Fabrication of Lithium Silicates As Highly Efficient High-Temperature CO₂ Sorbents from SBA-15 PrecursorYirong Pan,^{†,‡,§} Yu Zhang,[†] Tuantuan Zhou,[†] Benoît Louis,^{||} Dermot O'Hare,^{⊥,||} and Qiang Wang^{*,†,||}[†]College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, P. R. China[‡]Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, P. R. China[§]College of Resources and Environment, University of Chinese Academics of Science, 80 Zhongguancun East Road, Haidian District, Beijing 100190, P. R. China^{||}Laboratoire de Synthèse, Réactivité Organiques et Catalyse, Institut de Chimie, UMR 7177, Université de Strasbourg, 1 rue Blaise Pascal, 67000 Strasbourg, France[⊥]Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, United Kingdom

Supporting Information

ABSTRACT: A series of lithium silicates with improved CO₂ sorption capacity were successfully synthesized using SBA-15 as the silicon precursor. The influence of Li/Si ratio, calcination temperature, and calcination duration on the chemical composition and CO₂ capture capacity of obtained lithium silicates was systematically investigated. The correlation between CO₂ sorption performance and crystalline phase abundance was determined using X-ray diffraction and a normalized reference intensity ratio method. Under the optimized condition, Li-SBA15-4 prepared using Li/Si = 4 that contains mainly Li₄SiO₄ achieved an extremely high CO₂ capture capacity of 36.3 wt % (corresponding to 99% of the theoretical value of 36.7 wt % for Li₄SiO₄), which is much higher than the Li₄SiO₄ synthesized from conventional SiO₂ sources. It also showed very high cycling stability with only 1.0 wt % capacity loss after 15 cycles. Li-SBA15-10 (Li/Si = 10) that mainly contains Li₈SiO₆ displayed an extremely high CO₂ uptake of 62.0 wt %, but its regeneration capacity was poor, with only 10.5 wt % of reversible CO₂ capture capacity. The influence of CO₂ concentration on the CO₂ capture performance of Li-SBA15-4 and Li-SBA15-10 samples was also studied. With the decrease in CO₂ concentration, relatively lower temperatures are needed for its maximum CO₂ capture capacity. The CO₂ sorption kinetics and mechanism for Li-SBA15-4 and Li-SBA15-10 samples were explored. Overall, we have shown that the lithium silicates synthesized from SBA-15 possessed much improved CO₂ sorption performance than that attained from conventional SiO₂.

1. INTRODUCTION

CO₂ is one of the major greenhouse gases that contribute significantly to global warming, and its capture is an important prerequisite step for subsequent CO₂ storage or utilizations. The development of new solid-phase adsorbents/sorbents to capture CO₂ is a promising research topic.¹ Solid adsorbents/sorbent systems can be classified into low-temperature (<200 °C), intermediate-temperature (200–400 °C), and high-temperature (>400 °C) CO₂ adsorbents/sorbents according to their working temperature ranges.²

High-temperature CO₂ sorbents are mainly used in the sorption enhanced steam methane reforming process that operates at between 500 and 800 °C. Utilizing these sorbents, the conversion of methane to H₂ can be improved, and concurrently, pure CO₂ can be captured.³ To date, several types of high-temperature CO₂ sorbents have been developed such as CaO-based systems, alkali

dititanates, alkali zirconates, and alkali silicates.⁴ Alkali metal silicate-based sorbents have attracted tremendous attention owing to their high CO₂ capture capacity and relatively lower regeneration temperature. A series of alkali silicates including Li₄SiO₄, Li_{4-x}Na_xSiO₄, Li_{4+x}(Si_{1-x}Al_x)O₄, Li₈SiO₆, Li₆Si₂O₇, Li₂Si₂O₅, Li₂Si₃O₇, CaSiO₃, and (OH)₃Al₂O₃SiOH have been studied for CO₂ sorption.⁵ Among these, Li₄SiO₄ and Li₈SiO₆ are emerging as the most promising owing to their higher CO₂ sorption capacity and sorption/desorption kinetics.

Li₄SiO₄ was reported to possess outstanding CO₂ sorption behavior about 15 years ago.⁶ During the CO₂ sorption process, a reversible reaction as shown in eq 1 can readily occur. The theoretical CO₂ capture capacity of Li₄SiO₄ can be straightforwardly

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calculated as 36.7 wt %. Over the past few years, great effort has been devoted to the improvements of CO₂ uptake capacity and cycling stability of Li₄SiO₄. In parallel, several investigations have studied the use of alternative silicon sources loaded with alkali metals, and/or designing unique morphologies. Some alkali metal silicate-based sorption materials and their CO₂ capture performance are summarized in Table 1.

Olivares-Marín et al.⁷ developed K-doped Li₄SiO₄ from fly ash via a solid-state reaction with K₂CO₃, which exhibited a CO₂ uptake capacity of 10.7 wt %. Ortiz-Landeros et al.⁸ doped Li₄SiO₄ with aluminum and vanadium ions, and obtained a CO₂ uptake capacity of 17.1 wt %. Shan et al.²⁹ prepared Li₄SiO₄ from a diatomite precursor using a solid-state method, and the sample showed an increased CO₂ uptake capacity of 28.6 wt % (78% of theoretical sorption capacity). Xiang et al.¹⁰ synthesized a porous Li_{3.9}Na_{0.1}Si_{0.96}Ti_{0.04}O₄ sorbent using a sol-gel method and studied the relationship between Ti-doping and volume expansion for the first time. This sorbent showed a CO₂ uptake capacity of 31.6 wt % (86% of theoretical sorption value). Lee et al.¹¹ fabricated a coral-like Li₄SiO₄ by thermal conversion of a Li- and Si-containing metal-organic framework, and achieved a CO₂ uptake as high as 32.4 wt % at 550 °C. Wang et al.¹² designed a Li₄SiO₄ coupled with carbon coating using a sol-gel process, and this material exhibited a high CO₂ capture capacity of 34.2 wt % (93% of theoretical sorption value). Subha et al.¹³ used colloidal silica as the silicon source, and the CO₂ capture capacity of the as-prepared Li₄SiO₄ was further increased to 35.0 wt % (97% of theoretical sorption capacity). Particularly, it is noteworthy that another type of lithium silicate Li₈SiO₆ demonstrated an even higher CO₂ uptake capacity of 52.1 wt %.¹⁴

SBA-15 is an archetypal mesoporous silica and has been widely used as a catalysts, catalyst supports, and adsorbents, etc.¹⁵ SBA-15 type materials with different morphologies and structures can be readily obtained by changing synthesis parameters such as hydrothermal reaction duration and temperature, and hydrochloric acid concentration, etc.¹⁶ Thanks to its ordered pore channels, high specific surface area, and thin wall thickness, we speculated that SBA-15 could be a superior precursor and facilitates much better contact with lithium precursors than commercial SiO₂ so that highly pure lithium silicates could be obtained with shorter calcination time and lower calcination temperatures. To date, there has been no report of the use of SBA-15 as silica precursor for the fabrication of lithium silicates-based CO₂ sorbents. In this contribution, we describe a series of lithium silicates using SBA-15 precursor and comprehensively investigate their high temperature CO₂ capture performance.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. **2.1.1. Preparation of SBA-15.** SBA-15 was synthesized using a modified classical method.¹⁷ A total of 360 g of deionized water was mixed with 43 g of hydrochloric acid (36–38%, Beijing Chemical Works), followed by adding 12 g of P-123 block copolymer (Sigma-Aldrich Life Science & Technology Co., Ltd.) into the solution. The mixed solution was stirred vigorously at 35 °C until all the P-123 was dissolved completely, after which 24 g of tetraethyl orthosilicate (Sinopharm Chemical Reagent Co., Ltd.) was added dropwise. The mixture was kept stirring at 35 °C for 24 h. The resulting gel was transferred into a Teflon-lined autoclave and was hydrothermally treated at 100 °C for 24 h. The product was filtered and washed with deionized water until the pH = 7.0, followed by calcination at 550 °C for 6 h. After grinding, white powder of SBA-15 was obtained.

