Review

Performance of Li$_4$SiO$_4$ Material for CO$_2$ Capture: A Review

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Abstract: Lithium silicate (Li$_4$SiO$_4$) material can be applied for CO$_2$ capture in energy production processes, such as hydrogen plants, based on sorption-enhanced reforming and fossil fuel-fired power plants, which has attracted research interests of many researchers. However, CO$_2$ absorption performance of Li$_4$SiO$_4$ material prepared by the traditional solid-state reaction method is unsatisfactory during the absorption/regeneration cycles. Improving CO$_2$ absorption capacity and cyclic stability of Li$_4$SiO$_4$ material is a research highlight during the energy production processes. The state-of-the-art kinetic and quantum mechanical studies on the preparation and CO$_2$ absorption process of Li$_4$SiO$_4$ material are summarized, and the recent studies on the effects of preparation methods, dopants, and operating conditions on CO$_2$ absorption performance of Li$_4$SiO$_4$ material are reviewed. Additionally, potential research thoughts and trends are also suggested.

Keywords: CO$_2$ capture; energy production process; Li$_4$SiO$_4$ material; modification

1. Introduction

The emission of anthropogenic CO$_2$ into the environment has aggravated the trend of global warming [1], which has become one of the most threatening problems in recent decades, and the largest emission sources of CO$_2$ are fossil fuel-fired power plants [2]. Hence, various techniques have been reported to capture CO$_2$ from the flue gas released from fossil fuel-fired power plants [3], and CO$_2$ capture and storage (CCS) has been recognized as one of the most effective techniques to mitigate CO$_2$ emission [4,5]. In the process of CCS, CO$_2$ is captured from flue gas and stored for utilization and sequestration instead of being released to the environment directly. Recent studies have found that various lithium-based materials, such as LiFeO$_2$ [6], Li$_2$CuO$_2$ [7], Li$_2$ZrO$_3$ [7–9], Li$_8$SiO$_6$ [10,11], and Li$_4$SiO$_4$ [9], are capable of effective CO$_2$ capture. Among these materials, Li$_4$SiO$_4$, with a variety of applications [12,13], has better application potential, owing to its higher CO$_2$ sorption capacity, cyclic stability than LiFeO$_2$, Li$_2$CuO$_2$, and Li$_8$SiO$_6$, and lower cost than that of Li$_2$ZrO$_3$ [9]. Additionally, the regeneration temperature of Li$_4$SiO$_4$ material is much lower compared with the calcium-based CO$_2$ sorbents, indicating that lower energy consumption is required for the regeneration. Li$_4$SiO$_4$ material is usually obtained by the solid-state reaction method with Li$_2$CO$_3$ and SiO$_2$ at high temperature, which is shown in Equation (1) [14]:

$$2Li_2CO_3 + SiO_2 \leftrightarrow Li_4SiO_4 + 2CO_2 \tag{1}$$

The basic reversible reaction for CO$_2$ sorption by Li$_4$SiO$_4$ material follows Equation (2), and the process is shown in Figure 1. In the absorption reactor, CO$_2$ in flue gas from fossil fuel-fired power

plants or syngas from hydrogen plants based on sorption-enhanced reforming is absorbed by Li_4SiO_4 at 500 to 600 °C, thus the gas, almost free of CO_2, is exhausted from the reactor. The generated Li_2SiO_3 and Li_2CO_3 are transported to the regeneration reactor, where Li_4SiO_4 is regenerated at temperatures higher than 700 °C and sent to the absorption reactor for the next CO_2 absorption cycle, and CO_2-rich gas can be obtained in the regeneration reactor.

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3 \qquad (2)$$

It can be calculated according to Equation (2) that the theoretical CO_2 absorption capacity of Li_4SiO_4 is 367 mg CO_2/g Li_4SiO_4, which is much higher than that of Li_2ZrO_3 (125 mg/g) [9].
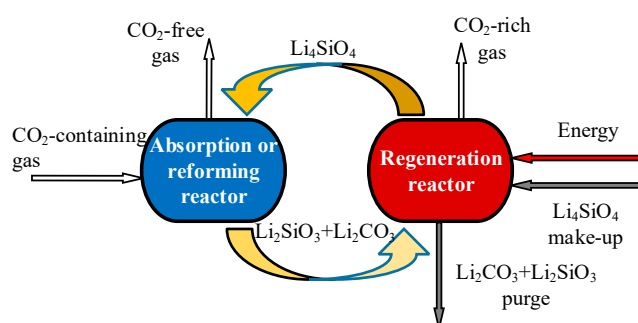

Figure 1. Application of Li_4SiO_4 material for CO_2 absorption for fossil fuel-fired power plants or hydrogen plants based on sorption-enhanced reforming.

Additionally, CO_2 absorption by Li_4SiO_4 material can also contribute to sorption-enhanced hydrogen production, as shown in Figure 1, where methane and ethanol are usually selected [15]. In the process of methane or ethanol reforming, CO_2 is a necessary while undesired product. With in situ CO_2 absorption by Li_4SiO_4 material, the concentration of CO_2 in syngas can be reduced, and the reaction equilibrium of reforming can be shifted to hydrogen production simultaneously, thus the CO_2 absorption capacity of Li_4SiO_4 material is the key factor to determine the hydrogen production efficiency [16,17]. This section will be discussed in detail in Section 6.

However, the CO_2 absorption capacity and cyclic stability of pristine Li_4SiO_4 material prepared by the solid-state reaction method is low, which is mainly due to the smooth surface of pristine Li_4SiO_4 particles generated at high temperature, thus the surface area and pore volume of Li_4SiO_4 material are low, and the reaction between CO_2 and Li_4SiO_4 is limited [18]. Therefore, a large number of works have been conducted to improve the pore structure of Li_4SiO_4, such as the application of organic precursors, which is conducive to the formation of pores, and doping with eutectic salts, which is favorable for the decrease of CO_2 diffusion resistance [19,20].

Since CO_2 absorption by Li_4SiO_4 material was firstly reported, abundant studies have been revealed the reaction mechanism and improved the cyclic CO_2 absorption performance [21]. This work introduces the latest research progress on CO_2 absorption performance of Li_4SiO_4 material. In addition, thermodynamic and kinetic comprehension of the reaction between CO_2 and Li_4SiO_4 are illustrated, and strategies to enhance the cyclic CO_2 absorption performance of Li_4SiO_4 material are summarized. Additionally, applications of Li_4SiO_4 material in sorption-enhanced hydrogen production are reviewed, and studies on CO_2 absorption by Li_4SiO_4 material at the molecular scale are also reviewed briefly. Finally, the major drawback that hinders the large-scale application of Li_4SiO_4 material for CO_2 absorption is introduced.

2. Thermodynamics and Kinetics of CO$_2$ Absorption by Li$_4$SiO$_4$

2.1. Reaction Model for Synthesis of Li$_4$SiO$_4$

Li$_4$SiO$_4$ material is usually synthesized by the solid-state reaction method, and the preparation process is illustrated by Equation (1) [22,23], and a core-shell model was suggested for the solid-state reaction between Li$_2$CO$_3$ and SiO$_2$, which is shown in Figure 2. In the first step, Li$_2$CO$_3$ reacts with SiO$_2$ at their contact part, and a thin Li$_2$SiO$_3$ layer is formed. Li$_2$SiO$_3$ is the intermediate product, which continues to react with Li$_2$CO$_3$ to form Li$_4$SiO$_4$ eventually. Li$_4$SiO$_4$ and Li$_2$SiO$_3$ layers become thicker with the reaction, and internal SiO$_2$ is covered by the layers in the meantime. Thus, Li$^+$ and O^{2-} must diffuse through the product layer before contacting with internal SiO$_2$, and it is the limited step that limiting the synthesis of Li$_4$SiO$_4$, because the diffusion process is much slower than the reaction. Consequently, alternative synthesis methods and precursors for the synthesis of Li$_4$SiO$_4$ have been reported, which will be discussed in the following section [24].
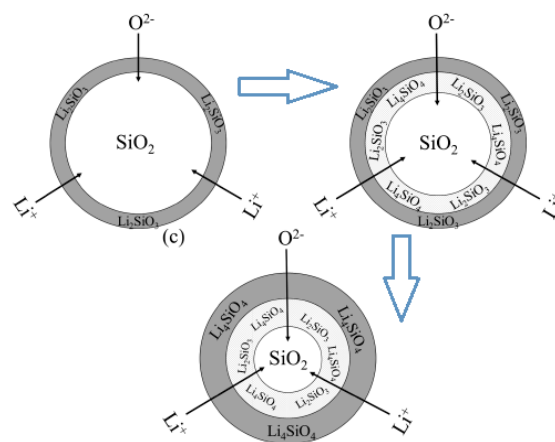

Figure 2. Core-shell model for synthesis of Li$_4$SiO$_4$ by the solid-state route [24].

2.2. Kinetic Study for CO$_2$ Absorption by Li$_4$SiO$_4$

Figure 3 shows the CO$_2$ absorption performance of Li$_4$SiO$_4$ materials prepared by the solid-state reaction method and the sol-gel method in a thermogravimetric analyzer (TGA) [25], and the CO$_2$ absorption amount (mg CO$_2$/g sorbent) was used to evaluate the CO$_2$ absorption capacity of Li$_4$SiO$_4$ materials, which is calculated according to Equation (3):

$$C_N = \frac{m_2 - m_1}{m_1} \tag{3}$$

where C_N is the amount of CO$_2$ absorbed by the Li$_4$SiO$_4$ material, mg/g; N represents the number of cycles; m_1 represents the initial mass of Li$_4$SiO$_4$ material, g; and m_2 represents the mass of the sample during CO$_2$ absorption, mg. The CO$_2$ absorption stage of Li$_4$SiO$_4$ occurs at temperatures lower than 400 °C, and the CO$_2$ absorption rate increases suddenly when the temperature reaches around 500–600 °C. Weight losses of two Li$_4$SiO$_4$ materials are observed when the temperature exceeds 720 °C, indicating the reaction converts to the regeneration of Li$_4$SiO$_4$ materials, and the regeneration reaction is much faster than the absorption process. As shown in Figure 3, the CO$_2$ absorption capacity of Li$_4$SiO$_4$ material prepared by the sol-gel method is higher than that prepared by the solid-state reaction method, which will be discussed in Section 3.3.3.
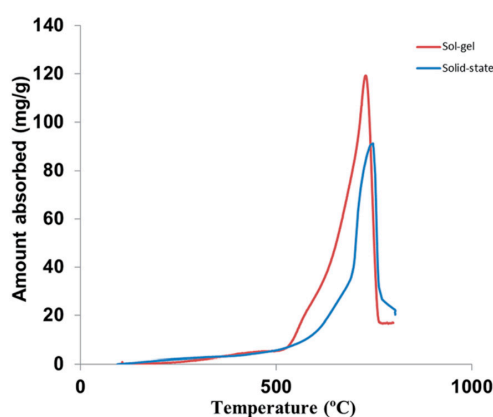
Figure 3. CO_2 absorption by Li_4SiO_4 material in pure CO_2 with respect to temperature [25].

2.3. Thermodynamic Study for CO_2 Capture by Li_4SiO_4

Figure 4 shows the equilibrium partial pressure of CO_2 over Li_4SiO_4 material as a function of temperature [26], and the maximum temperature of CO_2 absorption by Li_4SiO_4 material is determined by the corresponding CO_2 partial pressure. When CO_2 partial pressure is 100% at 1 atm, it can be inferred from Figure 4 that the equilibrium temperature is around 715 °C, which agrees well with the results that discussed above. The corresponding temperature of CO_2 absorption by Li_4SiO_4 material can be determined by the CO_2 partial pressure, and CO_2 absorption by Li_4SiO_4 material occurs when the temperature is lower than the equilibrium temperature, otherwise Li_4SiO_4 material is regenerated. As a result, CO_2 absorption and regeneration regions of Li_4SiO_4 material are divided by the equilibrium line.
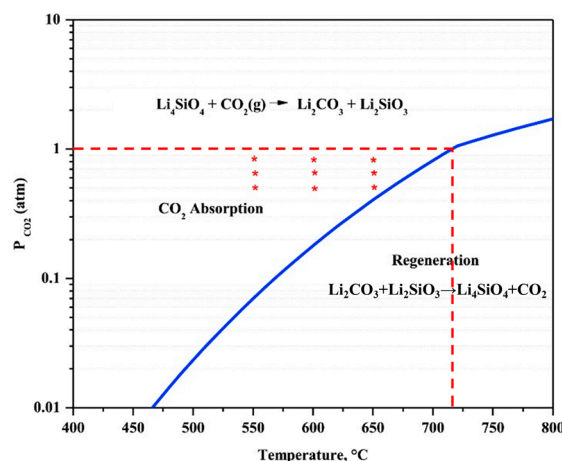

Figure 4. Equilibrium CO_2 partial pressure as a function of temperature for the absorption of CO_2 of Li_4SiO_4 [26].

