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]:

$$2\text{Li}_2\text{CO}_3 + \text{SiO}_2 \leftrightarrow \text{Li}_4\text{SiO}_4 + 2\text{CO}_2$$

(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$_4$SiO$_4$ at 500 to 600 °C, thus the gas, almost free of CO$_2$, is exhausted from the reactor. The generated Li$_2$SiO$_3$ and Li$_2$CO$_3$ are transported to the regeneration reactor, where Li$_4$SiO$_4$ 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.

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3
\]  

(2)

It can be calculated according to Equation (2) that the theoretical CO$_2$ absorption capacity of Li$_4$SiO$_4$ is 367 mg CO$_2$/g Li$_4$SiO$_4$, which is much higher than that of Li$_2$ZrO$_3$ (125 mg/g) [9].

Additionally, CO$_2$ absorption by Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ material prepared by the solid-state reaction method is low, which is mainly due to the smooth surface of pristine Li$_4$SiO$_4$ particles generated at high temperature, thus the surface area and pore volume of Li$_4$SiO$_4$ material are low, and the reaction between CO$_2$ and Li$_4$SiO$_4$ is limited [18]. Therefore, a large number of works have been conducted to improve the pore structure of Li$_4$SiO$_4$, 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$_4$SiO$_4$ 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$_4$SiO$_4$ material. In addition, thermodynamic and kinetic comprehension of the reaction between CO$_2$ and Li$_4$SiO$_4$ are illustrated, and strategies to enhance the cyclic CO$_2$ absorption performance of Li$_4$SiO$_4$ material are summarized. Additionally, applications of Li$_4$SiO$_4$ material in sorption-enhanced hydrogen production are reviewed, and studies on CO$_2$ absorption by Li$_4$SiO$_4$ material at the molecular scale are also reviewed briefly. Finally, the major drawback that hinders the large-scale application of Li$_4$SiO$_4$ material for CO$_2$ absorption is introduced.
2. Thermodynamics and Kinetics of CO₂ Absorption by Li₄SiO₄

2.1. Reaction Model for Synthesis of Li₄SiO₄

Li₄SiO₄ 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 Li₂CO₃ and SiO₂, which is shown in Figure 2. In the first step, Li₂CO₃ reacts with SiO₂ at their contact part, and a thin Li₂SiO₃ layer is formed. Li₂SiO₃ is the intermediate product, which continues to react with Li₂CO₃ to form Li₄SiO₄ eventually. Li₄SiO₄ and Li₂SiO₃ layers become thicker with the reaction, and internal SiO₂ is covered by the layers in the meantime. Thus, Li⁺ and O²⁻ must diffuse through the product layer before contacting with internal SiO₂, and it is the limited step that limiting the synthesis of Li₄SiO₄, because the diffusion process is much slower than the reaction. Consequently, alternative synthesis methods and precursors for the synthesis of Li₄SiO₄ have been reported, which will be discussed in the following section [24].

![Diagram of core-shell model for synthesis of Li₄SiO₄](image)

**Figure 2.** Core-shell model for synthesis of Li₄SiO₄ by the solid-state route [24].

2.2. Kinetic Study for CO₂ Absorption by Li₄SiO₄

Figure 3 shows the CO₂ absorption performance of Li₄SiO₄ materials prepared by the solid-state reaction method and the sol-gel method in a thermogravimetric analyzer (TGA) [25], and the CO₂ absorption amount (mg CO₂/g sorbent) was used to evaluate the CO₂ absorption capacity of Li₄SiO₄ materials, which is calculated according to Equation (3):

$$C_N = \frac{m_2 - m_1}{m_1}$$  \hspace{1cm} (3)

where \(C_N\) is the amount of CO₂ absorbed by the Li₄SiO₄ material, mg/g; \(N\) represents the number of cycles; \(m_1\) represents the initial mass of Li₄SiO₄ material, g; and \(m_2\) represents the mass of the sample during CO₂ absorption, mg. The CO₂ absorption stage of Li₄SiO₄ occurs at temperatures lower than 400 °C, and the CO₂ absorption rate increases suddenly when the temperature reaches around 500–600 °C. Weight losses of two Li₄SiO₄ materials are observed when the temperature exceeds 720 °C, indicating the reaction converts to the regeneration of Li₄SiO₄ materials, and the regeneration reaction is much faster than the absorption process. As shown in Figure 3, the CO₂ absorption capacity of Li₄SiO₄ 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.
which covers the internal Li$_2$O.

2.3. Thermodynamic Study for CO$_2$ Capture by Li$_4$SiO$_4$

Figure 4 shows the equilibrium partial pressure of CO$_2$ over Li$_4$SiO$_4$ material as a function of temperature [26], and the maximum temperature of CO$_2$ absorption by Li$_4$SiO$_4$ 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$_4$SiO$_4$ material can be determined by the CO$_2$ partial pressure, and CO$_2$ absorption by Li$_4$SiO$_4$ material occurs when the temperature is lower than the equilibrium temperature, otherwise Li$_4$SiO$_4$ material is regenerated. As a result, CO$_2$ absorption and regeneration regions of Li$_4$SiO$_4$ 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$_4$SiO$_4$ [26].

2.4. Reaction Mechanism and Reaction Model of CO$_2$ Capture by Li$_4$SiO$_4$

The double-shell mechanism is regarded as the most appropriate model for the reaction between CO$_2$ and Li$_4$SiO$_4$ [27], which is schematically illustrated in Figure 5. At the beginning of the reaction, CO$_2$ molecules react with Li$_4$SiO$_4$ particles to generate a double shell composed of Li$_2$CO$_3$ and Li$_2$SiO$_3$, which covers the internal Li$_4$SiO$_4$. 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$_4$SiO$_4$. 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.

![Double-shell mechanism of Li₄SiO₄ material for CO₂ absorption and regeneration](image)

Figure 5. Double-shell mechanism of Li₄SiO₄ material for CO₂ absorption and regeneration [27].