2.1.2. Preparation of Lithium Silicates. A solid-state reaction protocol was implemented to load SBA-15 with lithium nitrate. A total of 0.3 g of SBA-15 powders and a corresponding amount of lithium nitrate (SHFS Co.) were mixed mechanically at predefined ratios (Li/Si = 3–11) in an agate mortar, and a moderate amount of absolute ethanol (99.8%, Beijing Chemical Works) was added in order to ensure homogeneous mixing of the solids during grinding process. After being dried in an oven at 60 °C for 10 min, the mixed powders were calcined at 750 °C for 6 h. Other calcination temperatures and durations were also used in order to optimize the performance of the products for CO₂ capture. The molar ratio of Li/Si was controlled in the range of 3–11, and the correspondingly synthesized samples were noted as Li-SBA15-*x*, in which *x* represents the Li/Si ratio.

2.1.3. Preparation of Li₂SiO₃ and Its Mixtures with Li₄SiO₄. Pure Li₂SiO₃ was synthesized using a hydrothermal method.¹⁸ A total of 0.400 g of lithium nitrate was mixed with 0.522 g of SiO₂ powder (SHFS Co), and then the mixed powders were added into the 60 mL 0.3 M hot NaOH solution (Beijing Chemical Works). The mixed solution was stirred vigorously for 15 min and then was transferred into a Teflon-lined autoclave. After the hydrothermal treatment at 180 °C for 48 h, the product was filtered and washed with deionized water, followed by drying and grinding, and the powder of Li₂SiO₃ was obtained. The mixtures of 2 or 8 wt % Li₂SiO₃ with Li₄SiO₄ were simply obtained by mixing and grinding in a certain weight ratio, and the samples were noted as "Li₄SiO₄ + *x* wt % Li₂SiO₃".

2.2. Sample Characterization. Powder X-ray diffraction (XRD) analysis was performed in a Shimadzu XRD-7000 instrument in reflection mode with Cu K α radiation and a power of 40 kV $\times$ 40 mA. Within a wide-angle range of $2\theta = 5\text{--}80^\circ$, XRD patterns were recorded with a scanning speed of 5° per minute and a step size of 0.02° . Within a low-angle range of $2\theta = 0.5\text{--}5^\circ$, XRD patterns were recorded with a scanning speed of 1° per minute and a step size of 0.02° . To evaluate the pore size distribution and specific surface areas of samples, a N₂ adsorption/desorption test was conducted in a BET instrument (SSA-7000). The morphology and structure characterizations of samples were examined using scanning electronic microscopy (SEM, Hitachi S-3400N II) and transmission electronic microscopy (TEM, JEM-1010) analyses.

2.3. Evaluation of CO₂ Sorption Performance. CO₂ sorption capacity and cycling stability were both evaluated using a thermogravimetric analysis (TGA) apparatus (Q50 TA Instrument). An approximately 20 mg sample was loaded into a platinum tray and heated to the sorption temperature at a ramping rate of $5^\circ\text{C}/\text{min}$ under pure N₂ atmosphere. After the sorption temperature was kept for 30 min, N₂ was shifted to CO₂ with different concentrations and the sample was left to sorb CO₂ for 180 min. Cycling stability measurements were conducted with the similar conditions. A sorption and desorption temperature of 575, 600, and 650 °C was used for 100 vol %, 50 vol %, and 20 vol % CO₂, respectively. CO₂ sorption was performed for 60 min, and the desorption was performed at the same temperature for 30 min. During all evaluation processes, the flow rate of N₂ and CO₂ was kept at 40 and 20 mL/min, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Synthesized SBA-15. Synthesized SBA-15 sample was first thoroughly characterized using XRD, N₂ adsorption/desorption, SEM, and TEM analyses. Figure 1a shows the XRD pattern of SBA-15. In low 2θ range, three Bragg reflections are observed, which may be indexed as (100), (110), (200) reflections of the hexagonal arrangement of the pores in SBA-15.^{17,19} At higher 2θ , a broad reflection is observed at approximately $2\theta = 22^\circ$, which indicates that SBA-15 has amorphous silica wall features. Figure 1b shows the N₂ adsorption/desorption isotherm of the as-synthesized SBA-15. The curves of adsorption and desorption were parallel and show a H1-type hysteresis loop, which is the characteristic of a type IV isotherm, indicating that SBA-15 possessed regular and homogeneous mesopores.²⁰ The specific surface area and pore

