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JournalFacile synthesis of macroporous  $\text{Li}_4\text{SiO}_4$  with remarkably enhanced  $\text{CO}_2$  adsorption kineticsHyeonbin Kim<sup>a</sup>, Hee Dong Jang<sup>b,1</sup>, Minkee Choi<sup>a,\*</sup><sup>a</sup> Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea<sup>b</sup> Department of Industrial Materials Research, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea

## HIGHLIGHTS

- We synthesized macroporous  $\text{Li}_4\text{SiO}_4$  by solid-state method using LiOH and fumed silica.
- The use of LiOH decreased the synthesis temperature of  $\text{Li}_4\text{SiO}_4$  down to 600 °C.
- The decrease of synthesis temperature circumvents undesirable sintering of  $\text{Li}_4\text{SiO}_4$ .
- Macroporous  $\text{Li}_4\text{SiO}_4$  exhibited enhanced  $\text{CO}_2$  adsorption capacity and adsorption rate.
- During 10 cycles, the adsorption performance of macroporous  $\text{Li}_4\text{SiO}_4$  were maintained.

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## ABSTRACT

Lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) has attracted extensive scientific attention due to its large  $\text{CO}_2$  adsorption capacity at high temperature (650–700 °C) and low material cost. However, the conventional nonporous  $\text{Li}_4\text{SiO}_4$  ceramic shows very poor  $\text{CO}_2$  adsorption performance below 600 °C, which is a relevant condition for possible applications such as sorption-enhanced steam methane reforming. In the present work, in order to increase the  $\text{CO}_2$  adsorption kinetics below 600 °C,  $\text{Li}_4\text{SiO}_4$  was synthesized in the form of a macroporous structure by a simple solid-state transformation method using LiOH and fumed silica as a precursor for Li and  $\text{SiO}_2$ , respectively. The use of LiOH substantially decreased the synthesis temperature of  $\text{Li}_4\text{SiO}_4$  down to 600 °C, compared with the conventional syntheses using other lithium precursors such as  $\text{Li}_2\text{CO}_3$  and  $\text{LiNO}_3$  that require very high synthesis temperature (>700 °C). The decrease of the material synthesis temperature circumvents undesirable sintering of initially formed small  $\text{Li}_4\text{SiO}_4$  crystallites and leads to the formation of a highly macroporous (macropore volume >0.6 mL g<sup>-1</sup>)  $\text{Li}_4\text{SiO}_4$  framework that has a significantly higher BET surface area (15 m<sup>2</sup> g<sup>-1</sup>) than conventional nonporous  $\text{Li}_4\text{SiO}_4$  (<1.0 m<sup>2</sup> g<sup>-1</sup>). The macroporous  $\text{Li}_4\text{SiO}_4$  exhibited dramatically enhanced  $\text{CO}_2$  adsorption capacity (29.8 wt%) and rate (56.1 mg g<sup>-1</sup> min<sup>-1</sup>), compared with the  $\text{CO}_2$  adsorption capacities (1.40–7.79 wt%) and rates (0.420–2.95 mg g<sup>-1</sup> min<sup>-1</sup>) of nonporous  $\text{Li}_4\text{SiO}_4$  materials. Adsorption-desorption cycles at 550 °C could be repeated 10 times without a significant decrease in the adsorption capacity or the rate capability.

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## 1. Introduction

Developing adsorbents for carbon dioxide ( $\text{CO}_2$ ) capture at high temperature (450–700 °C) has recently drawn significant interest [1]. The flue gas from the coal-burner is hot and its temperatures vary from a few hundred to about a thousand degrees Celsius depending on the specific locations in the flue gas line in the power

plant [2]. Direct capture of  $\text{CO}_2$  at high temperature can improve the energy efficiency by overcoming the need to cool the gas to ambient temperature prior to  $\text{CO}_2$  removal [3]. Another important application of high-temperature  $\text{CO}_2$  adsorbent is sorption-enhanced steam methane reforming (SE-SMR) for hydrogen production [4,5]. The process utilizes a solid  $\text{CO}_2$  adsorbent to capture  $\text{CO}_2$  produced in the reforming reactor and thereby overcomes the thermodynamic limitations of the reaction via Le Chatelier's principle. SE-SMR consequently can be operated at lower temperatures (450–600 °C), which are significantly lower than those required for the traditional steam methane reforming process (750–900 °C)

