



Effects of porous carbon additives on the CO₂ absorption performance of lithium orthosilicate



Sungeun Jeoung^a, Jae Hwa Lee^a, Ho Young Kim^b, Hoi Ri Moon^{a,*}

^a Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 44919, Republic of Korea

^b Department of Chemical Engineering, School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 44919, Republic of Korea

ARTICLE INFO

Article history:

Received 30 March 2016
Received in revised form 18 May 2016
Accepted 20 May 2016
Available online 24 May 2016

Keywords:

Lithium orthosilicate
Porous carbon
CO₂ absorption
Gas pathway

ABSTRACT

Lithium orthosilicate (Li₄SiO₄) is an attractive high-temperature CO₂ sorbent (>650 °C) because of its large theoretical absorption capacity of up to 36.7 wt%. However, slow kinetics and partial reactions with CO₂ hinder its proper operation as a sorbent under practical conditions. To allow the use of this sorbent at lower operation temperatures, the present studies explored the way to improve the CO₂ absorption kinetics and increase the degree of reaction of Li₄SiO₄. Porous carbon materials such as CMK-3 were introduced into the sorbent to provide an internal gas pathway. Upon calcination conditions, the carbon amount was controlled in the composites (Li₄SiO₄@CMK-X%, where X represents the amounts of CMK-3). In Li₄SiO₄@CMK-1.8%, CMK-3 is distributed over the whole solid; in contrast, the additive in Li₄SiO₄@CMK-0.5% is mainly observed near the surface of the solid. CO₂ gas sorption study of the composites showed that pores of CMK-3 in Li₄SiO₄ aid the diffusion of CO₂. In addition, we found that the incorporation of porous carbon provides more active sites for interactions with CO₂ through the formation of cavities between Li₄SiO₄ and CMK-3. Li₄SiO₄@CMK-1.8% had an increased CO₂ absorption capacity (35.4 wt%) and rate (15.2 wt% for the first 5 min) at 600 °C, compared to the CO₂ absorption capacity (16.3 wt%) and rate (5.1 wt% for the first 5 min) of pristine Li₄SiO₄ (p-Li₄SiO₄). To confirm the influence of porous carbon on the CO₂ absorption properties, multi-walled carbon nanotube (MWCNT) was also examined as an additive instead of CMK-3. Li₄SiO₄@CNT showed similar trends with Li₄SiO₄@CMK sorbents.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Increasing atmospheric CO₂ concentration, which is mostly due to the burning of fossil fuels, has been identified as a major contributor to global warming [1]. Because the direct capture of CO₂ from power plants is economically viable, zeolites [2], amine-based materials [3], magnesium and calcium oxides [4–6], and lithium-based oxide composites [7–11] have been tested as high temperature CO₂ sorbents. In particular, among lithium-based oxide sorbents, lithium orthosilicate (Li₄SiO₄) has been recognized as an attractive sorbent, since it has theoretical CO₂ absorption capacity of up to 36.7 wt% of its original weight (Li₄SiO₄ + CO₂ ↔ Li₂CO₃ + Li₂SiO₃) [12]. It is also known to have reasonable material costs. However, most reported Li₄SiO₄ sorbents

have displayed slow kinetics and the partial reaction with CO₂, which lead low absorption capacities [13,14]. Because the introduction of a high concentration of active sites on Li₄SiO₄ sorbents can solve this problem, various efforts have been made to synthesize the Li₄SiO₄ with a large surface area and small particle size. For example, diatomite has been used as a silica precursor to yield Li₄SiO₄ having a higher surface area. This high surface area arises from the uniform pore structure of diatomite (pore size, ~500 nm), which can produce macropores in the Li₄SiO₄ sorbent unlike solids synthesized using analytically pure silica [15,16]. As a result, this Li₄SiO₄ with a high surface area had superior CO₂ absorption properties in terms of kinetics and capacity. Recently Choi et al. reported that decreasing the synthesis temperature prevented sintering, allowing the formation of a macroporous structure, and enhancing both the CO₂ absorption capacity and rate in comparison to nonporous Li₄SiO₄ [17]. Ball-milling is a facile method to reduce particle size and increase the surface area of the nanomaterials. In the synthesis of Li₄SiO₄, ball-milling resulted in the formation of sorbent particles that were 30-times smaller and had 12-times

