

Article

Stability of CO₂ Capture by Lithium Orthosilicate Under Various Conditions and the Presence of SO₂

Dien-Yi Wu ¹, Birgitta Narindri Rara Winayu ^{1,2} and Hsin Chu ^{1,*}

¹ Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan; z8008079@email.ncku.edu.tw (D.-Y.W.); birgittanarindri@yahoo.com (B.N.R.W.)

² Department of Biotechnology, Faculty of Biotechnology, Atma Jaya Catholic University of Indonesia, BSD Campus, Tangerang 15345, Indonesia

* Correspondence: chuhsin@mail.ncku.edu.tw

Abstract: Investigating effective sorbent materials in the CO₂ sorption process is crucial. Lithium-based sorbents combine high carbon capture efficiency with excellent mechanical stability. Lithium orthosilicate (Li₄SiO₄) was prepared for the CO₂ capture test in this study with a variety of variables, including the sorbent calcination temperature, space velocity, operation temperature, and water vapor and SO₂ concentrations. Several analyses were used in the characterization of the spent and fresh sorbents. Additionally, the CO₂ sorption reaction kinetics were investigated using deactivation models. The sorbent with the best utilization value was obtained via calcining Li₄SiO₄ at 700 °C for five hours. Li₄SiO₄ demonstrated exceptional stability in the 600–800 °C temperature and 1200–6000 mL/h/g space velocity ranges. The performance of the sorbent was not significantly affected by the water vapor content up to 10%. Nevertheless, further increasing the water vapor stream drastically declined its performance due to water masking on the sorbent's surface. Similar sorption trends were demonstrated by Li₄SiO₄ in all SO₂ content setups. The Type I deactivation model was well fitted to the experimental data.

Keywords: CO₂ capture; lithium orthosilicate; SO₂; H₂O; carbonation; sorbent



Academic Editor: Paola Ammendola

Received: 26 November 2024

Revised: 13 December 2024

Accepted: 24 December 2024

Published: 27 December 2024

Citation: Wu, D.-Y.; Narindri Rara Winayu, B.; Chu, H. Stability of CO₂ Capture by Lithium Orthosilicate Under Various Conditions and the Presence of SO₂. *Processes* **2025**, *13*, 41. <https://doi.org/10.3390/pr13010041>

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The elevation of CO₂ emissions, which is dominated by fossil-fuel burning from industry and anthropogenic activities, leads to a worsening of global warming [1]. Among the developed technologies for carbon capture, sorption is considered a promising strategy to be applied due to the simplicity of the process [2] through the supply of flue gas to the solid bed of sorbent [3].

Several factors are critical in choosing the sorbent materials for carbon capture, including a high diffusion rate, stability, and great kinetic and thermodynamic properties [4]. Lithium (Li)-based sorbents, such as lithium zirconate (Li₂ZrO₃) and lithium silicate (Li₄SiO₄), are favorable to be applied in carbon capture due to their fast regeneration rate [5] and high mechanical strength, especially when operated under high temperatures [6]. Several side effects, including sintering, fouling, loss of active species, a reduction in mechanical strength, and poisoning, can significantly decline the sorption performance. Nevertheless, some side effects are reversible and can be eliminated by the regeneration process [7]. The combination of Li with the Si element (Li₄SiO₄) has been reported to have a sorption capacity of 360 mg-CO₂/g-sorbent, which was higher than that when mixing with Zr(Li₂ZrO₃) [8]. Aside from considerations regarding the sorbent properties, sorption

of CO₂ is highly dependent on the operating temperature, the presence of other molecules in the flue gas [9], and the concentration of CO₂ in the inlet stream [10].

This study aimed to prepare a Li₄SiO₄ sorbent for CO₂ capture in a fixed-bed system. Other studies have reported the impact of a single operating parameter, while in this study, the influence of various calcination arrangements (temperature and period), operation setups (space velocity and temperature), contents of other molecules in the simulated flue gas (H₂O and SO₂), and characterization were tested. Analysis was also supported by the characterization of the fresh and spent sorbent to observe the change in properties due to the carbonation process. Furthermore, the study of reaction kinetics was also carried out using Type I and Type II deactivation models to build a comprehensive discussion. Thus, this study can provide a comprehensive analysis from the insight of material and environmental engineering.

2. Materials and Methods

2.1. Sorbent Preparation

Lithium orthosilicate (Li₄SiO₄) sorbent was prepared using sol-gel method by continuous mixing of 21.42 g of lithium nitrate/LiNO₃ (99.1%, J.T. Baker: Phillipsburg, NJ, USA) with 150 mL of ethanol (99.9%, J.T. Baker) at 400 rpm. After the mixture was completely dissolved, 16.77 mL of tetraethyl orthosilicate/TEOS (98%, Alfa Aesar: Ward Hill, MA, USA) was inserted and this was followed by the slow addition of 6 mL of nitric acid/HNO₃ (65%, Sigma-Aldrich: Burlington, MA, USA) under continuous stirring at a temperature of 70 °C. The product was then dried in an oven at 100 ± 5 °C for 24 h prior to the calcination process. Initially, calcination was conducted under various arrangements, including varying temperatures (600–800 °C, with heating rate of 10 °C/min) and heating periods (1–5 h). The calcined product was then ground and sieved using 200–400 mesh to obtain Li₄SiO₄ powder and applied for the assessment of carbon capture performance. The carbon capture test was conducted in a thermogravimetric analyzer/TG/DTA (Pyris Diamond, Perkin Elmer: Shelton, CT, USA) by purging 100% CO₂ under a heating rate of 5 °C/min, temperature range of 30–1000 °C, and flow rate of 100 mL/min. Utilization of the sorbent was calculated using Equation (1).

$$\tau(\%) = \frac{\int_0^t \frac{C(t)}{C_0} dt}{t^*} \times 100\% \quad (1)$$

where τ is the sorbent utilization (%), C_0 is the CO₂ inlet concentration (%), t is the experiment duration (min), $C(t)$ is the CO₂ concentration of the exhaust gas at time t (%), and t^* is the theoretical breakthrough time (min). Since the test for calculation of the utilization value that was obtained by Equation (1) was applied in a closed system, the loss of purged CO₂ can be implemented to measure the performance of the carbonation process over the prepared Li₄SiO₄ sorbents. Furthermore, the theoretical breakthrough time was obtained using Equation (2).

$$t^* = \frac{(\frac{WX}{M})A}{F} \quad (2)$$

where F is the flow rate of the CO₂ inlet (mol/min), M is the molecular weight of the active metal in sorbent (g/mol), W is the sorbent amount (g), X is the proportion of active metal in the sorbent (g/g), and A is the mole number of adsorbed CO₂ per mole active metal (mol/mol).

2.2. Arrangement of the Capture Test

The reactor setup comprised three groups with each specific function as illustrated in Figure S1. The inlet gas simulation system was arranged to supply the mixed gas in

various concentrations, including CO₂, water vapor, and SO₂ to the gas mixer and flow meter prior to implementation as the inlet of the reactor. In the case of water vapor, the gas was mixed with the distilled water under a controlled temperature and flow to create the required absolute humidity value.

The gas reactor part was made of a quartz tube with a size of 85 cm in length, 1.5 cm in inner diameter, and 1.8 cm in outer diameter. Inside the tube, a quartz bed was installed to place 1 g of Li₄SiO₄ on it. The inner top part of the reactor tube was connected to a thermocouple and the simulated gas system, while the bottom part was connected to the gas analysis system. Quartz wool was installed both at the bottom and just below the open area of the tube reactor's mouth to avoid leakage and inhibit an excessive pressure drop. The gas analysis system, composed of a CO₂ analyzer (T801 NDIR CO₂ analyzer, Thomson Environmental Systems: Kirrawee, NSW, Australia), was set to analyze the exhausted gas.

The carbon capture test was conducted using 100% CO₂, 6000 mL/g/h WHSV, 0% humidity, 0 ppm SO₂, and at temperature of 700 °C, if not specified. Examination of the sorbent performance was defined in the breakthrough time curve and was also conducted for conditions with various parameters including the weight hourly space velocity/WHSV (1200–12,000 mL/g/h), temperature (600–800 °C), water vapor content (0–30%), and SO₂ concentration (0–900 ppm).

