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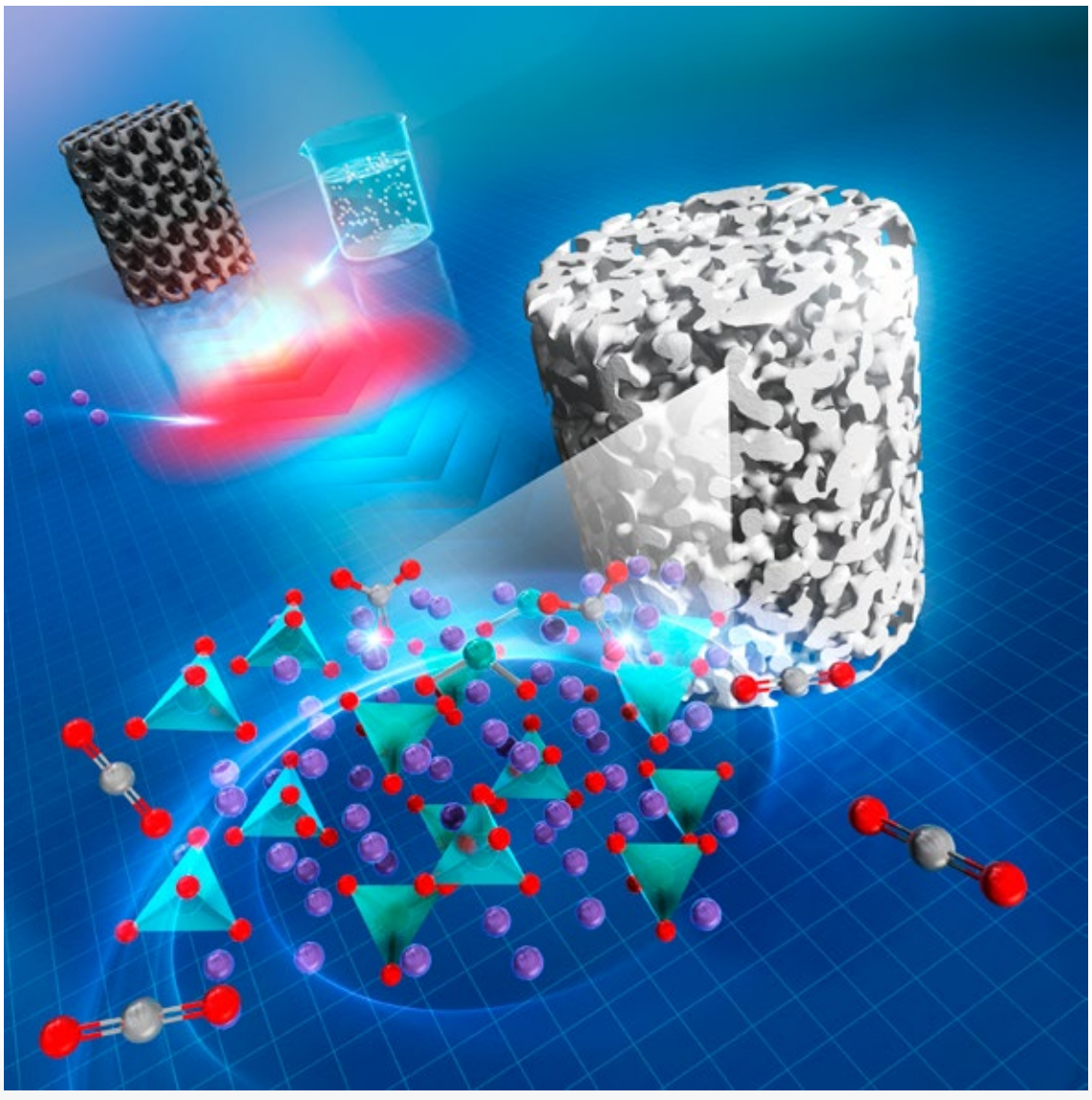

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FULL PAPER

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Lithium silicate (Li_4SiO_4) is one of the most promising carbon dioxide (CO_2) capture materials at high temperatures. In this study, Li_4SiO_4 on silica (SiO_2) porous structure was tried to fabricate in solid state reaction for CO_2 capture materials. Li_2CO_3 reacted with amorphous SiO_2 on the surface of silica porous structure made by template method, resulting in the formation of Li_4SiO_4 porous structure on silica support at 800 °C. The obtained Li_4SiO_4 porous structure can capture CO_2 at 600 °C and release it at 700 °C, and could be used stably and repeatedly. This Li_4SiO_4 porous structure is expected to be useful as a CO_2 capture material at high temperature.

