

# High Performance of Fly Ash Derived $\text{Li}_4\text{SiO}_4$ -Based Sorbents for High Temperature $\text{CO}_2$ Capture

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## Abstract

It is urgent to develop excellent solid  $\text{CO}_2$  sorbents with higher sorption capacity, simpler synthetic process, better thermal stability and lower costs of synthesis in  $\text{CO}_2$  capture and storage technologies. In this work, a number of  $\text{Li}_4\text{SiO}_4$ -based sorbents synthesized by lithium carbonate with three different kinds of fly ashes in various molar ratios were developed. The results indicate that the  $\text{Li}_2\text{CO}_3:\text{SiO}_2$  mole ratio used in the sorbents synthesis significantly affects the  $\text{CO}_2$  absorption properties. The sorption capacity increased with the excess of  $\text{Li}_2\text{CO}_3$  first and then decreased when the excessive quantity was beyond a certain amount. The experiments found that FA- $\text{Li}_4\text{SiO}_4_{0.6}$ , CFA- $\text{Li}_4\text{SiO}_4_{0.4}$ , HCl/CFA- $\text{Li}_4\text{SiO}_4_{0.3}$  presented the best sorption ability among these fly ash derived  $\text{Li}_4\text{SiO}_4$  samples, and the corresponding weight gain was 28.2 wt%, 25.1 wt% and 32.5 wt%, respectively. The three sorbents with the optimal molar ratio were characterized using various morphological characterization techniques and evaluated by thermogravimetric analysis for their capacity to chemisorb  $\text{CO}_2$  at  $450^\circ\text{C}$  -  $650^\circ\text{C}$ , diluted  $\text{CO}_2$  (10%, 20%) and in presence of water vapor (12%). The adsorption curve of FA- $\text{Li}_4\text{SiO}_4_{0.6}$  at different temperatures was simulated with the Jander-Zhang model to explore the influence of carbon dioxide diffusion on adsorption reaction. Further experiments showed that the adsorbent had a good sorption capacity in a lower partial pressure of  $\text{CO}_2$  and the presence of steam enhanced the mobility of  $\text{Li}^+$ . What's more, FA- $\text{Li}_4\text{SiO}_4_{0.6}$ , CFA- $\text{Li}_4\text{SiO}_4_{0.4}$  and HCl/CFA- $\text{Li}_4\text{SiO}_4_{0.3}$  particles showed satisfactory sorption capacity in fixed-bed reactor and excellent cyclic sorption stability during 10 sorption/desorption cycles.

## Keywords

Fly Ash, Lithium Orthosilicates, Molar Ratios,  $\text{CO}_2$  Capture

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is considered to be the main cause of greenhouse effect. The CO<sub>2</sub> atmospheric concentration has reached an unprecedented high level of 410.79 ppm in 2018 due to the massive emission of carbon dioxide derived from the large-scale combustion of fossil fuel [1] [2] [3]. Carbon capture and storage (CCS) has been proposed as one of the most promising technologies to mitigate CO<sub>2</sub> emissions from flue gases of coal-fired plants and industrial sites [2] [4] [5]. However, it is a big challenge to develop excellent CO<sub>2</sub> sorbents with high sorption capacity, simple synthetic process, high thermal stability and low costs of synthesis. The use of solid sorbents at high temperature is receiving increasing attention due to low energy and material consumption compared to low temperature capture system. High-temperature solid sorbents used in post-combustion system can avoid high regeneration requirements, equipment corrosion and high solvent costs problems, and can effectively use the waste heat from power or industrial sites [6]. The typical solid sorbents are hydrotalcite-like sorbents, CaO-based sorbents and Li<sub>4</sub>SiO<sub>4</sub>-based sorbents. Hydrotalcite-like sorbents absorb CO<sub>2</sub> in the temperature range of 200 °C - 400 °C and can be regenerated at a relatively low temperature. However, its moderate CO<sub>2</sub> sorption capacity has quite limited its practical application as a CO<sub>2</sub> sorbent. CaO-based sorbents have competitive advantages because of high theoretical sorption capacity and low cost [7]. But the rapid loss of reaction activity due to sintering, attrition and elutriation [8] and high desorption temperature during absorption/desorption cycles challenges its practical application [9].

Li<sub>4</sub>SiO<sub>4</sub> is a promising sorbent because of its high CO<sub>2</sub> capture capacity, rapid sorption rates and mild regeneration temperature (<750 °C) compared with the regeneration temperature of CaO (>900 °C) [10] [11] [12]. With the increasing demand of solid CO<sub>2</sub> sorbents, reducing the cost of synthesis will undoubtedly enhance the edge of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents for CO<sub>2</sub> capture in flue gas applications [13] [14]. Low cost materials like fly ash, rice husk ash, diatomite as SiO<sub>2</sub> precursors used to synthesize the Li<sub>4</sub>SiO<sub>4</sub>-based sorbents has attracted considerable attention in recent years due to their high availability and low cost [15] [16] [17]. Fly ash is a mineral residue resulting from the combustion of coal in power plants, and it contains considerable silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxides (Fe<sub>2</sub>O<sub>3</sub>), calcium oxides (CaO) [18]. Relevant research reported that Li<sub>4</sub>SiO<sub>4</sub> doping with Al, Fe, Ca could enhance its sorption ability and Li<sup>+</sup> mobility [19] [20] [21]. Therefore, the preparation of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from fly ash is expected. This practice not only can reduce the cost of CO<sub>2</sub> sorbents, but also can solve the problem of fly ash disposal to minimize significant economic and environmental impacts.

Olivares-Marín *et al.* [22] firstly reported novel Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from fly ash. The sorbent derived from fly ash in the presence of 40 mol% K<sub>2</sub>CO<sub>3</sub> presented a 10.7 wt% sorption capacity at 600 °C in 100% CO<sub>2</sub> atmosphere and reached the plateau of maximum capture capacity in less than 15 mins. Izquier-

do *et al.* [23] synthesized fly ash derived  $\text{Li}_4\text{SiO}_4$ -based sorbents and found that the sorption capacity of the sorbents from fly ash and  $\text{Li}_2\text{SiO}_3$  or  $\text{LiOH}$  via solid state method were 7.3 wt% and 11.3 wt% at  $600^\circ\text{C}$ , respectively. In our previous work [24],  $\text{Li}_4\text{SiO}_4$ -based sorbents from fly-ash(FA) subjected to different pre-treatments were synthesized for  $\text{CO}_2$  capture at high temperatures, finding that different preconditioned FA had different components and significantly affected the morphology, the porosity and the adsorption performance of the sorbents. However, the  $\text{Li}_2\text{CO}_3:\text{SiO}_2$  mole ratio used to synthesize  $\text{Li}_4\text{SiO}_4$ -based sorbents remains to be studied.