2.3. Characterization of Prepared Sorbents

The crystallography property of the sorbents was analyzed by X-ray diffraction spectroscopy/XRD (Model D/MAS IIIV, Rigaku, Tokyo, Japan) with a Cu K α target and scanning rate of 5 °C/min. Elemental analysis of the prepared sorbents was examined by inductively coupled plasma mass spectrometry/ICP-MS (SCIEX ELAN 5000, Perkin Elmer). Scanning electron microscopy/SEM with an energy-dispersive spectrometer/EDS (XLEG, Phillips: Amsterdam, The Netherlands) was applied for the observation of surface properties, while the porous properties were determined using a Brunauer Emmet Teller/BET analyzer (Micromeritics ASAP 2020, Micromeritics Instrument Corporation: Norcross, GA, USA). The electronic states of various elements in the prepared sorbents were detected by x-ray photoelectron spectroscopy/XPS (ULVAC PHI 5000 Versa Probe: Chigasaki, Japan). Chemical bondings in the prepared sorbents were observed by using Fourier-transform infrared spectroscopy/FTIR (Spectrum One B, Perkin Elmer).

2.4. The Study of Reaction Kinetics

CO₂ sorption over a lithium orthosilicate sorbent can be carried out through a physical transport and chemical reaction. The carbonation steps can be defined as (i) the diffusion of gaseous reactants through the gas-phase film on the surface of the sorbent; (ii) gas reactants passing through reacted layer of the sorbent's surface to the unreacted area via penetration and diffusion; and (iii) gas reactants reacting with the solid on the sorbent's surface. Therefore, kinetics analysis is necessary to analyze the mass transfer process. The raw data of the reaction kinetics analysis were obtained by conducting a short separate experiment using the same reactor arrangements under various operating temperatures in the range of 600–700 °C. Afterwards, the Type I and Type II deactivation models were applied in the study of reaction kinetics under assumptions including the following: (i) the carbonation process was carried out under isothermal conditions, (ii) restriction from bulk-phase transport was negligible, (iii) the fixed-bed system applied a pseudo-steady-state condition, and (iv) intermediates were not produced. Ther Type I deactivation model was calculated using Equation (3) while Type II was calculated using Equation (4).

$$\ln \left[\ln \left(\frac{C_0}{C} \right) \right] = \ln \left(\frac{k_0 W}{Q_0} \right) - k_d t \quad (3)$$

$$\frac{C}{C_0} = \exp \left\{ \frac{[1 - \exp(k_0 W / Q_0 (1 - \exp(-k_d t)))]}{(1 - \exp(-k_d t))} \exp(-k_d t) \right\} \quad (4)$$

where Q_0 is the flow rate (m^3/min), C is the CO_2 outlet concentration (kmol/m^3), C_0 is the CO_2 inlet concentration (kmol/m^3), k_d is the deactivation rate constant (min^{-1}), k_0 is the sorption rate constant ($\text{m}^3/\text{kg}/\text{min}$), t is time (min), and W is the weight of sorbent (kg). The sorption of CO_2 in the system will occupy the active sites of the sorbent and cause a deactivation process. Therefore, analysis or reaction kinetics by deactivation simulations could suitably represent the mechanism of carbonation process in this study.

Then, the activation energy/ E_a (kcal/mol) and frequency factor of collision (A) were carried out using the Arrhenius equation as given in Equation (5).

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where k is the reaction rate constant (s^{-1}), R is the ideal gas constant (1.987×10^{-3} kcal/mol/K), and T is temperature (K).

3. Results

3.1. Effect of Calcination Condition on the Sorption Performance

The influence of calcination temperature and period on the utilization values of sorbents is displayed in Figure 1a and Table 1. Increasing the calcination temperature up to 700°C and a prolonged heating period led to the elevation of utilization values of the prepared sorbents. Nevertheless, further increasing the heating temperature caused a declining utilization value. Considering the great CO_2 sorption performance, the calcination process at 700°C for 5 h was chosen to be implemented in the subsequent parts of the study. Comparison of the thermogravimetric analysis of commercial and self-prepared sorbents is presented in Figure 1b.

Table 1. Utilization values of Li_4SiO_4 sorbents under various calcination conditions.

Calcination Time (h)	Calcination Temperature ($^\circ\text{C}$)	Utilization (%)
1	600	56.3
1	700	79.9
1	800	82.8
3	600	71.5
3	700	83.2
3	800	83.9
5	600	77.9
5	700	88.0
5	800	84.5

Analysis of Li content of the sorbent by ICP is presented in Table S1 and imperfect recovery might be caused by the loss of material during the grinding and sieving process. BET analysis of Li_4SiO_4 for the pore size distribution and isothermal curve of N_2 adsorption are presented in Figure S2 and Figure 1c, respectively.

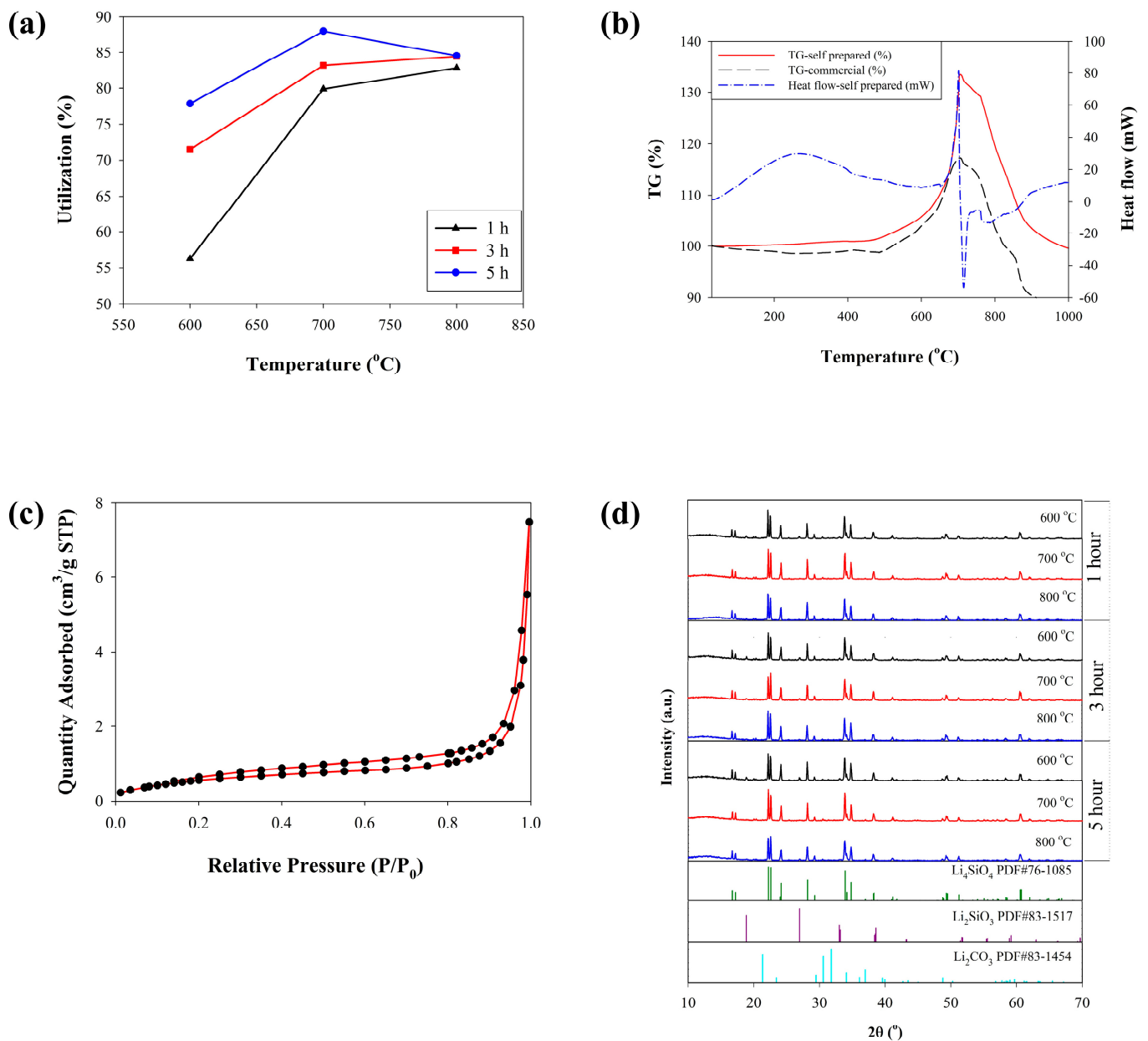


Figure 1. (a) Utilization of Li_4SiO_4 under various calcination conditions using the flow of 100 mL/min 100% CO_2 , along with the characterization of fresh sorbent after calcination at 700 °C for 5 h with (b) TGA and (c) BET. (d) XRD patterns of the prepared sorbents.