Key-words : Lithium silicate, CO_2 sorbent, CO_2 capture, Surface modification

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1. Introduction

The amount of carbon dioxide (CO_2) emitted from coal-fired power plants is more than 20 % worldwide, and about 60 % in the power generation sector. Because coal has abundant reserves and is cheaper than oil or natural gas, its use is increasing.[1)] CO_2 is greenhouse and acidic gas causing to global warming and acidification of seawater.[2)–4)] The reducing CO_2 emissions from coal-fired power plants is an important task.[5),6)] One solution of these problems is a CO_2 removal method using a capture material.[7)] Currently, various studies on CO_2 capture and storage (CCS) for reduction of CO_2 are being conducted around the world.[8)–10)] One of the CCS technologies is using absorption and adsorption. The selection of capture material is important to improve CO_2 storage efficiency.[11)]

The most practical method is chemical absorption reactions using amine solutions such as mono-ethanol amine, di-ethanol amine, and methyl diethylanamine, which has advantages for large-capacity processing and simple operation.[12)] However, this technology requires a cooling system because high-temperature CO_2 gas cannot be taken directly from flue gas or exhaust gas, caused to an increase in energy consumption and requirement of time and money. In addition, there are problems with environmental hazards due to the volatility of the absorbent and the corrosiveness of the absorbent itself.[13)] Therefore, it is necessary to develop a capture material at high temperatures. There are some literatures on calcium oxide (CaO) and lithium silicate (Li_4SiO_4) as high-temperature solid capture materials.[14)–16)] CaO has a high CO_2 capture capacity and wide availability, although its low cycle stability due to serious sintering problems.[17)] Li_4SiO_4 has a high lithium atom density, excellent chemical and mechanical stabilities at high temperatures, and low neutron activation properties,[18),19)] which has widely applied for catalysts, CO_2 capture materials, CO_2 separation membranes, cathodes in Li-ion batteries, and energy storage.[20)–24)] Li_4SiO_4 has a high selective CO_2 capture ability with a theoretical value of 36.7 wt % CO_2 in the temperature range of 450–700 °C according to the reaction shown in Eq. (1).[25)] The regeneration temperature of Li_4SiO_4 is less than 750 °C, which is lower than that of CaO, the energy consumption required for regeneration is low, and circulation stability is excellent.[26),27)]

$$Li_4SiO_4 + CO_2\ (g) \rightarrow Li_2SiO_3 + Li_2CO_3 \quad (1)$$

There are some studies on kinetic analysis for the carbonation of Li_4SiO_4.[28)–36)] Venegas et al. proposed two rate constants during CO_2 capture of Li_4SiO_4; one is a reaction rate constant between CO_2 and Li_4SiO_4, and the other is a diffusion rate constant of CO_2 into Li_2SiO_3 and Li_2CO_3 layer.[28)] This kinetic analysis can help us understand the CO_2 capture ability of Li_4SiO_4.

Regarding the reversible capture of CO_2, there are two main approaches with the use of liquid capture materials and solid capture materials.[37),38)] The method of using liquid capture materials has a limitation due to the decomposition of liquid during temperature cycles. The solid capture materials are relatively non-degradable, have a variety of capture functions and are renewable.[37)–39)] Most previously studied Li_4SiO_4 capture materials are not suita-

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ble for application in various fields due to easy elution and rapid pressure drop when used in a reactor as powder form.[40)–42)] Therefore, in order to be commercialized, development in bulk form is necessary. The capture materials of bulk form can be applied by strengthening their mechanical properties, which is a necessary element in renewable CO_2 capture materials.[43)] These bulk capture materials can be divided into pellet form, monolithic (honeycomb), and porous form. Monolithic and porous forms are more advantageous for separation and recovery, and have high mass transfer characteristics with low pressure drop.[44)–49)] Therefore, the development of capture materials such as monolithic and porous materials has been active in recent years.[46),47),50),51)] Inorganic porous capture materials have received industrial interest for use in CCS.[52)–55)] The presence of capture sites for CO_2 is the most important factor. The form, particle size, porosity, and specific surface area of the material are also important to determine capture efficiency.[56),57)] In particular, a large surface area is effective in higher capture amounts and longer capture life.[58)]

