station by 25 to 30 %, and reduce its operating efficiency from about 40 to 30 %. CO_2 capture process accounts for 70-80 % of the overall CCS (Lee and Park, 2015).

CO_2 capture technologies are categorized as post-combustion, pre-combustion, and oxy-fuel combustion. Among these, post-combustion CO_2 capture processes are regarded as being important green and economic technologies (Ahmad et al., 2015). Post-combustion capture uses wet/dry adsorbents, which are used for gas separation, and separates and collects CO_2 by adsorption/desorption. Currently, the commercially available technique for CO_2 capture is based on amine-scrubbing processes (Chavez et al., 2015). However, this technology is energy-intensive, due to the low operating temperature (40-150 °C) and the energy requirement for regeneration of the solutions, and involves environmental penalties, due to the degradation of the expensive amine-based solvents.

Recently, selective adsorption technology (solid sorbents) has been identified as one of the ways for post-combustion CO_2 capture at high temperature, without cooling the flue gas to ambient or even lower temperature (Puccini et al., 2013a). For the separation of carbon dioxide from hot gas stream, the adsorbent

Please cite this article as: Puccini M., Stefanelli E., Seggiani M., Vitolo S., 2016, Removal of co2 from flue gas at high temperature using novel porous solids, Chemical Engineering Transactions, 47, 139-144 DOI: 10.3303/CET1647024

must have high selectivity for CO_2 over N_2 at elevated temperatures and high adsorption capacity for carbon dioxide at the operating temperature.

Among the various solid sorbents that have been studied, lithium orthosilicate (Li_4SiO_4) is considered one of the most promising candidates for the post-combustion CO_2 capture at high temperature (500-700 °C), according to the following reaction r1:

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

Main advantages of this materials are their high CO_2 capture capacity (theoretically up to 360 mg/g sorbent), lower regeneration temperatures (< 750 °C) compared to other high-temperature sorbents, such as CaO, and their excellent stability that allow operation over a significant number of cycles without losing their sorption capacity.

For large-scale application of such sorbents, the looping cycles system might represent the optimal industrial technology: a typical reactor configuration consist of two interconnected fluidized beds, which allows the circulation of the solid between the reactors and ensures an appropriate contact between the solid and the gas phase, operating alternatively adsorption/regeneration cycles (looping process). Therefore, it is also required that these sorbents are used in the form of granules or pellets. For increasing the performance of the pellets over multiple cycles an activation strategy could be applied: a pelletization procedure of powdered sorbents with a binder (e.g. cellulose fibres) allows enhancing the porosity of pellets by applying a thermal activation before adsorption process (Puccini et al., 2013b).

In this study, pellets of Li_4SiO_4-based sorbents were developed for CO_2 capture at high temperature and low concentration, in view of industrial applications. A mechanical method was used for pelletization of the powdered materials, namely lithium silicate (Li_4SiO_4) doped with binders. The CO_2 sorption properties of the obtained pellets were investigated by using a thermal gravimetric analyzer (TGA) in a controlled gas flow environment at low CO_2 partial pressure (0.04 atm). Scanning electron microscopy (SEM) was used to characterise the prepared sorbents and to understand the relationship between the sorbent structure and CO_2 sorption properties. Besides, the cyclic stability of the pellets was investigated by carrying out multiple cycles of CO_2 sorption/desorption.

2. Experimental

2.1 Sorbent preparation and characterization

Li_4SiO_4 powders were prepared by the solid state method. Starting materials were reagent-grade Li_2CO_3 and SiO_2 (from Sigma-Aldrich) in a 2:1 molar ratio. The materials were weighed, mixed, and ground in an agate mortar with a suitable amount of water. Then, the mixtures were dried and calcined in air at 900 °C for 4 h. Both temperature increase and decrease ramping rates were set to 60 °C/h. The resulting powders were ground by agate mortar to break down any agglomeration and then sieved to produce Li_4SiO_4 particles with size below 10 µm. Promoted Li_4SiO_4-based sorbent, named LiK, was prepared mixing 30 wt% of potassium carbonate (K_2CO_3) with the previously synthesized pure Li_4SiO_4 powder.