In this work, three starting fly ashes (original fly ash, pre-calcined fly ash, further acid leached and pre-calcined fly ash) were utilized to develop fly ash derived  $\text{Li}_4\text{SiO}_4$ -based sorbents. The effects of the mole ratios of  $\text{Li}_2\text{CO}_3:\text{SiO}_2$  (fly ash) on sorption capacity, the sorbents compositions and particle size were investigated. The effects of experiment conditions, including the temperature,  $\text{CO}_2$  partial pressures and moisture were also studied. The fixed-bed reactor has been used to analyze the sorption performance of particle sorbents.

## 2. Experimental Section

### 2.1. Preparation of Sorbents

Different  $\text{Li}_4\text{SiO}_4$ -based sorbents were synthesized by using three kinds of fly ashes (FA, CFA, HCl/CFA) and excessive lithium carbonate (AR, Sinopharm Chemical Reagent Co. Ltd) as starting materials, and the  $\text{Li}_2\text{CO}_3:\text{SiO}_2$  molar ratio was  $(2 + x):1$ , where  $x$  varied in the range of 0.1 to 0.7. The CFA was obtained by calcining the original FA at  $900^\circ\text{C}$  for 10 h in air, and the HCl/CFA was obtained as follows: 1) immersing the CFA samples in 10% conc. (weight) HCl aqueous solution at  $60^\circ\text{C}$  for 2 h; 2) washing several times with deionized water until no acid was detected in the filtrate; 3) drying the resultant at  $100^\circ\text{C}$  for 12 h. The quantitative composition of the three fly ashes was analyzed by X-Ray Fluorescence Spectrometer and reported in our previous paper [24]. The mixed powder samples were calcined at  $750^\circ\text{C}$  for 6 h. After calcination, the obtained samples were grounded by using a mortar and were subsequently screened into 20 - 40 mesh large particles, and the rest were further homogenized into powder. The obtained samples from original fly ash, calcined fly ash, further acid leached and pre-calcined fly ash were named as FA- $\text{Li}_4\text{SiO}_4_x$ , CFA- $\text{Li}_4\text{SiO}_4_x$  and HCl/CFA- $\text{Li}_4\text{SiO}_4_x$ , respectively.

### 2.2. Characterization of Sorbents

The phase compositions of the developed  $\text{Li}_4\text{SiO}_4$ -based sorbents were analyzed by X-ray diffraction with a diffractometer (RIGAKU D/MAX 2550 VB/PC, Japan) coupled to a copper anode X-ray tube and XRD peaks were identified using Jade 6.0 software. The surface morphologies of the sorbents were observed by scanning electron microscope (SEM, JSM-6360LV). The specific surface area, pore volume and pore size distribution of the synthesized sorbents were deter-

mined using a Micromeritics 3H-2720PS4 instrument.

The CO<sub>2</sub> sorption isotherms of the synthesized Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were tested using a WRT-3P TG equipment. Before CO<sub>2</sub> sorption experiments, the sorbents were first heated from room temperature to 700 °C at a heating rate of 20 °C/min in N<sub>2</sub> flow (100 mL/min) to remove potential CO<sub>2</sub> and moisture until the weight stayed stable. Then, the temperature was changed to the desired sorption temperature, and the flow gas (100 mL/min) was switched to pure CO<sub>2</sub> flow or mixture gas (N<sub>2</sub> and 10 vol% or 20 vol% CO<sub>2</sub>) to start the reaction for 150 min. Steam was also introduced into the reaction system, and the concentration of steam was controlled by changing the temperature of the water bath (12 vol% of H<sub>2</sub>O concentration, vapor pressure of H<sub>2</sub>O at 50 °C = 0.12 atm). The line from the water bath to the TG was wrapped with thermostatic bandage. Cycling tests were carried out using TGA. Sorption was conducted at 600 °C in pure CO<sub>2</sub> flow of 100 mL/min for 30 mins, and desorption was carried out at 700 °C in pure N<sub>2</sub> flow of 100 mL/min for 60 mins.

The particles of three fly ash derived Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were tested in a fixed-bed reactor at various temperatures under pure CO<sub>2</sub> atmosphere. The adsorption section (60 mm long) was filled with 2 g of 20 - 40 mesh sorbent particles mixed with 20 - 40 mesh Rasching ring as a diluting agent. For the breakthrough experiments, the sorbent was heated to 700 °C in N<sub>2</sub> flow (100 mL/min) to remove potential CO<sub>2</sub> and moisture, and then switched the temperature to desired temperatures (450 °C - 600 °C) to adsorb CO<sub>2</sub> in pure CO<sub>2</sub> (30 mL/min). The exhaust was analyzed using an online M3000 micro gas chromatograph equipped with a TCD detector and a Porapak Q column. The equilibrium capacity was equal to the quantity of the absorbed CO<sub>2</sub> at equilibrium. The calculating equations were as follows [25]:

$$S_{\text{abs}} = S_{\text{blank}} - S_{\text{CO}_2}$$

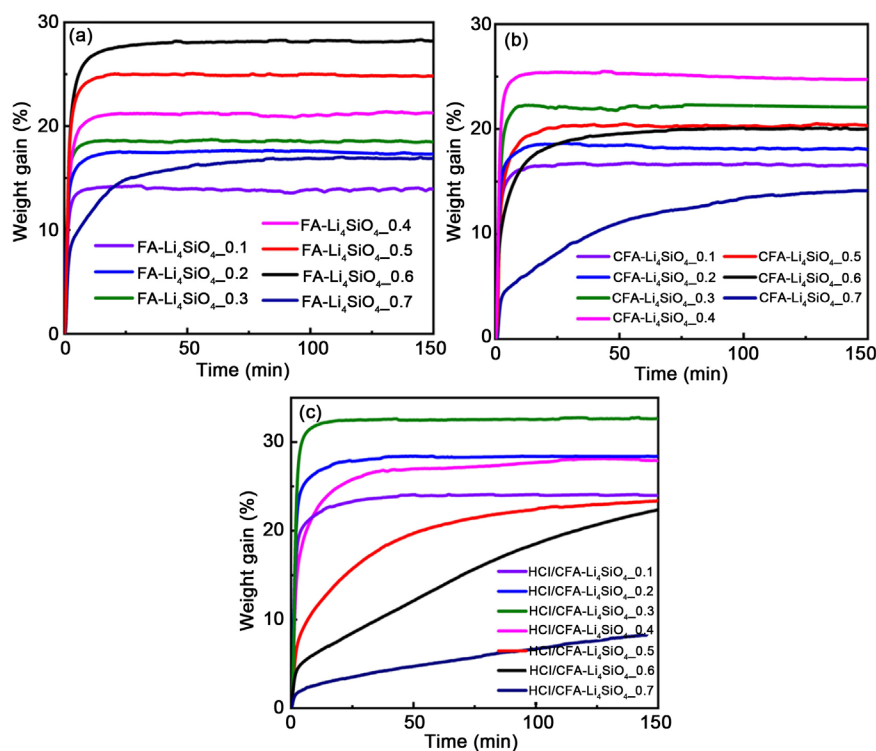
$$Q_{\text{abs}} = \frac{F \times S_{\text{abs}} \times M_{\text{CO}_2}}{24.5 \times m}$$

Among them,  $S_{\text{blank}}$  was the integral value of CO<sub>2</sub> concentration with time under the blank test condition;  $S_{\text{CO}_2}$  was the integral value of CO<sub>2</sub> concentration with time in the outlet gas after the CO<sub>2</sub> adsorption reaction; F was the inlet gas flow, in ml/min; 24.5 was the molar volume constant of gas at room temperature; m was the mass of adsorbent added during the reaction process in g;  $M_{\text{CO}_2}$  was the molar mass of carbon dioxide.