In this study, we attempted to fabricate a renewable high temperature CO_2 capture material, Li_4SiO_4, with a porous structure. There are few studies reporting the effectiveness and performance of CO_2 removal by Li_4SiO_4 capture material surface-modified on a porous support. Therefore, this study is meaningful in investigating the improvement effect of Li_4SiO_4 capture material surface-modified on SiO_2 porous sintered body. Li_4SiO_4 was synthesized on the surface of the SiO_2 porous glass support by an impregnation method. The characteristics and CO_2 capture ability of the Li_4SiO_4 porous sample were evaluated. The rate constant during the CO_2 capture process was obtained, and the effect of the porous structure on the reaction was investigated.

2. Experimental

2.1 Preparation of SiO_2 porous glass

The schematic diagram for sample preparation is shown in **Fig. 1**. SiO_2 ceramics of compositions 89 wt% SiO_2 (SS-10, Tokuyama Corp., Japan), 10 wt% mullite (KM101, KCM Corp., Japan), and 1 wt% K_2CO_3 (Special grade, KISHIDA CHEMICAL Co., Ltd., Japan) were used as starting materials for the preparation of porous glass supports. SiO_2, mullite and K_2CO_3 powders were mixed for 50 min using an agate mortar. A cubic open cell PU sponge (MF-30, INOAC Corp., Japan) with a cell density of 30 ppi was used as a template. Poly vinyl alcohol (PVA, special grade, FUJIFILM Wako Pure Chemical Corp., Japan) aqueous solution was used as a dispersant.

SiO_2 porous glass was prepared according to our previous report.[59)] 3 g of 5 wt% PVA aqueous solution was mixed with 3 g of SiO_2 powder using a kneading machine (AR-100, Thinky Corp., Japan). PU sponge with a diameter and height of 11.5 and 10.0 mm was dipped into the SiO_2 slurry before drying at room temperature for 24 h. The dried sample was calcined at 400 °C for 6 h, sintered at 1200 °C under atmospheric pressure with a heating rate of 10 °C/min. The obtained SiO_2 porous glass shrank to about 9.5 mm of diameter and 8.0 mm of height due to sintering.

2.2 Surface modification of SiO_2 porous glass with Li_4SiO_4

For the preparation of Li_4SiO_4 on SiO_2 porous glass named as Li_4SiO_4/SiO_2, Li_2CO_3 (Special grade, KISHIDA CHEMICAL Co., Ltd., Japan) was used as Li source. Li_2CO_3 slurry was prepared in the same way as SiO_2 slurry using 5 wt% PVA aqueous solution. The mixing composition was set at 6 g of 5 wt% PVA and 4 g of Li_2CO_3 powder. SiO_2 porous glass was dipped into the Li_2CO_3 slurry, and dried at room temperature for 24 h. The dried sample was heat-treated at 400 °C for 1 h and then at 800 °C for 1 h under atmospheric pressure at a heating rate of 10 °C/min.

2.3 Characterization

Phase analysis was performed using X-ray diffraction (XRD, SmartLab SE, Rigaku Corp., Japan). Amorphous and crystalline phase composition were calculated by Rietveld analysis. The microstructure of the sintered body was observed using JSM-6701F (JEOL Ltd., Japan).