Pellets were prepared using the powdered sorbent (LiK) mixed with weighed quantities of binder. Cylindrical pellets, with diameter of 6 mm and length of 2.5 mm, were produced by using a mechanical press, operating at 5 bar pressure applied for 3 min. Different pellet samples were prepared with different binder types and quantities (between 5 and 30 wt%, by weight of LiK). Binder-free pellet was also prepared for comparison purpose (LiK-p).

The sample morphology was observed with a JEOL 5600 LV scanning electron microscope (SEM).

2.2 CO_2 capture tests

Carbon dioxide adsorption on pellets was studied using a thermogravimetric analyzer (TGA Q500 TA Instrument). The pellet was placed in a sample pan and, prior to CO_2 sorption testing, the sample was heated (heating rate of 10 °C/min) in air to required temperature (750 °C) to thermally degrade the binder for developing porosity in the pellets. When the sample weight became stable, the operating temperature (580 °C) was reached, and the N_2 flow was switched to a mixture CO_2/N_2, containing 4 vol% of CO_2. The total feed gas flow rate was maintained at 100 mL/min at atmospheric pressure. The weight increase during the CO_2 sorption process, lasted 120 min, was recorded as a function of time.

Besides, to assess the stability of the optimized sorbent ten adsorption/desorption cycles were carried out. The adsorption of CO_2 was carried for 60 min at 580 °C in 4 vol% CO_2 flow. Afterwards, the feed gas stream was switched to a pure N_2 flow (100 mL/min) and the temperature was raised to 700 °C with heating rate of 20 °C/min. The sample was kept to the regeneration temperature until it was completely regenerated. The regeneration process lasted about 15 min. After that, a new cycle was carried out.

Since the promoters showed no affinity for the CO_2 capture but contributed to the sorbent weight, the conversion of Li_4SiO_4, $X_{Li4SiO4}$, was used to assess and compare the effect of the different promoters used on the CO_2 sorption reaction. The percentage conversion $X_{Li4SiO4}$ was calculated by using the Eq(1):

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

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 0.36 g of CO_2/g of Li_4SiO_4.

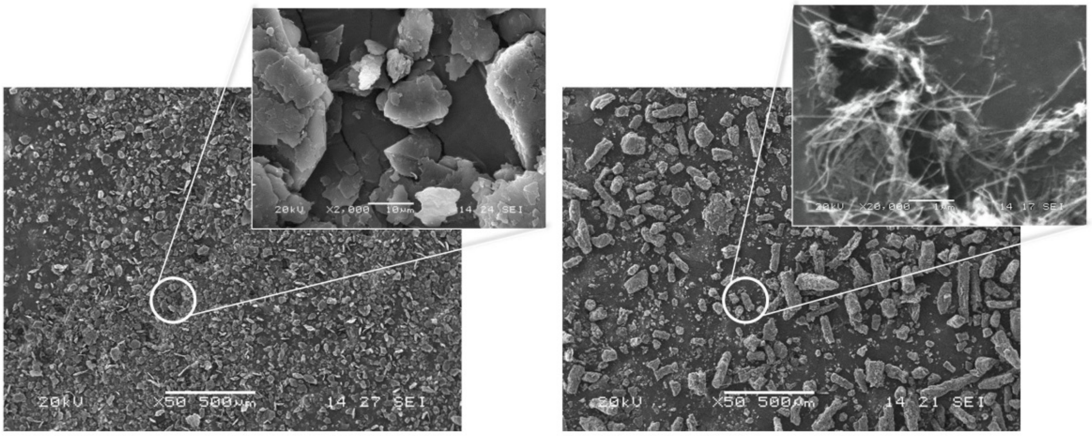
3. Results and discussion

Li_4SiO_4-based pellets were prepared by sintering the powdered sorbent with a binder. A thermal pre-treatment before adsorption process was applied for developing a porous structure into the pellets: during degradation the binder releases gases that alter the porosity of sorbent, and subsequently could enhance CO_2 capture. In a previous work (Puccini et al., 2013b), cellulose fibres was used as binder. In this study layered graphite (LG) and carbon nanotubes (CN) were used for developing a mesoporous structure. The SEM micrograph of the selected binders are reported in Figure 1. The layered graphite showed particles with size around 10 µm. The carbon nanotubes presented the typical structure constituted of fibres having with diameter of 7-15 nm and length of 0.5-10 µm.