Table 1. Summary of Silicate-Based Sorbents and Their CO₂ Capture Performance

schemes altering the silicon sources	materials	synthesis conditions	CO ₂ sorption performance	ref
designing special morphology	Li ₄ SiO ₄	solid-state route, rice husk ash, calcined at 800 °C for 4 h	32.4 wt % at 650 °C for 150 min, 100% CO ₂ , 33.0 wt % after 15 cycles, sorption: 650 °C for 15 min, desorption: 800 °C for 10 min	23a
	Li ₄ SiO ₄	solid-state route, diatomite, calcined at 700 °C for 2 h	28.6 wt % at 620 °C for 180 min, 100% CO ₂ , 32.3 wt % after 10 cycles, sorption and desorption at 700 °C for 30 min for each one	9
	Li ₄ SiO ₄	solid-state route, diatomite, calcined at 700 °C for 2 h	30.3 wt % at 620 °C for 100 min, 50% CO ₂ , 27.7 wt % after 16 cycles, sorption and desorption at 700 °C for 30 min for each one	29
	Li ₄ SiO ₄	solid-state route, water pretreatment rice straw ash, calcined at 800 °C for 4 h	31.6 wt % at 680 °C for 120 min, 100% CO ₂ , around 28.0 wt % after 15 cycles, sorption: 680 °C for 15 min, desorption: 800 °C for 10 min	23e
	Li ₄ SiO ₄	solid-state route, nanocitric acid pretreatment rice husk ash, calcined at 700 °C for 4 h	30.5 wt % at 680 °C for 120 min, 100% CO ₂ , around 27.0 wt % after 15 cycles, sorption: 680 °C for 15 min, desorption: 800 °C for 10 min	23d
loading with alkali metals	platelet-shaped Li ₄ SiO ₄	sol-gel approach, colloidal silica, calcined at 800 °C for 3 h	35.0 wt % at 700 °C, 100% CO ₂ , around 35.0 wt % after 5 cycles, sorption and desorption at 700 °C	13
	macroporous Li ₄ SiO ₄	solid-state route, fumed silica (Cab-O-Sil, MS), calcined at 600 °C for 7 h	29.8 wt % at 550 °C for 100 min, 100% CO ₂ , around 28.0 wt % after 10 cycles, sorption: 550 °C for 120 min, desorption: 550 °C for 300 min	3
	coral-like Li ₄ SiO ₄	a metal-organic frameworks as precursors, calcined at 700 °C for 6 h and further calcined at 650 °C for 2 h	32.4 wt % at 550 °C for 300 min, 15% CO ₂ , from 22.4 wt % to 7.7 wt % after 25 cycles, sorption: at 550 °C, desorption: at 650 °C, a cycle for 200 min	11
	macroporous Li ₄ SiO ₄ coupled with carbon coating	a sol-gel method combined with carbon coating, fumed silica, calcined at 700 °C for 4 h	34.2 wt % at 680 °C for 120 min, 100% CO ₂ , around 32.5 wt % after 20 cycles, sorption: 680 °C for 15 min, desorption: 800 °C for 10 min	12
	Li ₄ SiO ₄ + K ₂ CO ₃	solid-state route, SiO ₂ (quartz type), calcined at 1000 °C for 8 h	27.7 wt % at 500 °C for 60 min, 20% CO ₂	32
transition metal doping	Li ₄ SiO ₄ + K ₂ CO ₃	solid-state route, fly ashes, calcined at 950 °C for 8 h	10.7 wt % at 600 °C for 60 min, 100% CO ₂ , 10.1 wt % after 10 cycles, sorption and desorption at 600 °C for 15 min for each one	7
	Li ₄ SiO ₄ + K ₂ CO ₃	solid-state route, crystalline quartz, calcined at 900 °C for 4 h	27.0 wt % at 580 °C for 120 min, 4% CO ₂ , 23.0 wt % after 4 cycles, sorption: 580 °C for 60 min, desorption: 750 °C for 10 min	25
	Li ₄ SiO ₄ + K ₂ CO ₃ + Na ₂ CO ₃	solid-state route, quartz type, calcined at 900 °C for 4 h	23.0 wt % at 580 °C for 120 min, 4% CO ₂ , for K-Li ₃ SiO ₄ , 15.0 wt % after 25 cycles, sorption: 580 °C for 30 min, desorption: 700 °C for 15 min	27a
	Li ₄ SiO ₄ + K ₂ CO ₃	solid-state route, SiO ₂ (AR), calcined at 750 °C for 6 h	31.0 wt % at 575 °C for 200 min, 10% CO ₂ , 20% steam, 22.5 wt % after 10 cycles, sorption: 575 °C, 100% CO ₂ , desorption: 700 °C	33
	Al and Fe doped Li ₄ SiO ₄	solid-state route, SiO ₂ (AR), calcined at 850 °C for 8 h	22.0 wt % at 650 °C for 60 min, 100% CO ₂ , 18.7 wt % after 5 cycles, sorption and desorption at 650 °C for 60 min for each one	34
Li substitution by Na	Li _{4+x} (Si _{1-x} Al _x)O ₄	solid-state route, fumed silica, calcined at 850 °C for 12.5 h	17.2 wt % at 700 °C for 200 min, 100% CO ₂	23b
	Li _{4-x} Na _x SiO ₄	coprecipitation method, tetraethyl-orthosilicate, calcined at 900 °C for 6 h	19.4 wt % at 680 °C for 300 min, 100% CO ₂	30
	Li _{3.9} Na _{0.1} Si _{0.96} Ti _{0.04} O ₄	a sol-gel method, tetraethyl orthosilicate, calcined at 700 °C for 4 h	31.6 wt % at 650 °C for 180 min, 100% CO ₂ , 33.1 wt % after 10 cycles, sorption: 650 °C for 60 min, desorption: 650 °C for 40 min	10
	Li ₄ SiO ₄ modified by the ball milling	wet-mixing and solid-state route, fumed silica, calcined at 700 °C for 4 h	21.1 wt % at 600 °C for 240 min, 100% CO ₂ , 15.0 wt % after 10 cycles, sorption and desorption at 550 °C for 90 min for each one	23c
	Li ₄ SiO ₄	water-based sol-gel technique, SiO ₂ (AR), calcined at 700 °C for 4 h	32.3 wt % at 680 °C for 120 min, 100% CO ₂ , 28.6 wt % after 15 cycles, sorption: 680 °C for 15 min, desorption: 800 °C for 10 min	23d
others	fly ash based Na/Li silicates	solid-state route, fly ash, calcined at 800 °C for 8 h	16.2 wt % at 700 °C for 120 min, 14% CO ₂ , 12% H ₂ O, around 10 wt % after 10 cycles, sorption and desorption at 700 °C for 45 min for each other	27b
	Li ₄ SiO ₄	hydration-calcination technique, fumed silica, calcined at 800 °C for 4 h	27.5 wt % at 680 °C for 120 min, 100% CO ₂ , around 27.5 wt % after 15 cycles, sorption: 680 °C for 15 min, desorption: 800 °C for 10 min	35
	Li ₈ SiO ₆	solid-state reaction, silicon dioxide, calcined at 800 °C for 8 h	52.1 wt % at 650 °C for 180 min, 100% CO ₂	14
	Li ₈ SiO ₆ + K ₂ CO ₃ + Na ₂ CO ₃	solid-state reaction, silicon dioxide, calcined at 800 °C for 8 h	45.0 wt % at 650 °C for 180 min, 100% CO ₂ , 6.6 wt % after 10 cycles, sorption: 650 °C, desorption: 800 °C	24

Figure 1. (a) XRD patterns, (b) N_2 adsorption/desorption isotherm, (c) SEM images, and (d) TEM image of synthesized SBA-15.

size calculated by the BET method was $907.0 \text{ m}^2/\text{g}$ and 5.6 nm , respectively.

The morphology and mesoporous structure were then examined using SEM and TEM analyses. Figure 1c shows the SEM image of synthesized SBA-15, which indicates a fiber rod-like morphology. The TEM image in Figure 1d shows that the sample exhibits highly ordered mesopore channels.

3.2. Synthesis of Lithium Silicates (Li-SBA15- x). A comprehensive investigation on the synthesis of lithium silicates using SBA-15 as the silica source and LiNO_3 as lithium source was performed. Different ratios of SBA-15 and LiNO_3 were mixed together and calcined for different times and at temperatures to give samples designated as Li-SBA15- x ($x = \text{Li/Si ratio}$). The influence of synthesis parameters on the CO_2 sorption capacity of the obtained samples was then investigated. In order to correlate the CO_2 sorption capacity with their structure and chemical composition, all samples were characterized using XRD and analyzed using a normalized reference intensity ratio (RIR) method. Thus, the optimization of the synthesis of lithium silicates was based on both the CO_2 sorption capacity and the XRD and RIR analyses.