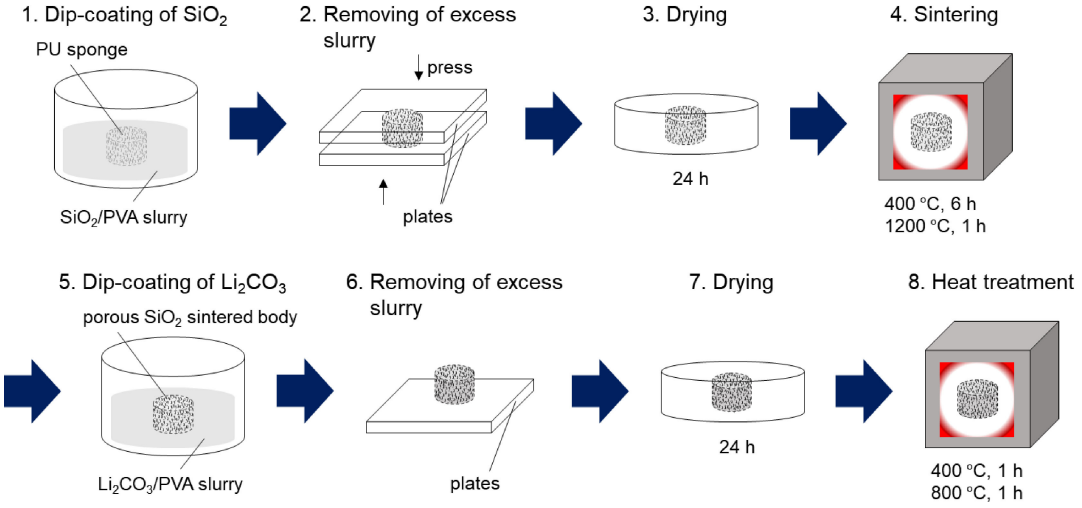

Fig. 1. Fabrication process of Li_4SiO_4 porous sorbent having a hierarchical structure using PU sponge.

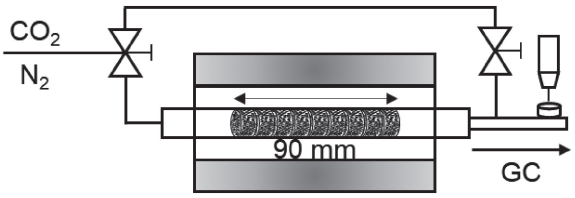

Fig. 2. Schematic diagram of the packed-bed system used for the CO_2 capture and regeneration experiments.

2.4 CO_2 capture and regeneration tests of Li_4SiO_4

CO_2 capture and regeneration tests were conducted in a fixed-bed stainless steel pipe reactor (internal diameter: 10 mm) heated by a tubular furnace. An overview of the device structure is shown in **Fig. 2**. The Li_4SiO_4/SiO_2 samples were filled in the stainless steel pipe reactor and heated at 600 and 700 °C during CO_2 capture and regeneration test. The flow gas condition was set with 0–15 vol % CO_2/N_2 balance at 100 or 200 mL/min under atmospheric pressure. The CO_2 concentration was analyzed at 5 min intervals by gas chromatography (GC-2014, Shimadzu Corp., Japan) with flame ionization detector (FID) mode using methanizer. The temperature was set at 100 °C as injector, 75 °C as Sunpak-A column, 150 °C as FID detector, and 150 °C as methanizer, respectively. The flow rate of N_2 as the carrier gas was set to 20.0 mL/min.

3. Results and discussion

3.1 Li_4SiO_4 surface modification conditions

The sintering of Li_4SiO_4 is quite difficult due to a low diffusion coefficient and thermal decomposition even at high temperature. In almost all cases, voids form and the densification do not occur.[59),60)] In this study, we focused on the surface modification of Li_4SiO_4 to SiO_2 porous support. For the application to CO_2 capture materials, the surface activity is required compared to bulk property. Two methods were tried to modify the surface of SiO_2 porous support to Li_4SiO_4: one was coating with Li_4SiO_4 on SiO_2 support named as Li_4SiO_4 on SiO_2, and the other was the reaction of Li_2CO_3 with SiO_2 surface named as Li_4SiO_4/SiO_2. Li_4SiO_4 and Li_2CO_3 slurries were prepared by mixing of PVA with each powder. Li_4SiO_4 powder was made by solid state reaction.[61)] The calcination at 400 °C for 1 h was carried out on both samples to remove PVA, and then the heat treatment was applied to Li_4SiO_4/SiO_2 sample at 800 °C for 1 h.