2.4. Reaction Mechanism and Reaction Model of CO_2 Capture by Li_4SiO_4

The double-shell mechanism is regarded as the most appropriate model for the reaction between CO_2 and Li_4SiO_4 [27], which is schematically illustrated in Figure 5. At the beginning of the reaction, CO_2 molecules react with Li_4SiO_4 particles to generate a double shell composed of Li_2CO_3 and Li_2SiO_3, which covers the internal Li_4SiO_4. Then the reactants diffuse through the double shell to continue the reaction, and the thickness of the double shell increases as the reaction proceeds. Thus, the second stage is much slower than the first stage, owing to the high diffusion resistance of the reactants. Therefore, decreasing the diffusion resistance is conducive to the reaction between CO_2 and Li_4SiO_4. The presence of steam and doping of molten salts are believed to reduce the diffusion resistance in the double shell,

which will be discussed in the following section. Additionally, the shrinking core model and the unreacted core model were well-reported in many studies, which are also involved with the external product shell and internal unreacted core, and the models are similar to that of the double-shell model.
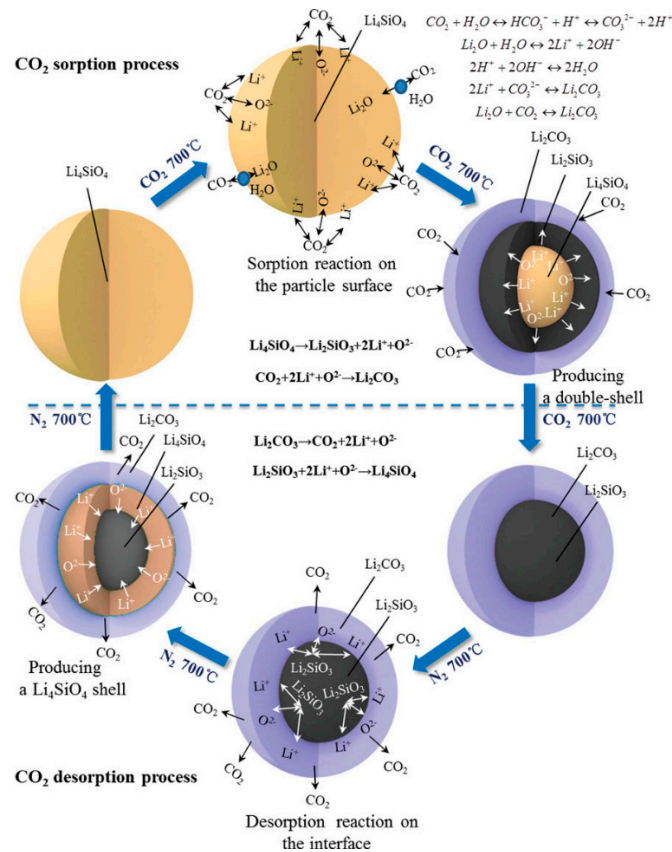

Figure 5. Double-shell mechanism of Li_4SiO_4 material for CO_2 absorption and regeneration [27].

TGA curves of CO_2 absorption by Li_4SiO_4 at various temperatures are present in Figure 6, and weight gain of Li_4SiO_4 was used to evaluate its CO_2 absorption performance, which can be calculated according to Equation (4):

$$W_N = (C_N + 1) \times 100\% \qquad (4)$$

where W_N is the weight gain of Li_4SiO_4 material during the Nth cycles, wt.%; and C_N is the amount of CO_2 absorbed by Li_4SiO_4 material during the Nth cycles, mg/g. CO_2 absorption capacity of Li_4SiO_4 increases with the temperature rising from 460 to 560 °C. Li_4SiO_4 shows a fast CO_2 absorption stage in a short time and a slow CO_2 absorption stage in the following long time, which are controlled by the chemical reaction and diffusion, respectively [28]. Most of the TGA curves are fitted to the double exponential model, which is shown in Equation (5):

$$y = A \exp^{-k_1 t} + B \exp^{-k_2 t} + C \qquad (5)$$

where y represents the weight gain of Li_4SiO_4 material after CO_2 absorption; k_1 and k_2 denote two exponential constants for the chemical reaction-controlled stage and the diffusion-controlled stage, respectively; and two pre-exponential factors A and B are the intervals that control the corresponding stages [28].
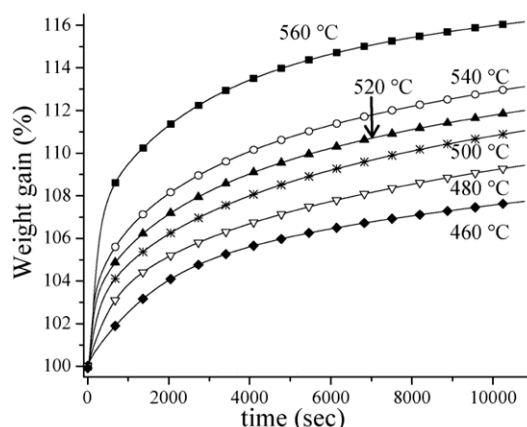
Figure 6. Isotherms obtained in a CO_2 atmosphere at various temperatures [28].

Table 1 presents the kinetic parameters of the double exponential model fitted to the reaction between CO_2 and Li_4SiO_4 [28]. As presented in Table 1, the values of k_1 are usually one order of magnitude higher than those of k_2, and B are always larger than A, indicating that CO_2 absorption over the surface of Li_4SiO_4 controlled by chemical reaction is a rapid process, and CO_2 absorption controlled by diffusion occurs in a large interval of time. Thus, CO_2 absorption controlled by diffusion is the limiting step hindering the absorption of CO_2 by Li_4SiO_4 [29,30].

Table 1. Kinetic parameters of reaction between Li_4SiO_4 and CO_2 for double exponential model [28].

T (°C)	$k_1(\text{sec}^{-1})$	$k_2(\text{sec}^{-1})$	A	B	C
460	8.0×10^{-4}	1.4×10^{-4}	−3.248	−5.560	108.8
480	1.72×10^{-3}	1.3×10^{-4}	−3.467	−7.821	111.2
500	2.96×10^{-3}	1.7×10^{-4}	−3.716	−8.668	112.3
520	4.26×10^{-3}	2.1×10^{-4}	−4.231	−8.711	112.8
540	4.17×10^{-3}	2.1×10^{-4}	−4.983	−9.003	113.8
560	4.27×10^{-3}	2.5×10^{-4}	−9.017	−8.911	116.6

Although the double exponential model is widely used due to its simplicity, Ortiz et al. [26] thought that this model was short of the theoretical mechanism to support its fitting with the experimental data. Zhang et al. [27] reported that the Avrami–Erofeev model was relevant to the reaction mechanism of the formation and growth of product crystals, which are shown as Equations (6) and (7):

$$\mathrm{d}\alpha/\mathrm{d}t = Kn(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{6}$$

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t \tag{7}$$

where α refers to the degree of conversion; K denotes the kinetic constant; k equals to K^n; and n is the kinetic parameter; t represents the time. Equation (7) is an equation of a straight line with slope n in the coordinates $\ln(-\ln(1-\alpha))$ vs. $\ln t$. If the value of n is higher than 1, the absorption reaction is controlled by the formation and growth of product crystals. When n equals to 0.5 approximately, the absorption reaction is controlled by the diffusion of ions [31].

As illustrated in Figure 7, the curves of Avrami–Erofeev model look similar to TGA curves obtained from 550 to 700 °C, and the rapid chemical reaction-controlled stage and the slow diffusion-controlled stage can be easily distinguished at every temperature. Additionally, Zhang et al. [27] reported that the Avrami–Erofeev model suited the regeneration process of Li_4SiO_4 material, and the entire regeneration process was controlled by the rate of the formation and growth of product crystals, which was also confirmed by Xiang et al. [32]. Thus, the Avrami–Erofeev model is more suitable for CO_2 absorption by Li_4SiO_4.
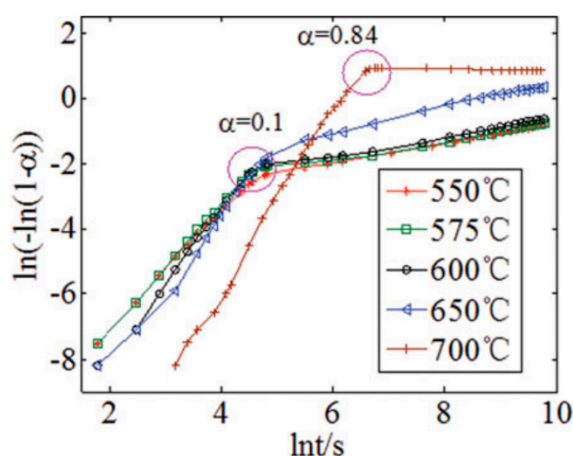
Figure 7. Fit of kinetic experimental data by the Avrami–Erofeev model [27].

3. Synthesis of Li_4SiO_4 Materials with Superior Cyclic Absorption/Regeneration Performance

It is clear that Li_4SiO_4 material synthesized by the solid-state reaction method from SiO_2 and Li_2CO_3 achieves low CO_2 absorption capacity, due to the low porosity of Li_4SiO_4 generated at high temperatures during the preparation. Thus, the CO_2 absorption capacity of Li_4SiO_4 decreases rapidly with the number of cycles, which is the main disadvantage of Li_4SiO_4 material in industrial applications. The various methods have been reported to enhance the cyclic performance of Li_4SiO_4 material prepared by solid-state reaction method, such as hydration [33] and ball milling [34,35]. The strategies to enhance the cyclic performance of Li_4SiO_4 can be categorized as follows: (i) reducing the diffusion resistance by adding solid solutions or molten salts; (ii) using alternative precursors; and (iii) using a more appropriate synthesis method.

3.1. Modification for Li_4SiO_4 Prepared by Solid-State Reaction

As discussed above, high temperature during the preparation by the solid-state reaction method of Li_4SiO_4 leads to sintering, and the core of Li_4SiO_4 usually cannot react with CO_2. Thus, Yin et al. [33] proposed a hydration process to improve the pore structure of Li_4SiO_4 material. First, Li_4SiO_4 material was prepared by the solid-state reaction method, and then distilled water was added to the samples and stirred at 80 °C for 4 h. They reported that dense particles formed during the solid-state reaction preparation could be split into fine particles, so the porous structure and high cyclic CO_2 absorption capacity of Li_4SiO_4 was obtained by hydration process.

Romero-Ibarra et al. [34] used the ball milling process to modify the surface properties of Li_4SiO_4 material, and they found that the ball milling process decreased the particle size and improved the surface area of Li_4SiO_4 material. Kanki et al. [35] reported that the ball milling process could promote CO_2 absorption of Li_4SiO_4 material at lower temperatures, and longer ball milling duration led to higher CO_2 absorption capacity. Additionally, the doping of K_2CO_3 in Li_4SiO_4 material improved its CO_2 absorption capacity under short ball milling duration.