Thermogravimetric analysis of binders under air was conducted to assess their thermal degradation behaviour, and then to set the pre-treatment procedure before sorption test. The thermal decomposition profiles of the binders (the mass loss as function of time) are shown in Figure 2. Layered graphite and carbon nanotubes exhibit similar curves: the LG sample showed thermal stability up to 630 °C and a single-step weight loss close to 870 °C, and the CN sample is thermally stable up to 730 °C and exhibits a a single-step weight loss around 900 °C. Both samples reached the complete degradation over 900 °C, keeping such temperature for 15 minutes (the selected materials are free ash). Therefore, the pre-treatment procedure was setted with a temperature of 750 °C (heating rate of 10 °C/min) lasting 30 minutes.

The SEM micrographs of pellet without binder, and the samples after the thermal activation are reported in Figure 3. The SEM images display the morphology of the section of the samples: the picture (a), pellet LiK-p, presents a compact structure without cavities, instead in the picture (a) and (b) holes and cavity are visible, due to the degradation of binders during the thermal pre-treatment.

Different ratios of binders were used in order to identify the optimal amount to ensure good hardness and a porous structure to the pellets. The tested percentage of LG was varied between 20 and 40 wt%. An amount of binder exceeding 40 wt% has not been considered appropriate since reduces the amount of active sorbent. Since problems in the production of pellets during mechanical compression of the powder containing the carbon nanotubes were occurred, the tested percentage of CN was varied between 5 and 15 wt%.



layered graphite *carbon nanotubes*

Figure 1: SEM micrograph of binders.

The Figures 4 shows the CO_2 uptake of the pellets as a result of tests in 4 vol% CO_2 stream at temperature of 580 °C. The profile of the cycle displays a typical solid–gas reaction profile. During carbonation, the low resistance diffusion of CO_2 through the pores enabled a fast reaction stage, followed by a slow reaction stage related to the closure of small pores and full masking of surface area by the product of carbonation, i.e. $CaCO_3$. The Table 1 reports the percentage conversion of the sorbents.

As shown, the LiK sample and the pellets containing carbon nanotubes exhibit similar CO_2 uptake profiles: the adsorbed amount of CO_2 after 2 hours was nearly 0.09 g CO_2/g sorbent corresponding to a 30 % conversion of Li_4SiO_4. The slow reaction stage where both profiles exhibited similar slopes suggests nearly identical diffusion rates of carbon dioxide in both sorbents, therefore a similar morphology of the pellets. The use of carbon nanotubes developed a structure with pores smaller than 1 μm that the $CaCO_3$ produced during carbonation could blocked, increasing the resistance to CO_2 diffusion.

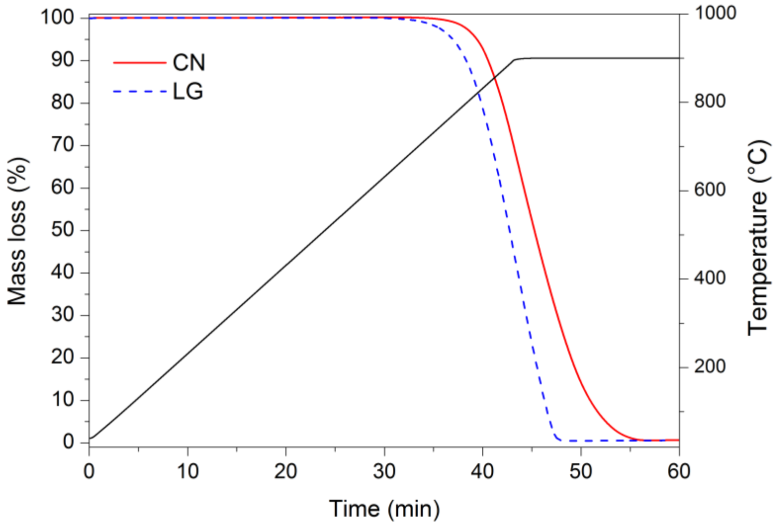


Figure 2: Thermal decomposition profiles of binders (in air and heating rate of 20 °C/min).