TGA curves of CO₂ absorption by Li₄SiO₄ at various temperatures are present in Figure 6, and weight gain of Li₄SiO₄ was used to evaluate its CO₂ absorption performance, which can be calculated according to Equation (4):

\[
W_N = (C_N + 1) \times 100\% \tag{4}
\]

where \(W_N\) is the weight gain of Li₄SiO₄ material during the \(N\)th cycles, wt.%; and \(C_N\) is the amount of CO₂ absorbed by Li₄SiO₄ material during the \(N\)th cycles, mg/g. CO₂ absorption capacity of Li₄SiO₄ increases with the temperature rising from 460 to 560 °C. Li₄SiO₄ shows a fast CO₂ absorption stage in a short time and a slow CO₂ 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):

\[
y = A \exp^{-k_1 t} + B \exp^{-k_2 t} + C \tag{5}
\]

where \(y\) represents the weight gain of Li₄SiO₄ material after CO₂ 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].
where \( \alpha \) 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\(_4\)SiO\(_4\). Zhang et al. [27] reported that the Avrami–Erofeev model suited the regeneration process of Li\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\).

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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\).

Table 1 presents the kinetic parameters of the double exponential model fitted to the reaction between CO\(_2\) and Li\(_4\)SiO\(_4\) [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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) [29,30].

![Figure 6. Isotherms obtained in a CO\(_2\) atmosphere at various temperatures [28].](image)

Table 1. Kinetic parameters of reaction between Li\(_4\)SiO\(_4\) and CO\(_2\) for double exponential model [28].

| T (°C) | \( k_1 \) (sec\(^{-1}\)) | \( k_2 \) (sec\(^{-1}\)) | \( A \)  | \( B \)  | \( C \)  |
|-------|-----------------|-----------------|-------|-------|-------|
| 460   | \( 8.0 \times 10^{-4} \) | \( 1.4 \times 10^{-4} \) | \(-3.248\) | \(-5.560\) | 108.8 |
| 480   | \( 1.72 \times 10^{-3} \) | \( 1.3 \times 10^{-4} \) | \(-3.467\) | \(-7.821\) | 111.2 |
| 500   | \( 2.96 \times 10^{-3} \) | \( 1.7 \times 10^{-4} \) | \(-3.716\) | \(-8.668\) | 112.3 |
| 520   | \( 4.26 \times 10^{-3} \) | \( 2.1 \times 10^{-4} \) | \(-4.231\) | \(-8.711\) | 112.8 |
| 540   | \( 4.17 \times 10^{-3} \) | \( 2.1 \times 10^{-4} \) | \(-4.231\) | \(-9.003\) | 113.8 |
| 560   | \( 4.37 \times 10^{-3} \) | \( 2.5 \times 10^{-4} \) | \(-9.017\) | \(-8.911\) | 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):

\[
\frac{da}{dt} = Kn(1-a)\left[-\ln(1-a)\right]^{(n-1)/n} \tag{6}
\]

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

where \( a \) 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 \( \ln [-\ln(1-a)] \) 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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\).
Figure 7. Fit of kinetic experimental data by the Avrami–Erofeev model [27].

3. Synthesis of Li4SiO4 Materials with Superior Cyclic Absorption/Regeneration Performance

It is clear that Li4SiO4 material synthesized by the solid-state reaction method from SiO2 and Li2CO3 achieves low CO2 absorption capacity, due to the low porosity of Li4SiO4 generated at high temperatures during the preparation. Thus, the CO2 absorption capacity of Li4SiO4 decreases rapidly with the number of cycles, which is the main disadvantage of Li4SiO4 material in industrial applications. The various methods have been reported to enhance the cyclic performance of Li4SiO4 material prepared by solid-state reaction method, such as hydration [33] and ball milling [34,35]. The strategies to enhance the cyclic performance of Li4SiO4 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 Li4SiO4 Prepared by Solid-State Reaction

As discussed above, high temperature during the preparation by the solid-state reaction method of Li4SiO4 leads to sintering, and the core of Li4SiO4 usually cannot react with CO2. Thus, Yin et al. [33] proposed a hydration process to improve the pore structure of Li4SiO4 material. First, Li4SiO4 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 CO2 absorption capacity of Li4SiO4 was obtained by hydration process.

Romero-Ibarra et al. [34] used the ball milling process to modify the surface properties of Li4SiO4 material, and they found that the ball milling process decreased the particle size and improved the surface area of Li4SiO4 material. Kanki et al. [35] reported that the ball milling process could promote CO2 absorption of Li4SiO4 material at lower temperatures, and longer ball milling duration led to higher CO2 absorption capacity. Additionally, the doping of K2CO3 in Li4SiO4 material improved its CO2 absorption capacity under short ball milling duration.

3.2. Doping of Solid Solutions or Molten Salts

3.2.1. Solid Solutions

The CO2 absorption rate of Li4SiO4 material is mainly controlled by the diffusion of ions and CO2. Zhao et al. [36] reported that solid solution usually formed with the doping of Al2O3 during solid-state preparation, thus increased oxygen vacancies could promote the diffusion in the product layer. Ortiz-Landeros et al. [37] reported that Al2O3 addition and ball milling could extend the range of CO2 absorption temperature. In addition, Ortiz-Landeros et al. [38] compared Li4+x(Si1−xAlx)O4 with Li4−x(Si1−xVx)O4 as the solid solutions, and the results showed that diffusion resistance of CO2
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$_4$SiO$_4$ material for CO$_2$ absorption could be resolved. The CO$_2$ absorption performance of various alkali metal-doped Li$_4$SiO$_4$ materials is summarized in Table 2 [39–46].