3.2. Doping of Solid Solutions or Molten Salts

3.2.1. Solid Solutions

The CO_2 absorption rate of Li_4SiO_4 material is mainly controlled by the diffusion of ions and CO_2. Zhao et al. [36] reported that solid solution usually formed with the doping of Al_2O_3 during solid-state preparation, thus increased oxygen vacancies could promote the diffusion in the product layer. Ortiz-Landeros et al. [37] reported that Al_2O_3 addition and ball milling could extend the range of CO_2 absorption temperature. In addition, Ortiz-Landeros et al. [38] compared $Li_{4+x}(Si_{1-x}Al_x)O_4$ with $Li_{4-x}(Si_{1-x}V_x)O_4$ as the solid solutions, and the results showed that diffusion resistance of CO_2

and ions in $Li_{4+x}(Si_{1-x}Al_x)O_4$ was diminished, while the presence of V was adverse to the diffusion through the product layer.

3.2.2. Molten Salts

The doping of alkali metals, such as Na and K, could produce a layer of molten salts with low eutectic temperature, which reduced diffusion resistance effectively, thus the limiting step of Li_4SiO_4 material for CO_2 absorption could be resolved. The CO_2 absorption performance of various alkali metal-doped Li_4SiO_4 materials is summarized in Table 2 [39–46].

Table 2. Summary of CO_2 absorption performance of Na and K doped Li_4SiO_4 materials.

Materials	Molar Ratio of Li/Alkali Metal	Preparation Method	Absorption Conditions	Regeneration Conditions	Cycle No.	Weight Increase (wt.%)	Refs.
SiO_2, Li_2CO_3, K_2CO_3	10.5:1	Solid-state reaction	4% CO_2/N_2; 580 °C; 60 min	N_2; 800 °C; 10 min	4	24	[39]
SiO_2, Li_2CO_3, K_2CO_3	10.83:1	Solid-state reaction	4% CO_2/N_2; 580 °C; 60 min	N_2; 700 °C; 15 min	25	16	[40]
SiO_2, Li_2CO_3, K_2CO_3	17.6:1	Solid-state reaction	CO_2; 575 °C; 25 min	N_2; 700 °C; 50 min	10	28	[41]
SiO_2, Li_2CO_3, K_2CO_3	17.6:1	Solid-state reaction	CO_2; 650 °C; 15 min	90% H_2O/N_2; 650 °C; 15 min	22	21	[42]
SiO_2, CH_3COOLi, K_2CO_3	43.7:1	Impregnated suspension	15% CO_2/N_2; 550 °C; 30 min	N_2; 750 °C; 10 min	40	315	[43]
SiO_2, CH_3COONa, Na_2CO_3	16:1	Impregnated suspension	15% CO_2/N_2; 550 °C; 30 min	N_2; 750 °C; 10 min	40	28	[43]
SiO_2, Li_2CO_3, Na_2CO_3	49:1	Solid state	CO_2; 700 °C; 30 min	Air; 900 °C; 30 min	5	32	[44]
SiO_2, $LiNO_3$, NaF	41:1	Template	15% CO_2/N_2; 600 °C; 35 min	N_2; 700 °C; 20 min	10	31	[45]
SiO_2, $LiNO_3$, NaCl	133:1	Solid state with hydration	15% CO_2/N_2; 575 °C; 40 min	N_2; 700 °C; 10 min	10	32	[46]

As presented in Table 2, Na and K were the most commonly reported alkali metals to enhance the CO_2 absorption performance of Li_4SiO_4 material. In order to determine the most appropriate doping method for K_2CO_3, Seggiani et al. [39] compared eutectic doping and simple mechanical addition of K_2CO_3, and they found that Li_4SiO_4 particles obtained from mechanical addition were smaller, as shown in Figure 8, so the mechanical doping method may be more appropriate for the doping of K_2CO_3. Olivares-Marín [47] et al. synthesized K_2CO_3-doped Li_4SiO_4 material with fly ash as the silicon precursor, and they reported that the CO_2 absorption capacity of the prepared Li_4SiO_4 material increased with the increase of the dopant amount. It is also worth noting that Zhang et al. [42] reported that the K_2CO_3 doped Li_4SiO_4 material cooperated well with the Ni/γ-Al_2O_3 catalyst in the sorption-enhanced steam methane reforming (SE-SMR) system, and high-purity hydrogen (>95%) could be obtained at lower temperatures ranging from 500 to 550 °C, and the presence of steam in the regeneration atmosphere could improve the reaction rate obviously. Mejía-Trejo et al. [48] prepared Na-doped Li_4SiO_4 material by doping Na_2CO_3 into the starting materials of TEOS and Li_2CO_3 through the co-precipitation route, and they noted that the addition of Na_2CO_3 increased the activity and reduced the equilibrium temperature of Li_4SiO_4 material for CO_2 absorption, and $Li_{3.85}Na_{0.15}SiO_4$ had the highest CO_2 absorption capacity among various Na-doped Li_4SiO_4 materials. Seggiani et al. [40] noted that dopants like K_2CO_3 and Na_2CO_3 could form eutectic mixtures with Li_2CO_3, which melted at high temperatures (>500 °C), so the diffusion of ions and CO_2 was enhanced in the diffusion-controlled stage. Yang et al. [43] reported that orderly crystalline arrangement of Li_4SiO_4 was broken by doped K_2CO_3 and Na_2CO_3 for their different crystal sizes, thus more pores and larger specific surface area were generated.
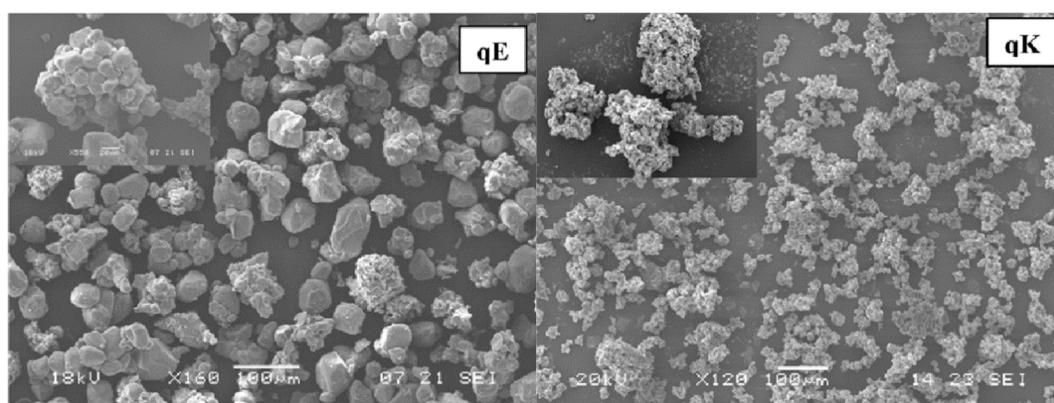
Figure 8. Scanning electron microscopy (SEM) images of Li_4SiO_4 samples obtained from different doping methods: eutectic doping (qE); simple mechanical addition (qK) [39].

3.2.3. Other Dopants

Wang et al. [49] prepared K-, Mg-, Cr-, and Ce-doped Li_4SiO_4 and found that Ce was the most difficultly doped into the Li_4SiO_4 crystal lattice among the four elements. However, Ce was the most effective to inhibit the aggregation of Li_4SiO_4 grains, so Ce-doped Li_4SiO_4 achieved the highest CO_2 absorption performance. Subha et al. [50] studied the CO_2 absorption by Li_4SiO_4 material doped with Y_2O_3, Gd_2O_3 or $LaPO_4$, and found that both Y_2O_3 and Gd_2O_3 improved the CO_2 absorption capacity of Li_4SiO_4, and Y_2O_3-doped Li_4SiO_4 retained the highest CO_2 absorption capacity due to the segregation of second phase created by the doped unreacted Y_2O_3. Chen et al. [51] reported that Ca-doped Li_4SiO_4 material achieved high CO_2 absorption capacity and they proposed a modified double-shell mechanism to describe the CO_2 absorption and regeneration mechanism of Ca-doped Li_4SiO_4 as shown in Figure 9. The transformation of Ca_2SiO_4 to Li_2CaSiO_4 during CO_2 absorption process was beneficial of transferring CO_2 from Li_4SiO_4 surface to the core, which reduced the diffusion resistance and improved CO_2 absorption, and regeneration was also correspondingly enhanced.
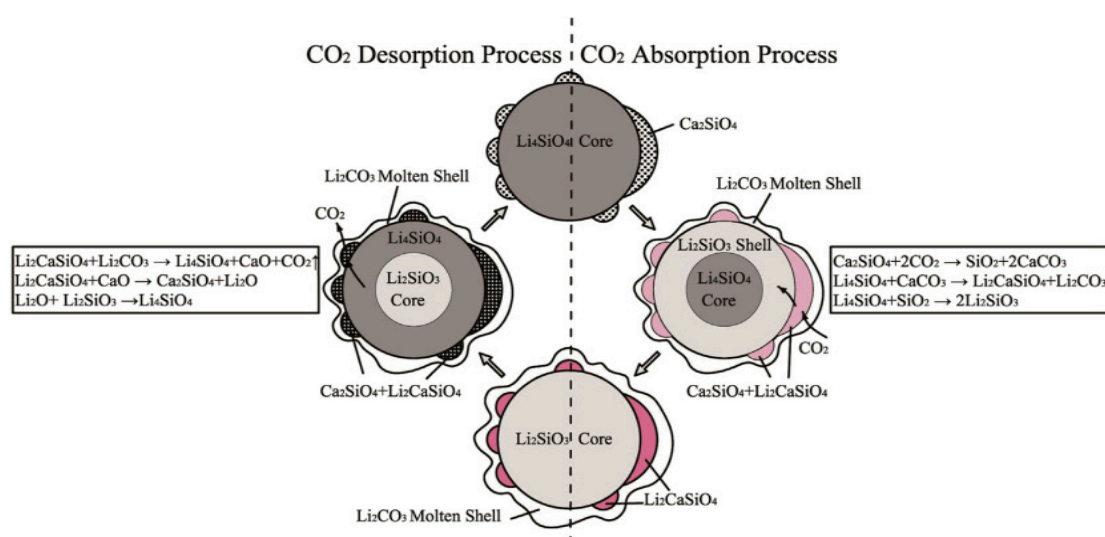

Figure 9. CO_2 absorption and regeneration mechanism of Ca-doped Li_4SiO_4 [51].

Additionally, doping of organic matter can also enhance the CO_2 absorption property of Li_4SiO_4 material due to the formation of the porous structure. Wang et al. [30,52] prepared carbon-coated Li_4SiO_4 material by the sol-gel method, and gluconic acid and citric acid were used as the complexing agents, respectively. During the carbonization stage, gluconic acid and citric acid decomposed, and a mesoporous carbon coating covered the surface of Li_4SiO_4 material, which suppressed the growth of

Li_4SiO_4 grains. As a result, the cyclic CO_2 absorption capacities and rates of carbon-coated Li_4SiO_4 materials were higher than that of uncoated Li_4SiO_4 during multiple absorption/regeneration cycles. Furthermore, CMK-3, as a kind of porous carbon material [53], was also introduced into the Li_4SiO_4 material. Jeoung et al. [54] prepared CMK-modified Li_4SiO_4, while the cyclic absorption capacity of CMK-modified Li_4SiO_4 decreased obviously with the number of cycles.

It has been reviewed in this part that doping of metal elements, such as K, Na, Ca, Ce, Y, Al, or organic matters, can enhance the CO_2 absorption capacities of Li_4SiO_4 material. The limitation in the diffusion-controlled stage for Li_4SiO_4 is reduced greatly with the doping of solid solution or molten salts, and the porous structure of Li_4SiO_4 by doping of organic matters is obtained. The additive amounts are minor, but the CO_2 absorption performance of Li_4SiO_4 can be greatly enhanced.

3.3. Selection of Alternative Precursors for Preparation of Li_4SiO_4

Li_4SiO_4 material is usually prepared from Li_2CO_3 and SiO_2, which are not able to create a favorable surface characteristic for CO_2 absorption. Recent studies have shown that Li_4SiO_4 materials prepared from alternative precursors, especially organic precursors, rather than Li_2CO_3 and SiO_2 achieve high CO_2 absorption capacities and cyclic stability. In this section, the effects of precursors on CO_2 absorption capacity of Li_4SiO_4 material are summarized.