3.2. Effect of WHSV on the Sorption Performance

Performance of CO_2 sorption during the test under various WHSV conditions are presented in Figure 2a and Table 2 along with the blank experiment in Figure S3.

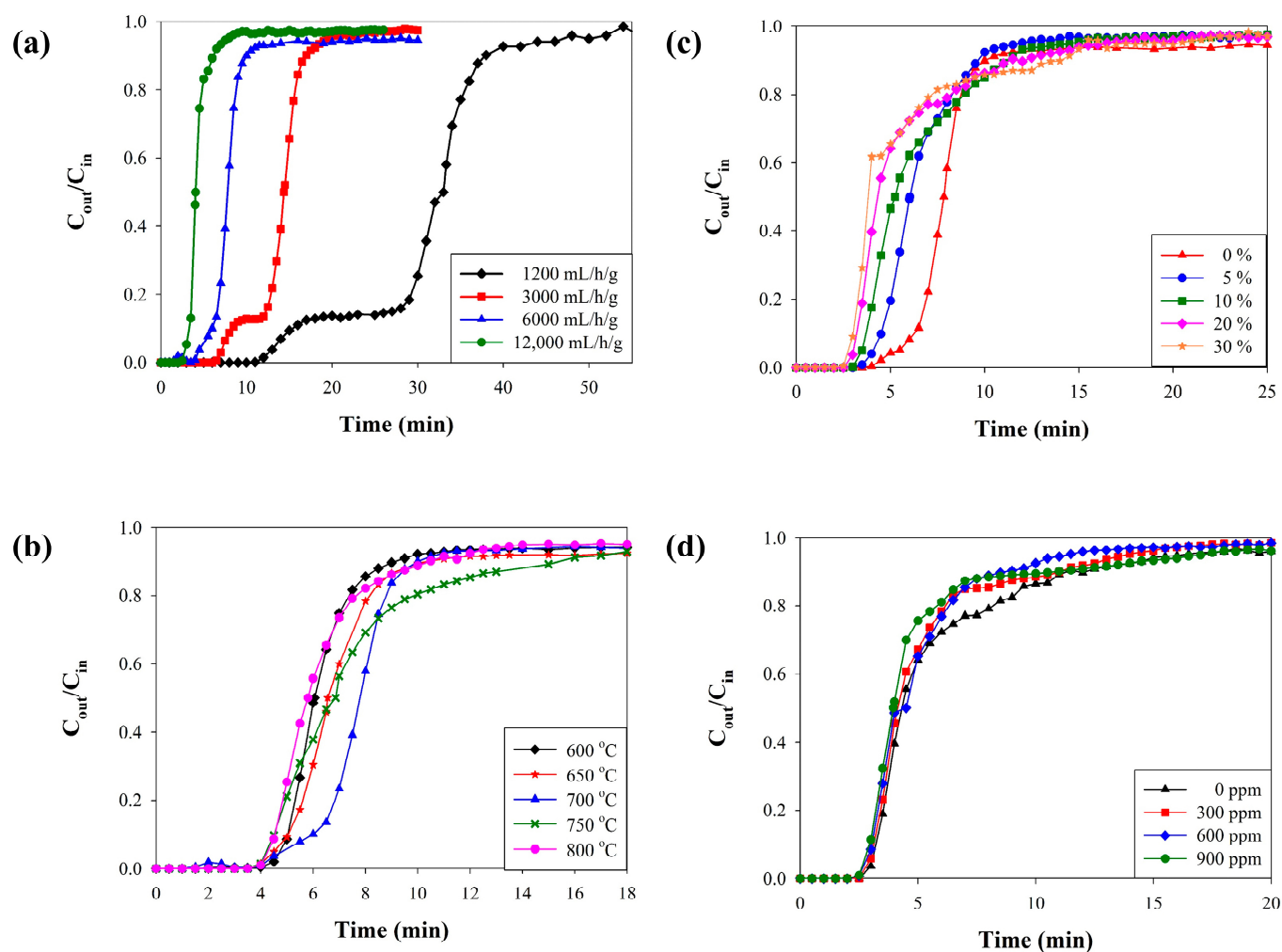


Figure 2. CO₂ capture performance of Li₄SiO₄ under various (a) WHSVs, (b) operating temperatures, (c) H₂O contents, and (d) SO₂ concentrations (combined with 20% water vapor). Test was conducted under 100% CO₂, 6000 mL/h/g WHSV, 0% H₂O, 0 ppm SO₂, and at 700 °C, if not specified.

Table 2. Utilization values of Li₄SiO₄ under various operating conditions.

Variation	Temperature (°C)	WHSV (mL/h/g)	H ₂ O Content (%)	SO ₂ Content (ppm)	Experimental Break-through Time (min)	Theoretical Break-through Time (min)	Li ₄ SiO ₄ Utilization (%)
Space velocity	700	1200	0	0	5.18	10.18	50.9
		3000			1.93	4.07	47.5
		6000			0.93	2.04	45.8
		12,000			0.38	1.02	37.3
Temperature	600	6000	0	0	0.24	2.04	12.0
	650				0.45	2.04	22.3
	700				0.93	2.04	45.8
	750				0.22	2.04	11.0
	800				0.13	2.04	6.1
Water content	700	6000	0	0	0.93	2.04	45.8
			5		0.83	2.14	38.7
			10		0.52	2.26	22.9
			20		0.41	2.55	16.1
			30		0.31	2.91	10.6

Table 2. Cont.

Variation	Temperature (°C)	WHSV (mL/h/g)	H ₂ O Content (%)	SO ₂ Content (ppm)	Experimental Break-through Time (min)	Theoretical Break-through Time (min)	Li ₄ SiO ₄ Utilization (%)
SO ₂ content	700	6000	20	0	0.41	2.55	16.1
				300	0.35	2.55	13.6
				600	0.29	2.55	11.4
				900	0.27	2.55	10.6

Arrangement of the space velocity in the system had a significant impact on the performance of the sorbent. The higher WHSV value resulted in lower sorbent utilization due to the short contact period with CO₂. Moreover, extremely high operating temperatures also led to the decline in sorbent performance. The presence of water content rapidly reduced the CO₂ sorption capacity of the sorbent. Nevertheless, compared to other reports on the CO₂ sorption process, the prepared Li₄SiO₄ sorbent in this study achieved a higher sorption capacity, as can be seen in Table 3.

Table 3. Performance of several previous reports on CO₂ sorption over solid sorbents.