* Corresponding author at: Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 689-798, Republic of Korea.
E-mail addresses: hoirimoon@unist.ac.kr, hoiri.moon@gmail.com (H.R. Moon).

the surface area of bulk Li_4SiO_4 [18]. The sol-gel method was also used to generate nano-sized particles, which result from the better mixing of reactants and the higher reaction rate, which showed the distinguishable properties like CO_2 absorption capacity and kinetics with Li_4SiO_4 synthesized by solid-state methods [19,20].

In spite of efforts to form advantageous structures for CO_2 absorption, these morphologies are often not maintained during high-temperature CO_2 absorption/desorption cycles, leading to capacity losses. Because Li_2CO_3 , which is formed from the reaction between Li_4SiO_4 and CO_2 , exists as a molten phase in the range of the absorption temperature, the initial textural properties are lost by severe agglomeration [21]. Previously, as a trial to maintain the original morphology of some oxide materials, various additives have been introduced in the synthetic process. The Carbon group used carbon-based material as an additive to prepare TiO_2 nanoparticles, which play a role in preventing the formation of an irregular morphology; furthermore, this additive leads to the formation of a high surface area [22]. Mahinpey et al. reported that the composite of CaO sorbents with Al_2O_3 additives showed the improved cyclability by retaining its original capacity. The authors claimed that this result was attributed to the more active CaO sites induced by the co-existing alumina. [23]. On this wise, the introduction of additives to Li_4SiO_4 sorbents can be a feasible solution to improve the textural properties and physical stability.

Our strategy is the introduction of porous materials to provide the CO_2 diffusion pathways and high surface area into Li_4SiO_4 sorbents. The additives chosen for use in the synthesis of Li_4SiO_4 must be non-reactive with the lithium precursors to avoid undesirable production of unnecessary species for CO_2 absorption. In this sense, we selected highly porous carbon, CMK-3, which has a surface area of $1520 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $1.3 \text{ cm}^3 \text{ g}^{-1}$, as an additive due to its low reactivity with lithium [24,25]. The embedded porous carbon in Li_4SiO_4 produced through the facile wet-mixing method affords more CO_2 diffusion pathways in the resultant Li_4SiO_4 sorbents; this is expected to affect their CO_2 absorption behavior. In this paper, we describe our investigation into the roles of the porous carbon materials on enhancing the CO_2 absorption properties of Li_4SiO_4 by synthesizing Li_4SiO_4 and carbon composites with different kinds and amounts of porous carbon.

2. Experimental

2.1. Materials

Analytical grade chemicals lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, >98.0%), silica, fumed (SiO_2 , 0.007 μm powder), and carbon nanotube, multi-walled, carboxylic acid functionalized (MWCNT, >8% carboxylic acid functionalized) were purchased from Aldrich. All of these chemicals have been used without additional purification. CMK-3 was synthesized according to a previous report [25].

2.2. Preparation of the sorbents

2.2.1. Pristine Li_4SiO_4 (p- Li_4SiO_4)

p- Li_4SiO_4 was synthesized according to a previous report [18]. $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.29 g, 6.8 mmol) and SiO_2 (0.10 g, 1.7 mmol) were dissolved in water with stirring at 70°C . Then, the mixture solution was heated at 105°C to evaporate water, and the resulting powder was collected and calcined at 700°C for 4 h in a tube furnace under nitrogen flow (500 mL min^{-1}).