### 3. Results and Discussion

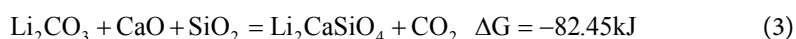
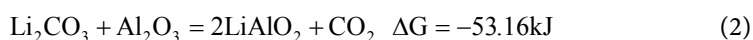
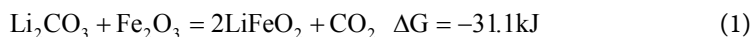
#### 3.1. Optimization and Characterization of Adsorbents

The CO<sub>2</sub> sorption isotherms of three kinds of sorbents from different pretreatments with different Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> molar ratios at 600 °C are shown in **Figure 1**. It can be seen that the Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> molar ratio had a significant influence on the synthesized sorbents. The overall weight gain of three kinds of sorbents increased



**Figure 1.** CO<sub>2</sub> sorption isotherms of three kinds of sorbents from different pretreatments with different Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> molar ratios at 600 °C: (a) FA-Li<sub>4</sub>SiO<sub>4</sub> sorbents; (b) CFA-Li<sub>4</sub>SiO<sub>4</sub> sorbents; (c) HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub> sorbents.

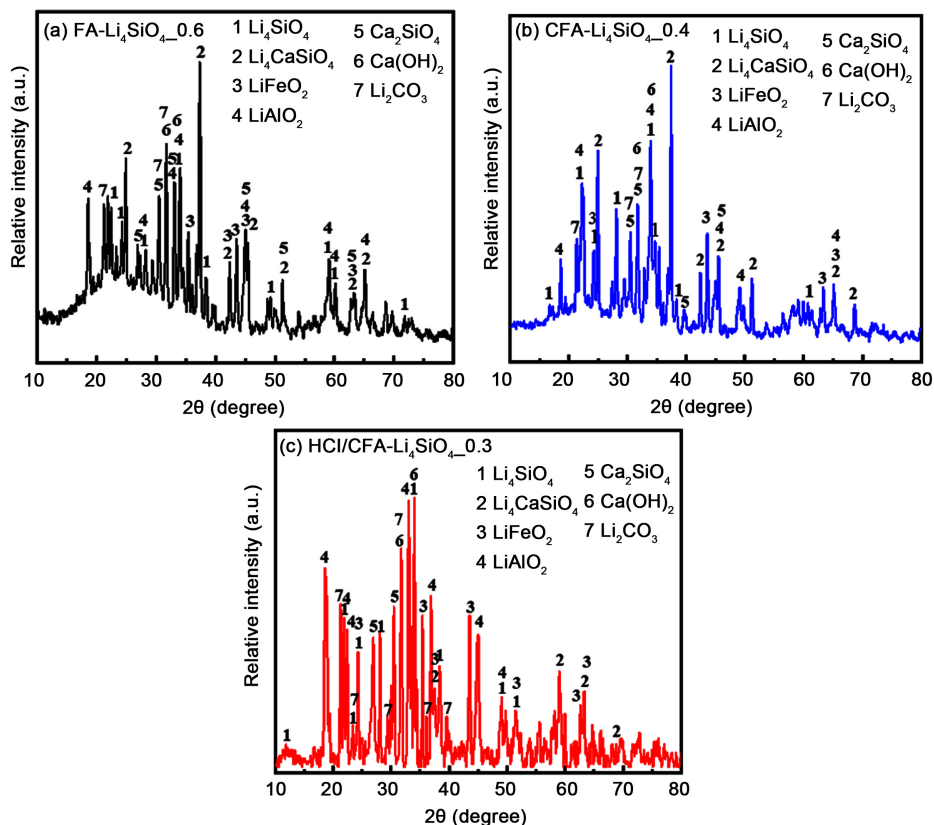
with the excess of Li<sub>2</sub>CO<sub>3</sub> first, then decreased when the excessive quantity was beyond a certain amount. Among these FA-Li<sub>4</sub>SiO<sub>4</sub> samples, as shown in **Figure 1(a)**, FA-Li<sub>4</sub>SiO<sub>4\_0.6</sub> sorbents presented the best sorption ability, whose weight gain was 28.2 wt%. While for CFA-Li<sub>4</sub>SiO<sub>4</sub> and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub> sorbents, as shown in the **Figure 1(b)** and **Figure 1(c)**, the optimal samples were CFA-Li<sub>4</sub>SiO<sub>4\_0.4</sub> and HCl/CFA-Li<sub>4</sub>SiO<sub>4\_0.3</sub> respectively, and the corresponding sorption capacity was 25.1 wt% and 32.5 wt% respectively. According to the calculation chemical Equation (1), (2), (3) of facts age 6.4, the lithium carbonate can react with the alkali oxides contained in three kinds of FA at 750 °C, and therefore the lithium carbonate was insufficient to produce enough lithium orthosilicate before the content of Li<sub>2</sub>CO<sub>3</sub> reached the optimal level. The by-product Li<sub>2</sub>SiO<sub>3</sub> that has no adsorption capacity at a temperature higher than 250 °C was easy to generate due to the insufficient content of Li, resulting in low adsorption capacity of the synthesized sorbents [25]. However, excessive lithium carbonate doping led to a decrease in the content of the active component lithium orthosilicate in the adsorbent, and thus the adsorption performance decreased.