**Table 2. Summary of CO$_2$ absorption performance of Na and K doped Li$_4$SiO$_4$ materials.**

| Materials | Molar Ratio of Li/Alkali Metal | Preparation Method | Absorption Conditions | Regeneration Conditions | Cycle No. | Weight Increase (wt.%) | Refs. |
|-----------|--------------------------------|--------------------|-----------------------|------------------------|-----------|-----------------------|-------|
| SiO$_2$, Li$_2$CO$_3$, K$_2$CO$_3$ | 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$_2$CO$_3$, K$_2$CO$_3$ | 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$_2$CO$_3$, K$_2$CO$_3$ | 17:1 | Solid-state reaction | CO$_2$: 575 °C; 25 min | N$_2$: 700 °C; 50 min | 10 | 28 | [41] |
| SiO$_2$, Li$_2$CO$_3$, K$_2$CO$_3$ | 17:1 | Solid-state reaction | CO$_2$: 650 °C; 15 min | 90% H$_2$O/N$_2$: 650 °C; 15 min | 22 | 21 | [42] |
| SiO$_2$, CH$_3$COONa, K$_2$CO$_3$ | 43:7 | Impregnated suspension | 15% CO$_2$/N$_2$: 550 °C; 30 min | N$_2$: 750 °C; 10 min | 40 | 315 | [43] |
| SiO$_2$, SiO$_2$, CH$_3$COONa, K$_2$CO$_3$ | 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$_2$CO$_3$, Na$_2$CO$_3$ | 49:1 | Solid state | CO$_2$: 700 °C; 30 min | Air: 900 °C; 30 min | 5 | 32 | [44] |
| SiO$_2$, Li$_2$CO$_3$, Na$_2$CO$_3$ | 49:1 | Solid state | CO$_2$: 700 °C; 30 min | Air: 900 °C; 30 min | 5 | 32 | [44] |
| SiO$_2$, Li$_2$CO$_3$, Na$_2$CO$_3$ | 49:1 | Solid state | CO$_2$: 700 °C; 30 min | Air: 900 °C; 30 min | 5 | 32 | [44] |
| SiO$_2$, Li$_2$CO$_3$, Na$_2$CO$_3$ | 49:1 | Solid state | CO$_2$: 700 °C; 30 min | Air: 900 °C; 30 min | 5 | 32 | [44] |

As presented in Table 2, Na and K were the most commonly reported alkali metals to enhance the CO$_2$ absorption performance of Li$_4$SiO$_4$ material. In order to determine the most appropriate doping method for K$_2$CO$_3$, Seggiani et al. [39] compared eutectic doping and simple mechanical addition of K$_2$CO$_3$, and they found that Li$_4$SiO$_4$ 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$_2$CO$_3$. Olivares-Marín et al. [47] et al. synthesized K$_2$CO$_3$-doped Li$_4$SiO$_4$ material with fly ash as the silicon precursor, and they reported that the CO$_2$ absorption capacity of the prepared Li$_4$SiO$_4$ material increased with the increase of the dopant amount. It is also worth noting that Zhang et al. [42] reported that the K$_2$CO$_3$ doped Li$_4$SiO$_4$ material cooperated well with the Ni/γ-Al$_2$O$_3$ 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$_4$SiO$_4$ material by doping Na$_2$CO$_3$ into the starting materials of TEOS and Li$_2$CO$_3$ through the co-precipitation route, and they noted that the addition of Na$_2$CO$_3$ increased the activity and reduced the equilibrium temperature of Li$_4$SiO$_4$ material for CO$_2$ absorption, and Li$_{3.85}$Na$_{0.15}$Si$_4$O$_9$ had the highest CO$_2$ absorption capacity among various Na-doped Li$_4$SiO$_4$ materials. Seggiani et al. [40] noted that dopants like K$_2$CO$_3$ and Na$_2$CO$_3$ could form eutectic mixtures with Li$_2$CO$_3$, 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$_4$SiO$_4$ was broken by doped K$_2$CO$_3$ and Na$_2$CO$_3$ for their different crystal sizes, thus more pores and larger specific surface area were generated.
with Y process was beneficial of transferring CO\textsubscript{2} from Li\textsubscript{4}SiO\textsubscript{4} surface to the core, which reduced the diffusion resistance shown in Figure 9. The transformation of Ca\textsubscript{2}SiO\textsubscript{4} to Li\textsubscript{2}CaSiO\textsubscript{4} during CO\textsubscript{2} absorption process was beneficial of transferring CO\textsubscript{2} from Li\textsubscript{4}SiO\textsubscript{4} surface to the core, which reduced the diffusion resistance and improved CO\textsubscript{2} absorption, and regeneration was also correspondingly enhanced.

3.2.3. Other Dopants

Wang et al. [49] prepared K\textsubscript{–}, Mg\textsubscript{–}, Cr\textsubscript{–}, and Ce-doped Li\textsubscript{4}SiO\textsubscript{4} and found that Ce was the most difficultly doped into the Li\textsubscript{4}SiO\textsubscript{4} crystal lattice among the four elements. However, Ce was the most effective to inhibit the aggregation of Li\textsubscript{4}SiO\textsubscript{4} grains, so Ce-doped Li\textsubscript{4}SiO\textsubscript{4} achieved the highest CO\textsubscript{2} absorption performance. Subha et al. [50] studied the CO\textsubscript{2} absorption by Li\textsubscript{4}SiO\textsubscript{4} material doped with Y\textsubscript{2}O\textsubscript{3}, Gd\textsubscript{2}O\textsubscript{3} or LaPO\textsubscript{4}, and found that both Y\textsubscript{2}O\textsubscript{3} and Gd\textsubscript{2}O\textsubscript{3} improved the CO\textsubscript{2} absorption capacity of Li\textsubscript{4}SiO\textsubscript{4}, and Y\textsubscript{2}O\textsubscript{3}-doped Li\textsubscript{4}SiO\textsubscript{4} retained the highest CO\textsubscript{2} absorption capacity due to the segregation of second phase created by the doped unreacted Y\textsubscript{2}O\textsubscript{3}. Chen et al. [51] reported that Ca-doped Li\textsubscript{4}SiO\textsubscript{4} material achieved high CO\textsubscript{2} absorption capacity and they proposed a modified double-shell mechanism to describe the CO\textsubscript{2} absorption and regeneration mechanism of Ca-doped Li\textsubscript{4}SiO\textsubscript{4} as shown in Figure 9. The transformation of Ca\textsubscript{2}SiO\textsubscript{4} to Li\textsubscript{2}CaSiO\textsubscript{4} during CO\textsubscript{2} absorption process was beneficial of transferring CO\textsubscript{2} from Li\textsubscript{4}SiO\textsubscript{4} surface to the core, which reduced the diffusion resistance and improved CO\textsubscript{2} absorption, and regeneration was also correspondingly enhanced.