To confirm that Li_4SiO_4 was coated on the SiO_2 surface, the sample was cut and the SEM image was checked. **Figure 3** shows the SEM images of cross-section view of (a) Li_4SiO_4 on SiO_2 and (b) Li_4SiO_4/SiO_2. The interface of Li_4SiO_4 and SiO_2 was clearly observed on coating sample, whereas that of reacting one was ambiguous. This suggests that Li_2CO_3 and SiO_2 were reacted very well, resulting in tight bonding. The high reactivity between Li_2CO_3 and SiO_2 might be due to the high activity of SiO_2 glass surface sintered at low temperature. Thus, silica porous materials with amorphous phase prepared by sintering is

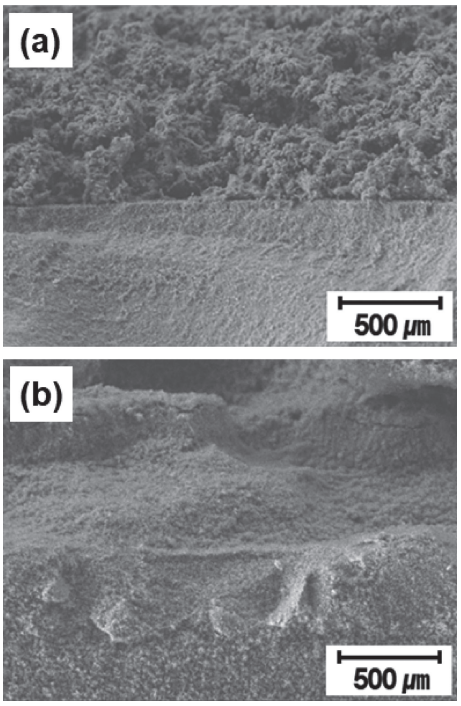

Fig. 3. SEM images of cross-section view of (a) Li_4SiO_4 on SiO_2 and (b) Li_4SiO_4/SiO_2.

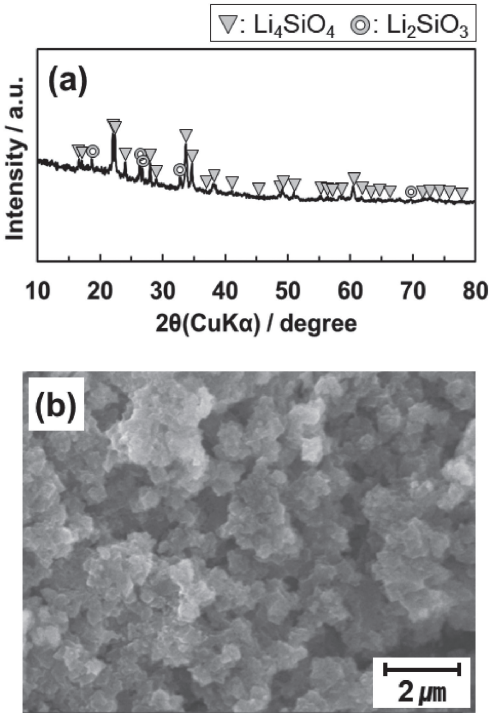

Fig. 4. (a) XRD pattern and (b) SEM image of Li_4SiO_4/SiO_2 surface.

effective for the fabrication of environmental catalyst by surface modification.

Figure 4 shows the XRD pattern and SEM image of Li_4SiO_4/SiO_2 surface prepared by heating at 800 °C for 1 h Li_2CO_3 on silica porous material. Li_4SiO_4 mainly formed beside small amount of Li_2SiO_3. The crystalline phase con-