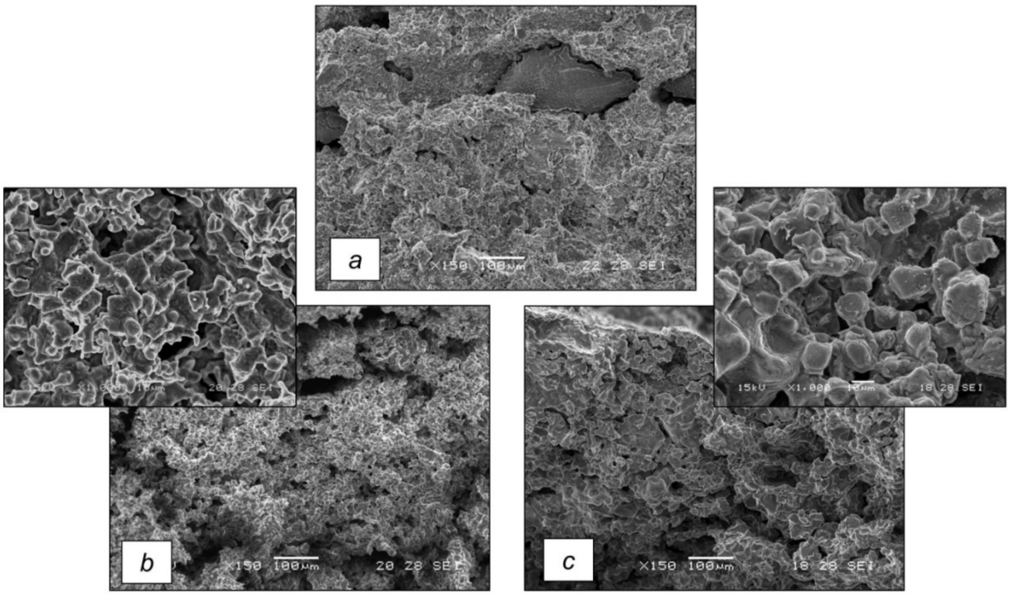


Figure 3: SEM micrograph of cross-section of LiK pellets: (a) without binder, after activation (b) with 20 wt% of layered graphite, (c) with 15 wt% of carbon nanotubes.

Table 1: Percentage conversion of Li_4SiO_4.

Pellets LiK		$X_{Li_4SiO_4}$ (%)
Binder	wt%	
LG	20	72.1
LG	30	69.1
LG	40	57.7
CN	5	30.6
CN	10	27.1
CN	15	28.9

Instead, the use of layered graphite enhanced the CO_2 uptake: the adsorbed amount of CO_2 after 2 hours was nearly 0.2 g CO_2/g sorbent corresponding to a 72 % conversion of Li_4SiO_4 for the sample produced with 20 % of LG. No significant variation on CO_2 adsorption capacity was observed varying the binder content. This result can be attributed to the different morphology of the pellets: the porosity created as a result of the graphite degradation increased the surface area of the pellets by developing larger pores than CN, and, consequently, their sorption capacity increased.

The cyclic stability of the pellets was investigated by carrying out 10 cycles of CO_2 sorption/desorption (Figure 5). The pellet produced without cellulose fibres (LiK) showed a remarkable decay in CO_2 absorption capacity after the first cycle: the conversion dropped off from 32 % to 13 %, and remained essentially constant during the subsequent cycles. The other pellet, produced using LiK containing the 20 % of layered graphite, showed a different behaviour: the sorption capacity decreased during first four cycles and remained nearly constant for cycles 5-10 (around a 45 % conversion of Li_4SiO_4).

sorption strongly varies and remains almost constant. The decrease of CO_2 uptake with increasing number of cycles demonstrates that the structure of Li_4SiO_4-base pellets experiences sintering typical of such sorbents, e.g. excessive loss of narrow pores useful for carbonation (Fennell et al., 2007).