Additionally, doping of organic matter can also enhance the CO\textsubscript{2} absorption property of Li\textsubscript{4}SiO\textsubscript{4} material due to the formation of the porous structure. Wang et al. [30,52] prepared carbon-coated Li\textsubscript{4}SiO\textsubscript{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\textsubscript{4}SiO\textsubscript{4} material, which suppressed the growth of...
Li$_4$SiO$_4$ grains. As a result, the cyclic CO$_2$ absorption capacities and rates of carbon-coated Li$_4$SiO$_4$ materials were higher than that of uncoated Li$_4$SiO$_4$ during multiple absorption/regeneration cycles. Furthermore, CMK-3, as a kind of porous carbon material [53], was also introduced into the Li$_4$SiO$_4$ material. Jeoung et al. [54] prepared CMK-modified Li$_4$SiO$_4$, while the cyclic absorption capacity of CMK-modified Li$_4$SiO$_4$ 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$_4$SiO$_4$ material. The limitation in the diffusion-controlled stage for Li$_4$SiO$_4$ is reduced greatly with the doping of solid solution or molten salts, and the porous structure of Li$_4$SiO$_4$ by doping of organic matters is obtained. The additive amounts are minor, but the CO$_2$ absorption performance of Li$_4$SiO$_4$ can be greatly enhanced.

3.3. Selection of Alternative Precursors for Preparation of Li$_4$SiO$_4$

Li$_4$SiO$_4$ material is usually prepared from Li$_2$CO$_3$ and SiO$_2$, which are not able to create a favorable surface characteristic for CO$_2$ absorption. Recent studies have shown that Li$_4$SiO$_4$ materials prepared from alternative precursors, especially organic precursors, rather than Li$_2$CO$_3$ 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$_4$SiO$_4$ material are summarized.

3.3.1. Lithium Precursors

Kim et al. [29] synthesized Li$_4$SiO$_4$ material from LiOH and fumed silica 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$_4$SiO$_4$ 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$_4$SiO$_4$ with LiOH by the sol-gel technique and they found that LiOH-synthesized Li$_4$SiO$_4$ particles were primarily composed of porous grains, and the average grain size of Li$_4$SiO$_4$ prepared by the sol-gel method was much smaller than that synthesized by the solid-state reaction method.

Weng et al. [56] synthesized Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ material. Yang et al. [19] used lithium acetate and lithium lactate to prepare novel Li$_4$SiO$_4$ materials by the impregnated suspension method. As shown in Figure 10, the two novel Li$_4$SiO$_4$ materials showed a bulgier morphology and more porous structure, compared with Li$_4$SiO$_4$ synthesized by the solid-state reaction method. Absorption capacities of Li$_4$SiO$_4$ material prepared from lithium acetate or lithium lactate as the lithium precursors were almost six times higher than that of a conventional Li$_4$SiO$_4$ material. Additionally, the CO$_2$ absorption capacities and conversions of Li$_4$SiO$_4$ material prepared from lithium acetate or lithium lactate showed an incremental tendency over 40 cycles, and the conversion of Li$_4$SiO$_4$ prepared from lithium acetate was approximately 70% even in the last cycle, which was calculated according to Equation (8):

$$X_N = \frac{C_N}{m_0}$$  \hspace{1cm} (8)

where $X_N$ is the conversion of Li$_4$SiO$_4$ during the Nth cycle, %; and $m_0$ is the theoretical CO$_2$ absorption capacity of Li$_4$SiO$_4$ 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$_4$SiO$_4$ material was able
to convert into Li$_4$SiO$_4$ thermally. The as-prepared material had a coral-like morphology, so the contact area between CO$_2$ and Li$_4$SiO$_4$ material was enhanced, and the Li$_4$SiO$_4$ material showed higher CO$_2$ absorption capacity than that prepared by the conventional solid-state reaction method.

![SEM images of three kinds of Li$_4$SiO$_4$ materials prepared with Li$_2$CO$_3$ (RS), lithium acetate (ORC) and lithium lactate (ORL) [19].](image)

In this section, CO$_2$ absorption performance of Li$_4$SiO$_4$ 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$_2$CO$_3$, 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$_4$SiO$_4$ material.

3.3.2. Silicon Precursors

SiO$_2$ is an essential raw material for the synthesis of Li$_4$SiO$_4$. 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$_4$SiO$_4$ material are critically reviewed.