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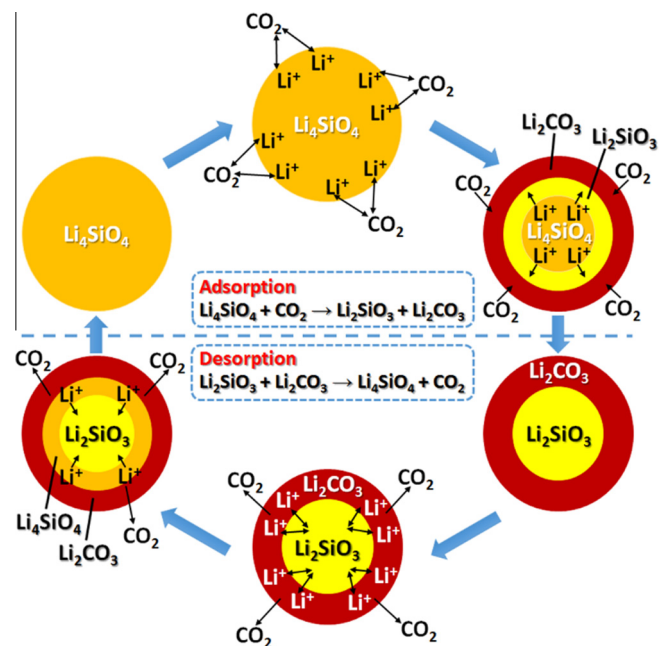
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[5,6]. This can reduce energy consumption, coking, and sintering of the catalyst, and enables the use of less expensive reactor wall materials. The main requirements for designing an adsorbent for SE-SMR [7] are (1) a high CO<sub>2</sub> adsorption rate in a temperature range of 450–600 °C; (2) stable performance during repeated regeneration cycles; (3) low cost; and (4) high adsorption capacity.

Adsorbents based on calcium oxide (CaO) have been widely investigated as high-temperature CO<sub>2</sub> adsorbents [4,6–9]. These materials are highly available, inexpensive, and show high CO<sub>2</sub> adsorption capacities. However, they require excessively high temperature for the desorption of CO<sub>2</sub> (>800 °C) [7,10]. Such high regeneration temperature causes sintering of the CaO adsorbents, thereby reducing the cyclic performance [7,9], and also requires the use of costly metallurgy for the reactor design. Recently, lithium-based ceramics such as Li<sub>2</sub>ZrO<sub>3</sub> [2,3,11], LiFeO<sub>2</sub> [12], Li<sub>2</sub>TiO<sub>3</sub> [13], Li<sub>5</sub>AlO<sub>4</sub> [14], and Li<sub>4</sub>SiO<sub>4</sub> [15–21] have been extensively studied as high-temperature CO<sub>2</sub> adsorbents, because desorption of CO<sub>2</sub> can be carried out at much lower temperature than with CaO-based materials. Among various lithium ceramics, lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) is considered one of the most promising materials due to its large adsorption capacity and low material cost [11,15–19]. Li<sub>4</sub>SiO<sub>4</sub> can chemisorb CO<sub>2</sub> according to the reaction scheme shown in Scheme 1, which allows a theoretical maximum CO<sub>2</sub> capacity of 36.7 wt%.

Although conventional Li<sub>4</sub>SiO<sub>4</sub> exhibits reasonably fast CO<sub>2</sub> adsorption kinetics above 650 °C, it shows very slow CO<sub>2</sub> adsorption kinetics below 600 °C, thus presenting a significant hurdle for directly using it in applications such as SE-SMR [6,22]. At mild temperatures (<600 °C), the CO<sub>2</sub> adsorption process is limited to the Li<sub>4</sub>SiO<sub>4</sub> surface and only a superficial reaction occurs, leading to the formation of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) and lithium metasilicate (Li<sub>2</sub>SiO<sub>3</sub>) external shell. Under these conditions, the bulk framework of Li<sub>4</sub>SiO<sub>4</sub> does not effectively participate in the CO<sub>2</sub> adsorption due to very slow interstitial Li<sup>+</sup> diffusion within the material framework [19,22]. One possible strategy to enhance the low-temperature CO<sub>2</sub> adsorption kinetics is to dope the Li<sub>4</sub>SiO<sub>4</sub> with heteroatoms such as Al [23,24], Fe [24], K [15,22], and Na [16]. Alternatively, in principle, structuring Li<sub>4</sub>SiO<sub>4</sub> into a highly porous structure can also significantly increase the CO<sub>2</sub> adsorption kinetics by shortening the diffusion path length (thinner framework) for Li<sup>+</sup> diffusion. Unfortunately, Li<sub>4</sub>SiO<sub>4</sub> has been mostly obtained as a nonporous structure with extremely low surface area (<5 m<sup>2</sup> g<sup>-1</sup>) [18,23,25]. Li<sub>4</sub>SiO<sub>4</sub> adsorbents commonly have been synthesized by the reaction between various silica (quartz, silica gel, Ludox, fumed silica, and diatomite) and Li precursors (Li<sub>2</sub>CO<sub>3</sub>, LiNO<sub>3</sub>, and LiOH) under dry or wet conditions, followed by heat treatment [15–25]. Previous studies [15–19,22,25] frequently have used Li<sub>2</sub>CO<sub>3</sub> as a Li precursor, which requires a synthesis temperature above 720 °C to obtain a pure Li<sub>4</sub>SiO<sub>4</sub> phase [21]. Syntheses using other Li precursors such as LiNO<sub>3</sub> and LiOH were also carried out at similarly high temperature without careful optimization of the synthesis conditions [23,25,26]. Because the Li<sub>4</sub>SiO<sub>4</sub> phase is synthesized at very high temperature, significant sintering of the Li<sub>4</sub>SiO<sub>4</sub> framework takes place concurrently with the phase formation, which leads to the formation of nonporous and low-surface-area Li<sub>4</sub>SiO<sub>4</sub>. Several researchers have reported the methods for obtaining a pure Li<sub>4</sub>SiO<sub>4</sub> phase with relatively smaller crystallite sizes [27,28], which used the additives such as citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) [27] and polyvinyl alcohol (PVA) [28].