No.	Sorbent	Special Operating Condition	CO ₂ Sorption Capacity (g-CO ₂ /g-sorbent)	Ref.
1	Tertiary amine	Under 10% CO ₂ and 88% He	0.13	[1]
2	SBA-HA (aziridine monomer with hyperbranched aminosilica)	Under 15% CO ₂ and 85% N ₂ , 20 mL/min rate of H ₂ O	0.09	[2]
3	Synthetic hydrotalcite	With chemisorption cell with 20% CO ₂ and 80% N ₂	0.02	[3]
4	Basic alumina	Under isotherm vacuum condition	0.03	[4]
5	LiYO ₂ and NaYO ₂	Preparation with calcination at 800 °C, operating temperature of 650 °C	0.17, 0.15, respectively	[5]
6	Li ₄ SiO ₄	Preparation with calcination at 700 °C, operating under 700 °C, 6000 mL/h/g WHSV, 0% H ₂ O and SO ₂ contents	0.17	This study

Successful CO₂ capture was indicated by the presence of Li₂SiO₃ and Li₂CO₃ in the XRD spectra (Figure 3a). Intensities of Li₂CO₃ peaks after the sorption tests with 1200–6000 mL/h/g were similar; however, the lower intensity of this compound was found in the case of 12,000 mL/h/g. SEM images (Figure 3b,c) and EDS scanning (Table 4) indicated the change in the sorbent after the carbonation process. The fresh prepared sorbent presented an irregular diamond shape with flat surface. The carbonation process led to the conversion of an irregular diamond shape in the fresh sorbents into stacks of granular shapes due to the formation of Li₂CO₃. However, the XPS deconvolution of the sorbents are presented in Figure 4. Characteristic peaks at 55.2, 531.6, and 102.2 eV in the region of Li1s, O1s, and Si2p, respectively, were detected in both fresh and used sorbents.

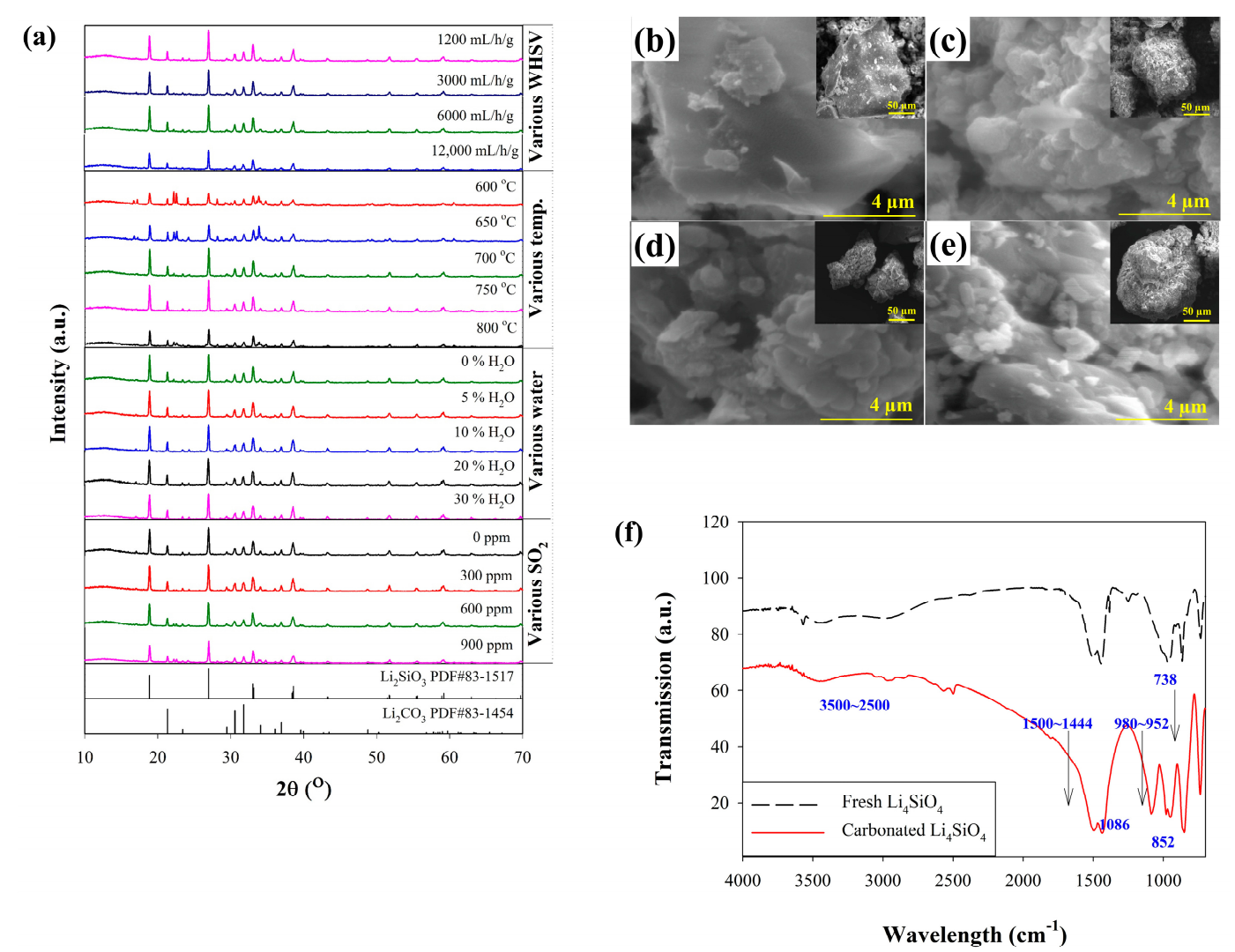


Figure 3. Characterization of spent Li_4SiO_4 by analysis using (a) XRD, (b,c) SEM images for fresh, carbonated Li_4SiO_4 , with the presence of (d) H_2O or (e) SO_2 , and (f) FTIR. Test was conducted under 100% CO_2 , 6000 mL/h/g WHSV, 0% H_2O , 0 ppm SO_2 , and at 700 °C, if not specified.

Table 4. Percentage of weighted and atomic element of Li_4SiO_4 from EDS scanning. Test was conducted under 100% CO_2 , 6000 mL/h/g WHSV, 0% H_2O , 0 ppm SO_2 , and at 700 °C, if not specified.

Element	Weight (%)					Atomic (%)				
	Li	Si	O	C	S	Li	Si	O	C	S
Fresh	N.D	25.6	55.5	18.9	N.D	N.D	15.3	58.3	26.4	N.D
100% CO_2	N.D	21.8	53.0	25.2	N.D	N.D	12.6	53.6	33.9	N.D
20% H_2O	N.D	16.5	59.4	24.1	N.D	N.D	9.3	58.9	31.8	N.D
300 ppm SO_2	N.D	24.1	50.6	24.3	1.0	N.D	14.2	52.0	33.3	0.5