In order to determine the appropriate sorption temperature regime, the effects of sorption temperature on the CO_2 capture capacity of a model sample was initially studied. Li-SBA15-4 (Li/Si = 4) was synthesized by calcination at 750°C for 6 h, and its CO_2 uptake capacity with the increase in sorption temperature from 550 to 700°C is shown in Figure 2a. The CO_2 sorption capacity first increased from 550 to 650°C and then started to decrease from 650 to 700°C . At 550°C , the diffusion process is kinetically controlled, and the diffusion barrier is the main reason for the low CO_2 sorption capacity at low temperature. And with the increase in sorption temperature to 650°C , the diffusion

process could be accelerated so that the sorption rate becomes much faster, which leads to higher overall CO_2 sorption capacity over the same testing period. But if the temperature (700°C) is too high, the sorbed CO_2 may start to desorb. And in the meantime, too high a temperature is more likely to cause sintering, which has a negative effect on CO_2 sorption capacity. It is clear that the sample shows the best sorption performance at 650°C , and therefore, we reasonably selected 650°C as the optimal sorption temperature for further studies.

3.2.1. Influence of Li/Si Molar Ratio (x) on CO_2 Uptake Capacity. The influence of Li/Si molar ratio (x) on the formation of lithium silicates and their subsequent CO_2 sorption capacity was explored. The uptake data are shown in Figure 2b,c. All Li-SBA15- x ($x = 3, 4, 5, 6, 7, 8, 9, 10, 11$) samples were synthesized at 750°C for 6 h and were then tested at 650°C . For Li-SBA15-3, the CO_2 sorption curve sharply increased to a plateau within 10 min. As the Li/Si molar ratio was increased to 4, the CO_2 sorption capacity of the sample was increased to $35.6 \text{ wt } \%$, which corresponds to 97.1% of the theoretical value. With a further increase of the Li/Si molar ratio from 5 to 7, the CO_2 sorption capacity of samples continuously increased, but it took a longer time to reach a plateau in comparison with Li-SBA15-3 and Li-SBA15-4. A similar tendency was also observed; as the Li/Si molar ratio was increased from 8 to 10, the CO_2 uptake capacity of Li-SBA15-10 increased tremendously to $59.8 \text{ wt } \%$. However, for Li-SBA15-11, almost no change was observed in CO_2 sorption capacity compared to Li-SBA15-10.

In order to correlate the CO_2 sorption capacity with the composition of sorbents, the chemical composition of samples with different Li/Si molar ratios were then determined using XRD and RIR analyses, as shown in Figure 3 and Table 2. For Li-SBA15-3 and Li-SBA15-4, Li_4SiO_4 was the main crystalline

Figure 2. (a) The effect of sorption temperature on the CO₂ capture performance of Li-SBA15-4, and (b) and (c) the CO₂ capture capacity of Li-SBA15-*x* at 650 °C.

phase, with a certain amount of Li₂SiO₃ detected at $2\theta = 18.84^\circ$ and 26.92° . However, as *x* was increased to 5, only the main characteristic peak of Li₄SiO₄ was observed at $2\theta = 22.14^\circ$, which indicated that pure Li₄SiO₄ phase was obtained. Compared to Li-SBA15-4, the CO₂ sorption capacity of Li-SBA15-5 was slightly lower (Figure 2c). This might be due to the existence of Li₂SiO₃ impurity in Li-SBA15-4, which can act as a lithium ion conductor and thus promote the bulk diffusion.²¹

In order to further confirm that the presence of a certain amount of Li₂SiO₃ phase can promote the CO₂ capture performance of Li₄SiO₄, pure Li₂SiO₃ and Li₄SiO₄ were synthesized using

Figure 3. XRD patterns of Li-SBA-*x* with different Li/Si (*x*) molar ratios from 3 to 11.

hydrothermal¹⁸ and solid-state methods, respectively. These two pure phases were then mixed physically by simply grinding in a mortar. Two wt % and 8 wt % of Li₂SiO₃ were charged for this studies. The XRD patterns of pure Li₂SiO₃, pure Li₄SiO₄, and the mixtures of them were analyzed and summarized in Figure S1. The characteristic peaks of Li₂SiO₃ at $2\theta = 18.84^\circ$, 26.92° , and 33.15° were observed for both Li₄SiO₄ + 2 wt % Li₂SiO₃ and Li₄SiO₄ + 8 wt % Li₂SiO₃, indicating the Li₂SiO₃ phase was successfully introduced to the Li₄SiO₄ phase. The CO₂ sorption performance of these two mixtures was evaluated at 650 °C for 2 h, as shown in Figure S2. The results indicated that the CO₂ sorption capacity of pure Li₄SiO₄ can be significantly increased by adding a certain amount of Li₂SiO₃. With 2 or 8 wt % of Li₂SiO₃, the CO₂ sorption capacity within 2 h was increased from 25.6 wt % to 30.5 and 29.5 wt %, respectively. The obtained CO₂ sorption capacities of these two mixtures are somehow lower than that of Li-SBA15-4 (35.5 wt %) over the same testing period. This is reasonable because the dispersion of Li₂SiO₃ within Li₄SiO₄ prepared by physical mixing is relatively worse. Thus, this designed experiment clearly demonstrated that the existence of a small amount of Li₂SiO₃ can promote the CO₂ sorption capacity of Li₄SiO₄.

With the increase in *x*, the Li₄SiO₄ phase was always detected, and in the meantime, the Li₈SiO₆ phase ($2\theta = 25.24^\circ$) started to appear in the Li-SBA15-6 sample. Furthermore, the LiOH phase was observed at 2θ ca. 32.50° in Li-SBA15-9 and SBA15-10 samples. Owing to the existence of Li₈SiO₆ and LiOH, the CO₂ sorption capacity of Li-SBA15-9 and SBA15-10 was significantly increased. Nevertheless, when the Li/Si molar ratio was increased to 11, the characteristic reflection of LiOH was replaced by that of Li₂O at $2\theta = 33.44^\circ$. Because Li₂O possesses a higher theoretical capacity than LiOH, it is reasonable that Li-SBA15-11 showed a slightly higher CO₂ uptake than Li-SBA15-10.

