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GHGT-12

Novel Na-silicates CO₂ sorbents from fly ash

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Abstract

Despite the very good CO₂ uptake of lithium based silicates at high temperature, this material is expensive and not very abundant. Therefore, there is the need to develop high temperature sorbents based on low-cost and widely available materials. In this work, Na-silicates prepared by mixing sodium carbonate with fly ash (FA) in the molar ratio of Na₂CO₃:SiO₂ of 1:1 and 4:1 were evaluated for their capacity to chemisorb CO₂ at 700°C. This temperature was chosen as it is compatible with post-combustion technologies. Pure Na-FA sorbent (NaCO₃:SiO₂ molar ratio of 1:1) was able to adsorb 1.8 mmol CO₂/g sorbent. The CO₂ uptake capacity increased to 2mmol CO₂/g sorbent in presence of 20% Li₂CO₃ as additive. Therefore, this work suggests that Na-silicate materials with acceptable CO₂ uptake can be developed as high temperature sorbents for post-combustion technologies.

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Keywords: CO₂ capture, Na-based sorbents, solid sorbents, carbonation/calcination cycles.

1. Introduction

Alkaline ceramics, mainly lithium and sodium containing compounds, have recently been used as CO₂ sorbents [1-5]. Typically, these ceramics present a double-step sorption mechanism, with an initial chemical sorption of CO₂ over the ceramic surface, which forms a carbonate shell, followed by the CO₂ diffusing through the carbonate external layer to reach the surface and further react with the alkaline element [1].

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At low temperature (100°C), Na sorbents have shown better CO₂ capture capacity compared to Li-based sorbents. For example, Na₂ZrO₃ absorbs twice more CO₂ than Li₂ZrO₃ (1.1 mmolCO₂/g sorbent vs 0.67 mmol CO₂/g sorbent), and its reaction rate is faster as well (100 min vs 200 min) [2]. CO₂ capture at high temperatures (450-700°C) based on regenerable sorbent materials produced from waste feedstocks has also received increasing attention [5]. Amongst the wide range of materials tested, lithium silicate (Li₄SiO₄) has shown the largest CO₂ sorption capacity and the fastest CO₂ sorption rate over a wide range of temperatures and CO₂ concentrations [5-7]. The authors have reported that the presence of carbonates (e.g. K₂CO₃) and high temperatures affect the CO₂ sorption capacity for the Li-based sorbents prepared from fly ashes [5], where at 600°C, both the CO₂ sorption capacity and the sorption rate increase significantly to a maximum CO₂ sorption capacity of 107 mg CO₂/g sorbent in the presence of 40 mol% K₂CO₃. It was also reported that Li₄SiO₄-based sorbents maintained their original capacity over 10 cycle processes [5].

Despite the very good performance of these materials, it should be noted that the lithium carbonate used to produce the Li-silicate is expensive and toxic, and not very abundant. Therefore, the aim of this work is to develop high temperature sorbents based on low-cost and widely available Na and mixtures of Na and Li silicates. CO₂ capture using sodium metasilicates (Na₂SiO₃) has not been studied at high temperature thus far, although it has been shown that Na₂SiO₃ was able to trap very low quantities of CO₂ at low temperatures (130°C) under dry conditions [1]. The CO₂ adsorption occurs as follows: Na₂SiO₃ + 2CO₂ → 2NaHCO₃ + SiO₂. As expected, the presence of water vapour strongly favoured the CO₂ chemisorption on Na₂SiO₃ [6].

2. Methodology

In this work, Na -meta and -ortho silicates were prepared by mixing fly ash (FA) with Na₂CO₃ (Acros Organics) in the molar ratio of Na₂CO₃:SiO₂ of 1:1 and 4:1 by using an agate mortar and pestle. The mixed powder was then calcined in an alumina crucible in a muffle furnace at 800°C for 8 hours. The FA samples were collected from a coal-fired power plant in the UK.

The resulting sorbents were grinded and characterized by different techniques, including powder thermogravimetric analysis (TGA) and Fourier Transformed Infrared (FTIR). The CO₂ capture capacity of the resultant samples was measured by using a TGA (TA Q500) in a controlled gas flowing environment. Li₂CO₃ was used also as additives (20 mol%) to promote CO₂ sorption. Prior to CO₂ sorption testing, the samples were dried in flowing N₂ (100 mL/min) at 25 °C/min for 30 min. The flowing gas was then changed to 100% CO₂ to allow reaction and determine CO₂ adsorption capacity. The weight increase due to CO₂ sorption (mg CO₂/g sorbent) was measured as a function of time at a constant temperature (700 °C) and constant concentration of CO₂ (95 mL/min) at atmospheric pressure.