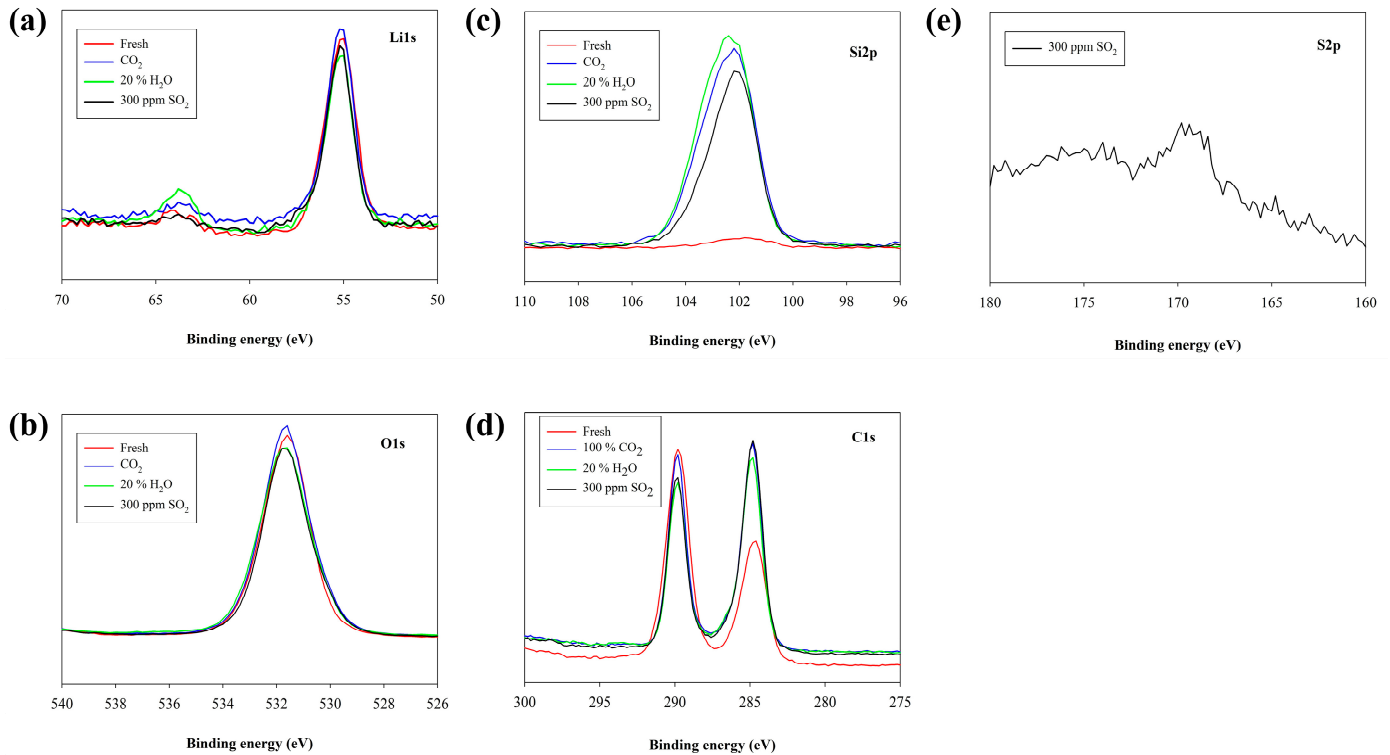


Figure 4. XPS spectra of fresh and spent Li_4SiO_4 for the regions of (a) Li1s, (b) O1s, (c) Si2p, (d) C1s, and (e) S2p.

3.3. Effect of Operating Temperature on the Sorption Performance

The operating temperature is one of the essential influencing factors during the capture process by the prepared sorbent, as can be seen in Figure 2b and Table 2. The increasing utilization value of the sorbent to 45.8% was detected under an elevation of operating temperature until 700 °C. Among the tested operating temperatures, XRD analysis of the spent sorbents also indicated a similar tendency for the formation of Li_2CO_3 and Li_2SiO_3 , as can be seen in Figure 3a.

3.4. Effect of Water Content on the Sorption Performance

The presence of water vapor content over 5% drastically reduced the performance of the sorbent, as can be seen in Figure 2c and Table 2. The tendency of crystallography change from the spent sorbent after the test using various H_2O contents was not significantly different from the observation of the test under various velocities or temperatures, as can be seen in Figure 3a. Compared to the SEM image of fresh sorbent (Figure 3b), slightly different surface properties were found for the carbonated sorbent after the test with the presence of 20% water vapor (Figure 3d). A similar result of XPS spectra was also obtained in the spent sorbent after the test with the presence of water vapor, which indicated an insignificant effect of H_2O on the sorption activity (Figure 4a–d).

3.5. Effect of SO_2 Content on the Sorption Performance

Compared to the other parameters, with the presence of SO_2 in the system, obvious decline in the sorption performance was detected, as can be seen in Figure 2d and Table 2. Furthermore, similar tendencies in the formation of Li_2SiO_3 and Li_2CO_3 were still presented but in lower intensities from the XRD analysis (Figure 3a). A different SEM image is presented from the spent sorbent after the test with the presence of 300 ppm SO_2 in Figure 3e compared to the fresh Li_4SiO_4 in Figure 3b. XPS spectra in the region of Si2p from

the spent sorbent after the test with 300 ppm SO₂ had the lowest intensity compared to fresh sorbent or after examination using other parameters (Figure 4c). A similar tendency to have the lowest intensity was also presented for the region C1s (Figure 4d). A peak at the binding energy of 169.8 eV was detected in the XPS deconvolution of spent sorbent for the region S2p (Figure 4e), which might be due to the presence of S⁶⁺ in the bond formation of SO₄^{2−} of Li₂SO₄. Furthermore, following the study of the functional groups in the spent sorbent after the test with the presence of SO₂, this was also checked using FTIR, as presented in Figure 3f. The presence of a characteristic peak at 1086 cm^{−1} was attributed to the SO₄^{2−} [11]. However, a carbonation process was indicated by the bond of C=O with the characteristic peaks at 1500–1444 cm^{−1} [12].

3.6. Reaction Kinetics Study

In the kinetics study using Type I and Type II deactivation models, as can be seen in Figures S4 and 5a,c, a high value of R² in the range of 0.97–0.99 was achieved. Moreover, after the further analysis using the Arrhenius equation (Figure 5b and Table 5), the calculated activation energies (E_a) of 51.5 and 5.2 kJ/mol were obtained.

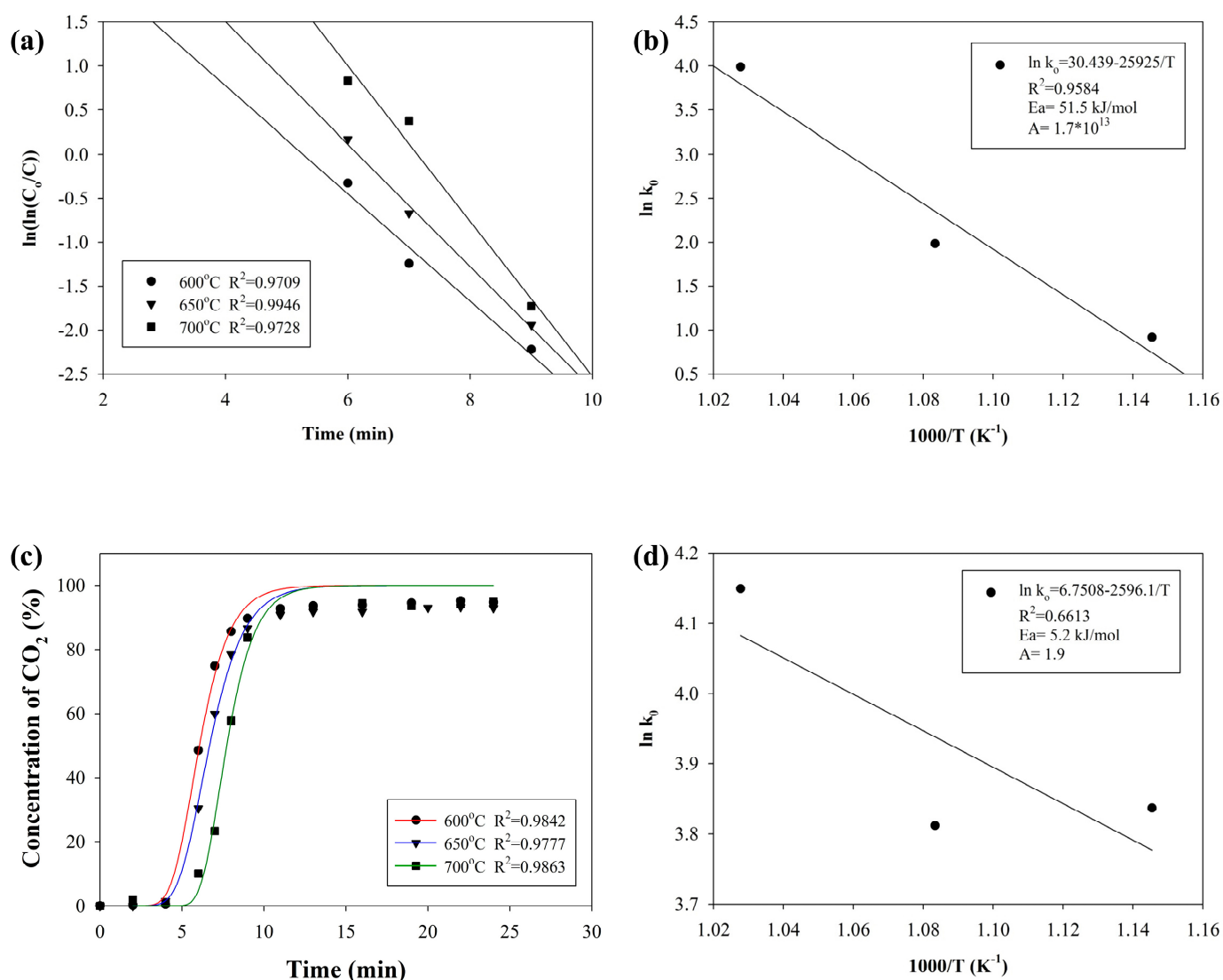


Figure 5. Study of reaction kinetics using (a,b) Type I and (c,d) Type II deactivation model.