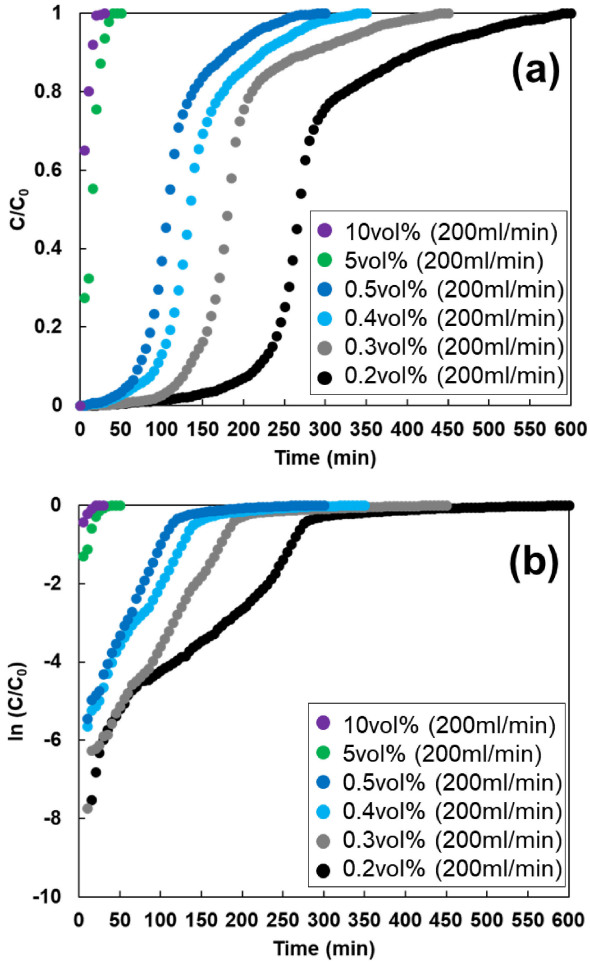

Fig. 5. CO_2 capture performance [C/C_0-time (a) and ln(C/C_0)-time (b)] of prepared Li_4SiO_4/SiO_2 porous samples with different initial concentration of CO_2 at 200 mL/min at 600 °C.

Table 1. Rate constant values calculated from the ln(C/C_0)-time slope

Flow rate (mL/min)	Concentration (vol %)	k_1 (s^{-1})	k_2 (s^{-1})
200	0.2	0.0075	0.0058
	0.3	0.0075	0.0057
	0.4	0.0075	0.0058
	0.5	0.0075	0.0058
	5	—	0.0058
	10	—	0.0058

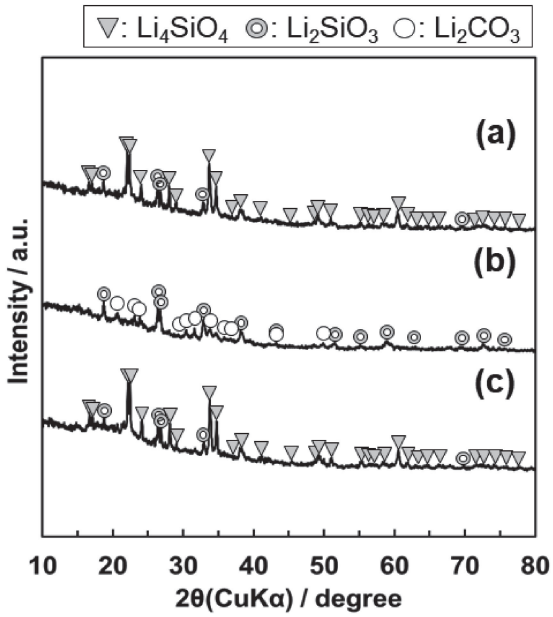

Fig. 6. XRD patterns of (a) Li_4SiO_4/SiO_2 porous sample after (b) CO_2 capture at 600 °C and (c) regeneration at 700 °C.

tent was 88 wt % (0.00063 mol) for Li_4SiO_4 and 12 wt % (0.00011 mol) for Li_2SiO_3 estimated using the Rietveld method. The particles of about 500 nm were observed on the surface of Li_4SiO_4/SiO_2, indicating that Li_4SiO_4 was synthesized by solid reaction of Li_2CO_3 and SiO_2.

3.2 CO_2 capture characteristics of Li_4SiO_4/SiO_2

The CO_2 capture ability of the Li_4SiO_4/SiO_2 porous sample was measured using 0.2–10 vol % CO_2 gas with N_2 balance of 200 mL/min at 600 °C. **Figure 5** shows the change in CO_2 concentration at reactor outlet with time, which means break through curve. The outlet CO_2 concentration C normalized by initial concentration C_0. Li_4SiO_4/SiO_2 porous sample can capture CO_2 until Li_4SiO_4 completely changed to Li_2CO_3. When CO_2 initial concentration was high over 5 vol %, CO_2 was immediately permeated the test samples. Below 0.5 %, the increase in CO_2 concentration changed from gradually to sharply and gradually again with time, forming an S-curve. Especially at 0.2 and 0.3 %, CO_2 was completely captured during the initial 5–10 min of the reaction. These results indicate that CO_2 and Li_4SiO_4 react rapidly at the initial stage of reaction and the Li_2CO_3 formed on the surface of Li_4SiO_4 prevent the reaction of CO_2 and Li_4SiO_4 from middle to final stage of reaction. CO_2 should diffuse the Li_2CO_3 layer to react Li_4SiO_4, leading to diffusion rate-limited state.