Wang et al. [20] selected two kinds of RHA samples as the silicon precursors for the preparation of Li$_4$SiO$_4$ 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$_4$SiO$_4$ materials were synthesized by the solid-state reaction method with Li$_2$CO$_3$. The employment of RHA produced a smaller particle size, larger pore volume, and surface area compared with pure Li$_4$SiO$_4$ material. They reported a weight gain of nearly 135 % over 15 cycles, which was much higher than that of pure Li$_4$SiO$_4$ 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$_4$SiO$_4$ materials pretreated at 1000 °C achieved better CO$_2$ absorption performance, which was similar to that of the RHA-derived Li$_4$SiO$_4$ material mentioned above. To study the effects of RHA as the silicon precursor on the CO$_2$ absorption properties of Li$_4$SiO$_4$ material, Wang et al. [59] selected RHA and two kinds of nanosilica (Aerosil and quartz) to prepare Li$_4$SiO$_4$ materials by solid-state reaction method, and SEM images and BET analysis indicated that RHA-synthesized Li$_4$SiO$_4$ material possessed higher surface area and larger pore volume. Furthermore, the weight gain of RHA-synthesized Li$_4$SiO$_4$ material was higher and faster than that of the two nanosilica-synthesized Li$_4$SiO$_4$ 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$_4$SiO$_4$ material prepared from RHA over multiple absorption/regeneration cycles.
cycles. Qiao et al. [60] also noted that RHA-derived Li$_4$SiO$_4$ 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$_4$SiO$_4$ materials can also be prepared from FA as a silicon precursor. Olivares-Marin et al. [47] fabricated Li$_4$SiO$_4$ material from Li$_2$CO$_3$ and three kinds of FA, and the samples were doped with several amounts ranging from 5 to 40 mol% of K$_2$CO$_3$. The cyclic CO$_2$ absorption capacity of one of the doped FA-Li$_4$SiO$_4$ was approximately 100 mg/g over 10 cycles, which was far below the theoretical absorption capacity of Li$_4$SiO$_4$ material synthesized from pure SiO$_2$, but it was relatively stable over multiple cycles. Sanna et al. [63] synthesized Na/Li-FA Li$_4$SiO$_4$ material with different molar ratios of Li$_2$CO$_3$, FA, and Na$_2$CO$_3$, and the material was doped with K$_2$CO$_3$. They reported that the CO$_2$ absorption capacity of the obtained Li$_4$SiO$_4$ 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$_4$SiO$_4$ was synthesized by the solid-state reaction method. Li$_4$SiO$_4$ synthesized from diatomite showed higher CO$_2$ absorption capacity. Li$_4$SiO$_4$ 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$_2$CO$_3$ to SiO$_2$, Shan et al. [65] prepared a series of Li$_4$SiO$_4$ containing the molar ratios of Li$_2$CO$_3$ 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.

| 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$_2$CO$_3$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ easily, so they selected the impregnation precipitation method to prepare Li$_4$SiO$_4$ materials, which was operated at lower temperature. Diatomite, LiNO$_3$, and NH$_3$·H$_2$O 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$_4$SiO$_4$ 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.

\[
\text{LiNO}_3 + \text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{NH}_4\text{NO}_3 \\
4\text{LiOH} + \text{SiO}_2 \rightarrow \text{Li}_4\text{SiO}_4 + 2\text{H}_2\text{O}
\]

Halloysite is also a SiO$_2$-containing material with a SiO$_2$ content of about 50 wt.% [68]. Niu et al. [69] synthesized Li$_4$SiO$_4$ from treated halloysite nanotubes (HNTs) with HCl aqueous solution and Li$_2$CO$_3$ by the solid-state reaction method at 800 °C. The content of Al$_2$O$_3$ of HNTs is 43.859%, and the presence of Al$^{3+}$ was beneficial to the enlargement of Li$_4$SiO$_4$ crystalline structure, which is beneficial for its CO$_2$ absorption performance [37]. The CO$_2$ absorption capacity of halloysite-synthesized Li$_4$SiO$_4$ material was approximately 30 wt.% over 10 cycles, which was higher than that of SiO$_2$-synthesized Li$_4$SiO$_4$ material.
In this section, CO₂ absorption performances of Li₄SiO₄ materials synthesized from various silicon precursors were reviewed. Li₄SiO₄ synthesized from RHA, diatomite and halloysite exhibited high CO₂ absorption capacity, while fly ash was not a good lithium precursor. Some elements in these silicon precursors other than pure SiO₂ are possibly beneficial for the CO₂ absorption properties of Li₄SiO₄ 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 Li₄SiO₄ materials have obtained great progress, while the major problem that limits the practical application of Li₄SiO₄ is the high price of Li-containing materials, and the cost of Li₄SiO₄ will not be reduced by much even if SiO₂ is free of charge, so the future research should focus on alternative lithium precursors.

3.3.3. Synthesis Methods

Most of the Li₄SiO₄ 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 Li₄SiO₄ 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 Li₄SiO₄ material and they found that the conversion of the obtained Li₄SiO₄ 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 Li₄SiO₄ material synthesized from LiNO₃ and colloidal silica by a sol-gel method achieved an absorption capacity of 350 mg/g. Additionally, the platelet-shaped Li₄SiO₄ material was coated with a porous carbon mesh, and the cyclic absorption/regeneration performance of the platelet-shaped Li₄SiO₄ material retained approximately 120 mg/g over eight cycles. The CO₂ absorption rates of the coated Li₄SiO₄ 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 Li₄SiO₄ materials synthesized by the sol-gel method was not completely pure, probably because the use of a microwave oven resulted in the sublimation of Li₄SiO₄.

4. Effects of Particle Properties on CO₂ Absorption Performance of Li₄SiO₄ Material

The newly synthesized Li₄SiO₄ powder is too fine, and elutriation might occur in the reactor, especially in fluidized bed reactors, in industrial applications. In addition, powdery Li₄SiO₄ materials cannot create effective fluidization, while most of the studies on CO₂ absorption by Li₄SiO₄ material were conducted on fixed bed reactors or TGA. Thus, pelletization may be an effective method for the practical application of Li₄SiO₄ materials. The effects of the particle properties on CO₂ absorption performance of Li₄SiO₄ material were critically reviewed in this section.

Pacciani et al. [71] studied the CO₂ absorption by the pelletized Li₄SiO₄ materials, which were doped with less than 10 vol.% K₂CO₃ and Li₂TiO₃ as a binder. The CO₂ absorption capacity of the pelletized Li₄SiO₄ material was 23 wt.% carbonated in 10 vol.% CO₂. However, Kato et al. [72] reported that the pelletized Li₄SiO₄ 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 K₂CO₃ doped Li₄SiO₄ materials with the diameter of 3 mm and length of 6 mm, while the CO₂ absorption capacity of a Li₄SiO₄ pellet was not so high as that of Li₄SiO₄ powder. Puccini et al. [74] synthesized K₂CO₃-doped Li₄SiO₄ by the solid-state reaction method, and they selected cellulose fiber as the binder. The Li₄SiO₄ material pellets with a diameter of 6 mm and lengths of 1.5, 2.5, and 3.5 mm were prepared, but the prepared Li₄SiO₄-based pellets did not show
superior cyclic performance and the conversion of the Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ materials with different binders [74,75].](image)

Pelletization is an essential procedure for the practical application of Li$_4$SiO$_4$, but few researchers studied the CO$_2$ absorption performance of the pelletized Li$_4$SiO$_4$ materials in fluidized bed reactors. Additionally, mechanical intensity and wearing characteristics of pelletized Li$_4$SiO$_4$ materials have seldom been reported.