3.3.1. Lithium Precursors

Kim et al. [29] synthesized Li_4SiO_4 material from LiOH and fumed silicate by the solid-state reaction method. They reported that the synthesis temperature could be reduced to 600 °C due to the use of LiOH, and the obtained Li_4SiO_4 showed higher CO_2 absorption capacity compared with those synthesized at 700 °C and 800 °C, which achieved 298 mg/g after 10 cycles. Wang et al. [55] synthesized Li_4SiO_4 with LiOH by the sol-gel technique and they found that LiOH-synthesized Li_4SiO_4 particles were primarily composed of porous grains, and the average grain size of Li_4SiO_4 prepared by the sol-gel method was much smaller than that synthesized by the solid-state reaction method.

Weng et al. [56] synthesized Li_4SiO_4 from $LiNO_3$ as lithium precursor and tetraethyl orthosilicate (TEOS) as a silicon precursor by the sol-gel method. The CO_2 absorption capacity of the obtained Li_4SiO_4 material increased with increasing temperature from 400 to 500 °C in 2% CO_2. Bretado et al. [14] reported that the solid-state reaction method was more appropriate than the sol-gel method for the preparation of Li_4SiO_4 material when $LiNO_3$ was used as the lithium precursor. However, Subha et al. [25] reported that the sol-gel method was superior to the solid-state reaction method for Li_4SiO_4 material prepared from $LiNO_3$ and colloidal silica. This indicates that the most appropriate synthesis method depends on the lithium and silicon precursors simultaneously.

Compared with inorganic lithium precursors, organic lithium-containing materials seems more appropriate as the lithium precursor for the preparation of Li_4SiO_4 material. Yang et al. [19] used lithium acetate and lithium lactate to prepare novel Li_4SiO_4 materials by the impregnated suspension method. As shown in Figure 10, the two novel Li_4SiO_4 materials showed a bulgier morphology and more porous structure, compared with Li_4SiO_4 synthesized by the solid-state reaction method. Absorption capacities of Li_4SiO_4 material prepared from lithium acetate or lithium lactate as the lithium precursors were almost six times higher than that of a conventional Li_4SiO_4 material. Additionally, the CO_2 absorption capacities and conversions of Li_4SiO_4 material prepared from lithium acetate or lithium lactate showed an incremental tendency over 40 cycles, and the conversion of Li_4SiO_4 prepared from lithium acetate was approximately 70% even in the last cycle, which was calculated according to Equation (8):

$$X_N = \frac{C_N}{m_0} \qquad (8)$$

where X_N is the conversion of Li_4SiO_4 during the Nth cycle, %; and m_0 is the theoretical CO_2 absorption capacity of Li_4SiO_4 material, which is 367 mg/g. Lee et al. [57] used Li and a Si-containing metal-organic framework (MOF) as the silicon precursor, and the prepared Li_4SiO_4 material was able

to convert into Li_4SiO_4 thermally. The as-prepared material had a coral-like morphology, so the contact area between CO_2 and Li_4SiO_4 material was enhanced, and the Li_4SiO_4 material showed higher CO_2 absorption capacity than that prepared by the conventional solid-state reaction method.
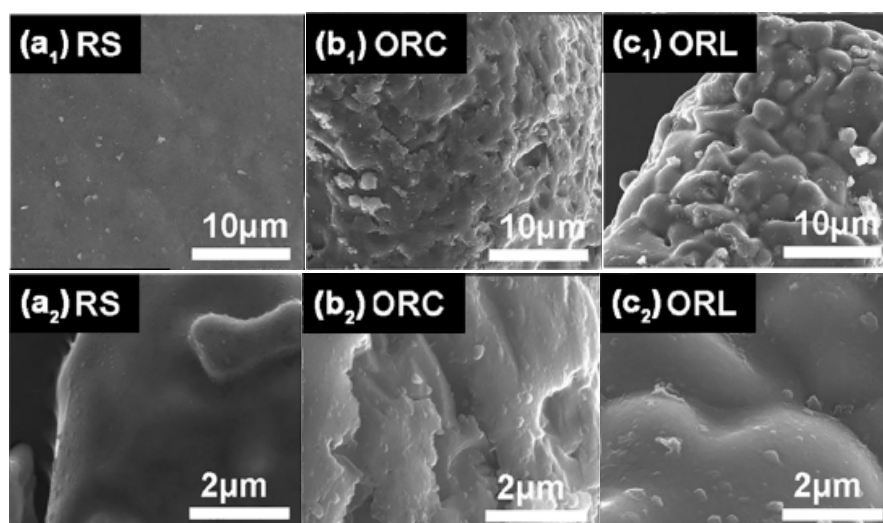

Figure 10. SEM images of three kinds of Li_4SiO_4 materials prepared with Li_2CO_3 (RS), lithium acetate (ORC) and lithium lactate (ORL) [19].

In this section, CO_2 absorption performance of Li_4SiO_4 material synthesized from various lithium sources was reviewed. It is known to all that the price of Li-containing materials is quite high now, including Li_2CO_3, LiOH, $LiNO_3$ or organic lithium precursors mentioned above, so it is necessary to find other alternative Li-containing materials, especially wastes, with lower prices as the lithium precursor for the preparation of Li_4SiO_4 material.

3.3.2. Silicon Precursors

SiO_2 is an essential raw material for the synthesis of Li_4SiO_4. In addition to pure SiO_2, there are many SiO_2-rich industrial wastes which have attracted researchers' interests, such as rice husk ash (RHA) and fly ash (FA). In this section, the effects of alternative silicon precursors on CO_2 absorption performance of Li_4SiO_4 material are critically reviewed.

Wang et al. [20] selected two kinds of RHA samples as the silicon precursors for the preparation of Li_4SiO_4 material, which contained the SiO_2 contents of 94.71 and 98.84 wt.%, respectively. HCl aqueous solution was used to pretreat the two RHA samples, then Li_4SiO_4 materials were synthesized by the solid-state reaction method with Li_2CO_3. The employment of RHA produced a smaller particle size, larger pore volume, and surface area compared with pure Li_4SiO_4 material. They reported a weight gain of nearly 135 % over 15 cycles, which was much higher than that of pure Li_4SiO_4 material. Furthermore, Wang et al. [58] pretreated rice husk samples at 600 and 1000 °C, respectively, and cyclic performances of the two RHA-synthesized Li_4SiO_4 materials pretreated at 1000 °C achieved better CO_2 absorption performance, which was similar to that of the RHA-derived Li_4SiO_4 material mentioned above. To study the effects of RHA as the silicon precursor on the CO_2 absorption properties of Li_4SiO_4 material, Wang et al. [59] selected RHA and two kinds of nanosilica (Aerosil and quartz) to prepare Li_4SiO_4 materials by solid-state reaction method, and SEM images and BET analysis indicated that RHA-synthesized Li_4SiO_4 material possessed higher surface area and larger pore volume. Furthermore, the weight gain of RHA-synthesized Li_4SiO_4 material was higher and faster than that of the two nanosilica-synthesized Li_4SiO_4 materials, and its cyclic CO_2 absorption capacity reached nearly 30 wt.% over 15 cycles. The authors ascribed this phenomenon to the almost unchanged surface morphology of Li_4SiO_4 material prepared from RHA over multiple absorption/regeneration

cycles. Qiao et al. [60] also noted that RHA-derived Li_4SiO_4 material could enhance the yield of H_2 and reduce the energy consumption in the process of sorption-enhanced steam ethanol reforming.

Fly ash (FA) is a kind of hazardous mineral residue released from coal-fired power plants, and it accounts for approximately 88% in the total coal ash content, which contains a high silicon content, thus it has been used to fabricate useful materials [61,62]. Therefore, Li_4SiO_4 materials can also be prepared from FA as a silicon precursor. Olivares-Marín et al. [47] fabricated Li_4SiO_4 material from Li_2CO_3 and three kinds of FA, and the samples were doped with several amounts ranging from 5 to 40 mol% of K_2CO_3. The cyclic CO_2 absorption capacity of one of the doped FA-Li_4SiO_4 was approximately 100 mg/g over 10 cycles, which was far below the theoretical absorption capacity of Li_4SiO_4 material synthesized from pure SiO_2, but it was relatively stable over multiple cycles. Sanna et al. [63] synthesized Na/Li-FA Li_4SiO_4 material with different molar ratios of Li_2CO_3, FA, and Na_2CO_3, and the material was doped with K_2CO_3. They reported that the CO_2 absorption capacity of the obtained Li_4SiO_4 material was approximately 50 mg/g in low CO_2 concentration in the presence of water vapor, and water vapor had no effect on the cyclic CO_2 absorption capacity.

Shan et al. [64] selected diatomite as silicon precursor, containing the SiO_2 content of approximately 75% [65], and zeolite was also chosen as precursor for comparison. Li_4SiO_4 was synthesized by the solid-state reaction method. Li_4SiO_4 synthesized from diatomite showed higher CO_2 absorption capacity. Li_4SiO_4 material synthesized from diatomite achieved better CO_2 absorption performance than that synthesized from pure SiO_2 because of the higher specific surface area of the former [66]. In order to determine the optimum molar ratio of Li_2CO_3 to SiO_2, Shan et al. [65] prepared a series of Li_4SiO_4 containing the molar ratios of Li_2CO_3 to SiO_2 ranging from 2.0 to 2.8 and their CO_2 absorption capacities carbonated under 50 vol.% CO_2 at 620 °C for 30 min were shown in Table 3.

Table 3. CO_2 absorption performances of Li_4SiO_4 materials with different molar ratios of Li_2CO_3 to SiO_2 [65].

Molar Ratio	2.0:1	2.1:1	2.2:1	2.3:1	2.4:1	2.6:1	2.8:1
Weight gain (%)	116	122	124	129	129	130	116

As presented in Table 3, when molar ratio of Li_2CO_3 to SiO_2 was 2.6:1, CO_2 absorption capacity reached 30.32 wt.% (82.62% of the theoretical value). The CO_2 absorption capacity of Li_4SiO_4 material with this molar ratio decreased from 34.14 to 27.70 wt.% over 16 cycles. However, Shan et al. [67] pointed out that high temperature (900 °C) during the solid-state reaction preparation process resulted in the sintering of Li_4SiO_4 easily, so they selected the impregnation precipitation method to prepare Li_4SiO_4 materials, which was operated at lower temperature. Diatomite, $LiNO_3$, and $NH_3·H_2O$ were selected as the starting materials with the Li:Si molar ratio of 5.2:1, and the reactions involved are shown in Equations (9) and (10). When carbonated in 50 vol.% CO_2 and regenerated in pure N_2 at 700 °C, both for 30 min, cyclic CO_2 absorption capacity of Li_4SiO_4 synthesized by the impregnation precipitation method was quite stable, which decreased from 34.14 to 33.09 wt.% as the cycle number increases from 1 to 15.

$$LiNO_3 + NH_3 · H_2O \rightarrow LiOH + NH_4NO_3 \qquad (9)$$

$$4LiOH + SiO_2 \rightarrow Li_4SiO_4 + 2H_2O \qquad (10)$$

Halloysite is also a SiO_2-containing material with a SiO_2 content of about 50 wt.% [68]. Niu et al. [69] synthesized Li_4SiO_4 from treated halloysite nanotubes (HNTs) with HCl aqueous solution and Li_2CO_3 by the solid-state reaction method at 800 °C. The content of Al_2O_3 of HNTs is 43.859%, and the presence of Al^{3+} was beneficial to the enlargement of Li_4SiO_4 crystalline structure, which is beneficial for its CO_2 absorption performance [37]. The CO_2 absorption capacity of halloysite-synthesized Li_4SiO_4 material was approximately 30 wt.% over 10 cycles, which was higher than that of SiO_2-synthesized Li_4SiO_4 material.