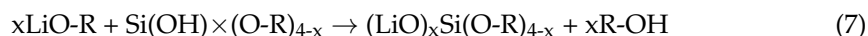
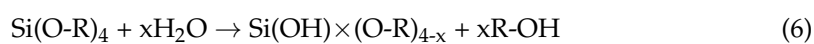
Table 5. Rate constants in reaction kinetics study using Type I and II deactivation models.

Type I Deactivation Model			
Temperature (K)	873	923	973
k_d (min ^{−1})	0.611	0.696	0.882
$\ln(k_0 W/Q)$	3.219	4.287	6.291
k_0 (cm ³ /min/g)	2501	7275	53,980
Type II Deactivation Model			
Temperature (K)	873	923	973
k_d (min ^{−1})	0.819	0.726	0.866
$k_0 W/Q$	4.638	4.523	6.3385
k_0 (cm ³ /min/g)	46,375	45,234	63,385

4. Discussion

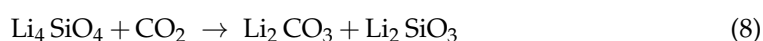
4.1. Effect of Calcination Condition on the Sorption Performance

A prolonged calcination period and increasing calcination temperature led to the promotion of performance but only until 700 °C (Figure 1a). Moreover, at the temperature of 700 °C, an insignificant performance difference was found among various calcination periods. A temperature of 700 °C during preparation of the Li₄SiO₄ sorbent played an important role due to the proper control of porosity formation [13] from the generation of Li₄SiO₄ with higher purity but further heating resulted in a lower surface area. Therefore, the further study implemented the sorbent calcinated at 700 °C for 5 h, which is similar to the method of a previous study of Zubbri et al. [14]. Conversion of the precursors during calcination can be explained by Equations (6) and (7).



where O is the organic ligand from the dealcoholization process (O-R) and dehydration (OH).

An extreme increase in the weight occurred at a temperature of 500–700 °C due to the sorption of CO₂. The weight increasing during the carbonation process reached 32.3% and was close to the theoretical weight gain (36.7%). CO₂ capture by Li₄SiO₄ can be described in Equation (8).



The double-shell mechanism in CO₂ sorption at high temperatures by Li₄SiO₄ has been reported previously by Li et al. [15], which would be initiated by the formation of dense lithium carbonate (Li₂CO₃) and followed by lithium metasilicate (Li₂SiO₃) in the inner layer of the reacted sorbent. An endothermic peak at 700 °C in the heat flow curve was consistent with the carbonation reaction of Li₄SiO₄ and conversion of Li₂CO₃ into Li₂O for the desorption (Figure 1b). However, cracking under a high temperature occurred for some parts of Li₂CO₃, which can be used to indicate the equilibrium time for the double-shell reaction. The rapid weight loss at 700–760 °C should be mostly due to the conversion of LiCO₃ to Li₂O. The self-prepared sorbent presented a similar weight gain trend to the commercial sorbent (Figure 1b—blue dashed line). However, the self-prepared Li₄SiO₄ indicated a better mechanical strength and performance since complete desorption occurred at a higher temperature (900 °C) with a utilization value of 88.0% (Table 1), than that of the commercial sorbent (800 °C, utilization value of 47%).

The measured specific surface area reached 2.5 m²/g with the total pore volume of 0.005 cm³/g and the average pore size of 23.0 nm. The isothermal adsorption curve shown in Figure 1c indicated the presence of the type IV isothermal adsorption diagram. Figure 1d

presents a further analysis of crystallography properties of the prepared sorbents by XRD. Compared to the higher calcination temperature, calcination with 600 °C presented a higher trace content of Li_2SiO_3 due to incomplete calcination of the TEOS precursor.

4.2. Effect of WHSV on the Sorption Performance

Under the space velocity rates of 1200–6000 mL/h/g, the sorbent utilizations ranged from 45–51% (Table 2), and a lower velocity led to a prolonged breakthrough time (Figure 2a). However, the extreme high velocity presented poor performance due to the difficulty of the gas diffusion under a short contact time. Wang and Luo [16] indicated that the overall sorption highly depended on the mass transfer. Since the differences in performance for the tests under a velocity range of 1200–6000 mL/h/g were insignificant, the velocity of 6000 mL/h/g was chosen to be applied in the further test with other parameters due to the consideration of an efficient carbonation process.

For the case of SEM images, after the carbonation process, the surface of fresh sorbent (irregular diamond shape on flat surface) changed into stacks of granular shapes from the generated Li_2CO_3 (Figure 3c). However, the increment of the C element (Table 4) also proved the occurrence of the carbonation process (0.18–0.22 g- CO_2 /g-sorbent). Moreover, after the carbonation, a significant reduction in the Si element was detected due to the production of Li_2CO_3 covering the surface of the sorbent.

A similar trend was presented for the XPS spectra of fresh and carbonated sorbents with the presence of characteristic peaks at 55.2, 531.6, and 102.2 eV in the region of Li1s, O1s, and Si2p, respectively (Figure 4). The presence of peaks at 284.8 and 289.9 eV in the region of C1s also appeared in fresh and carbonated sorbents and indicated the presence of carbon and carbonate, respectively [17]. Similar result of Li_2CO_3 detection with a characteristic peak at 290.1 eV was previously reported by Li et al. [18].

The detected C from the fresh sorbent might be caused by the residue of a TEOS precursor. The peak in Li1s was attributed to Li^+ with the bond type of Li-O [19]. However, the observed peak in the O1s region indicated the presence of LiSiO_4 [20]. The Si^{4+} of Li_2SiO_3 was indicated by a peak located at 102.3 eV from the spent sorbent [21].

4.3. Effect of Operating Temperature on the Sorption Performance

Elevation of the operating temperature until 700 °C led to the promotion of the utilization value of the sorbent to 45.8% (Table 2). Nevertheless, further increasing the temperature reduced the performance of the sorbent, which might be caused by the presence of crack in the Li_2CO_3 layer, as was also found in the TGA result (Figure 1b). However, a previous study of Seggiani et al. [22] also detected the presence of dense morphology agglomeration on Li_4SiO_4 at a high temperature that might lower the surface area.

However, in the XRD pattern of the test at 600–650 °C, peaks for the remaining Li_4SiO_4 were still detected, which indicated their slower reaction rates than those under higher temperatures (Figure 3a). Moreover, sintering phenomena also rapidly reduced the number of active sites and the availability of Li_4SiO_4 for the carbonation process. Starting from the temperature of 750 °C and above, a slight decrease in the peak intensity of Li_2CO_3 was observed, which was also in accordance with the reduction in the utilization value under these temperatures (Table 2). Thus, the temperature of 700 °C was chosen as the operating condition for the further test using other parameters.

4.4. Effect of Water Content on the Sorption Performance

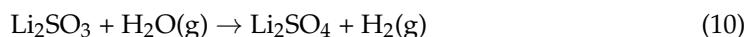
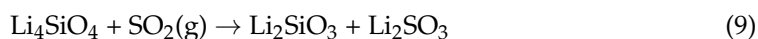
When the water vapor content was 30%, the sorbent utilization dropped to 10.6% (Table 2). A reduction in the sorbent's performance by the presence of water vapor might be caused by several mechanisms including sintering, partition of the material, and evaporation of the active sites [23,24]. However, mass transfer of the CO_2 might also be inhibited

by a change in the crystal structure of the sorbent. Moreover, the competitive sorption between the water vapor and CO₂ might occur on the sorbent surface. Li₄SiO₄ has been acknowledged to have a higher affinity for water than that of soda lime [25]. In contrast, in the previous report of Quinn et al. [26], the presence of water vapor promoted the CO₂ capture by Li₄SiO₄ due to the formation of a layer on the sorbent surface with an alkaline condition. The presence of water vapor might cause the formation of LiOH on the surface of Li₄SiO₄ [25].