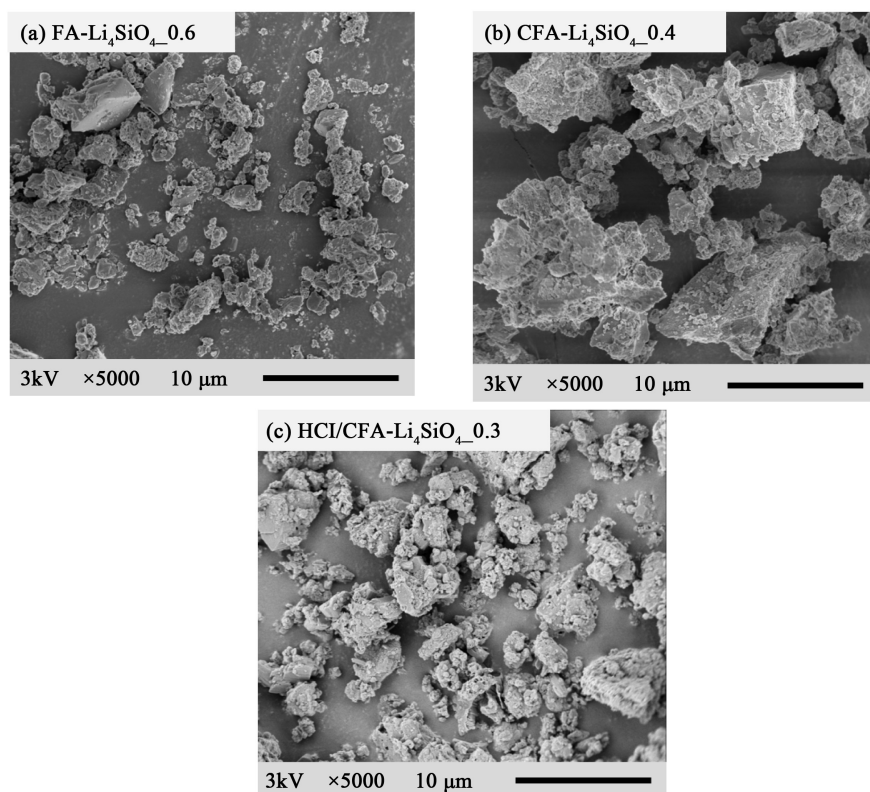
Three optimal Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were further characterized by XRD, and

the results are shown in **Figure 2**. The main components of the three sorbents were  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{CaSiO}_4$ ,  $\text{LiFeO}_2$  and  $\text{LiAlO}_2$ , and a small amount of  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Li}_2\text{SiO}_3$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$ . The existence of a small amount of  $\text{Li}_2\text{CO}_3$  indicates that  $\text{Li}_2\text{CO}_3$  was added in excess, which could avoid the formation of  $\text{Li}_2\text{SiO}_3$  due to insufficient  $\text{Li}_2\text{CO}_3$  and made sure the full reaction of  $\text{SiO}_2$  and other metal elements. The FA- $\text{Li}_4\text{SiO}_4_{-0.6}$  sorbent had a broad hump in the  $2\theta$  region between  $18^\circ$  and  $35^\circ$  which showed the presence of amorphous glassy phase [26]. This was because the calcination temperature was not enough high to release all amounts of amorphous glassy phase. Compared with FA- $\text{Li}_4\text{SiO}_4_{-0.6}$  and CFA- $\text{Li}_4\text{SiO}_4_{-0.4}$ , HCl/CFA- $\text{Li}_4\text{SiO}_4_{-0.3}$  had no sharp peak of  $\text{Li}_2\text{CaSiO}_4$ , and the Ca species mainly existed in the form of  $\text{Ca}(\text{OH})_2$ . The decomposition product of  $\text{Ca}(\text{OH})_2$  was  $\text{CaO}$ , which could improve the  $\text{CO}_2$  sorption capability of the sorbent by the occurrence of Li-Ca- $\text{CO}_2$  interactions ( $\text{Li}_4\text{SiO}_4 + \text{CaO} + \text{CO}_2 \rightarrow \text{Li}_2\text{CaSiO}_4 + \text{Li}_2\text{CO}_3$ ) [13] [21]. Moreover, the peak of  $\text{LiAlO}_2$  of HCl/CFA- $\text{Li}_4\text{SiO}_4_{-0.3}$  sorbents increased more remarkably. Relevant literature [20] has reported that  $\text{LiAlO}_2$  can promote the diffusion of  $\text{Li}^+$  which is beneficial to the increase of the sorption capacity of these three sorbents.

**Figure 3** shows the SEM morphologies of the three optimal fly ash  $\text{Li}_4\text{SiO}_4$ -based sorbents. It can be seen that CFA- $\text{Li}_4\text{SiO}_4_{-0.4}$  was mainly composed of irregular particle sizes, and its average particle sizes were as large as  $9\ \mu\text{m}$ .



**Figure 2.** XRD patterns of FA- $\text{Li}_4\text{SiO}_4_{-0.6}$ , CFA- $\text{Li}_4\text{SiO}_4_{-0.4}$  and HCl/CFA- $\text{Li}_4\text{SiO}_4_{-0.3}$  sorbents.

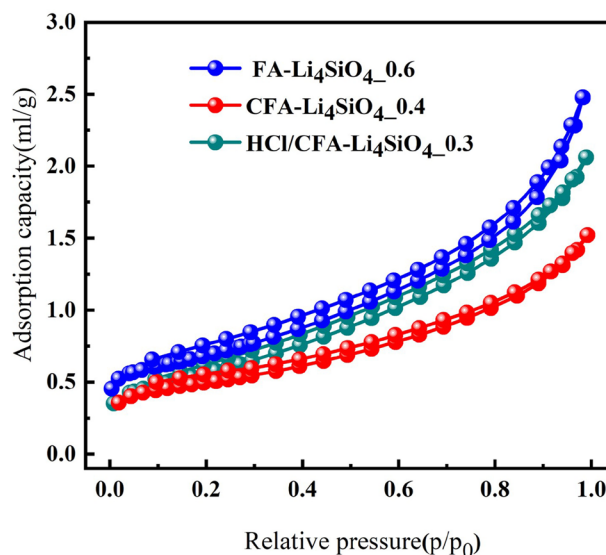


**Figure 3.** SEM images of the three optimal sorbents.

Moreover, there were grain agglomerates between particles. This kind of surface morphology is mainly related to the high-temperature solid phase synthesis method because sorbent particles are easy to migrate and aggregate together at high temperatures [27]. While the surface morphologies of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 were obviously different from that of CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4. Their particles were relatively looser and the average particle size was smaller (about 3 μm and 5 μm, respectively). And there were also fewer agglomerations between particles. FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 exhibited the smallest particle size of the three sorbents. It was reported that that alkali metal, alkaline earth metal, Mg, Al and other elements can inhibit the growth of sorbent grains and reduce the sintering effect of sorbent particles [28] [29]. Since the FA was not calcined and contained a large amount of hetero elements such as an alkali metal, the FA derived FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 had smaller particle size.

**Figure 4** compares the N<sub>2</sub> adsorption/desorption isotherms of three optimal Li<sub>4</sub>SiO<sub>4</sub>-based sorbents. These three sorbents presented similar adsorption/desorption isotherms belonging to “type II” isotherm [30], indicating that the resulting sorbent samples had non-porous structure and aggregates of plate-like particles. According to the IUPAC classification, the three sorbents exhibited narrow “H3” hysteresis loops, indicating that the sorbents contained irregular stacked pores or slit-like pores.