5. Effects of Reaction Conditions on CO$_2$ Absorption Performance of Li$_4$SiO$_4$ Material

Realistic reaction conditions for CO$_2$ absorption by Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$, 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$_4$SiO$_4$ material in low CO$_2$ concentrations.

Pacciani et al. [71] reported that the CO$_2$ absorption rate of Li$_4$SiO$_4$ material rose apparently when CO$_2$ concentration in absorption atmosphere increased from 2.5 to 24.5 vol.% [77]. Essaki et al. [77] prepared the pelletized Li$_4$SiO$_4$ materials with an average particle size of 5 mm and K$_2$CO$_3$ and Li$_2$ZrO$_3$ were doped into the materials to promote the absorption reaction and prevent reduction of absorption capacity, respectively. The absorption property of Li$_4$SiO$_4$ 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$_4$SiO$_4$. 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 CO2 concentration, and the weight increase was used to evaluate the CO2 absorption performance of Li4SiO4 material, which can be calculated according to Equation (11):

\[ I_N = \frac{W_N - W_0}{W_0} \times 100\% \]  

where \( I_N \) is the weight increase of Li4SiO4 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 CO2 absorption process of Li4SiO4 was limited in low CO2 concentration (5 vol.%), while it was controlled by the diffusion of Li\(^+\) and O\(^{2-}\) in high CO2 concentration (15 vol.%).

![Figure 12. Weight increase of Li4SiO4 at different temperatures in different CO2 concentrations [77].](image)

Researchers found that the limits of low CO2 concentration could be counteracted by the addition of dopants. Puccini et al. [78] found Li4SiO4 material doped with 30 wt.% K2CO3 maintained a stable CO2 absorption capacity (approximately 160 mg/g) after 25 cycles in 4 vol.% CO2 at 580 °C. It is worth noting that Seggiani et al. [39] reported that CO2 absorption capacity of K2CO3-doped Li4SiO4 material was superior than 20 wt.% over four cycles in 4 vol.% CO2. Furthermore, Seggiani et al. [40] also reported that the CO2 absorption capacity of Na2CO3-doped Li4SiO4 material in 4 vol.% CO2 was 7 wt.%, and it was quite stable over 25 cycles. Adding some dopants can improve the CO2 absorption capacity of Li4SiO4 material, but the improvement in lower CO2 concentration is still relatively lower compared with that in higher CO2 concentration. The CO2 absorption performance of Li4SiO4 material in high CO2 concentration has been well studied by researchers. Thus, Li4SiO4 materials with high absorption capacity, fast absorption rate, and good cyclic stability in low CO2 concentrations should be investigated for industrial application.

5.1.2. Presence of Steam

Apart from CO2, steam also exists in realistic CO2 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 CO2 absorption reaction could be reduced. Thus, the presence of steam in the absorption atmosphere also has non-negligible effect on the CO2 absorption capacity of Li4SiO4 material.

Ochoa-Fernández et al. [80] reported that the presence of 10 vol.% steam in the absorption atmosphere could raise the CO2 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 CO2 absorption performance of Li4SiO4 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 Li4SiO4 materials for CO2 absorption in 14.7% CO2, 2.6% steam in N2 at 550 °C, and they found that the CO2 absorption capacity after 10 min was almost three times higher than that in dry atmosphere. Furthermore, Sanna et al. [63] synthesized Li4SiO4 material from FA as SiO2 precursor, and the CO2 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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) material should be considered. The effects of NO\(_x\) and SO\(_2\) on the CO\(_2\) absorption performance of Li\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) material. Furthermore, when the concentration of SO\(_2\) in the absorption atmosphere increased from 0 to 2000 ppm, the weight change of Li\(_4\)SiO\(_4\) material increased with the increase of SO\(_2\) concentration, but the regeneration performance of Li\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\), as shown in Equations (12) and (13):

\[
\text{Li}_4\text{SiO}_4 + \text{SO}_2 \rightarrow \text{Li}_2\text{SO}_3 + \text{Li}_2\text{SiO}_3 \quad (12)
\]
\[
\text{Li}_2\text{SiO}_3 + \text{SO}_2 \rightarrow \text{Li}_2\text{SO}_4 + \text{SiO} \quad (13)
\]

The formation of Li\(_2\)SO\(_3\) and Li\(_2\)SO\(_4\) 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\(_4\)SiO\(_4\) material [82]. In general, NO had no negative impact on the CO\(_2\) absorption property of Li\(_4\)SiO\(_4\) materials, while SO\(_2\) had an adverse effect due to the formation of the irreversible Li\(_2\)SO\(_3\) and Li\(_2\)SO\(_4\), 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\(_2\)S, on the CO\(_2\) absorption by Li\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) 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\(_4\)SiO\(_4\) pellets in a pure CO\(_2\) atmosphere. This confirmed the conclusion that the equilibrium temperature of the reaction between Li\(_4\)SiO\(_4\) and CO\(_2\) rising with increasing CO\(_2\) partial pressure.

Different kinds of Li\(_4\)SiO\(_4\) materials accommodate diverse appropriate absorption temperatures. Qiao et al. [60] synthesized Li\(_4\)SiO\(_4\) material from RHA and Li\(_2\)CO\(_3\), 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\(_4\)SiO\(_4\) materials, and Wang et al. [30] pointed out that 575 °C was the most appropriate for the CO\(_2\) absorption by Li\(_4\)SiO\(_4\).