However, lower peak intensities of Li₂CO₃ were detected under the test with higher water vapor contents. Nevertheless, in the industrial flue gas, the average water vapor in the range of 10–30% could be detected; thus, the 20% water vapor was applied for the further parameter tests. The SEM image of spent sorbent after the test with the presence of 20% water vapor showed a bigger particle structure on the surface (Figure 3d). Enlargement of the particle might be caused by the melting and agglomeration process during the carbonation reaction. However, the Si contents of spent sorbents after the test under various water vapor contents were lower than the fresh sorbents and other parameter settings (Table 4). A lower utilization value by the presence of water vapor was also proved by the lower C content in the spent sorbent after the carbonation.

4.5. Effect of SO₂ Content on the Sorption Performance

For the case of SO₂ content in the system, a reduction in the performance was detected in all tested SO₂ concentrations (Table 2). This result indicated that carbonation and sulfurization of the prepared sorbent occurred at the same time, as can be explained by Equations (9) and (10).



The presence of SO₂ decreased the utilization value; however, the differences between various added concentrations were not significant, which indicated that the capacity of the sorbent to conduct the sulfurization process was limited by the 20% H₂O. The presence of 20% water vapor in the test of various SO₂ contents promoted the sulfurization reaction and led to the formation of lithium sulfate. The great affinity of the prepared sorbent to carry out the sulfidation process resulted in competitive sorption with the carbonation reaction. Therefore, the lower availability of the active sites further decreased the utilization value.

Moreover, only slightly different utilization was observed between the tested SO₂ contents (Figure 2d and Table 2). Although the sorbent indicated the capability of sulfurization, the XRD spectra could not demonstrate the presence of the S compound, which might be due to the tiny amount of S or less crystalline material. In the SEM images, compared to the test using other parameters, carbonation under the presence of 300 ppm SO₂ demonstrated a surface with debris, which also covered the pores to make the structure tighter (Figure 3e).

However, a slight shift by 0.2 eV to the higher binding energy for the peak in the XPS deconvolution region O1s (Figure 4b) was detected in the spent sorbent under the test with SO₂, which might be caused by the interruption from the large electronegativity of the S element. The analysis of region S2p indicated that the peak at the binding energy around 169.8 eV might be attributed to the presence of S⁶⁺ with the bond formation of SO₄^{2−} for Li₂SO₄. This result is in accordance with Equation 9 for the formation of Li₂SO₃ (Figure 4e) in the reaction.

For the FTIR patterns (Figure 3f), peaks at 3500–2500 cm^{−1} indicated the adsorbed water on the surface of sorbent [27]. The presence of SO₄^{2−} was indicated by the characteristic peaks at 1086 cm^{−1} [11]. The carbonation process was indicated by the presence of peaks at

1500–1444 cm^{-1} for the C=O [12]. Functional groups with the Si element were indicated by the peaks at 980–952 cm^{-1} (Si-OH) [28], 738 cm^{-1} (Si-O), and 852 cm^{-1} (Si-O-Si) [29–31].

4.6. Reaction Kinetics Study

The result of the kinetics study could indicate the suitability of the Type I deactivation model with a deactivation constant (k_d), reaction rate constant (k_0), and E_a of 0.882 min^{-1} , 53,980 $\text{cm}^3/\text{min/g}$ and 51.5 KJ/mol, respectively (Figure 5a,b and Table 5).

The Type II deactivation model assumes that constant decay of sorbent will be related to the first order of carbon dioxide concentration. The study of the Type II deactivation model, as presented in Figure 5c, also indicated a great R^2 value in the range of 0.98–0.99. However, from the further analysis for exploration of the kinetics parameter (Figure 5d and Table 5), an E_a value of 5.2 kJ/mol was detected, which was lower than that for the Type I deactivation model.

The common activation energy of a gas–solid reaction is greater than 50 kJ/mol. Moreover, since CO_2 sorption by Li_4SiO_4 in this study was conducted under a high temperature, the value of surface collision is essential. The value of frequency collision from Type I and Type II deactivation models were 1.7×10^{13} and 1.9 s^{-1} , respectively. Thus, this result indicated a well-fitted result to the Type I deactivation model for CO_2 sorption using Li_4SiO_4 in this study.

5. Conclusions

Li_4SiO_4 has been prepared under various calcination temperatures and periods, and the best utilization value for carbon capture was achieved by the sorbent calcinated at 700 °C for 5 h with the carbon removal capacity of 0.17 g- CO_2 /g-sorbent. Further assessment was conducted under various operating conditions. The highest space velocity led to a decline in the utilization value to 37.3%. Either the presence of water vapor or SO_2 reduced the sorption capacity of Li_4SiO_4 due to the hindering effect from competitive sorption on the active sites. Moreover, water vapor in the system resulted in a larger particle size due to the melting and agglomeration processes, while SO_2 created debris on the surface of the sorbent. The Type I deactivation model for the reaction kinetics study indicated a well-fitted result with an E_a value of 51.5 kJ/mol.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr13010041/s1>, Figure S1: Schematic diagram of the experimental setup; Figure S2: Pore size distribution of Li_4SiO_4 from BET analysis; Figure S3: The result of the blank test experiment of the reactor without the presence of sorbent; Figure S4: Raw data of the CO_2 sorption by Li_4SiO_4 for the study of reaction kinetics using Type I deactivation model. Table S1: Analysis of Li content in Li_4SiO_4 by ICP.

Author Contributions: Conceptualization, H.C.; methodology, H.C. and D.-Y.W.; validation, D.-Y.W. and B.N.R.W.; formal analysis, D.-Y.W. and B.N.R.W.; investigation, D.-Y.W. and B.N.R.W.; resources, D.-Y.W. and B.N.R.W.; writing—original draft preparation, D.-Y.W. and B.N.R.W.; writing—review and editing, H.C. and B.N.R.W.; visualization, B.N.R.W.; supervision, H.C.; project administration, H.C.; funding acquisition, H.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Taiwan National Science and Technology Council, grant number NSC 101-3113-P-110-002.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

WHSV	Weight hourly space velocity
TGA	Thermogravimetric analysis
BET	Brunauer–Emmet–Teller analysis
FTIR	Fourier-transform infrared spectroscopy
NDIR	Nondispersive infrared spectroscopy
XRD	X-ray diffraction spectroscopy
XPS	X-ray photoelectron spectroscopy
SEM	Scanning electron microscope
EDS	Energy dispersive X-ray