3. Results and Discussion

3.1 FTIR study

Information on the mineral phases formed during calcination was obtained by FTIR. Figure 1 presents the IR fingerprint of the Na-FA CO₂ sorbents between 2000 and 600 cm⁻¹ and those of standard silica and Na₂CO₃ for comparison. As can be seen in Figure 1, the peak representing SiO₂ is not present in the calcined Na-FA sorbents, indicating that the calcination process at 800°C mostly converted the SiO₂ from fly ash and the Na₂CO₃ into Na-silicates. The large peak at ~1427 cm⁻¹ in Figure 1 (c) suggests that unreacted sodium remains when a Na₂CO₃:SiO₂ ratio of 4:1 is used. Overall, major peaks shift to lower energy as the concentration of silica increases. [8]. Different forms of silicates from structured crystalline solids can be distinguished by the stretching energy between 1200 and 750 cm⁻¹ where species with higher connectivity values absorb at higher energies. Vibrations at 1200, 1050, 950 and 750 cm⁻¹ correspond to (SiO₂), (Si₂O₅²⁻), (Si₂O₆⁴⁻), and (Si₂O₇⁶⁻ or SiO₄⁻) silicon centres, respectively. They appear to broaden and their frequencies decrease in intensity as species depolymerise and the Si-O-Si bond angle decreases [9]. Key IR bands appear at near 800, 877, 952 and 1427 cm⁻¹. The peak at 1427 cm⁻¹ can be attributed to CO₃²⁻ anion originating from the sodium carbonate, while the band with maximum at 963 cm⁻¹ is due to deformation

vibration of the atom in O-C-O bond of the same carbonate [10]. The remnant peaks are characteristic of meta-silicate structure. The IR spectra of sodium silicate present the most prominent bands between 1000 and 800 cm^{-1} caused by un-dissociated Na-silicate species. Based on previous studies, the IR bands at ~ 890 and 1020 cm^{-1} could be assigned to Si-O stretching vibration involving the Si-O-Si entity [9].

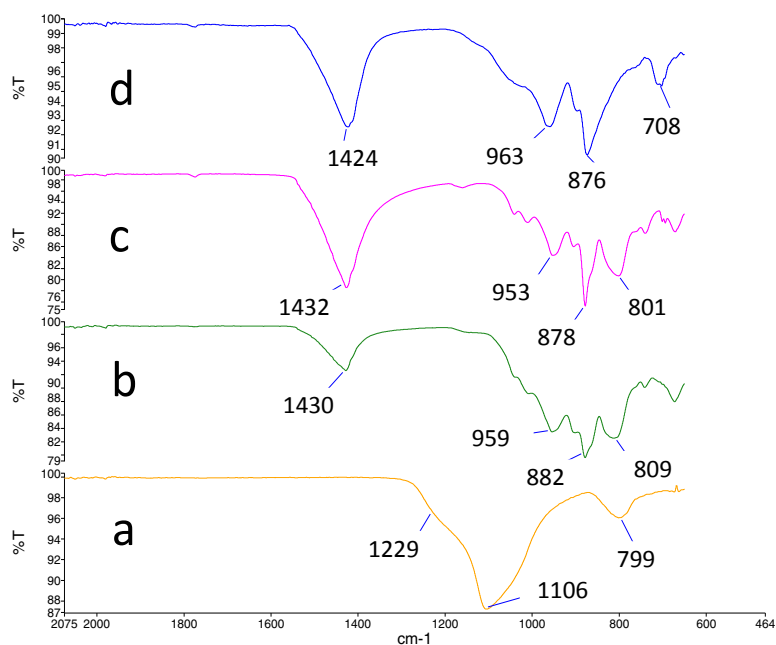


Figure 1. FTIR of SiO_2 standard (a); Na-FA 1:1 (b), Na-FA 4:1 (c) and Na_2CO_3 standard (d).

The band at around $959\text{-}950 \text{ cm}^{-1}$ represents silicate phase and the shifting to lower wavelength (953 cm^{-1} for the Na-FA 4:1) is characteristic of high silica-silicates. Absence of asymmetric Si-O-Si band at 1100 cm^{-1} in synthesized Na-FA sorbents (Figure 1b, 1c) indicates that the SiO_2 from FA has disappeared by the formation of Na-silicate. Some peaks seem somehow shifted to higher energies compared to typical Na_2SiO_3 peaks and may be associable to amorphous silicate phase (800 cm^{-1}).