In this section, CO_2 absorption performances of Li_4SiO_4 materials synthesized from various silicon precursors were reviewed. Li_4SiO_4 synthesized from RHA, diatomite and halloysite exhibited high CO_2 absorption capacity, while fly ash was not a good lithium precursor. Some elements in these silicon precursors other than pure SiO_2 are possibly beneficial for the CO_2 absorption properties of Li_4SiO_4 materials, which will be discussed in the following sections. There are a large number of Si-containing materials, especially industrial wastes like steel slag, so the following research will focus on these materials. The studies on alternative silicon precursors for the preparation of Li_4SiO_4 materials have obtained great progress, while the major problem that limits the practical application of Li_4SiO_4 is the high price of Li-containing materials, and the cost of Li_4SiO_4 will not be reduced by much even if SiO_2 is free of charge, so the future research should focus on alternative lithium precursors.

3.3.3. Synthesis Methods

Most of the Li_4SiO_4 materials were synthesized by the traditional solid-state reaction method at a relatively high temperature (900 °C). The solid-state reaction method has been widely used because of its simplicity, while Bretado et al. [14] reported that high temperature during the solid-state reaction process resulted in contamination and volatilization. In addition, the microstructure and composition of Li_4SiO_4 materials were difficult to control and agglomeration and sintering of the materials also occurred in the preparation process [24,29]. Thus, Bretado et al. [14] selected the impregnated suspension method to prepare Li_4SiO_4 material and they found that the conversion of the obtained Li_4SiO_4 material (98.4%) was higher than that prepared by the solid-state reaction method (94.9%).

Subha et al. [25] reported that the platelet-shaped Li_4SiO_4 material synthesized from $LiNO_3$ and colloidal silica by a sol-gel method achieved an absorption capacity of 350 mg/g. Additionally, the platelet-shaped Li_4SiO_4 material was coated with a porous carbon mesh, and the cyclic absorption/regeneration performance of the platelet-shaped Li_4SiO_4 material retained approximately 120 mg/g over eight cycles. The CO_2 absorption rates of the coated Li_4SiO_4 materials were faster than those of the uncoated ones. Additionally, the sol-gel method was superior to the solid-state reaction method when LiOH was selected as the lithium precursor [29,55]. However, the impregnation precipitation method was superior to the solid-state reaction method when diatomite was selected as the silicon precursor [67]. Venagas et al. [70] reported that Li_4SiO_4 materials synthesized by the sol-gel method was not completely pure, probably because the use of a microwave oven resulted in the sublimation of Li_4SiO_4.

4. Effects of Particle Properties on CO_2 Absorption Performance of Li_4SiO_4 Material

The newly synthesized Li_4SiO_4 powder is too fine, and elutriation might occur in the reactor, especially in fluidized bed reactors, in industrial applications. In addition, powdery Li_4SiO_4 materials cannot create effective fluidization, while most of the studies on CO_2 absorption by Li_4SiO_4 material were conducted on fixed bed reactors or TGA. Thus, pelletization may be an effective method for the practical application of Li_4SiO_4 materials. The effects of the particle properties on CO_2 absorption performance of Li_4SiO_4 material were critically reviewed in this section.

Pacciani et al. [71] studied the CO_2 absorption by the pelletized Li_4SiO_4 materials, which were doped with less than 10 vol.% K_2CO_3 and Li_2TiO_3 as a binder. The CO_2 absorption capacity of the pelletized Li_4SiO_4 material was 23 wt.% carbonated in 10 vol.% CO_2. However, Kato et al. [72] reported that the pelletized Li_4SiO_4 materials were more prone to lose their cyclic stability due to the sintering which was caused by the short length of material particles. Essaki et al. [73] prepared cylinder-type K_2CO_3 doped Li_4SiO_4 materials with the diameter of 3 mm and length of 6 mm, while the CO_2 absorption capacity of a Li_4SiO_4 pellet was not so high as that of Li_4SiO_4 powder. Puccini et al. [74] synthesized K_2CO_3-doped Li_4SiO_4 by the solid-state reaction method, and they selected cellulose fiber as the binder. The Li_4SiO_4 material pellets with a diameter of 6 mm and lengths of 1.5, 2.5, and 3.5 mm were prepared, but the prepared Li_4SiO_4-based pellets did not show

superior cyclic performance and the conversion of the Li_4SiO_4 pellets decreased to below 28% after 10 cycles. Furthermore, Puccini et al. [75] selected layered graphite and carbon nanotubes as the binders, and thermogravimetric analysis showed that layered graphite was a more suitable binder than carbon nanotubes. It is noteworthy that the cyclic performance of Li_4SiO_4 pellets with a binder of layered graphite was more superior than that of the pellets mentioned in [74], as shown in Figure 11.
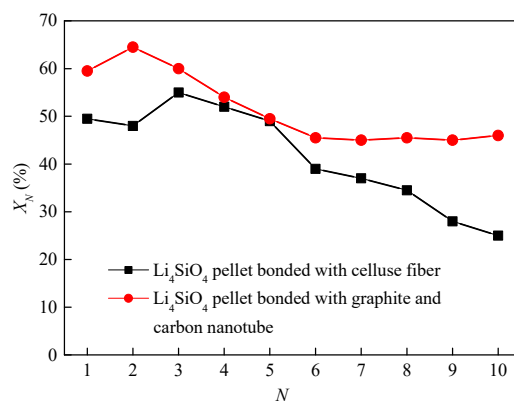

Figure 11. Cyclic CO_2 absorption by Li_4SiO_4 materials with different binders [74,75].

Pelletization is an essential procedure for the practical application of Li_4SiO_4, but few researchers studied the CO_2 absorption performance of the pelletized Li_4SiO_4 materials in fluidized bed reactors. Additionally, mechanical intensity and wearing characteristics of pelletized Li_4SiO_4 materials have seldom been reported.

5. Effects of Reaction Conditions on CO_2 Absorption Performance of Li_4SiO_4 Material

Realistic reaction conditions for CO_2 absorption by Li_4SiO_4 material is very complicated, which involves the absorption atmosphere, absorption temperature, regeneration (desorption) temperature, and operating pressure, etc. Hence, the effects of reaction conditions on the CO_2 absorption performance of Li_4SiO_4 materials are reviewed in this section.

5.1. Reaction Atmosphere

5.1.1. CO_2 Concentration

The practical CO_2 concentration in the flue gas from fossil fuel-fired power plant is about 15 vol.% [76], but pure CO_2 is usually selected as the absorption atmosphere of Li_4SiO_4, and the CO_2 absorption performance under the practical lower CO_2 concentration has been overlooked. In fact, CO_2 concentration in sorption-enhanced hydrogen production process is also usually low. Therefore, it is necessary to investigate the CO_2 absorption performance of Li_4SiO_4 material in low CO_2 concentrations.

Pacciani et al. [71] reported that the CO_2 absorption rate of Li_4SiO_4 material rose apparently when CO_2 concentration in absorption atmosphere increased from 2.5 to 24.5 vol.%. Essaki et al. [77] prepared the pelletized Li_4SiO_4 materials with an average particle size of 5 mm and K_2CO_3 and Li_2ZrO_3 were doped into the materials to promote the absorption reaction and prevent reduction of absorption capacity, respectively. The absorption property of Li_4SiO_4 pellets was investigated in 5 vol.% CO_2 at first, and they found that 500 °C was the most appropriate temperature in the range of 400–600 °C for the CO_2 absorption by Li_4SiO_4. However, when the absorption tests were carried out in 10 or 15 vol.% CO_2, it was found that the CO_2 absorption capacity rose as the temperature increased from 400 to 600 °C. Essaki et al. [77] ascribed this phenomenon to the influence of reaction equilibrium, as shown in Figure 12. The equilibrium temperature of CO_2 absorption and regeneration showed an

increasing trend with increasing CO_2 concentration, and the weight increase was used to evaluate the CO_2 absorption performance of Li_4SiO_4 material, which can be calculated according to Equation (11):

$$I_N = W_N - 100\% \tag{11}$$

where I_N is the weight increase of Li_4SiO_4 material during the Nth cycle, wt.%; W_N is the weight gain, wt.%; N is the number of cycles. It was also noteworthy that the CO_2 absorption process of Li_4SiO_4 was limited in low CO_2 concentration (5 vol.%), while it was controlled by the diffusion of Li^+ and O^{2-} in high CO_2 concentration (15 vol.%).
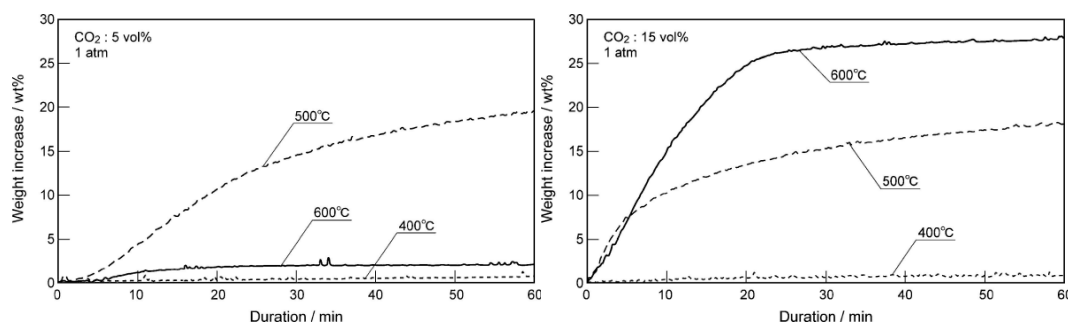

Figure 12. Weight increase of Li_4SiO_4 at different temperatures in different CO_2 concentrations [77].

Researchers found that the limits of low CO_2 concentration could be counteracted by the addition of dopants. Puccini et al. [78] found Li_4SiO_4 material doped with 30 wt.% K_2CO_3 maintained a stable CO_2 absorption capacity (approximately 160 mg/g) after 25 cycles in 4 vol.% CO_2 at 580 °C. It is worth noting that Seggiani et al. [39] reported that CO_2 absorption capacity of K_2CO_3-doped Li_4SiO_4 material was superior than 20 wt.% over four cycles in 4 vol.% CO_2. Furthermore, Seggiani et al. [40] also reported that the CO_2 absorption capacity of Na_2CO_3-doped Li_4SiO_4 material in 4 vol.% CO_2 was 7 wt.%, and it was quite stable over 25 cycles. Adding some dopants can improve the CO_2 absorption capacity of Li_4SiO_4 material, but the improvement in lower CO_2 concentration is still relatively lower compared with that in higher CO_2 concentration. The CO_2 absorption performance of Li_4SiO_4 material in high CO_2 concentration has been well studied by researchers. Thus, Li_4SiO_4 materials with high absorption capacity, fast absorption rate, and good cyclic stability in low CO_2 concentrations should be investigated for industrial application.

5.1.2. Presence of Steam

Apart from CO_2, steam also exists in realistic CO_2 absorption conditions, and the content of steam during the typical sorption-enhance hydrogen production process is more than 30%. Ochoa-Fernández et al. [79] reported that steam could promote the mobility of alkaline ions, indicating that the limiting resistance of the CO_2 absorption reaction could be reduced. Thus, the presence of steam in the absorption atmosphere also has non-negligible effect on the CO_2 absorption capacity of Li_4SiO_4 material.

Ochoa-Fernández et al. [80] reported that the presence of 10 vol.% steam in the absorption atmosphere could raise the CO_2 capacity from 9.5 to 29 wt.%. Additionally, they also found that the presence of steam accelerated the regeneration reaction: the regeneration process became faster and more thorough with the presence of steam, and cyclic CO_2 absorption performance of Li_4SiO_4 material degraded slightly after eight cycles with the presence of steam, almost the same as the experimental data obtained in dry atmosphere. Quinn et al. [81] used pelletized Li_4SiO_4 materials for CO_2 absorption in 14.7% CO_2, 2.6% steam in N_2 at 550 °C, and they found that the CO_2 absorption capacity after 10 min was almost three times higher than that in dry atmosphere. Furthermore, Sanna et al. [63] synthesized Li_4SiO_4 material from FA as SiO_2 precursor, and the CO_2 absorption capacity was enhanced by steam.