**Table 1** summarizes the BET surface area, average pore diameter and pore volume for three samples. As can be seen from the table, FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and



**Figure 4.** N<sub>2</sub> adsorption/desorption isotherms of three optimal Li<sub>4</sub>SiO<sub>4</sub>-based sorbents.

**Table 1.** Physicochemical properties of three optimal Li<sub>4</sub>SiO<sub>4</sub>-based sorbents.

Sorbents	BET surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	Pore volume (ml/g)
FA-Li <sub>4</sub> SiO <sub>4</sub> _0.6	1.97	6.36	0.0038
CFA-Li <sub>4</sub> SiO <sub>4</sub> _0.4	1.01	6.27	0.0021
HCl/CFA-Li <sub>4</sub> SiO <sub>4</sub> _0.3	1.94	5.60	0.0034

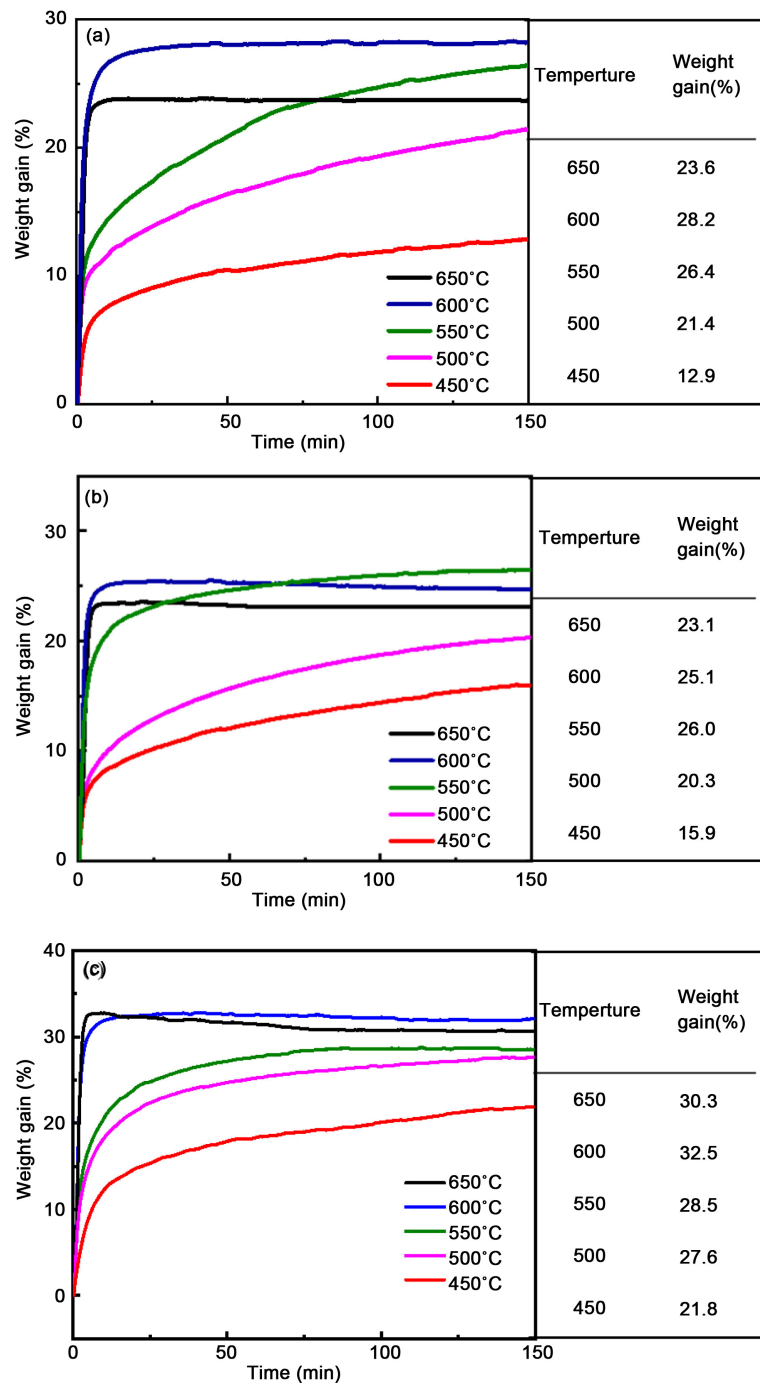
HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 had higher specific surface areas (1.97 and 1.94 m<sup>2</sup>/g respectively) than CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 (1.0087 m<sup>2</sup>/g). This result was consistent with the particle size distribution of SEM images. The adsorbent with smaller particles had larger specific surface area. The average pore diameters of three Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were between 2 - 50 nm, which belonged to mesoporous materials.

## 3.2. CO<sub>2</sub> Capture Studies

### 3.2.1. Effect of Temperature

**Figure 5** shows the CO<sub>2</sub> uptake isotherms of the three sorbents at pure CO<sub>2</sub> at different sorption temperatures to evaluate the effect of temperature on CO<sub>2</sub> uptake. The CO<sub>2</sub> adsorption capacity of these three adsorbents first increased with an increasing temperature and then decreased when the experimental temperature exceeded 600 °C, which showed a similar sorption trend to previous literature [22] [24] [29]. This phenomenon could be mainly attributed to the disappearance of the mesopore on the external shell of the Li<sub>4</sub>SiO<sub>4</sub> at high temperature [29]. FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 obtained its maximum CO<sub>2</sub> sorption capacity of 28.2 wt% at 600 °C. Furthermore, when the sorption temperature was 600 °C or 650 °C, the sorption rate of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 was exactly rapid to obtain the maximum capacity





**Figure 5.** CO<sub>2</sub> sorption isotherms of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 under pure CO<sub>2</sub> at different temperatures.