It is still unclear why some samples have a similar chemical composition but different sorption capacities. We performed a semiquantitative analysis of the XRD Bragg peak intensities using a normalized RIR method, as given in eq 2.²² By semiquantitatively determining the crystalline phases in each sample, we hoped to achieve a deeper understanding on how *x* influences the CO₂ sorption performance. In eq 2, *x* means one phase in the all definite crystalline phases of the analyzed sample and *W_x* represents the phase abundance of *x* phase. *A* is representative for the phase selected to work as an internal standard, and *I_x* denotes the intensity of a specific pattern of the *x* phase which

Table 2. Phase Abundance of All Synthesized Samples Calculated Using the Normalized RIR Method

calcination T (°C)	calcination duration (h)	samples	chemical components (wt %)						calculated Li/Si	
			Li ₈ SiO ₆	Li ₄ SiO ₄	Li ₂ SiO ₃	LiOH	Li ₂ O	SiO ₂		
750	6	Li-SBA15-3		71.84	28.16				3.31	
		Li-SBA15-4		98.09	1.91				3.95	
		Li-SiO ₂ -4		80.99	17.08			1.93	3.43	
		Li-SBA15-5		100.00					4.00	
		Li-SBA15-6	22.59	77.41					4.65	
		Li-SBA15-7	40.33	59.67					5.24	
		Li-SBA15-8	36.48	63.52					5.11	
		Li-SBA15-9	30.23	34.90		34.87			8.63	
		Li-SBA15-10	40.62	18.28		41.10			10.92	
		6	Li-SBA15-4		98.09	1.91				3.94
	Li-SBA15-10		40.62	18.28		41.10			10.92	
	4		Li-SBA15-4		97.08	2.92				3.92
			Li-SBA15-10	58.78	19.88		21.34			8.46
			Li-SiO ₂ -10	32.16	27.92		39.92			9.79
	2		Li-SBA15-4		92.13	7.87				3.80
			Li-SiO ₂ -4		72.58	2.46			24.95	2.36
			Li-SBA15-10	17.47	36.36		46.16			9.78
	0.5		Li-SBA15-4		94.03	5.97				3.84
			Li-SBA15-10	11.25	31.98		45.22	11.54		12.83
	650		2	Li-SBA15-4		93.92	6.08			3.84
	750			Li-SBA15-4		92.13	7.87			3.80
	850			Li-SBA15-4		93.87	6.13			3.84
	650		4	Li-SBA15-10	24.45	75.55				4.71
	750			Li-SBA15-10	58.78	19.88		21.34		8.46
	850	Li-SBA15-10		15.66	57.63			26.70	7.76	

can be obtained from the peak reported in Jade analysis software. Finally, K_A^x can be calculated from eq 3. In this equation, K_x is equal to the RIR value of the x phase, which can be referred to with the relevant PDF card. All calculated results are summarized in Table 2.

$$W_x = \left(\frac{K_A^x}{I_x} \sum_{i=A}^n \frac{I_i}{K_A^i} \right)^{-1} \quad (2)$$

$$K_A^x = \frac{K_x}{K_A} \quad (3)$$

Table 2 shows that the CO₂ sorption capacity of Li-SBA15-3 and Li-SBA15-4 samples increased with the increase of Li₄SiO₄ phase abundance. It was noteworthy that the abundance of the Li₄SiO₄ phase attained 98 wt % when $x = 4$. For a comparison purpose, a control sample (Li-SiO₂-4) was synthesized using SiO₂ powder instead of SBA-15, and the Li₄SiO₄ phase abundance was only ca. 80 wt % in this sample. In the conventional synthesis process,^{3,23} it is common to add excess lithium for preventing the sublimation. Under the same synthesis condition, SBA-15 as a silicon source produced a much pure Li₄SiO₄ phase, which may be attributed to its ordered mesoporous structure that promoted lithium dispersion and complete reaction. For Li-SBA15-5 sample, only the Li₄SiO₄ phase can be detected, and its abundance was calculated as 100 wt %. With the increase in x , Li₈SiO₆, LiOH, and Li₂O phases with higher theoretical sorption values appeared one by one. The CO₂ uptake of Li-SBA15-6 and Li-SBA15-7 increased with the increase in the Li₈SiO₆ phase abundance. However, the Li₈SiO₆ phase abundance confusingly decreased in Li-SBA15-8 so that its CO₂ uptake capacity also reduced. For Li-SBA15-9 and Li-SBA15-10, their CO₂ uptake

capacity also increased owing to the increase in both Li₈SiO₆ and LiOH phase fractions.

The Li/Si ratios calculated from RIR results are also provided in Table 2. The calculated Li/Si ratios based on RIR results are close to the original added Li/Si ratios, suggesting that the RIR analysis is quite reliable. One exception is the Li-SBA15-10 sample that calcined at 650 °C for 4 h, whose calculated value (4.71) is much lower than the added Li/Si ratio of 10. This might be caused by the incomplete reaction between Li and Si when the original Li/Si ratio was high but the calcination temperature was low (650 °C), and the remaining Li may remain in an amorphous phase so the XRD analysis cannot detect it.

In addition to the influences of the chemical compositions with different Li/Si molar ratios, the effects of structures and morphological features have been also considered (Table S1 and Figures S3–S4). All samples presented the typical isotherm corresponding to nonporous materials, and their specific surface areas are all very low (1–1.5 m²/g). The N₂ adsorption/desorption results indicate that the ordered mesoporous structure of SBA-15 was destroyed during thermal treatment²² and the chemical compositions showed little effect on the structure of sorbents. The SEM images of Li-SBA15- x in Figure S4 show that most of samples possess smooth surfaces, corresponding to low specific surface area and morphological features of materials calcined at high temperature as the previous literature reports.^{13,22}

3.2.2. Influence of Calcination Time on CO₂ Uptake Capacity. On the basis of the above results, Li-SBA15-4 mainly containing Li₄SiO₄ and Li-SBA15-10 mainly containing Li₈SiO₆ were selected as the representative sorbents for further studies. The influence of calcination time of Li-SBA15-4 and Li-SBA15-10 on their CO₂ uptake capacity was investigated at a fixed calcination temperature at 750 °C. Figure 4a shows that the CO₂

Figure 4. CO₂ sorption isotherms of (a) Li-SBA15-4 and (b) Li-SBA15-10 calcined at 750 °C for different calcination times, and XRD patterns of (c) Li-SBA15-4 samples and (d) Li-SBA15-10 calcined at 750 °C for different calcination times.

sorption capacity of Li-SBA15-4 first increases and then decreases with an increase of calcination duration from 0.5 to 6 h. The highest CO₂ sorption capacity of 36.3 wt % was obtained with the sample calcined for 2 h, corresponding to 99% of the theoretical value. We further noted that materials prepared using the SBA-15 precursor exhibited a high CO₂ uptake even after a very short calcination time such as 0.5 h. Figure 4a (the dash line) illustrates the CO₂ sorption curve of the sample synthesized from SiO₂ at 750 °C for 2 h. The measured CO₂ uptake of this sample is only 23.5 wt %, which is significantly lower than that using the SBA-15 precursor.

According to Figure 4b, the CO₂ sorption capacity of Li-SBA15-10 displayed a similar variation trend to Li-SBA15-4. What is more, the weight dramatically increased after 2 min, and the highest capacity (62.0 wt %) was observed for a sample calcined for 4 h. The CO₂ sorption capacity of an equivalent sample using silica as a silicon source exhibited significantly less CO₂ uptake capacity (50.5 wt %), compared to the sample prepared from SBA-15 under the same synthesis condition.