Puccini et al. [82] also noted that the CO_2 absorption rate was accelerated correspondingly with increasing steam concentration from 10 to 30 vol.%.

As mentioned above, the presence of steam contributes to the CO_2 absorption by Li_4SiO_4 material, because the addition of steam maybe enhances the mobility of Li^+ and O^{2-} [27,83], thus the resistance of diffusion is reduced, so the CO_2 absorption capacity of Li_4SiO_4 is enhanced by steam.

5.1.3. Gas Contaminants

NO_x and SO_2 are common gas contaminants which have done great harm to the environment and people's health. Thus, the effects of NO_x and SO_2 in the flue gas on the CO_2 absorption by Li_4SiO_4 material should be considered. The effects of NO_x and SO_2 on the CO_2 absorption performance of Li_4SiO_4 material could be great despite of their minor contents [82].

Puccini et al. [82] performed CO_2 absorption tests in an atmosphere of 4 vol.% CO_2 and various concentrations of NO, and the results showed that NO in the absorption atmosphere does not show a harmful effect on the CO_2 absorption capacity of Li_4SiO_4 material. Furthermore, when the concentration of SO_2 in the absorption atmosphere increased from 0 to 2000 ppm, the weight change of Li_4SiO_4 material increased with the increase of SO_2 concentration, but the regeneration performance of Li_4SiO_4 material in the presence of SO_2 was worse compared with that in the absence of SO_2. Additionally, the cyclic CO_2 absorption performance of Li_4SiO_4 material was negatively influenced in the presence of SO_2 under absorption and regeneration atmospheres [71]. The authors ascribed this phenomenon to the nonreversible reaction between SO_2 and Li_4SiO_4, as shown in Equations (12) and (13):

$$Li_4SiO_4 + SO_2 \rightarrow Li_2SO_3 + Li_2SiO_3 \tag{12}$$

$$Li_2SiO_3 + SO_2 \rightarrow Li_2SO_4 + SiO \tag{13}$$
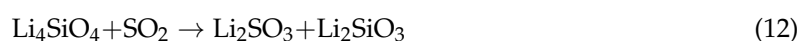
The formation of Li_2SO_3 and Li_2SO_4 prevented the regeneration of the materials, indicating that the presence of SO_2 in the absorption atmosphere has an adverse effect on the absorption performance of Li_4SiO_4 material [82]. In general, NO had no negative impact on the CO_2 absorption property of Li_4SiO_4 materials, while SO_2 had an adverse effect due to the formation of the irreversible Li_2SO_3 and Li_2SO_4, so SO_2 must be scrubbed prior to the trapping of CO_2. However, the exact joint role and acting mechanism of NO and SO_2 in the process of CO_2 capture are still unknown, and the effects of other contaminants, like HCl or H_2S, on the CO_2 absorption by Li_4SiO_4 material are not clear, thus further research is necessary.

5.2. Reaction Temperature

As shown in Figure 4, the equilibrium temperatures of absorption and regeneration increase as the CO_2 partial pressure rises monotonously. In other words, each equilibrium temperature corresponds with a partial pressure of CO_2 in the absorption atmosphere. Essaki et al. [77] reported that when the absorption temperature of Li_4SiO_4 pellets provided by Toshiba varied from 400 to 600 °C in 5 vol.% CO_2, and results showed that weight increase at 500 °C was 20 wt.%, which was much higher than those at 400 °C and 600 °C. Additionally, Quinn et al. [81] reported that 625 °C was the most appropriate temperature for the absorption of Toshiba-provided Li_4SiO_4 pellets in a pure CO_2 atmosphere. This confirmed the conclusion that the equilibrium temperature of the reaction between Li_4SiO_4 and CO_2 rises with increasing CO_2 partial pressure.

Different kinds of Li_4SiO_4 materials accommodate diverse appropriate absorption temperatures. Qiao et al. [60] synthesized Li_4SiO_4 material from RHA and Li_2CO_3, and they found that the most suitable temperature for absorption was 650 °C in a pure CO_2, while Puccini et al. [78] reported that 580 °C was the optimum temperature for K-doped Li_4SiO_4 materials, and Wang et al. [30] pointed out that 575 °C was the most appropriate for the CO_2 absorption by Li_4SiO_4.

Temperature during the regeneration process also had a deep effect on CO_2 absorption performance on Li_4SiO_4 material. Ochoa-Fernández et al. [80] reported that the ratio and degree

of regeneration increased when the regeneration temperature rose from 525 to 575 °C. This indicates that a higher regeneration temperature is possibly advantageous for the regeneration of Li_4SiO_4 material, while too high a regeneration temperature intensifies the sintering of the material, which is extremely harmful.

6. Application of Li_4SiO_4 Material in Sorption-Enhanced Hydrogen Production

Sorption-enhanced hydrogen production is one of the most important applications of Li_4SiO_4 material as a CO_2 acceptor, which mainly consists of sorption-enhanced steam methane reforming (SE-SMR) and sorption-enhance steam ethanol reforming (SE-SER). Overall reactions of SE-SMR and SE-SER are shown in Equations (14) and (15), respectively:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{14}$$

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{15}$$
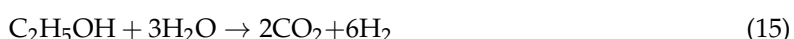
In the SE-SMR and SE-SER processes, in situ CO_2 removal of Li_4SiO_4 material as the CO_2 acceptor shifts the reaction equilibrium to hydrogen production, and exothermal absorption of CO_2 by the Li_4SiO_4 material provides heat for reforming, thus high hydrogen yield can be achieved.

Rusten et al. [84] conducted SE-SMR with CO_2 absorption by Li_4SiO_4 material in a fixed bed reactor at 848 K and 2 MPa, and syngas with the hydrogen concentration of 87% was obtained, which was higher than that obtained when Li_2ZrO_3 was used as a CO_2 acceptor. Essaki et al. [85] introduced commercial Li_4SiO_4 pellets into SE-SMR process, and the experiments were carried out on a vertical furnace. It was reported that methane conversion at 550 °C was 80%, and hydrogen concentration reached 93.6 vol.% in syngas. The performance of Li_4SiO_4 pellets in the SE-SER process was also tested, and the results showed that the concentrations of hydrogen and CO in syngas were higher than 99 vol.% and less than 0.12 vol.%, respectively, indicating that Li_4SiO_4 pellets were promising as the CO_2 acceptor for the SE-SER process [86]. Zhang et al. [42] reported K_2CO_3-doped Li_4SiO_4 material coupled well with the Ni/γ-Al_2O_3 catalyst, and hydrogen concentration in the syngas was higher than 95 vol.%. In addition, they found that homogeneous distribution of Li_4SiO_4 material and catalyst led to higher hydrogen concentration in the syngas.

It can be concluded from the studies above that hydrogen yield and concentration were mainly dependent on the performance of Li_4SiO_4 materials, thus Li_4SiO_4 materials with superior CO_2 absorption performance should be investigated. Additionally, Li_4SiO_4 materials may be applicable to various sorption-enhanced hydrogen production, and raw materials for gasification could be biomass, sludge, coal, etc.

7. Density Functional Theory Studies on Li_4SiO_4 Material

Duan et al. [87] studied CO_2 absorption performance on monoclinic and triclinic phases of Li_4SiO_4 using density functional theory, and they found that the thermodynamic properties of the two phases were similar to each other. The calculation results showed that reaction heat of the reaction between Li_4SiO_4 and CO_2 was consistent with the experimental data. Kong et al. [88] reported that the (0 1 0) plane was the most stable low-Miller index plane of Li_4SiO_4, and the adsorption and dissociation behaviors of molecular H_2O on the Li_4SiO_4 (0 1 0) plane were investigated. They found that molecular H_2O was more inclined to be absorbed on O atoms on the surface.

8. Conclusions

Research progress of Li_4SiO_4 materials for CO_2 capture in energy production processes, including hydrogen plants based on sorption-enhanced reforming and fossil fuel-fired power plants, were reviewed in this paper. Thermodynamic and kinetic studies on the preparation and CO_2 absorption of Li_4SiO_4 material were demonstrated, and the diffusion of CO_2 and ions through the product layer seemed to be the limiting step for CO_2 absorption by Li_4SiO_4 material. Since Li_4SiO_4

material prepared by the traditional solid-state reaction method only achieved low CO_2 absorption capacity, methods to enhance the CO_2 absorption performance of Li_4SiO_4 material were illustrated. Introducing a solid solution and molten salts could reduce the diffusion resistance in the product layer, and using hydration, ball milling, or organic precursors could increase the contact area of CO_2 and Li_4SiO_4, which is beneficial for CO_2 absorption by Li_4SiO_4 material. The sol-gel method seemed to be most appropriate for preparation of Li_4SiO_4 material, which is beneficial for the formation of porous structure. The effects of gas contaminants and reaction conditions on CO_2 absorption performance of Li_4SiO_4 material and the applications of Li_4SiO_4 material in the sorption-enhanced hydrogen production process were summarized. In view of the current studies reviewed in this work, potential research thoughts and trends are suggested as follows:

(i) Most of the laboratory experiments were carried out on TGA or fixed-bed reactors, while fluidized bed was the common equipment in practical application for the absorption of CO_2 under most energy production conditions. Additionally, powdery Li_4SiO_4 materials could not create effective fluidization, while studies on the performance of pelletized Li_4SiO_4 materials were insufficient. As a result, more focus should be attached to the CO_2 absorption performance of pelletized Li_4SiO_4 material in fluidized bed reactors.

(ii) Application of Li_4SiO_4 materials on sorption-enhanced hydrogen production is an important aspect, and hydrogen yield and concentration were considerable, while fewer studies involved this area. Additionally, CO_2 absorption performance of Li_4SiO_4 materials in realistic sorption-enhanced hydrogen production conditions (i.e., low CO_2 concentration in the presence of steam) deserves to be studied.

(iii) Preparation cost of Li_4SiO_4 materials is the main problem that limits its industrial application, thus many studies investigated the feasibility of silicon-containing solid wastes as a silicon precursor. However, the main factor that controls the cost of Li_4SiO_4 materials is the expensive lithium precursor. As a result, it is suggested that lithium-containing wastes can be tested for the possibility as a lithium precursor, and Li_4SiO_4 materials prepared from inexpensive lithium-containing wastes may be promising for large-scale CO_2 absorption.