In the present work, macroporous Li<sub>4</sub>SiO<sub>4</sub> was synthesized by a simple solid-state transformation method using LiOH and fumed silica as a precursor for Li and SiO<sub>2</sub>, respectively. These inorganic precursors were chosen because LiOH is the most reactive Li precursor and the highly porous, large-surface-area structure of fumed silica allows uniform distribution of LiOH over the silica framework. This can significantly reduce the formation temperature of



**Scheme 1.** Reaction scheme for CO<sub>2</sub> adsorption and desorption on Li<sub>4</sub>SiO<sub>4</sub>. This scheme is a simplified cartoon. Li<sub>4</sub>SiO<sub>4</sub> particle morphology does not need to be spherical, and Li<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>SiO<sub>3</sub> generated during the CO<sub>2</sub> adsorption can also exist as a dispersed domains rather than a well-defined core–shell structure.

the Li<sub>4</sub>SiO<sub>4</sub> phase down to 600 °C. The Li<sub>4</sub>SiO<sub>4</sub> synthesized at 600 °C showed a highly macroporous structure that has significantly higher BET surface area than that of conventional nonporous Li<sub>4</sub>SiO<sub>4</sub>, which allows efficient CO<sub>2</sub> adsorption and desorption at a mild temperature regime.

## 2. Experimental section

### 2.1. Material preparation

Li<sub>4</sub>SiO<sub>4</sub> samples were synthesized by using a solid-state transformation method. In a typical synthesis, 2.01 g of LiOH (Daejung), 1.14 g of fumed silica (Cab-O-Sil M5, Cabot), and 5 mL of H<sub>2</sub>O were mechanically ground in an agate mortar for 30 min. The Li:Si molar ratio was 4.4:1. To improve the synthesis, 10% excess lithium (compared to the required molar stoichiometry of 4.0:1) was added in order to compensate the sublimated lithium amount during the synthesis [18]. The resultant slurry was dried at 100 °C for 1 h. The resultant solid was heat-treated in alumina crucibles at 600, 700, and 800 °C (temperature ramp: 5 °C min<sup>-1</sup>) for 7 h under flowing dry air (500 mL min<sup>-1</sup>). The resultant samples were denoted as ‘LH-*n*’, where *n* indicates the thermal treatment temperature. For comparison, Li<sub>4</sub>SiO<sub>4</sub> samples were also prepared by using Li<sub>2</sub>CO<sub>3</sub> (Junsei) and LiNO<sub>3</sub> (Aldrich) as a Li precursor following the same solid-state transformation method. In all cases, the Li:Si molar ratio was fixed at 4.4:1. The resultant samples synthesized using Li<sub>2</sub>CO<sub>3</sub> and LiNO<sub>3</sub> as Li precursors were respectively denoted as ‘LC-*n*’ and ‘LN-*n*’, where *n* again indicates the synthesis temperature.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a D2-phaser (Bruker) equipped with Cu K $\alpha$  radiation (30 kV, 10 mA) and a LYNXEYE detector. Diffractograms were collected from 10.0° to 60.0° (2 $\theta$ ) with a resolution of 0.01° and a count time of 2.5 s at

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