To calculate the CO_2 capture rate, the natural logarithmic scale was used. As shown in Fig. 5(b), there were two slopes at initial stage and final stage, indicating the existence of two rate constants. The rate constant values calculated from the ln(C/C_0)-time slope are summarized in **Table 1**. The initial (k_1) and final (k_2) rate constants were 0.0075 and 0.0058 (s^{-1}), respectively, which was same value regardless of initial CO_2 concentration. At the initial stage, CO_2 react with Li_4SiO_4 immediately. Thus, k_1 means the reaction rate between CO_2 and Li_4SiO_4. As a reaction time was longer, the diffusion of CO_2 into Li_2CO_3 layer dominated the reaction. Therefore, the meaning of k_2 is the diffusion rate of CO_2.

The XRD patterns and SEM images of Li_4SiO_4/SiO_2 sample with CO_2 capture at 600 °C and regeneration at 700 °C are shown in **Figs. 6** and **7**, respectively. In the initial Li_4SiO_4/SiO_2 sample, Li_4SiO_4 mainly formed beside Li_2SiO_3 and polygonal particles with the size of about 500 nm were observed. With CO_2 capture sample,

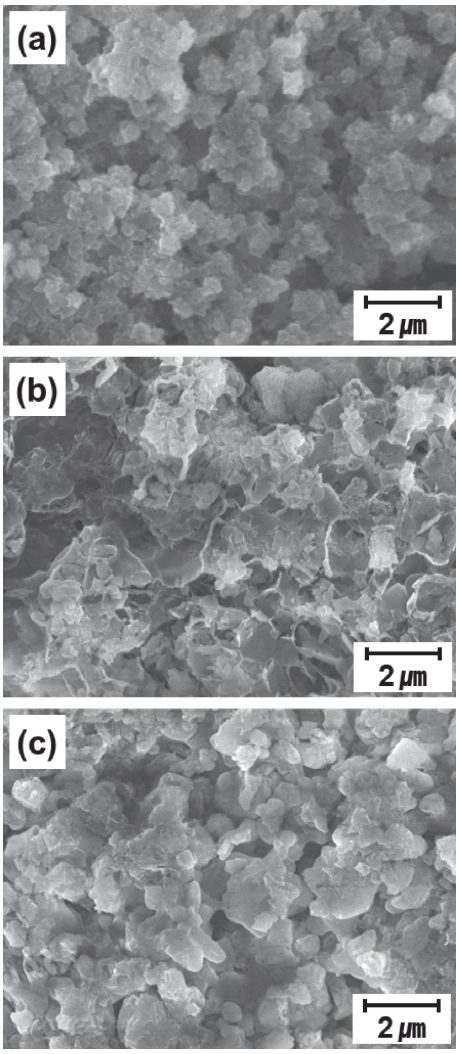

Fig. 7. SEM images of surface of (a) Li_4SiO_4/SiO_2 porous sample after (b) CO_2 capture at 600 °C and (c) regeneration at 700 °C.

the peaks of Li_2SiO_3 and Li_2CO_3 were detected and irregular morphology was observed, indicating that CO_2 completely reacts with Li_4SiO_4. After heat treatment at 700 °C under N_2 flow, Li_4SiO_4 peaks were detected with slight peaks of Li_2SiO_3, indicating almost all regeneration was achieved. However, particles morphology did not return to initial state, which was with wide size distribution.

Table 2 summarizes the rate constant values obtained in this study and several literatures.[29)–36)] Compared to other studies, the k_1 in this study was not so much high, which means the reaction rate between CO_2 and Li_4SiO_4 was low. This was due to a large flow rate and low CO_2 concentration in this study. On the other hand, the k_2 was highest among them. This indicates that the diffusion of CO_2 into Li_2SiO_3 and Li_2CO_3 layer was quite accelerated. There are two possible reasons for a high k_2 value. One is a low reaction rate of Li_4SiO_4 and CO_2. The other is porous structure accelerated CO_2 diffusion. Anyway, we achieved the enhancement of CO_2 diffusion in this study.