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References

1. Fiore, A.D.; Alterio, V.; Monti, S.M.; Simone, G.D.; Ambrosio, K.D. Thermostable carbonic anhydrases in biotechnological applications. *Int. J. Mol. Sci.* **2015**, *16*, 15456–15480. [CrossRef] [PubMed]
2. Hu, Y.H. Advances in Catalysts for CO_2 Reforming of Methane. *ACS Symp. Ser.* **2010**, *1056*, 155–174.
3. Ma, X.; Li, Y.; Shi, L.; He, Z.; Wang, Z. Fabrication and CO_2 capture performance of magnesia-stabilized carbide slag by by-product of biodiesel during calcium looping process. *Appl. Energy* **2016**, *168*, 85–95. [CrossRef]
4. Kezhen, Y.; James, G.D.; Zimmerman, W.B. Periodic CO_2 Dosing Strategy for Dunaliella salina Batch Culture. *Int. J. Mol. Sci.* **2015**, *16*, 11509–11521.
5. Kierzkowska, A.M.; Pacciani, R.; Müller, C.R. CaO-Based CO_2 Sorbents: From Fundamentals to the Development of New, Highly Effective Materials. *Chemsuschem* **2013**, *6*, 1130–1148. [CrossRef] [PubMed]
6. Kato, M.; Essaki, K.; Nakagawa, K.; Suyama, Y.; Terasaka, K. CO_2 absorption properties of lithium ferrite for application as a high-temperature CO_2 absorbent. *J. Ceram. Soc. Jpn.* **2005**, *113*, 684–686. [CrossRef]
7. Lara-Garcia, H.A.; Ramírez-Moreno, M.J.; Ortiz-Landeros, J.; Pfeiffer, H. CO_2 chemisorption in Li_2CuO_2 microstructurally modified by ball milling process: Study performed with different physicochemical CO_2 capture conditions. *RSC Adv.* **2016**, *6*, 57880–57888. [CrossRef]
8. Yamaguchi, K.; Murayama, N.; Shibata, J. Absorption and release of carbon dioxide with various metal oxides and hydroxides. *Mater. Trans.* **2007**, *48*, 2739–2742. [CrossRef]

9.　Kato, M.; Yoshikawa, S.; Nakagawa, K. Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. *J. Mater. Sci. Lett.* **2002**, *21*, 485–487. [CrossRef]

10.　Romero-Ibarra, I.C.; Durán-Muñoz, F.; Pfeiffer, H. Influence of the K-, Na- and K-Na-carbonate additions during the CO_2 chemisorption on lithium oxosilicate (Li_8SiO_6). *Greenh. Gases Sci. Technol.* **2014**, *4*, 145–154. [CrossRef]

11.　Durán-Muñoz, F.; Romero-Ibarra, I.C.; Pfeiffer, H. Analysis of the CO_2 chemisorption reaction mechanism in lithium oxosilicate (Li_8SiO_6): A new option for high-temperature CO_2 capture. *J. Mater. Chem. A* **2013**, *1*, 3919–3925. [CrossRef]

12.　Spataru, C.I.; Ianchis, R.; Petcu, C.; Nistor, C.L.; Purcar, V.; Trica, B.; Nitu, S.G.; Somoghi, R.; Alexandrescu, E.; Oancea, F. Synthesis of non-toxic silica particles stabilized by molecular complex oleic-acid/sodium oleate. *Int. J. Mol. Sci.* **2016**, *17*, 1936. [CrossRef] [PubMed]

13.　Hua, R.; Chao, Z.; Zhao, L.; Wei, Y.; Song, E. Emodin-loaded magnesium silicate hollow nanocarriers for anti-angiogenesis treatment through inhibiting VEGF. *Int. J. Mol. Sci.* **2014**, *15*, 16936–16948.

14.　Bretado, M.E.; Guzmán Velderrain, V.; Lardizábal Gutiérrez, D.; Collins-Martínez, V.; Ortiz, A.L. A new synthesis route to Li_4SiO_4 as CO_2 catalytic/sorbent. *Catal. Today* **2005**, *107–108*, 863–867. [CrossRef]

15.　Arstad, B.; Prostak, J.; Blom, R. Continuous hydrogen production by sorption enhanced steam methane reforming (SE-SMR) in a circulating fluidized bed reactor: Sorbent to catalyst ratio dependencies. *Chem. Eng. J.* **2012**, *189–190*, 413–421. [CrossRef]

16.　Rout, K.R.; Jakobsen, H.A. A numerical study of pellets having both catalytic- and capture properties for SE-SMR process: Kinetic- and product layer diffusion controlled regimes. *Fuel Process. Technol.* **2013**, *106*, 231–246. [CrossRef]

17.　Wang, J.; Wang, Y.; Jakobsen, H.A. The modeling of circulating fluidized bed reactors for SE-SMR process and sorbent regeneration. *Chem. Eng. Sci.* **2014**, *108*, 57–65. [CrossRef]

18.　Wang, Y.; Liu, J. The influencing factor for CO_2 absorption of Li_4SiO_4 at high temperature. In Proceedings of the Third International Conference on Measuring Technology and Mechatronics Automation, Shangshai, China, 6–7 January 2011; pp. 839–841.

19.　Yang, X.; Liu, W.; Sun, J.; Hu, Y.; Wang, W.; Chen, H.; Zhang, Y.; Li, X.; Xu, M. Preparation of novel Li_4SiO_4 sorbents with superior performance at low CO_2 concentration. *ChemSusChem* **2016**, *9*, 1607–1613. [CrossRef] [PubMed]

20.　Wang, K.; Guo, X.; Zhao, P.; Wang, F.; Zheng, C. High temperature capture of CO_2 on lithium-based sorbents from rice husk ash. *J. Hazard. Mater.* **2011**, *189*, 301–307. [CrossRef] [PubMed]

21.　Xiang, M.; Zhang, Y.; Hong, M.; Liu, S.; Zhang, Y.; Liu, H.; Gu, C. CO_2 absorption properties of Ti- and Na-doped porous Li_4SiO_4 prepared by a sol–gel process. *J. Mater. Sci.* **2015**, *50*, 4698–4706. [CrossRef]

22.　Tang, T.; Zhang, Z.; Meng, J.B.; Luo, D.L. Synthesis and characterization of lithium silicate powders. *Fusion Eng. Des.* **2009**, *84*, 2124–2130. [CrossRef]

23.　Carella, E.; Hernandez, M. High lithium content silicates: A comparative study between four routes of synthesis. *Ceram. Int.* **2014**, *40*, 9499–9508. [CrossRef]

24.　Xu, H.; Cheng, W.; Jin, X.; Wang, G.; Lu, H.; Wang, H.; Chen, D.; Fan, B.; Hou, T.; Zhang, R. Effect of the particle size of quartz powder on the synthesis and CO_2 Absorption properties of Li_4SiO_4 at high temperature. *Ind. Eng. Chem. Res.* **2013**, *52*, 1886–1891. [CrossRef]

25.　Subha, P.V.; Nair, B.N.; Hareesh, P.; Mohamed, A.P.; Yamaguchi, T.; Warrier, K.G.K.; Hareesh, U.S. Enhanced CO_2 absorption kinetics in lithium silicate platelets synthesized by a sol-gel approach. *J. Mater. Chem. A* **2014**, *2*, 12792–12798. [CrossRef]

26.　López Ortiz, A.; Escobedo Bretado, M.A.; Guzmán Velderrain, V.; Meléndez Zaragoza, M.; Salinas Gutiérrez, J.; Lardizábal Gutiérrez, D.; Collins-Martínez, V. Experimental and modeling kinetic study of the CO_2 absorption by Li_4SiO_4. *Int. J. Hydrogen Energy* **2014**, *39*, 16656–16666. [CrossRef]

27.　Zhang, Q.; Han, D.; Liu, Y.; Qian, Y.; Zhu, Z. Analysis of CO_2 sorption/desorption kinetic behaviors and reaction mechanisms on Li_4SiO_4. *AIChE J.* **2013**, *59*, 901–911.

28.　Rodríguez-Mosqueda, R.; Pfeiffer, H. Thermokinetic analysis of the CO_2 chemisorption on Li_4SiO_4 by using different gas flow rates and particle sizes. *J. Phys. Chem. A* **2010**, *114*, 4535–4541. [CrossRef] [PubMed]

29.　Kim, H.; Jang, H.D.; Choi, M. Facile synthesis of macroporous Li_4SiO_4 with remarkably enhanced CO_2 adsorption kinetics. *Chem. Eng. J.* **2015**, *280*, 132–137. [CrossRef]

30. Wang, K.; Zhou, Z.; Zhao, P.; Yin, Z.; Su, Z.; Sun, J. Synthesis of a highly efficient Li_4SiO_4 ceramic modified with a gluconic acid-based carbon coating for high-temperature CO_2 capture. *Appl. Energy* **2016**, *183*, 1418–1427. [CrossRef]

31. Zagorowsky, G.; Prikhod'ko, G.; Ogenko, V.; Koval'chuk, G. Investigation of kinetics of solid-phase synthesis of lithium orthosilicate. *J. Therm. Anal. Calorim.* **1999**, *55*, 699–705. [CrossRef]

32. Xiang, M.; Zhang, Y.; Zhang, Y.; Liu, W.; Wang, C.; Yu, Y. Reaction kinetics for the synthesis of li_4sio_4 by solid state reaction from Li_2SiO_3 and Li_2CO_3 for tritium breeder. *J. Fusion Energy* **2016**, *35*, 652–659. [CrossRef]

33. Yin, Z.; Wang, K.; Zhao, P.; Tang, X. Enhanced CO_2 Chemisorption properties of Li_4SO_4, Using a water hydration-calcination technique. *Ind. Eng. Chem. Res.* **2016**, *55*, 1142–1146. [CrossRef]

34. Romero-Ibarra, I.C.; Ortiz-Landeros, J.; Pfeiffer, H. Microstructural and CO_2 chemisorption analyses of Li_4SiO_4: Effect of surface modification by the ball milling process. *Thermochim. Acta* **2013**, *567*, 118–124. [CrossRef]

35. Kanki, K.; Maki, H.; Mizuhata, M. Carbon dioxide absorption behavior of surface-modified lithium orthosilicate/potassium carbonate prepared by ballmilling. *Int. J. Hydrogen Energy* **2016**, *41*, 18893–18899. [CrossRef]

36. Zhao, L.; Long, X.; Chen, X.; Xiao, C.; Gong, Y.; Guan, Q.; Li, J.; Xie, L.; Chen, X.; Peng, S. Design, synthesis and characterization of the advanced tritium breeder: $Li_{4+x}Si_{1-x}Al_xO_4$ ceramics. *J. Nucl. Mater.* **2015**, *467*, 911–916. [CrossRef]

37. Ortiz-Landeros, J.; Romero-Ibarra, I.C.; Gómez-Yáñez, C.; Lima, E.; Pfeiffer, H. $Li_{4+x}(Si_{1-x}Al_x)O_4$ solid solution mechanosynthesis and kinetic analysis of the CO_2 chemisorption process. *J. Phys. Chem. C* **2013**, *117*, 6303–6311. [CrossRef]

38. Ortiz-Landeros, J.; Gómez-Yáñez, C.; Palacios-Romero, L.M.; Lima, E.; Pfeiffer, H. Structural and thermochemical chemisorption of CO_2 on $Li_{4+x}(Si_{1-x}Al_x)O_4$ and $Li_{4-x}(Si_{1-x}V_x)O_4$ solid solutions. *J. Phys. Chem. A* **2012**, *116*, 3163–3171. [CrossRef] [PubMed]

39. Seggiani, M.; Puccini, M.; Vitolo, S. High-temperature and low concentration CO_2 sorption on Li_4SiO_4 based sorbents: Study of the used silica and doping method effects. *Int. J. Greenh. Gas Control* **2011**, *5*, 741–748. [CrossRef]

40. Seggiani, M.; Puccini, M.; Vitolo, S. Alkali promoted lithium orthosilicate for CO_2 capture at high temperature and low concentration. *Int. J. Greenh. Gas Control* **2013**, *17*, 25–31. [CrossRef]

41. Zhang, S.; Zhang, Q.; Wang, H.; Ni, Y.; Zhu, Z. Absorption behaviors study on doped Li_4SiO_4 under a humidified atmosphere with low CO_2 concentration. *Int. J. Hydrogen Energy* **2014**, *39*, 17913–17920. [CrossRef]

42. Zhang, Q.; Shen, C.; Zhang, S.; Wu, Y. Steam methane reforming reaction enhanced by a novel K_2CO_3-doped Li_4SiO_4 sorbent: Investigations on the sorbent and catalyst coupling behaviors and sorbent regeneration strategy. *Int. J. Hydrogen Energy* **2016**, *41*, 4831–4842. [CrossRef]

43. Yang, X.; Liu, W.; Sun, J.; Hu, Y.; Wang, W.; Chen, H.; Zhang, Y.; Li, X.; Xu, M. Alkali-doped lithium orthosilicate sorbents for carbon dioxide capture. *Chemsuschem* **2016**, *9*, 2480–2487. [CrossRef] [PubMed]

44. Wang, Y.; Qi, L.; Dai, K. Effect of Na-doping on CO_2 absorption of Li_4SiO_4. *Acta Phys.-Chim. Sin.* **2006**, *22*, 860–863.