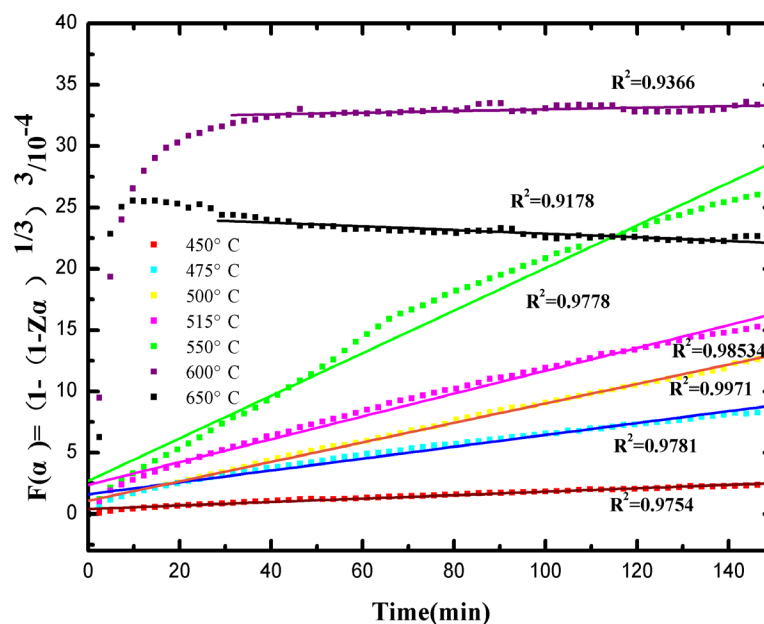
within 10 mins, which was faster than other reported low-cost ashes derived from Li<sub>4</sub>SiO<sub>4</sub>-based sorbents [17] [22] [27] [31] [32] [33]. For CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4, the sorption capacity was 25.1 wt% at 600°C. However, its sorption performance at 550°C reached 26 wt%, beyond that of 600°C with the sorption time prolonging enough, which is probably attributed to the relatively high content of LiFeO<sub>2</sub> in CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 sorbent. The thermodynamic equilibrium temperature of

LiFeO<sub>2</sub> was about 550 °C via FactSage 6.4 software analysis [24], indicating LiFeO<sub>2</sub> can adsorb CO<sub>2</sub> at the temperature of 550 °C to a certain extent while it cannot capture CO<sub>2</sub> at 600 °C. HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 showed the most excellent sorption capacity among these three sorbents at 450, 500, 550, 600 and 650 °C due to its relatively high surface area and content of LiAlO<sub>2</sub>. The maximum CO<sub>2</sub> sorption capacity for HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 was 32.5 wt% at 600 °C. When the temperature was 650 °C, the CO<sub>2</sub> uptake of the sorbent showed a decreasing trend at the later stage of reaction. This is because that too high temperature will lead to an increase in the CO<sub>2</sub> equilibrium concentration of the sorbent, while the concentration of CO<sub>2</sub> in the gas phase does not change. Therefore, an increase in temperature will lead to a decrease in the driving force of CO<sub>2</sub> diffusion to adsorbent particles, which is not conducive to the adsorption reaction, and even leads to the occurrence of a desorption reaction.

In order to understand the reaction mechanism of fly ash derived Li<sub>4</sub>SiO<sub>4</sub>-based sorbents, FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 adsorbents in pure CO<sub>2</sub> atmosphere at different temperatures were fitted to the Jander-Zhang model. Compared with other simulation methods, the Jander-Zhang model can well explain the influence of the diffusion of CO<sub>2</sub> in the shell on the CO<sub>2</sub> adsorption characteristics. The Jander-Zhang model assumes that the adsorption reaction is kinetically controlled by the diffusion of CO<sub>2</sub>, and the effects of the CO<sub>2</sub> surface adsorption reaction rate of the adsorbent are not considered. The Jander-Zhang model can be described by the following formula:

$$\left[1 - (1 - Z\alpha)^{1/3}\right]^3 = k(P_{\text{CO}_2})^n t$$

where  $k$  is the reaction rate constant.  $Z\alpha$  represents the proportion of Li<sub>2</sub>CO<sub>3</sub> in the products layer (Li<sub>2</sub>SiO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>), and  $(1 - Z\alpha)$  represents the proportion of unreacted Li<sub>4</sub>SiO<sub>4</sub> and generated Li<sub>2</sub>SiO<sub>3</sub>. Because the ratio of density to molar mass of Li<sub>2</sub>CO<sub>3</sub> is similar to Li<sub>2</sub>SiO<sub>3</sub>, theoretically  $Z$  is supposed to be around 0.5. According to previous literature reports, the products of Li<sub>4</sub>SiO<sub>4</sub> exist in the form of double shells, and the CO<sub>2</sub> concentration is nonlinearly distributed in the product layer. During the adsorption process of the Li<sub>4</sub>SiO<sub>4</sub> sorbent, Li<sup>+</sup> and O<sup>2-</sup> are generated on the surface of the unreacted Li<sub>4</sub>SiO<sub>4</sub> and diffuse to the outer surface of Li<sub>2</sub>SiO<sub>3</sub>; CO<sub>2</sub> diffuses through the solid Li<sub>2</sub>CO<sub>3</sub> layer and reacts with Li<sup>+</sup> and O<sup>2-</sup> on the outer surface of Li<sub>2</sub>SiO<sub>3</sub>. Since the size of Li<sup>+</sup> and O<sup>2-</sup> are smaller than CO<sub>2</sub> molecules, the diffusion of CO<sub>2</sub> in the solid Li<sub>2</sub>CO<sub>3</sub> layer is expected to be much slower than the diffusion of Li<sup>+</sup> and O<sup>2-</sup> in Li<sub>2</sub>SiO<sub>3</sub>. Therefore, CO<sub>2</sub> diffusion is more likely to be a reaction speed control step [31]. The fitting results of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 adsorbents in pure CO<sub>2</sub> atmosphere at different temperatures are shown in **Figure 6**. The Jander-Zhang model can fit the experimental results well at 450 °C, 475 °C, 500 °C, 525 °C, 550 °C, which means that the diffusion rate of CO<sub>2</sub> plays a decisive role in the whole CO<sub>2</sub> adsorption process of the adsorbents at a lower temperature. The fact is in agreement with the fitting results of double exponential model reported in previous literature



**Figure 6.** Fit of CO<sub>2</sub> sorption on FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 sorbent with Jander-Zhang model.