Figure 4c,d shows the XRD pattern of Li-SBA15-4 and Li-SBA15-10 after different calcination times. According to literature reports, Li₄SiO₄ and Li₈SiO₆ have different optimal calcination times for the complete reaction between silicon and lithium sources.^{8,12,13,22,23,28} It was estimated that the optimal calcination time for Li₄SiO₄ is ca. 2–4 h and the optimal calcination time for Li₈SiO₆ is around 8 h. The Li-SBA15-4 sample was mainly composed of Li₄SiO₄ with a tiny amount of Li₂SiO₃. The phase fraction of Li₄SiO₄ first decreased and then increased as the calcination duration decreased from 6 to 0.5 h. The lowest fraction of Li₄SiO₄ was obtained with the sample calcined for 2 h (Table 2). It is thought that Li₂SiO₃ can improve the CO₂ sorption capacity, and hence a moderate phase fraction of both Li₄SiO₄ and Li₂SiO₃ may be the reason why the sample

calcined for 2 h possesses the highest CO₂ sorption capacity. For comparison purposes, a control sample synthesized from SiO₂ by calcining for 2 h was also prepared, which contained much less Li₄SiO₄ and a relatively larger amount of SiO₂. This indicates that the reaction between silicon source and lithium nitrate was incomplete. For Li-SBA15-10, all calcined samples contained Li₈SiO₆, Li₄SiO₄, and LiOH phases, but the abundance of each phase was different. As the calcination time decreased from 6 to 0.5 h, the fraction of Li₈SiO₆ first increased and then sharply decreased. The sample calcined for 4 h possessed the maximum Li₈SiO₆ phase fraction and the highest CO₂ sorption capacity.

3.2.3. The Influence of Calcination Temperature on CO₂ Uptake Capacity. The influence of calcination temperature on the synthesis of lithium silicates was investigated with selected Li-SBA15-*x* samples and calcination times. Both Li-SBA15-4 and Li-SBA15-10 were calcined at different temperatures for 2 and 4 h, respectively. Figure 5a,b shows the CO₂ sorption isotherms for Li-SBA15-4 and Li-SBA15-10 after different calcination temperatures. The results indicate that 750 °C is the optimal calcination temperature for both samples, which resulted in the highest CO₂ sorption capacity.

The XRD patterns and phase abundances of these samples are shown in Figure 5c,d and Table 2. For Li-SBA15-4, all the samples consisted of a mixture of Li₄SiO₄ and Li₂SiO₃. The sample calcined at 750 °C contained slightly more Li₂SiO₃, which might be the reason for its better CO₂ capture performance. For Li-SBA15-10, in addition to Li₈SiO₆ and Li₄SiO₄, LiOH, and Li₂O were formed in sequence as the calcination temperature increased from 650 to 850 °C. The sample containing the highest Li₈SiO₆ phase fraction exhibited the highest CO₂ sorption capacity (Figure 5b and Table 2).

Figure 6 shows the comparison of the CO₂ capture capacity of our synthesized Li₄SiO₄ (noted as Li-SBA15-4) with some recent

Figure 5. CO₂ sorption performance of (a) Li-SBA15-4 and (b) Li-SBA15-10 calcined at different calcination temperatures for 2 and 4 h, respectively, and XRD patterns of (c) Li-SBA15-4 samples and (d) Li-SBA15-10 calcined at different calcination temperatures for 2 and 4 h, respectively.

Figure 6. Comparison of the CO₂ capture capacity of optimized Li-SBA15-4 (Li₄SiO₄) with other Li₄SiO₄ samples that were reported in the literature.

literature reports. As a result of the significant effort of various researchers, the CO₂ capture capacity of Li₄SiO₄ was increased incrementally from 28.6 wt % to 35 wt %, corresponding to 78% to 95% of the theoretical uptake of Li₄SiO₄ (36.67 wt %). To the best of our knowledge, prior to our present work, the highest CO₂ uptake for Li₄SiO₄ was 35 wt %.^{29–13} In this contribution, the CO₂ uptake capacity of Li₄SiO₄ (Li-SBA15-4) synthesized from the SBA-15 precursor was increased to 36.3 wt %, corresponding to 99% of its theoretical CO₂ uptake. In addition, Li₈SiO₆ (Li-SBA15-10) synthesized from the SBA-15 precursor also resulted in a higher CO₂ uptake (62.0 wt %) comparing to previous literature reports.^{14,24} Therefore, these two excellent sorbents, Li-SBA15-4 and Li-SBA15-10, were further comprehensively investigated in the following sections.

3.3. Characterization of Optimized Lithium Silicates Sorbents.

Li-SBA15-4 synthesized at 750 °C for 2 h and Li-SBA15-10 synthesized at 750 °C for 4 h were investigated using BET N₂ adsorption/desorption and SEM. As shown in Figure 7a,b, both samples presented a type III isotherm with a narrow H3 hysteresis loop in a wide relative pressure range, corresponding to a nonporous or macroporous material. The N₂ BET specific surface areas of both samples were low, being 1.0 and 1.5 m²/g for Li-SBA15-4 and Li-SBA15-10, respectively. These data indicate that the ordered mesoporous structure of SBA-15 has been destroyed during thermal treatment.^{12,23d} Figure 7c,d shows the SEM images of Li-SBA15-4 and Li-SBA15-10, both of which were composed of dense agglomerate particles with a large size. A slight difference is that the surface roughness was observed for Li-SBA15-10. This morphology may be related to the high calcination temperature and was in agreement with previous literature reports.^{12,14,23a,c,d}

3.4. CO₂ Sorption Performance of Optimized Li-SBA15-4 and Li-SBA15-10.

3.4.1. Influence of CO₂ Concentration on Sorption Capacity. Considering the practical applications of CO₂ sorbents, the influence of CO₂ concentration on the sorption performance of optimized Li-SBA15-4 and Li-SBA15-10 was studied at 650 °C, as shown in Figure 8a,b. For Li-SBA15-4, the sorption capacity dramatically dropped with the decrease in CO₂ concentration, particularly when the CO₂ concentration was 20 vol %. When the CO₂ concentration was 100 vol %, the CO₂ sorption capacity was 36.7 wt %. However, it decreased to only 25.8 and 0.7 wt % when the CO₂ concentration was 50 vol % and 20 vol %, respectively. A similar CO₂ sorption performance was observed with Li-SBA15-10. The CO₂ sorption capacity dropped sharply from 62.0 wt % to 37.8 wt % as the CO₂ concentration decreased from 100 vol % to 50 vol %. However, the capacity did not further decrease significantly with 20 vol % CO₂.

Figure 7. N₂ adsorption/desorption isotherms of (a) Li-SBA15-4 synthesized at 750 °C for 2 h and (b) Li-SBA15-10 synthesized at 750 °C for 4 h, SEM images of (c) Li-SBA15-4 synthesized at 750 °C for 2 h and (d) Li-SBA15-10 synthesized at 750 °C for 4 h.

This phenomenon can be explained by the fact that the reverse reaction (CO₂ desorption) will be accelerated when the CO₂ concentration is low.²⁵ Moreover, the sorption temperature should be lower since CO₂ sorption is exothermic.²⁶ To determine the optimal sorption temperature under different CO₂ concentrations, temperature-programmed sorption of CO₂ was performed by heating the samples from room temperature to 800 °C at a ramping rate of 10 °C/min, as shown in Figure 8c,d. All samples displayed similar profiles; the weight of sample first increased due to sorption and then sharply decreased once the reverse reaction was activated. For Li-SBA15-4, it was evident that the maximum peak temperature shifted to lower values with the decrease in CO₂ concentration. When the CO₂ concentration was low, it can be expected that a sorption temperature of 650 °C is too high to sorb CO₂, so overall it showed worse sorption performance in Figure 8a. However, for Li-SBA15-10, the shift of the peak temperature was not obvious (Figure 8d).