45. Wang, K.; Zhou, Z.; Zhao, P.; Yin, Z.; Su, Z.; Sun, J. Molten sodium-fluoride-promoted high-performance Li_4SiO_4-based CO_2 sorbents at low CO_2 concentrations. *Appl. Energy* **2017**, *204*, 403–412. [CrossRef]

46. Wang, K.; Li, W.; Yin, Z.; Zhou, Z.; Zhao, P. High-capacity Li_4SiO_4-based CO_2 sorbents via a facile hydration-nacl doping technique. *Energy Fuels* **2017**, *31*, 6257–6265. [CrossRef]

47. Olivares-Marín, M.; Drage, T.C.; Maroto-Valer, M.M. Novel lithium-based sorbents from fly ashes for CO_2 capture at high temperatures. *Int. J. Greenh. Gas Control* **2010**, *4*, 623–629. [CrossRef]

48. Mejía-Trejo, V.L.; Fregoso-Israel, E.; Pfeiffer, H. Textural, Structural, and CO_2 chemisorption effects produced on the lithium orthosilicate by its doping with sodium ($Li_{4-x}Na_xSiO_4$). *Chem. Mater.* **2008**, *20*, 7171–7176. [CrossRef]

49. Wang, K.; Yin, Z.; Zhao, P.; Zhou, Z.; Su, Z.; Sun, J. Development of metallic element-stabilized Li_4SiO_4 sorbents for cyclic CO_2 capture. *Int. J. Hydrogen Energy* **2016**, *42*, 4224–4232. [CrossRef]

50. Subha, P.V.; Nair, B.N.; Hareesh, P.; Mohamed, A.P.; Yamaguchi, T.; Warrier, K.G.K.; Hareesh, U.S. CO_2 absorption studies on mixed alkali orthosilicates containing rare-earth second-phase additives. *J. Phys. Chem. C* **2015**, *119*, 5319–5326. [CrossRef]

51. Chen, X.; Xiong, Z.; Qin, Y.; Gong, B.; Tian, C.; Zhao, Y.; Zhang, J.; Zheng, C. High-temperature CO_2 sorption by Ca-doped Li_4SiO_4 sorbents. *Int. J. Hydrogen Energy* **2016**, *41*, 13077–13085. [CrossRef]

52. Wang, K.; Yin, Z.; Zhao, P. Synthesis of macroporous Li_4SiO_4 via a citric acid-based sol–gel route coupled with carbon coating and its CO_2 chemisorption properties. *Ceram. Int.* **2016**, *42*, 2990–2999. [CrossRef]

53. Jun, S.; Joo, S.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Ohsuna, T.; Terasaki, O. Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure. *J. Am. Chem. Soc.* **2000**, *122*, 10712–10713. [CrossRef]

54. Jeoung, S.; Lee, J.H.; Kim, H.Y.; Moon, H.R. Effects of porous carbon additives on the CO_2 absorption performance of lithium orthosilicate. *Thermochim. Acta* **2016**, *637*, 31–37. [CrossRef]

55. Wang, K.; Wang, X.; Zhao, P.; Guo, X. High temperature capture of CO_2 on lithium-based sorbents prepared by a water-based sol-gel technique. *Chem. Eng. Technol.* **2014**, *37*, 1552–1558. [CrossRef]

56. Weng, D.; Wan, J. Synthesis and adsorption process of lithium taking used as high-temperature CO_2 sorbents. *Sci. Technol. Rev.* **2011**, *29*, 25–30.

57. Lee, J.H.; Moon, B.; Kim, T.K.; Jeoung, S.; Moon, H.R. Thermal conversion of a tailored metal-organic framework into lithium silicate with an unusual morphology for efficient CO_2 capture. *Dalton Trans.* **2015**, *44*, 15130–15134. [CrossRef] [PubMed]

58. Wang, K.; Zhang, G.; Zhao, P.; Wang, J. Effects of calcination temperature on the structure and CO_2 sorption properties of Li_4SiO_4 sorbents from Rice Husk Ash. In Proceedings of the International Conference on Mechatronics, Electronic, Industrial and Control Engineering, Shenyang, China, 15–17 November 2014; pp. 760–763.

59. Wang, K.; Zhao, P.; Guo, X.; Li, Y.; Han, D.; Chao, Y. Enhancement of reactivity in Li_4SiO_4-based sorbents from the nano-sized rice husk ash for high-temperature CO_2 capture. *Energy Convers. Manag.* **2014**, *81*, 447–454. [CrossRef]

60. Qiao, X.; Lisbona, P.; Guo, X.; Lara, Y.; Romeo, L.M. Energy assessment of ethanol-enhanced steam reforming by means of Li_4SiO_4 carbon capture. *Energy Fuels* **2016**, *30*, 1879–1886. [CrossRef]

61. Abdullah, M.; Jamaludin, L.; Hussin, K.; Bnhussain, M.; Ghazali, C.; Ahmad, M. Fly Ash Porous Material using Geopolymerization Process for High Temperature Exposure. *Int. J. Mol. Sci.* **2012**, *13*, 4388–4395. [CrossRef] [PubMed]

62. Abdullah, M.; Hussin, K.; Bnhussain, M.; Ismail, K.; Yahya, Z.; Razak, R. Fly Ash-based Geopolymer Lightweight Concrete Using Foaming Agent. *Int. J. Mol. Sci.* **2012**, *13*, 7186–7198. [CrossRef] [PubMed]

63. Sanna, A.; Ramli, I.; Mercedes Maroto-Valer, M. Development of sodium/lithium/fly ash sorbents for high temperature post-combustion CO_2 capture. *Appl. Energy* **2015**, *156*, 197–206. [CrossRef]

64. Shan, S.; Jia, Q.; Jiang, L.; Wang, Y. Effect of different silicon sources on CO_2 absorption properties of Li_4SiO_4 at high temperature. *Adv. Mater. Res.* **2011**, *213*, 515–518. [CrossRef]

65. Shan, S.; Jia, Q.; Jiang, L.; Li, Q.; Wang, Y.; Peng, J. Novel Li_4SiO_4-based sorbents from diatomite for high temperature CO_2 capture. *Ceram. Int.* **2013**, *39*, 5437–5441. [CrossRef]

66. Shan, S.; Jia, Q.; Jiang, L.; Li, Q.; Wang, Y.; Peng, J. Preparation and kinetic analysis of Li_4SiO_4 sorbents with different silicon sources for high temperature CO_2 capture. *Chin. Sci. Bull.* **2012**, *57*, 2475–2479. [CrossRef]

67. Shan, S.; Li, S.; Jia, Q.; Jiang, L.; Wang, Y.; Peng, J. Impregnation Precipitation Preparation and Kinetic Analysis of Li_4SiO_4-Based Sorbents with Fast CO_2 Adsorption Rate. *Ind. Eng. Chem. Res.* **2013**, *52*, 6941–6945. [CrossRef]

68. Joussein, E.; Petit, S.; Churchman, J.; Theng, B.; Righi, D.; Delvaux, B. Halloysite clay minerals—A review. *Clay Miner.* **2005**, *40*, 383–426. [CrossRef]

69. Niu, M.; Li, X.; Ouyang, J.; Yang, H. Lithium orthosilicate with halloysite as silicon source for high temperature CO_2 capture. *RSC Adv.* **2016**, *6*, 44106–44112. [CrossRef]

70. Venegas, M.J.; Fregoso-Israel, E.; Escamilla, R.; Pfeiffer, H. Kinetic and reaction mechanism of CO_2 sorption on Li_4SiO_4: Study of the particle size effect. *Ind. Eng. Chem. Res.* **2007**, *46*, 2407–2412. [CrossRef]

71. Pacciani, R.; Torres, J.; Solsona, P.; Coe, C.; Quinn, R.; Hufton, J.; Golden, T.; Vega, L.F. Influence of the concentration of CO_2 and SO_2 on the absorption of CO_2 by a lithium orthosilicate-based absorbent. *Environ. Sci. Technol.* **2011**, *45*, 7083–7088. [CrossRef] [PubMed]

72. Kato, M.; Nakagawa, K.; Essaki, K.; Maezawa, Y.; Takeda, S.; Kogo, R.; Hagiwara, Y. Novel CO_2 absorbents using lithium-containing oxide. *Int. J. Appl. Ceram. Technol.* **2005**, *2*, 467–475. [CrossRef]

73. Essaki, K.; Kato, M.; Nakagawa, K. CO_2 removal at high temperature using packed bed of lithium silicate pellets. *J. Ceram. Soc. Jpn.* **2006**, *114*, 739–742. [CrossRef]

74. Puccini, M.; Seggiani, M.; Vitolo, S. Lithium silicate pellets for CO_2 capture at high temperature. *Chem. Eng. Trans.* **2003**, *35*, 373–378.

75. Puccini, M.; Stefanelli, E.; Seggiani, M.; Vitolo, S. Removal of CO_2 from flue gas at high temperature using novel porous solids. *Chem. Eng. Trans.* **2016**, *47*, 139–144.

76. Aaron, D.; Tsouris, C. Separation of CO_2 from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40*, 321–348. [CrossRef]

77. Essaki, K.; Kato, M.; Uemoto, H. Influence of temperature and CO_2 concentration on the CO_2 absorption properties of lithium silicate pellets. *J. Mater. Sci.* **2005**, *40*, 5017–5019. [CrossRef]

78. Puccini, M.; Seggiani, M.; Vitolo, S. CO_2 capture at high temperature and low concentration on Li_4SiO_4 based sorbents. *Chem. Eng. Trans.* **2013**, *32*, 1279–1284.

79. Ochoa-Fernandez, E.; Rønning, M.; Yu, X.; Grande, T.; Chen, D. Compositional effects of nanocrystalline lithium zirconate on its CO_2 capture properties. *Ind. Eng. Chem. Res.* **2008**, *47*, 434–442. [CrossRef]

80. Ochoa-Fernández, E.; Zhao, T.; Rønning, M.; Chen, D. Effects of steam addition on the properties of high temperature ceramic CO_2 acceptors. *J. Environ. Eng.* **2009**, *135*, 397–403. [CrossRef]

81. Quinn, R.; Kitzhoffer, R.J.; Hufton, J.R.; Golden, T.C. A high temperature lithium orthosilicate-based solid absorbent for post combustion CO_2 capture. *Ind. Eng. Chem. Res.* **2012**, *51*, 9320–9327. [CrossRef]

82. Puccini, M.; Stefanelli, E.; Seggiani, M.; Vitolo, S. The effect of flue gas contaminants on CO_2 capture at high temperature by Li_4SiO_4- based sorbents. *Chem. Eng. Trans.* **2015**, *43*, 1093–1098.

83. Essaki, K.; Nakagawa, K.; Kato, M.; Uemoto, H. CO_2 absorption by lithium silicate at room temperature. *J. Ceram. Soc. Jpn.* **2004**, *37*, 772–777. [CrossRef]

84. Rusten, H.K.; Ochoa-Fernández, E.; Lindborg, H.; Chen, D.; Jakobsen, H.A. Hydrogen production by sorption-enhanced steam methane reforming using lithium oxides as CO_2-acceptor. *Ind. Eng. Chem. Res.* **2017**, *46*, 8729–8737. [CrossRef]

85. Essaki, K.; Muramatsu, T.; Kato, M. Effect of equilibrium shift by using lithium silicate pellets in methane steam reforming. *Int. J. Hydrogen Energy* **2008**, *33*, 4555–4559. [CrossRef]

86. Essaki, K.; Muramatsu, T.; Kato, M. Effect of equilibrium-shift in the case of using lithium silicate pellets in ethanol steam reforming. *Int. J. Hydrogen Energy* **2008**, *33*, 6612–6618. [CrossRef]

87. Duan, Y.; Parlinski, K. Density functional theory study of the structural, electronic, lattice dynamical, and thermodynamic properties of Li_4SiO_4 and its capability for CO_2 capture. *Phys. Rev. B* **2011**, *84*, 3382–3391. [CrossRef]

88. Kong, X.; Yu, Y.; Ma, S.; Gao, T.; Xiao, C.; Chen, X. Adsorption mechanism of H_2O molecule on the Li_4SiO_4 (0 1 0) surface from first principles. *Chem. Phys. Lett.* **2018**, *691*, 1–7. [CrossRef]