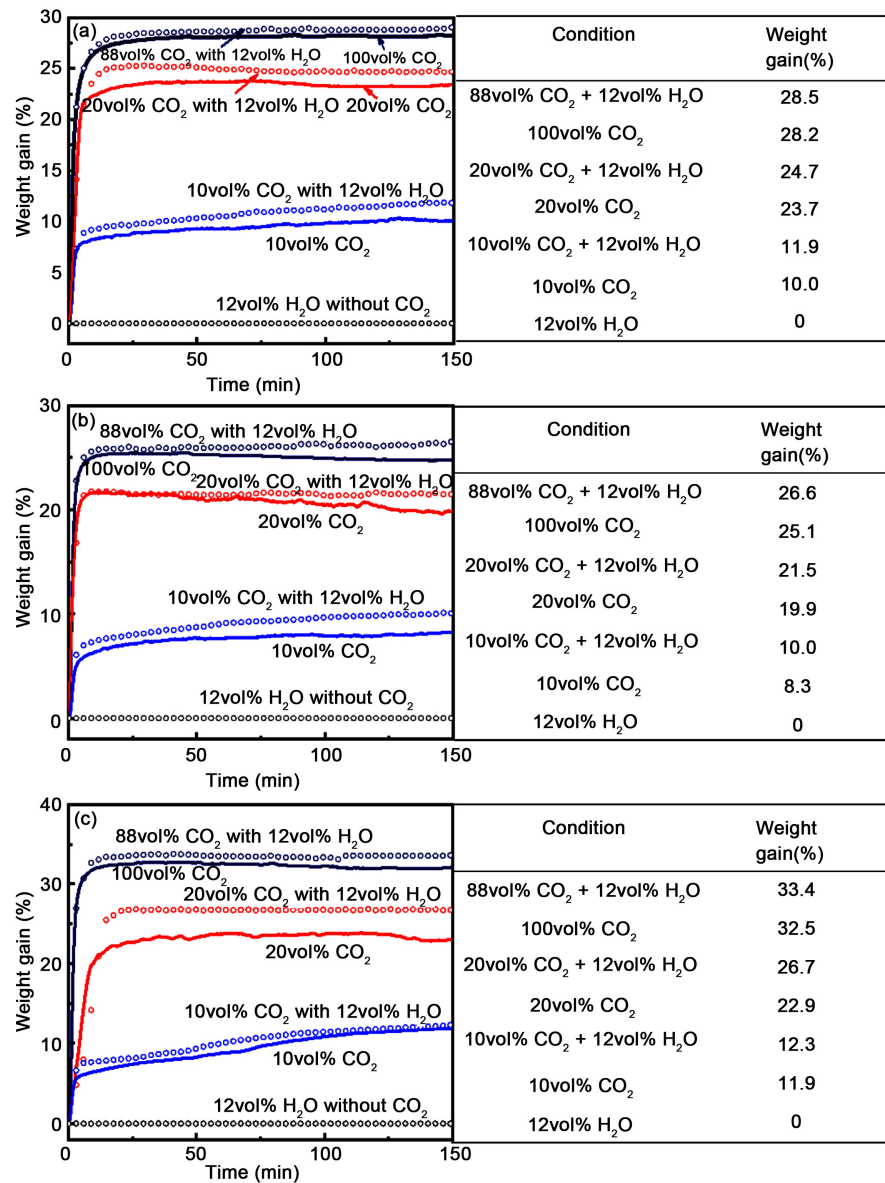
[32] [33]. However, when the reaction temperature is more than 600°C, the Jander-Zhang model cannot fit the initial stage of CO<sub>2</sub> adsorption well, which illustrates that at high temperatures, the reaction rate is determined by the surface chemisorption reaction rate in the initial stage of the reaction and by the diffusion rate of CO<sub>2</sub> in the later stage of the reaction.

### 3.2.2. Effect of Diluted CO<sub>2</sub> and Moisture on Sorption

The effects of various CO<sub>2</sub> concentration and humidity atmosphere on the sorption behavior of the three sorbents were investigated. In this experiment, moisture content of 12 vol% and different CO<sub>2</sub> partial pressures (from 10 vol% to 100 vol%) at 600°C were used to evaluate the influences of humidity and various CO<sub>2</sub> partial pressures on the developed Li<sub>4</sub>SiO<sub>4</sub>-based sorbents. As can be seen from **Figure 7**, due to the limitation of sorption equilibrium of Li<sub>4</sub>SiO<sub>4</sub>, the weight gain of the three sorbents in the presence and absence of steam decreased when the CO<sub>2</sub> partial pressure reduced from 100 vol% to 10 vol% [31]. The adsorption capacity of the three adsorbents in the presence of 20 vol% CO<sub>2</sub> can achieve about 70% - 80% of that of the three adsorbents under pure carbon dioxide, indicating that the Li<sub>4</sub>SiO<sub>4</sub>-based sorbents have a good practicability at a lower partial pressure of CO<sub>2</sub>. And the presence of 12 vol% steam enhanced the sorption uptake due to the enhancement of the mobility of Li<sup>+</sup> in the diffusion control stage according to double-shell mechanism [34]. As a result, the absorption capability and sorption rate of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were improved.

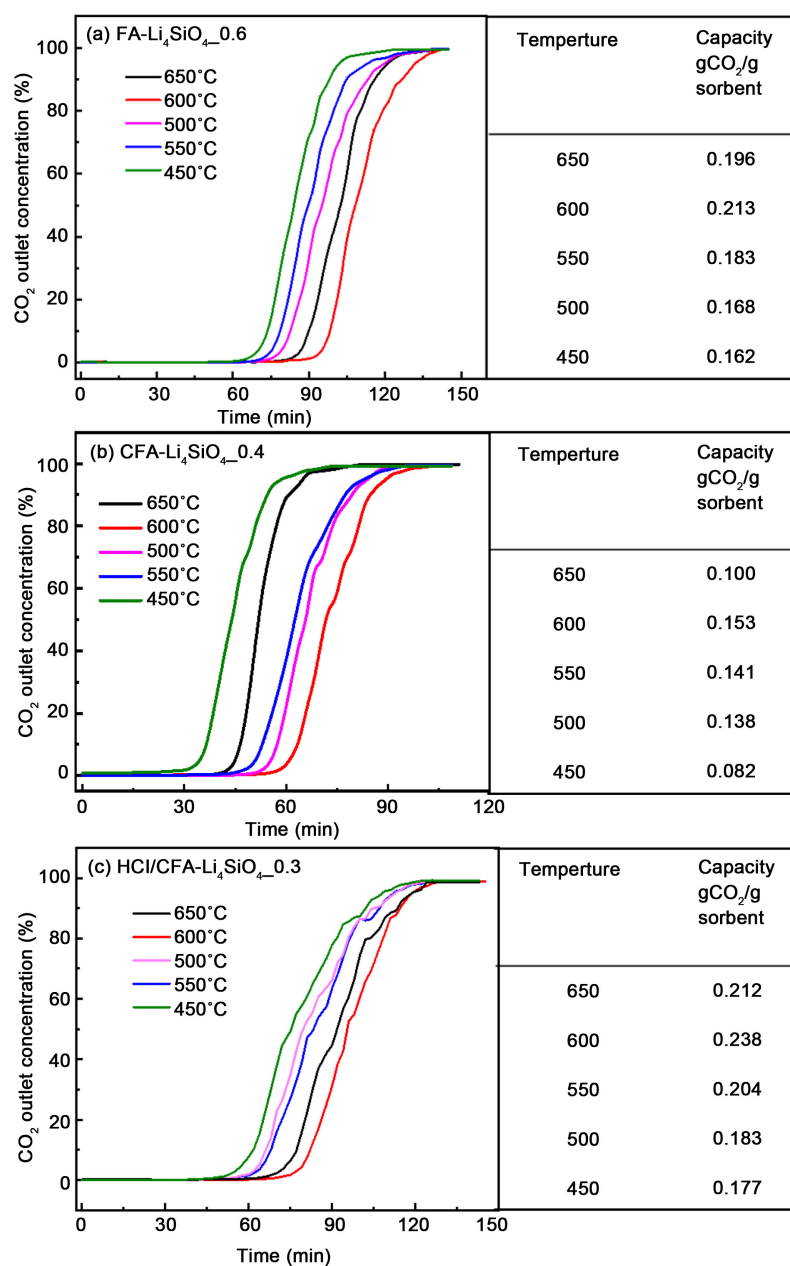
### 3.2.3. Fixed-Bed Reactor Test and Stability Test

Besides, a fixed-bed reactor was used to investigate CO<sub>2</sub> sorption on the prepared fly ash derived Li<sub>4</sub>SiO<sub>4</sub>-based sorbents. Compared to thermogravimetric



**Figure 7.** CO<sub>2</sub> sorption isotherms of (a) FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and (b) CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and (c) HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 under different CO<sub>2</sub> pressure with 12 vol% H<sub>2</sub>O.