Similarly, the peaks of the other synthesised sodium silicates present their main peaks at similar wavelength. Considering the two main factors determining the properties of sodium silicate solutions, namely silica to alkali ratio and silicate concentration, a solution with lower ratio of silica to alkali should imply a higher pH value [11]. This can be beneficial to CO_2 adsorption of the materials surface. Figure 2 shows the FTIR peaks of Na-FA 1:1 before (a) and after 1 adsorption/desorption cycle (b) at 700°C . The IR spectrum suggests that desorption of CO_2 was not completed and required more time. This can be deduced by the similarity of the band that represent the carbonates (1429 cm^{-1}) and those representing the silicate phase $1000\text{-}800 \text{ cm}^{-1}$ after the adsorption/desorption cycle.

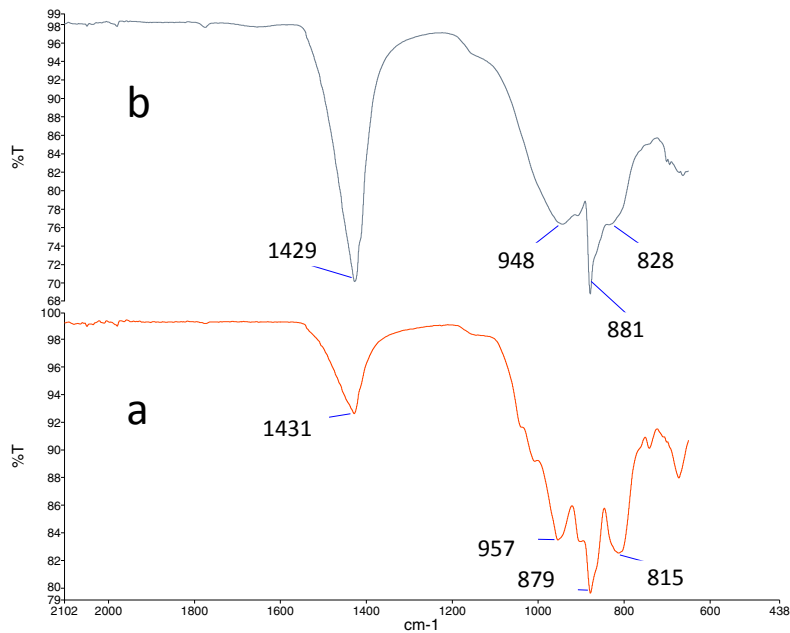


Figure2. FTIR of Na-FA samples obtained using a 1:1 before (a) and after 1 adsorption/desorption cycle (b) at 700°C.

3.2 CO₂ uptake

Different Na-FA sorbents have been evaluated for their capacity to chemisorb CO₂ at 700°C. This temperature was chosen as it is compatible with post-combustion technologies and industrial CO₂ emitters (e.g. cement plants steel works).

Figure 3 shows the effect of the different Na₂CO₃:FA molar ratio on CO₂ sorption and desorption at 700°C. Na-FA sorbent had its better performance at molar ratio 1:1 (a) with 1.8 mmol CO₂ / g sorbent, while a Na-FA ratio of 4:1 (b) was able to chemisorb only 0.45 mmol CO₂ / g sorbent. It is interesting to note that these materials can be regenerated by inert purge at the adsorption temperature. Both adsorption and desorption are rapid at the beginning of the process but then, the complete desorption requires about 1.6 h. For a commercial point of view, these long time may be a deterrent. However, 1.2 mmol/CO₂ / g sorbent can be adsorbed/desorbed in about 30 minutes.

Figure 4 compares the CO₂ sorption capacity of Na-FA 1:1 with and without additives at 700°C. Addition of lithium carbonate to the starting Na-silicate promoted CO₂ uptake and adsorption/desorption rate. The Na-FA 1:1 doped with 20% Li₂CO₃ was able to capture 2 mmol CO₂/g sorbent. Previous studies indicated that addition of up to 30 mol% K and Na carbonates promoted CO₂ sorption [12]. The addition of Li₂CO₃ to the Na-FA sorbent accelerated also the CO₂ adsorption and desorption steps, resulting in 1.4 mmol/CO₂ / g sorbent adsorbed/desorbed in about 25 minutes. Previous studies indicate that Na₂SiO₃ is not a good CO₂ sorbent at low temperature and under dry conditions, with a CO₂ uptake < 0.25 mmol CO₂/g sorbent [1]. Instead, this work suggests that Na-silicate materials may be developed as high temperature sorbents.