Temperature during the regeneration process also had a deep effect on CO\(_2\) absorption performance on Li\(_4\)SiO\(_4\) 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$_4$SiO$_4$ material, while too high a regeneration temperature intensifies the sintering of the material, which is extremely harmful.

6. Application of Li$_4$SiO$_4$ Material in Sorption-Enhanced Hydrogen Production

Sorption-enhanced hydrogen production is one of the most important applications of Li$_4$SiO$_4$ 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:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad (14)
\]

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \quad (15)
\]

In the SE-SMR and SE-SER processes, in situ CO$_2$ removal of Li$_4$SiO$_4$ material as the CO$_2$ acceptor shifts the reaction equilibrium to hydrogen production, and exothermal absorption of CO$_2$ by the Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_2$ZrO$_3$ was used as a CO$_2$ acceptor. Essaki et al. [85] introduced commercial Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ pellets were promising as the CO$_2$ acceptor for the SE-SER process [86]. Zhang et al. [42] reported K$_2$CO$_3$-doped Li$_4$SiO$_4$ material coupled well with the Ni/γ-Al$_2$O$_3$ catalyst, and hydrogen concentration in the syngas was higher than 95 vol.%. In addition, they found that homogeneous distribution of Li$_4$SiO$_4$ 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$_4$SiO$_4$ materials, thus Li$_4$SiO$_4$ materials with superior CO$_2$ absorption performance should be investigated. Additionally, Li$_4$SiO$_4$ 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$_4$SiO$_4$ Material

Duan et al. [87] studied CO$_2$ absorption performance on monoclinic and triclinic phases of Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$, and the adsorption and dissociation behaviors of molecular H$_2$O on the Li$_4$SiO$_4$ (0 1 0) plane were investigated. They found that molecular H$_2$O was more inclined to be absorbed on O atoms on the surface.

8. Conclusions

Research progress of Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ material. Since Li$_4$SiO$_4$
material prepared by the traditional solid-state reaction method only achieved low CO₂ absorption capacity, methods to enhance the CO₂ absorption performance of Li₄SiO₄ 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 CO₂ and Li₄SiO₄, which is beneficial for CO₂ absorption by Li₄SiO₄ material. The sol-gel method seemed to be most appropriate for preparation of Li₄SiO₄ material, which is beneficial for the formation of porous structure. The effects of gas contaminants and reaction conditions on CO₂ absorption performance of Li₄SiO₄ material and the applications of Li₄SiO₄ 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 CO₂ under most energy production conditions. Additionally, powdery Li₄SiO₄ materials could not create effective fluidization, while studies on the performance of pelletized Li₄SiO₄ materials were insufficient. As a result, more focus should be attached to the CO₂ absorption performance of pelletized Li₄SiO₄ material in fluidized bed reactors.

(ii) Application of Li₄SiO₄ materials on sorption-enhanced hydrogen production is an important aspect, and hydrogen yield and concentration were considerable, while fewer studies involved this area. Additionally, CO₂ absorption performance of Li₄SiO₄ materials in realistic sorption-enhanced hydrogen production conditions (i.e., low CO₂ concentration in the presence of steam) deserves to be studied.

(iii) Preparation cost of Li₄SiO₄ 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 Li₄SiO₄ 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 Li₄SiO₄ materials prepared from inexpensive lithium-containing wastes may be promising for large-scale CO₂ 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 CO₂ Reforming of Methane. *ACS Symp. Ser.* 2010, 1056, 155–174.
3. Ma, X.; Li, Y.; Shi, L.; He, Z.; Wang, Z. Fabrication and CO₂ 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 CO₂ 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 CO₂ 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. CO₂ absorption properties of lithium ferrite for application as a high-temperature CO₂ absorbent. *J. Ceram. Soc. Jpn.* 2005, 113, 684–686. [CrossRef]
7. Lara-Garcia, H.A.; Ramirez-Moreno, M.J.; Ortiz-Landeros, J.; Pfeiffer, H. CO₂ chemisorption in Li₂CuO₂ microstructurally modified by ball milling process: Study performed with different physiochemical CO₂ 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]

---

*Int. J. Mol. Sci.* 2019, 20, 928
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 CO₂ chemisorption on lithium oxosilicate (Li₄SiO₄). *Greenh. Gases Sci. Technol.* 2014, 4, 145–154. [CrossRef]

11. Durán-Muñoz, F.; Romero-Ibarra, I.C.; Pfeiffer, H. Analysis of the CO₂ chemisorption reaction mechanism in lithium oxosilicate (Li₄SiO₄): A new option for high-temperature CO₂ capture. *J. Mater. Chem. A* 2013, 1, 3919–3925. [CrossRef]

12. Sapatru, C.I.; Ianchis, R.; Petcu, C.; Nistor, C.I.; 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.* 2019, 20, 16936–16948.

14. Bretado, M.E.; Guzmán Velderrain, V.; Lardizábal Gutiérrez, D.; Collins-Martínez, V.; Ortiz, A.L. A new synthesis route to Li₄SiO₄ as CO₂ 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. Wux, Y.; Liu, J. The influencing factor for CO₂ absorption of Li₄SiO₄ at high temperature. In Proceedings of the Third International Conference on Measuring Technology and Mechatronics Automation, Shanghai, China, 6–7 January 2011; pp. 839–841.