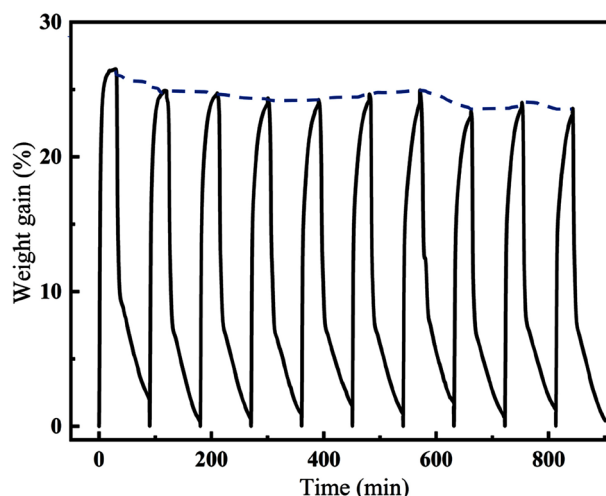
analysis (TGA), fixed-bed reactors can provide more reliable sorption capacity in formation in practical application. **Figure 8** shows the CO<sub>2</sub> sorption performance of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 sorbent particles (20 - 40 mesh) in the temperature range from 450 °C to 650 °C in pure CO<sub>2</sub> flow in a fixed-bed reactor. It can be seen that the three sorbents had a similar tendency of sorption performance. The equilibrium and breakthrough capacities of three sorbents initially increased and then decreased with the increase of temperature. All of the three sorbents reached the highest sorption capacity at 600 °C, and the maximum sorption capacities of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 were 0.213 g CO<sub>2</sub>/g sorbent, 0.153 g CO<sub>2</sub>/g sorbent and 0.238 g CO<sub>2</sub>/g sorbent respectively. The experimental results



**Figure 8.** CO<sub>2</sub> capture breakthrough curves of (a) FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and (b) CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 (c) HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 in the fixed-bed reactor at different temperatures in 100 vol% CO<sub>2</sub> atmosphere.

in the fixed-bed reactor were consistent with the sorption trends of the powder sorbents tested via TG. Compared with the sorption capacity of the powdered sorbents, the sorption capacity of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 particles was lower than that of the powdered sorbents, which was attributed to the larger diffusion resistance of CO<sub>2</sub> in the particulate sorbents than that in the powdered sorbent.

HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 is the best sorbent in terms of sorption capacity, while FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 sorbent has the advantage of simple synthetic process and relatively



**Figure 9.** Stability test of CO<sub>2</sub> sorption-desorption cycles on FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 sorbent (absorption: 600°C, 100 vol% CO<sub>2</sub>; desorption: 700°C, 100 vol% N<sub>2</sub>).

good adsorption performance, the industrial prospect is promising. Our previous literature [24] has reported the HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub> sorbent had an excellent cyclic performance. In order to investigate the cyclic stability of FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, ten sorption and desorption cycles were carried out in a pure CO<sub>2</sub> flow at 600°C. The results are shown in **Figure 9**. It can be seen that FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 presented an excellent cycling stability. Its CO<sub>2</sub> sorption capacity reduced slightly from 26 wt% to 24 wt% after 10 cycling processes. However, it should be pointed out that during the desorption process, the desorption rate was fast in the early stage, but became slower in the later stage, which resulted in the extension of the whole desorption time. Longer desorption time may be due to the lack of loose porous surface of the sorbent, which leads to a slower desorption rate at a later stage.

#### 4. Conclusions

Li<sub>2</sub>CO<sub>3</sub> and three kinds of fly ash from different pretreatments were used to synthesize Li<sub>4</sub>SiO<sub>4</sub>-based sorbents in different Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> molar ratios. The results indicate that the weight gain of three kinds of sorbents first increased with the excess of Li<sub>2</sub>CO<sub>3</sub>, and then decreased when the excess exceeded a certain amount. The optimal fly ash derived Li<sub>4</sub>SiO<sub>4</sub>-based sorbents with the best sorption ability among these samples are FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6, CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3, whose weight gain was 28.2 wt%, 25.1 wt% and 32.5 wt%, respectively. SEM and BET analyses indicate that FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 had smaller particle sizes and higher specific surface areas than that of CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.4. And XRD analyses indicate that HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 had a relatively high content of Ca(OH)<sub>2</sub> and LiAlO<sub>2</sub>, which were beneficial to the improvement of the sorption capacity.

The three kinds of optimal sorbents were tested in the temperature range of 450°C - 650°C, diluted CO<sub>2</sub> (10%, 20%) and in the presence of water vapor

(12%). The optimal sorbents showed the best adsorption performance at 600 °C. When the CO<sub>2</sub> partial pressure reduced from 100% to 10%, 20%, the CO<sub>2</sub> sorption capacity decreased due to the limitation of sorption equilibrium of Li<sub>4</sub>SiO<sub>4</sub>. And the adsorption capacity of sorbents at 20 vol% CO<sub>2</sub> can reach 70% - 80% of that of the sorbents at 100 vol% CO<sub>2</sub>. The presence of water vapor enhanced CO<sub>2</sub> absorption capacity at 600 °C due to enhancement of the mobility of Li<sup>+</sup> in the diffusion control stage according to double-mechanism.

The experimental results indicate that FA-Li<sub>4</sub>SiO<sub>4</sub>\_0.6 and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub>\_0.3 showed excellent sorption capacity at 600 °C in fixed-bed reactor. Compared with the sorption capacity of the powdered sorbents, the sorption capacity of particles was lower than that of the powdered sorbents. The excellent cyclic sorption stability of FA-Li<sub>4</sub>SiO<sub>4</sub> and HCl/CFA-Li<sub>4</sub>SiO<sub>4</sub> during 10 sorption/desorption cycles were confirmed by previous literature and work in this article respectively.

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### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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