Thus, in order to achieve good CO₂ sorption performance under specific CO₂ concentrations, selecting a proper sorption temperature is very important. In Figure 8e, under 20 vol % CO₂ atmosphere, Li-SBA15-4 exhibited extremely low capacity at 625 °C (2.0 wt %) and 650 °C (0.7 wt %). However, its CO₂ sorption capacity was dramatically increased to 29.5 wt % once the sorption temperature was decreased to 575 °C, which is a superior performance when compared with similar literature reports.^{11,25–27} Under 50 vol % CO₂ atmosphere, the optimal sorption temperature was 600 °C for Li-SBA15-4, with the highest CO₂ sorption capacity of 29.9 wt % (Figure 8f). These results clearly demonstrated that the sorption performance of Li-SBA15-4 was highly dependent on both the CO₂ concentration and the sorption temperature.

Figure 8g,h shows the sorption performance of Li-SBA15-10 under 20 vol % and 50 vol % CO₂ atmosphere, respectively. It is clear that in both cases Li-SBA15-10 exhibited slow kinetics when the sorption temperature was low (600 °C). While if the sorption temperature was too high (750 °C), the equilibrated CO₂ capture capacity was also reduced. The optimal sorption temperature was 650 °C for both cases, with the highest capacity of 36.4 and 37.8 wt % for 20 vol % and 50 vol % CO₂ concentrations, respectively. The influence of CO₂ concentration for Li-SBA15-10 is different from that for Li-SBA15-4, which is still unclear for us at the present time. We postulate that the sorption of CO₂ on the Li-SBA15-10 is more complex and might involve multiple steps. In general, we can conclude that the CO₂ sorption performance is lowered to some degree with decreasing CO₂ concentration. In order to have good CO₂ sorption performance under low CO₂ concentrations, a relatively low temperature should be selected.

3.4.2. Cycling and Stability Tests. The cycling stability is critical for the practical use of any CO₂ sorbent. To evaluate the regenerative properties and thermal stability of these optimized Li-SBA15-4 and Li-SBA15-10 sorbents, CO₂ sorption/desorption cycling tests were performed. Before performing the cycling tests, the optimum desorption temperatures for both Li-SBA15-4 and Li-SBA15-10 were determined by temperature-programmed desorption using TGA, as shown in Figure 9a,b. For Li-SBA15-4, the sorbed CO₂ mainly desorbed in the temperature range of 600–650 °C, indicating that the suitable desorption temperature should be chosen between 600–650 °C. At these temperatures, the sorbed CO₂ can be completely and rapidly desorbed from sample. However, for Li-SBA15-10, even with a temperature as high as 900 °C, the weight of sample only decreased by 17.6 wt %, which is much less than its sorption capacity. For a comparison, we chose 650 °C as the desorption temperature for both Li-SBA15-4 and Li-SBA15-10.

Figure 8. CO₂ sorption isotherms of (a) optimized Li-SBA15-4 and (b) optimized Li-SBA15-10 under different CO₂ concentrations, respectively, temperature-programmed sorption of CO₂ for (c) optimized Li-SBA15-4 and (d) optimized Li-SBA15-10 under different CO₂ concentrations, respectively, CO₂ sorption isotherms at different sorption temperatures of optimized Li-SBA15-4 under the CO₂ concentration of (e) 20 vol % and (f) 50 vol %, respectively, and CO₂ sorption isotherms at different sorption temperatures of optimized Li-SBA15-10 under the CO₂ concentration of (g) 20 vol % and (h) 50 vol %, respectively.

For Li-SBA15-4, the sorption capacity reached 32.5 wt % after the third cycle, and was maintained at 31.5 wt % even after 15 cycles. After 15 cycles, only 1 wt % capacity was lost, suggesting that the Li-SBA15-4 has excellent regenerative properties and thermal stability. However, for Li-SBA15-10, only 10.5 wt % of reversible CO₂ sorption/desorption capacity was obtained from its second cycle. Poor multicycle performance weakened its potential application, and more investigations are needed to improve its performance in the future.

Li-SBA15-4 showed excellent cycling performance with 100 vol % CO₂ (in Figure 9c) at 650 °C. We also studied its CO₂ sorption/desorption cycling performance at lower CO₂ concentrations, which is a more meaningful test for practical applications (Figure 9e). When the CO₂ concentration was 50 vol %, both the CO₂ sorption and desorption were conducted at 600 °C, and Li-SBA15-4 resulted in a reversible capacity of 27.4 wt % after 15 cycles. As the CO₂ concentration was decreased to 20 vol %, both the CO₂ sorption and desorption were conducted at 575 °C, and the capacity also dropped to

Figure 9. Temperature program desorption of sorbed CO₂ on (a) Li-SBA15-4 and (b) Li-SBA15-10, and CO₂ sorption/desorption cycling performance of (c) Li-SBA15-4 and (d) Li-SBA15-10 under 100 vol % CO₂ (sorption and desorption at 650 °C), and CO₂ sorption/desorption cycling performance of Li-SBA15-4 under (e) 50 vol % CO₂ (sorption and desorption at 600 °C) and (f) 20 vol % CO₂ (sorption and desorption at 575 °C).

18.2 wt % after 15 cycles. It is apparent that more cycles are needed for the Li-SBA15-4 sorbent to achieve its equilibrium capacity with the decrease in CO₂ concentration. It can be concluded that the CO₂ concentration has a great influence on the sorption and desorption performance of sorbents.

3.5. CO₂ Sorption Kinetics and Mechanism. **3.5.1. CO₂ Sorption Kinetics.** The CO₂ sorption kinetics of Li-SBA15-4 and Li-SBA15-10 were investigated by fitting their sorption curves using a well accepted double exponential function (eq 4).^{3,23c,28} We assume that two different sorption processes occur across the whole sorption process. First, an external layer of mixed solid forms after the initial carbonation reaction. Second, the continuous sorption depends on the bulk diffusion process of lithium. In eq 4, y represents the CO₂ sorption capacity in the form of mass percentage, t is the sorption time in seconds, k_1 and k_2 are the kinetic parameters in the surface chemical reaction and bulk diffusion process, respectively. Constants A and B are the intervals at each process that controls the whole CO₂ sorption process, and C indicates the y -intercept. All the kinetic analysis data are summarized in Table 3. In the case of Li-SBA15-4,

Li₄SiO₄ is the main composition phase. Samples synthesized either from SBA-15 or SiO₂ both had a high k_1 value that was 1 order of magnitude higher than the k_2 value, which indicates that the bulk diffusion process was the limiting step.^{3,12,13,27b,9} Table 3 shows that both samples synthesized from SBA-15 and SiO₂ had a similar