19. Yang, Y.; Liu, W.; Sun, J.; Hu, Y.; Wang, W.; Chen, H.; Zhang, Y.; Li, X.; Xu, M. Preparation of novel Li₄SiO₄ sorbents with superior performance at low CO₂ concentration. *ChemSusChem* 2016, 9, 1607–1613. [CrossRef] [PubMed]

20. Wang, K.; Guo, X.; Zhao, P.; Wang, F.; Zheng, C. High temperature capture of CO₂ 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. CO₂ absorption properties of Ti- and Na-doped porous Li₄SiO₄ 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 CO₂ Absorption properties of Li₄SiO₄ at high temperature. *Ind. Eng. Chem. Res.* 2013, 52, 1886–1891. [CrossRef]

25. Subba, P.V.; Nair, B.N.; Hareesh, P.; Mohamed, A.P.; Yamaguchi, T.; Warrier, K.G.K.; Hareesh, U.S. Enhanced CO₂ absorption kinetics in lithium silicate platelets synthesized by a sol-gel approach. *J. Mater. Chem. A* 2014, 2, 12792–12798. [CrossRef]

26. Lpez 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 CO₂ absorption by Li₄SiO₄. *Int. J. Hydrogen Energy* 2014, 39, 16656–16666. [CrossRef]

27. Zhang, Q.; Han, D.; Liu, Y.; Qian, Y.; Zhu, Z. Analysis of CO₂ sorption/desorption kinetic behaviors and reaction mechanisms on Li₄SiO₄. *AIChE J.* 2013, 59, 901–911.

28. Rodríguez-Mosqueda, R.; Pfeiffer, H. Thermokinetic analysis of the CO₂ chemisorption on Li₄SiO₄ 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 Li₄SiO₄ with remarkably enhanced CO₂ 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$_4$SiO$_4$ 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$_4$si$_4$ by solid state reaction from Li$_2$SiO$_3$ and Li$_2$CO$_3$ 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$_4$SO$_4$. 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$_4$SiO$_4$: 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 ball milling. *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$_x$O$_4$ 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 mechanochemistry 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. Saggiani, M.; Puccini, M.; Vitolo, S. High-temperature and low concentration CO$_2$ sorption on Li$_4$SiO$_4$ based sorbents: Study of the used silica and doping method effects. *Int. J. Greenh. Gas Control* **2011**, *5*, 741–748. [CrossRef]

40. Saggiani, 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$_4$SiO$_4$ 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$_2$CO$_3$-doped Li$_4$SiO$_4$ 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$_4$SiO$_4$. *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$_4$SiO$_4$-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$_4$SiO$_4$-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$_x$SiO$_4$). *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$_4$SiO$_4$ 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 CO2 sorption by Ca-doped Li4SiO4 sorbents. *Int. J. Hydrogen Energy* **2016**, *41*, 13077–13085. [CrossRef]
52. Wang, K.; Yin, Z.; Zhao, P. Synthesis of macroporous Li4SiO4 via a citric acid-based sol–gel route coupled with carbon coating and its CO2 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 CO2 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 CO2 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 CO2 capture. *Adv. Mater. Res.* **2011**, *383–426*. [CrossRef]
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 CO2 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 CO2 sorption properties of Li4SiO4 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 Li4SiO4-based sorbents from the nano-sized rice husk ash for high-temperature CO2 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 Li4SiO4 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 with carbon coating and its CO2 chemisorption properties. *Ceram. Int.* **2013**, *39*, 15130–15134. [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 CO2 capture. *Appl. Energy* **2015**, *156*, 197–206. [CrossRef]
64. Shan, S.; Jia, Q.; Jiang, L.; Wang, Y. Effect of different silicon sources on CO2 absorption properties of Li4SiO4 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 Li4SiO4-based sorbents from diatomite for high temperature CO2 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 Li4SiO4 sorbents with different silicon sources for high temperature CO2 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 Li4SiO4-Based Sorbents with Fast CO2 Adsorption Rate. *Ind. Eng. Chem. Res.* **2013**, *52*, 6941–6945. [CrossRef]
68. Joussine, 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 CO2 capture. *RSC Adv.* **2016**, *6*, 44106–44112. [CrossRef]
70. Venegas, M.J.; Fregoso-Israel, E.; Escamilla, R.; Pfeiffer, H. Kinetic and reaction mechanism of CO2 sorption on Li4SiO4: Study of the particle size effect. *Ind. Eng. Chem. Res.* **2007**, *46*, 2407–2412. [CrossRef]
71. Pacchioni, R.; Torres, J.; Solsona, P.; Coe, C.; Quinn, R.; Huftron, J.; Golden, T.; Vega, L.F. Influence of the concentration of CO2 and SO2 on the absorption of CO2 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 CO2 absorbers using lithium-containing oxide. *Int. J. Appl. Ceram. Technol.* **2005**, *2*, 467–475. [CrossRef]
73. Essaki, K.; Kato, M.; Nakagawa, K. CO₂ 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 CO₂ capture at high temperature. *Chem. Eng. Trans.* 2003, 35, 373–378.

75. Puccini, M.; Stefanelli, E.; Seggiani, M.; Vitolo, S. Removal of CO₂ from flue gas at high temperature using novel porous solids. *Chem. Eng. Trans.* 2016, 47, 139–144.

76. Aaron, D.; Tsouris, C. Separation of CO₂ from Flue Gas: A Review. *Sep. Sci. Technol.* 2005, 40, 321–348. [CrossRef]

77. Essaki, K.; Kato, M.; Uemoto, H. Influence of temperature and CO₂ concentration on the CO₂ absorption properties of lithium silicate pellets. *J. Mater. Sci.* 2005, 40, 5017–5019. [CrossRef]

78. Puccini, M.; Seggiani, M.; Vitolo, S. CO₂ capture at high temperature and low concentration on Li₄SiO₄ based sorbents. *Chem. Eng. Trans.* 2013, 32, 1279–1284.

79. Ochoa-Fernández, E.; Rønning, M.; Yu, X.; Grande, T.; Chen, D. Compositional effects of nanocrystalline lithium zirconate on its CO₂ 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 CO₂ 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 absorber for post combustion CO₂ 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 CO₂ capture at high temperature by Li₄SiO₄ based sorbents. *Chem. Eng. Trans.* 2015, 32, 1093–1098.

83. Essaki, K.; Nakagawa, K.; Kato, M.; Uemoto, H. CO₂ 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 CO₂-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 Li₄SiO₄ and its capability for CO₂ 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 H₂O molecule on the Li₄SiO₄ (0 1 0) surface from first principles. *Chem. Phys. Lett.* 2018, 691, 1–7. [CrossRef]