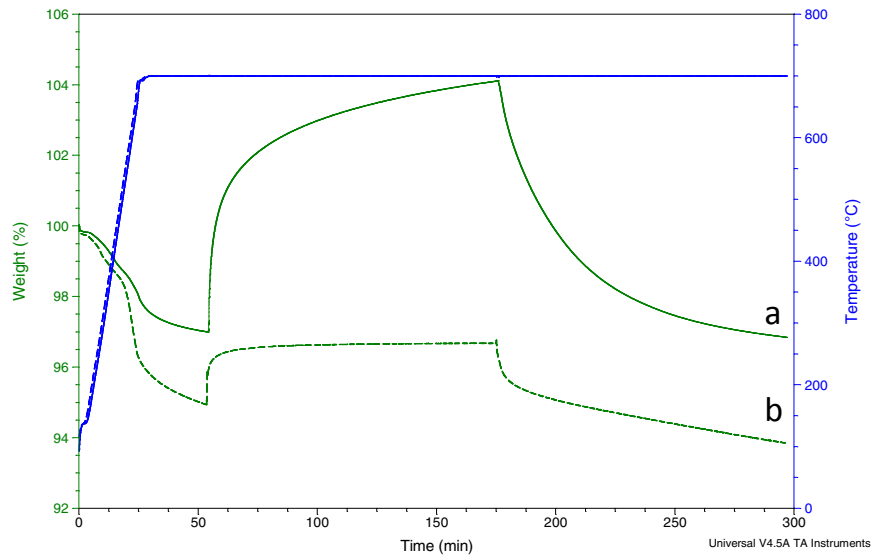


Figure 3. TGA of Na-FA 1:1 (a); Na-FA 4:1 (b).

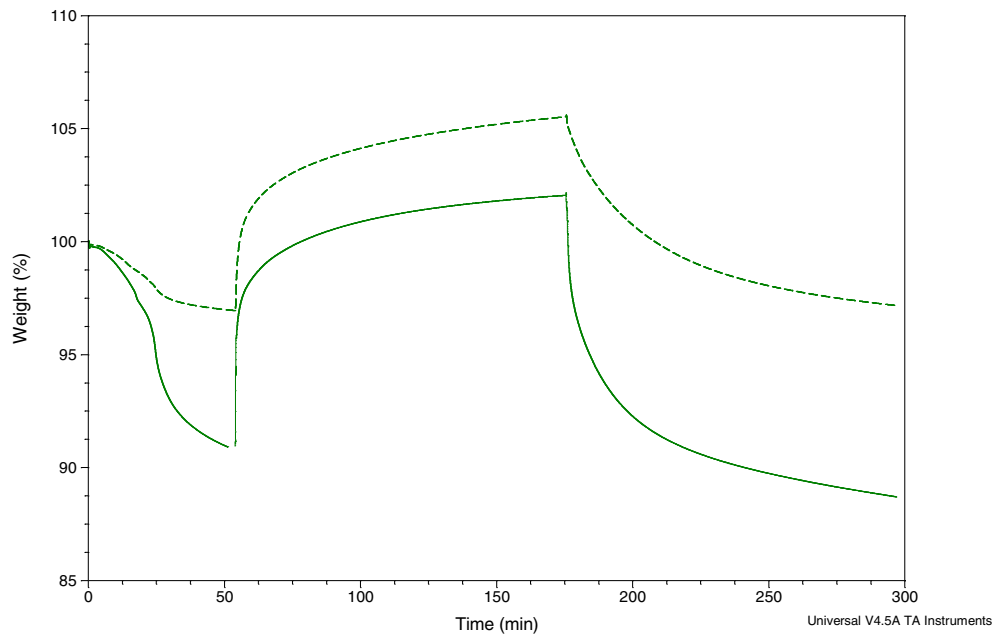


Figure 4. TGA of Na-FA 1:1 (a); Na-FA 1:1 20% Li_2CO_3 (b).

4. Conclusions

Na-FA sorbents with a $\text{Na}_2\text{CO}_3:\text{SiO}_2$ molar ratio of 1:1 obtained using fly ash as source of SiO_2 were developed and tested as CO_2 sorbent at high temperature. Na-FA had its better performance on CO_2 sorption (1.8 mmol CO_2) and desorption at 700°C . Its performance was enhanced when the material was doped with 20% Li_2CO_3 . In that case, it was able to capture 2 mmol CO_2/g . The CO_2 uptake at high temperature resulted much higher than found in previous experiments at temperature $< 100^\circ\text{C}$ (< 0.25 mmol CO_2/g sorbent) in dry conditions.

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