Table 3. Kinetics Parameters Obtained by Fitting the CO₂ Sorption Curves for Li-SBA15-4, Li-SiO₂-4, Li-SBA15-10, and Li-SiO₂-10 to eq 4

samples	k_1	k_2	R^2
Li-SBA15-4	0.0042	0.00078	0.9907
Li-SiO ₂ -4	0.0040	0.00035	0.9954
Li-SBA15-10-S1 ^a	0.0056		0.9965
Li-SiO ₂ -10-S1 ^a	0.0049		0.9981
Li-SBA15-10-S2 ^a	0.0039	0.00026	0.9997
Li-SiO ₂ -10-S2 ^a	0.0018	0.00007	0.9999

^aS1 denotes the very beginning process within a short period of time and S2 denotes the rest process of the whole reaction for CO₂ sorption on Li₈SiO₆.

performance during the initial carbonation reaction. However, the sample synthesized from SBA-15 had a higher k_2 value that was more than twice as high as that of the sample synthesized from SiO_2 , which suggests its excellent kinetics.

$$y = A \exp^{-k_1 t} + B \exp^{-k_2 t} + C \quad (4)$$

For Li-SBA15-10, the main phase is Li_8SiO_6 which may involve a much complicated reaction mechanism than with Li_4SiO_4 and is therefore not suitable for the exponential model. Considering that the reactions were conducted under the excess CO_2 atmosphere, a first-order reaction can be expected at the beginning of the reaction.²⁴ The first-order reaction is expressed in eq 5. Where m and m_0 represent the sample mass during and before sorption process, respectively, t is the sorption time in second, and k is the kinetics constant. Figure 10a shows the plots of $\ln\left(\frac{m}{m_0}\right)$ as a function of time for Li-SBA15-10 and Li-SiO₂-10. In the case of Li-SBA15-10, its fitting curve showed a much higher slope than that for Li-SiO₂-10, demonstrating that Li-SBA15-10 possesses a much faster sorption rate.

$$\ln\left(\frac{m}{m_0}\right) = kt \quad (5)$$

3.5.2. Reaction Mechanism. To gain insights into the CO_2 sorption mechanism of the optimized samples, the products after sorption were analyzed further. Figure 10b shows the XRD patterns of these samples after CO_2 sorption at 650 °C for 3 h, which indicate both samples produced Li_4SiO_4 , Li_2SiO_3 , and Li_2CO_3 after sorption. For Li-SBA15-10, Li_8SiO_6 accounts for the major phase, as shown in Table 2. Figure 10b confirms that no characteristic Bragg reflections for Li_8SiO_6 were detected after CO_2 sorption, indicating a complete reaction of Li_8SiO_6 . The possible reactions during the carbonation process are proposed in eq 6.³⁰ Considering the final products contain Li_4SiO_4 , Li_2SiO_3 , and Li_2CO_3 , we propose that the CO_2 sorption on Li_8SiO_6 may occur according to reaction 6. Li_4SiO_4 can sequentially react further with CO_2 to form Li_2SiO_3 according to reaction 1. This means that Li_8SiO_6 plays a significant role in the rapid initial CO_2 sorption for Li-SBA15-10 (Figure 4b).

To prove this hypothesis, the product after only 5 min CO_2 sorption was analyzed by XRD, and the whole sorption curve of Li-SBA15-10 sorbents was fitted using the kinetics models that were applied to both Li_8SiO_6 and Li_4SiO_4 . In Figure 10c, compared with raw Li-SBA15-10, no characteristic Bragg reflections of Li_8SiO_6 were detected after 5 min CO_2 sorption, which indicated a complete and rapid reaction of Li_8SiO_6 and meanwhile confirmed the hypothesis that Li_8SiO_6 plays a significant role in the initial rapid sorption. It is universally valid that a double exponential model is utilized to fit the whole sorption curve of Li_4SiO_4 , and a first-order reaction can be adapted to fit the sorption curve of Li_8SiO_6 at the beginning of reaction.^{24,28} Hence, the whole sorption curve of Li-SBA15-10 may be fitted by using these two models. And all fitted kinetics parameters are summarized in Table 3. The high R square indicated both models can fit the sorption curve well, which further supports the hypothesis that Li_8SiO_6 can sorb CO_2 much faster than Li_4SiO_4 in Li-SBA15-10. Li-SiO₂-10 was also analyzed using the same method, confirming Li-SBA15-10 is much better than Li-SiO₂-10.

It is generally accepted that the double shell mechanism can be applied to describe the CO_2 sorption process on Li_4SiO_4 .^{13,21,31}

Figure 10. (a) Plots of $\ln[m/m_0]$ as a function of time for Li-SBA15-10 and Li-SiO₂-10. Data were obtained in an extremely short time, which may correspond to a stage where the diffusion process did not occur. (b) XRD patterns of products after CO_2 sorption for 3 h from Li-SBA15-4 and Li-SBA15-10. (c) XRD patterns of products after CO_2 sorption on Li-SBA15-10 for only 5 min.

However, the use of Li_8SiO_6 as a novel high-temperature CO_2 sorbent candidate has not yet been investigated in detail. In summary, we proposed that the CO_2 entrapment in Li_8SiO_6 might occur in two steps: first Li_8SiO_6 reacts with 2 equiv of CO_2 to produce Li_4SiO_4 , and second Li_4SiO_4 reacts with further CO_2 to form Li_2SiO_3 and Li_2CO_3 .

4. CONCLUSIONS

We have demonstrated that SBA-15 is an excellent silicon precursor for the synthesis of lithium silicates with significantly improved CO_2 capture performance. The Li/Si ratio in the

precursors, calcination temperature, and calcination duration all showed a great effect on the chemical composition and the CO₂ capture capacity of the as-prepared lithium silicates. XRD and a normalized reference intensity ratio analyses suggest that the CO₂ sorption performance of synthesized lithium silicates can be correlated to their crystalline phase fractions. Under the optimized conditions, the Li-SBA15-4 sample that mainly contains Li₄SiO₄ achieved an extremely high CO₂ capture capacity of 36.3 wt %, by far the highest capacity among all reported Li₄SiO₄ sorbents. RIR analyses indicated that SBA-15 can result in a much higher abundance of the Li₄SiO₄ phase (98 wt %) than SiO₂ powder (80 wt %), which explains why SBA-15 is better than SiO₂ as a precursor for Li₄SiO₄. Li-SBA15-4 also showed a very high cycling stability with only 1.0 wt % capacity loss after 15 cycles. Another sample Li-SBA15-10 that mainly contains Li₈SiO₆ displayed a very high CO₂ uptake of 62.0 wt %, while its regeneration capacity was very poor, demonstrating only a 10.5 wt % reversible CO₂ capture capacity. The influence of CO₂ concentration (20 vol %, 50 vol %, and 100 vol %) on the CO₂ capture performance of Li-SBA15-4 and Li-SBA15-10 was also studied. At low CO₂ concentrations, relatively lower sorption temperatures are needed to achieve its maximum CO₂ capture capacity. Kinetic studies showed that the lithium silicates synthesized from SBA-15 exhibited much higher CO₂ sorption kinetics, more than twice as fast as that of the sample synthesized from SiO₂, suggesting SBA-15 as the silicon source promotes not only the CO₂ sorption capacity but also sorption rates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00559.

Additional BET analyses data, XRD patterns, SEM images, and isothermal CO₂ sorption results (PDF)

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Notes

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