2.2.2. Li_4SiO_4 @CMK

$\text{LiOH}\cdot\text{H}_2\text{O}$ (0.29 g, 6.8 mmol) and SiO_2 (0.10 g, 1.7 mmol) were dissolved in water (10 mL) at 70°C , and CMK-3 (0.02 g) was added to

the mixture solution with vigorous stirring. Then, water was evaporated from the suspension by heating at 105°C , and the obtained powder was calcined at 700°C for 4 h in a tube furnace under nitrogen flow (500 mL min^{-1}). The resultant greyish powder was calcined again at 700°C in air in muffle furnace. Upon retention time at 700°C , the carbon contents in the final product can be varied; no retention time yielded 1.8 wt% of carbon with respect to Li_4SiO_4 , designated as Li_4SiO_4 @CMK-1.8%; and retention for 4 h produced 0.5 wt%-carbon containing Li_4SiO_4 , designated as Li_4SiO_4 @CMK-0.5%.

2.2.3. Li_4SiO_4 @CNT

The same experiment was performed to synthesize Li_4SiO_4 @CNT with MWCNT (0.02 g) instead of CMK-3. After the first calcination under N_2 flow, the powder was calcined at 700°C in air without retention.

2.3. Material characterization

Elemental analyses (for C, H, N, S, and O) were performed by using a Thermo Scientific Flash 2000 series CHNS/O analyser. Thermogravimetric analyses (TGA) was performed under carbon dioxide atmosphere at a scan rate of $10^\circ\text{C min}^{-1}$, using Q50 from TA instruments. X-ray powder diffraction (XRPD) patterns were recorded on a Bruker D2 phaser diffractometer at 30 kV and 10 mA using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) with a step size of 0.02° in 2θ at room temperature. Scanning electron microscope (SEM) images were taken using a Quanta 200 microscope (FEI) operating at 18 kV. Transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDS) were obtained with a JEOL JEM-2100F microscope.

2.4. CO_2 uptake performance tests

CO_2 chemisorption experiments of dynamics, kinetics, and cyclability were performed using Q50 from TA instruments. To scan the absorption-desorption behavior of the prepared Li_4SiO_4 sorbents, dynamic thermograms were measured at a heating rate of $10^\circ\text{C min}^{-1}$ and a gas flow of 15% (v/v) CO_2 in N_2 , which mimics flue gas, as well as 100% CO_2 atmosphere from room temperature to 800°C . The isothermal curves of the sorbents were obtained for 200 min at 500, 550, 600, and 625°C under 15% (v/v) CO_2 in N_2 , and also at 550, 600, and 625°C under 100% CO_2 atmosphere. The stability of the Li_4SiO_4 sorbents was tested by cyclic absorption/desorption experiments as follows: absorption curves were obtained under a 15% (v/v) CO_2 flow in N_2 at 550°C , and the desorption process was performed after switching the gas flow to N_2 at 650°C . The gas flow rate for all of the thermogravimetric analyses was 60 mL min^{-1} , and the sample amount used in each CO_2 absorption experiment was ca. 10 mg.

3. Results and discussion

3.1. Synthesis and characterizations of p- Li_4SiO_4 and porous carbon-containing Li_4SiO_4 (Li_4SiO_4 @CMK)

CMK-3 was added and well-dispersed in the water solution of the Li_4SiO_4 precursors ($\text{LiOH}\cdot\text{H}_2\text{O}$ and SiO_2) to intermingle it with Li_4SiO_4 homogeneously, and then water was eliminated by heating. Because, at high absorption temperatures, porous carbon species are not expected to absorb CO_2 , the excess quantity of CMK-3 can cause a gravimetric disadvantage. Thus, to control the effective amount of CMK-3, additional calcination was conducted in air at 700°C (Scheme 1). For the second calcination, the reaction was carried out at 700°C with no retention time, resulting in 1.8 wt% CMK-3 contained in the Li_4SiO_4 , designated as Li_4SiO_4 @CMK-1.8%.

Download English Version:

<https://daneshyari.com/en/article/672696>

Download Persian Version:

<https://daneshyari.com/article/672696>

[Daneshyari.com](https://daneshyari.com)