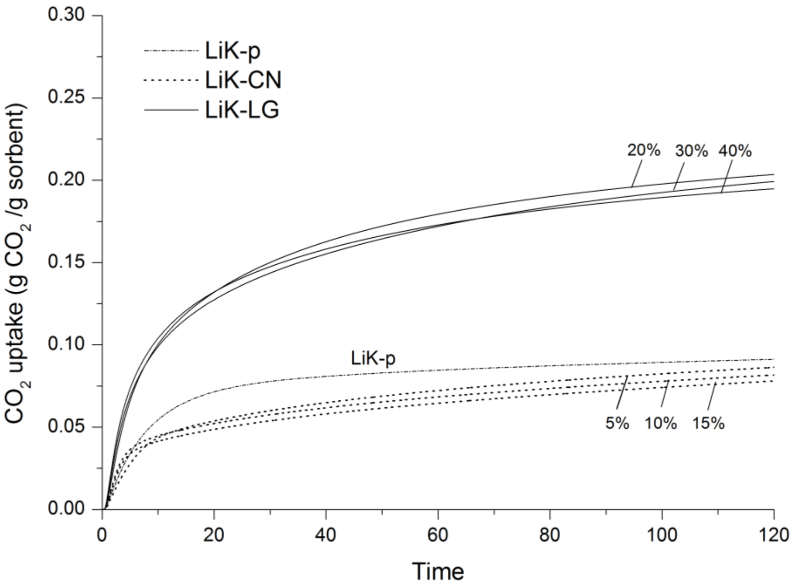


Figure 4: CO_2 uptake in 4 vol% CO_2 stream at 580 °C.

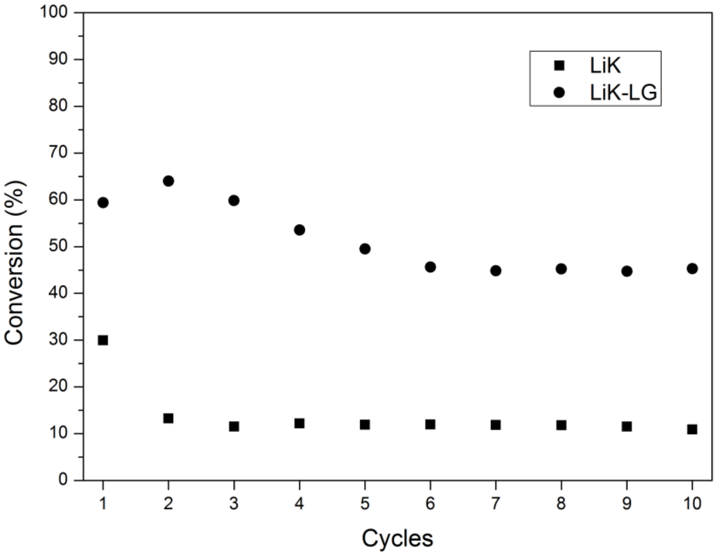


Figure 5: Multiple cycles of CO_2 sorption desorption (in 4 vol% CO_2 stream at 580 °C) on pellets LiK and LiK with 20 wt% of layered graphite

4. Conclusions

In this study novel Li_4SiO_4 based-sorbents in form of pellets for CO_2 capture at high temperature (500 - 600 °C) were developed. A mechanical method was used for pelletization of the powdered materials, namely lithium silicate (Li_4SiO_4) doped with carbonates. Binders were used to make porous the structure as evidenced by the morphology of the produced pellets. The CO_2 sorption properties of the pellets were investigated by using a thermal gravimetric analyzer (TGA). The curves uptake revealed that the use of layered graphite enhanced the CO_2 sorption capacity of the Li_4SiO_4-based pellets. At 580 °C and under a 4 vol% CO_2 flow the CO_2 sorption capacity for the pellets (diameter 6 mm and length 3.5 mm) produced using 20 wt% of graphite was about 200 mg CO_2/g sorbent after 120 minutes corresponding to a Li_4SiO_4 -conversion of 72.1 %. These results can be attributed to the morphology of the pellets: the porosity created by the graphite degradation in air (before the first sorption run) increased the surface area of the pellets and, consequently, their sorption capacity.

During 10 CO_2 sorption/desorption cycles, the sorption capacity of the pellets remained nearly constant only for the first 5 cycles and, then, decreased markedly because of a partial sintering of the material, as shown by SEM morphological analysis. Future work will focus on the use of an appropriate inert binder for the pelletization process in order to improve the cyclic stability and the mechanical resistance of the produced pelletized Li_4SiO_4-based sorbents.

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