3.3 Cycle performance test

The CO_2 capture and regeneration test of Li_4SiO_4/SiO_2 sample was measured in several cycles to investigate the cycle performance. **Figure 8** shows the relationship between the number of cycles and the CO_2 capture amount. The test conditions were set with 15 vol% CO_2 at 600 °C for CO_2 capture and with N_2 gas at 700 °C for regeneration. The CO_2 capture ability of Li_4SiO_4/SiO_2 per 1 g was 42.2 mg at 1st cycle and kept a stable over several cycles. The CO_2 capture capacity slightly decreased with an increase in cycle number, reaching 40.9 mg at the 20th cycle. This decrease in CO_2 capture ability was due to the particle growth during heat treatment at high temperature like Fig. 7.

4. Conclusions

SiO_2 porous glass modified with Li_4SiO_4 can be successfully development by the solid-state reaction method

Table 2. Kinetic constants compared to literatures

Sample feature	Temperature (°C)		Flow rate (ml/min)		Composition (vol%)		k_1 (s^{-1})	k_2 (s^{-1})	Ref.
	CO_2 sorption	CO_2 desorption	CO_2 sorption	CO_2 desorption	CO_2 sorption	CO_2 desorption			
Li_2SiO_3, Li_3NaSiO_4 powder	575	>650	—	—	CO_2: 100	N_2: 100	0.0050	0.0002	29)
Li_2SiO_3, Li_4SiO_4 powder	650	750	50	50	CO_2: 100	N_2: 100	0.0420	0.0010	30)
Li_4SiO_4 powder	550	550	50	50	CO_2: 100	N_2: 100	0.0088	0.0002	31)
Li_4SiO_4 powder	550	650	60	60	CO_2: 15 N_2: 85	N_2: 100	0.0650	0.0061	32)
LiOH, Li_2SiO_3, Li_4SiO_4 powder	700	725	100	100	CO_2: 60 N_2: 40	N_2: 100	0.0220	0.0004	33)
Li_2SiO_3, Li_4SiO_4 powder	610	700	50	50	CO_2: 30 Ar: 70	Ar: 100	0.0230	0.0011	34)
Li_2SiO_3, Li_4SiO_4 powder	590	700	60	60	CO_2: 50 Ar: 50	N_2: 100	0.0140	0.0006	35)
Li_2CO_3, Li_2SiO_3, Li_4SiO_4 powder	650	>700	—	—	CO_2: 60 N_2: 40	N_2: 100	0.0654	0.0016	36)
Li_4SiO_4/SiO_2 porous body	600	700	200	200	CO_2: 0.2–10 N_2: balance	N_2: 100	0.0075	0.0058	This work

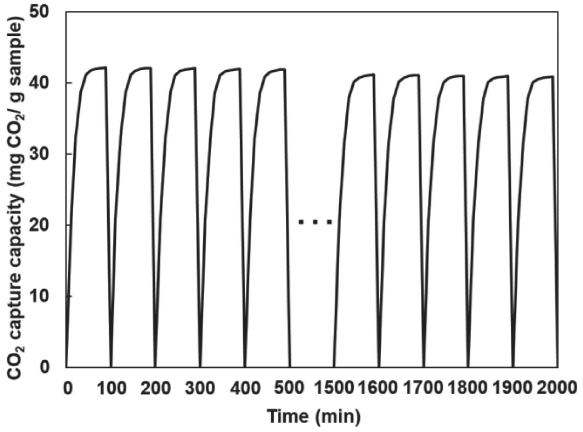

Fig. 8. CO_2 capture cycle performance of the Li_4SiO_4/SiO_2 sample at 100 mL/min of flow rate. The test conditions were set with 15 vol% CO_2 at 600 °C for CO_2 capture and with N_2 gas at 700 °C for regeneration.

with CO_2 capture ability at high temperature. The Li_4SiO_4/SiO_2 capture material was confirmed to have a low reaction rate but quite high diffusion rate. The CO_2 capture ability was stable over several cycles with a capture capacity of 42.2 to 40.9 mg per gram for 20 cycles at 600 °C. Li_4SiO_4 completely reacted with CO_2 and was completely regenerated into the original Li_4SiO_4 phase at 700 °C for several cycles. The porous Li_4SiO_4/SiO_2 capture material developed in this study has a high potential in applications for high-temperature CO_2 capture.

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