References

- Li, J.; Jia, K.; Wei, X.; Xia, M.; Chen, Z.; Yao, Y.; Zhang, X.; Jiang, H.; Yuan, B.; Tao, G.; et al. High-spatiotemporal resolution mapping of spatiotemporally continuous atmospheric CO₂ concentrations over the global continent. *Int. J. Appl. Earth Obs. Geoinf.* **2022**, *108*, 102743. [\[CrossRef\]](#)
- Ramar, V.; Balraj, A. Critical Review on Carbon-Based Nanomaterial for Carbon Capture: Technical Challenges, Opportunities, and Future Perspectives. *Energy Fuels* **2022**, *36*, 13479–13505. [\[CrossRef\]](#)
- Akeeb, O.; Wang, L.; Xie, W.; Davis, R.; Alkasrawi, M.; Toan, S. Post-combustion CO₂ capture via a variety of temperature ranges and material adsorption process: A review. *J. Environ. Manag.* **2022**, *313*, 115026. [\[CrossRef\]](#) [\[PubMed\]](#)
- Villa-Pérez, C.; Arneodo Larochette, P.; Soria, D.B.; Gennari, F.C. Thermodynamic and kinetic properties of Li₃BO₃ modified by the alkali fluorides addition in the CO₂ capture process. *Chem. Eng. J.* **2022**, *450*, 138118. [\[CrossRef\]](#)
- Stefanelli, E.; Vitolo, S.; Puccini, M. Single-step fabrication of templated Li₄SiO₄-based pellets for CO₂ capture at high temperature. *J. Environ. Chem. Eng.* **2022**, *10*, 108389. [\[CrossRef\]](#)
- Soto-Pacheco, S.A.; Pfeiffer, H.; Arturo Mendoza-Nieto, J. Li₂ZrO₃ modified with molten salts as potential materials for CO elimination: Effect of carbonate type and oxygen addition. *Chem. Eng. Sci.* **2023**, *278*, 118884. [\[CrossRef\]](#)
- Jo, S.; Cruz, L.; Shah, S.; Wasantwisut, S.; Phan, A.; Gilliard-AbdulAziz, K.L. Perspective on Sorption Enhanced Bifunctional Catalysts to Produce Hydrocarbons. *ACS Catal.* **2022**, *12*, 7486–7510. [\[CrossRef\]](#)
- Lee, S.C.; Kim, M.J.; Kwon, Y.M.; Chae, H.J.; Cho, M.S.; Park, Y.K.; Seo, H.M.; Kim, J.C. Novel regenerable solid sorbents based on lithium orthosilicate for carbon dioxide capture at high temperatures. *Sep. Purif. Technol.* **2019**, *214*, 120–127. [\[CrossRef\]](#)
- Ketabchi, M.R.; Babamohammadi, S.; Davies, W.G.; Gorbounov, M.; Masoudi Soltani, S. Latest advances and challenges in carbon capture using bio-based sorbents: A state-of-the-art review. *Carbon Capture Sci. Technol.* **2023**, *6*, 100087. [\[CrossRef\]](#)
- Yang, Y.; Chen, Z.; Sun, X.; Yao, S.; Zhang, X.; Liu, W. Li₄SiO₄ adsorbent derived from industrial biomass fly ash for high-temperature CO₂ capture. *Fuel* **2023**, *337*, 126853. [\[CrossRef\]](#)
- Li, X.; He, C.; Liang, H.; Chen, K.; Yao, Q.; Guo, C.; Lu, G.; Dang, Z. Investigation of the Interactions Occurring Between Cr(VI) and Citric Acid-Schwertmannite Composites: A Macroscopic and In Situ ATR-FTIR Study. *ACS Earth Space Chem.* **2022**, *6*, 391–402. [\[CrossRef\]](#)
- Fang, M.; Yi, Y.; Ma, W.; Lin, Y.; Li, J.; Liu, W. Performance analysis of coagulation hardening effect of geopolymer prepared from high calcium-based ladle furnace slag. *Constr. Build. Mater.* **2023**, *374*, 130963. [\[CrossRef\]](#)
- Rossi, D.; Anguillesi, I.; Desideri, U.; Seggiani, M. Easy fabrication method of Li₄SiO₄-K₂CO₃ based pellets for CO₂ capture at high temperature. *Chem. Eng. J.* **2024**, *481*, 148615. [\[CrossRef\]](#)
- Zubbri, N.A.; Mohamed, A.R.; Mohammadi, M. Parametric study and effect of calcination and carbonation conditions on the CO₂ capture performance of lithium orthosilicate sorbent. *Chin. J. Chem. Eng.* **2018**, *26*, 631–641. [\[CrossRef\]](#)
- Li, F.; Wang, Y.; Liu, K.; Wu, Y.; Ai, J.; Zhang, J. Preparation of Li₄SiO₄-based adsorbents with coal slag for high temperature cyclic CO₂ capture. *Fuel* **2022**, *310*, 121687. [\[CrossRef\]](#)
- Wang, M.; Luo, J. A coupled electrochemical system for CO₂ capture, conversion and product purification. *eScience* **2023**, *3*, 100155. [\[CrossRef\]](#)
- Qiu, H.; Li, M.; Lu, Y.; Cheng, H.; Chen, H.; Zheng, Y. Ultraviolet and infrared excitable inorganic-organic hybrid materials: Synthesis, characterization and anti-counterfeiting applications. *Mater. Today Phys.* **2023**, *31*, 100970. [\[CrossRef\]](#)
- Li, P.; Cheng, Z.; Liu, J.; Che, L.; Zhou, Y.; Xu, E.; Tian, X.; Yuan, Z. Solvation Structure Tuning Induces LiF/Li₃N-Rich CEI and SEI Interfaces for Superior Li/CF_x Batteries. *Small* **2023**, *19*, e2303149. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, Y.; Wang, J.; Wang, J.; Yang, M.; Zou, G.; Li, L.; Tse, J.S.; Fernandez, C.; Peng, Q. Towards an ultra-long lifespan Li-CO₂: Electron structure and charge transfer pathway regulation on hierarchical architecture. *Chem. Eng. J.* **2023**, *451*, 138953. [\[CrossRef\]](#)
- Vendra, S.S.L.; Singh, G.; Kumar, R. Single source precursor-derived SiOC/TiO_xC_y as an anode component for Li-ion batteries. *Int. J. Appl. Ceram. Technol.* **2023**, *20*, 70–83. [\[CrossRef\]](#)

21. Luo, Q.; Kang, J.; Liao, Z.; Feng, X.; Zou, H.; Yang, W.; Pai, C.; Waiyin Sun, R.; Chen, S. Modification Strategy for Constructing Li Gradient Combined with Spinel Phase Coating on Li-Rich Mn-Based Materials. *ACS Appl. Energy Mater.* **2022**, *5*, 4641–4650. [\[CrossRef\]](#)
22. Seggiani, M.; Puccini, M.; Vitolo, S. Alkali promoted lithium orthosilicate for CO₂ capture at high temperature and low concentration. *Int. J. Greenh. Gas Control* **2013**, *17*, 25–31. [\[CrossRef\]](#)
23. Karimi, M.; Shirzad, M.; Silva JA, C.; Rodrigues, A.E. Biomass/Biochar carbon materials for CO₂ capture and sequestration by cyclic adsorption processes: A review and prospects for future directions. *J. CO₂ Util.* **2022**, *57*, 101890. [\[CrossRef\]](#)
24. Kolle, J.M.; Fayaz, M.; Sayari, A. Understanding the Effect of Water on CO₂ Adsorption. *Chem. Rev.* **2021**, *121*, 7280–7345. [\[CrossRef\]](#)
25. Grasso, M.L.; Arneodo Larochette, P.; Gennari, F.C. CO₂ capture properties of Li₄SiO₄ after aging in air at room temperature. *J. CO₂ Util.* **2020**, *38*, 232–240. [\[CrossRef\]](#)
26. Quinn, R.; Kitzhoffer, R.J.; Hufton, J.R.; Golden, T.C. A High Temperature Lithium Orthosilicate-Based Solid Absorbent for Post Combustion CO₂ Capture. *Ind. Eng. Chem. Res.* **2012**, *51*, 9320–9327. [\[CrossRef\]](#)
27. Salimi, A.; Kavosi, B.; Navaee, A. Amine-functionalized graphene as an effective electrochemical platform toward easily miRNA hybridization detection. *Measurement* **2019**, *143*, 191–198. [\[CrossRef\]](#)
28. Qiao, Y.; Li, W.; Bao, J.; Zheng, Y.; Feng, L.; Ma, Y.; Yang, K.; Wu, A.; Bai, H.; Yang, Y. Controlled synthesis and luminescence properties of core-shell-shell structured SiO₂@AIPA-S-Si-Eu@SiO₂ and SiO₂@AIPA-S-Si-Eu-phen@SiO₂ nanocomposites. *Sci. Rep.* **2020**, *10*, 3522. [\[CrossRef\]](#)
29. Ortiz-Landeros, J.; Martinez-dlCruz, L.; Gomez-Yanez, C.; Pfeiffer, H. Towards understanding the thermoanalysis of water sorption on lithium orthosilicate (Li₄SiO₄). *Thermochim. Acta* **2011**, *515*, 73–78. [\[CrossRef\]](#)
30. Zhang, B.; Nieuwoudt, M.; Eastal, A.J. Sol-gel route to nanocrystalline lithium metasilicate particles. *J. Am. Ceram. Soc.* **2008**, *91*, 1927–1932. [\[CrossRef\]](#)
31. Ravikrishna, R.; Green, R.; Valsaraj, K. Polyaphrons as templates for the sol-gel synthesis of macroporous silica. *J. Sol-Gel Sci. Technol.* **2005**, *34*, 111–122. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.