Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 5437–5441

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Novel Li_4SiO_4-based sorbents from diatomite for high temperature CO_2 capture

ShaoYun Shan[a,b,*], QingMing Jia[b], LiHong Jiang[b], QinChao Li[b], YaMing Wang[b], JinHui Peng[a,*]

[a]School of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b]School of Chemical Engineering, Kunming University of Science and Technology, Kunming 650093, China

Received 21 October 2012; received in revised form 16 December 2012; accepted 16 December 2012
Available online 25 December 2012

Abstract

Using inexpensive porous diatomite as silicon source, novel Li_4SiO_4-based sorbents for high temperature CO_2 capture were prepared through the solid-state reaction method at lower temperature (700 °C). Effect of different raw material ratios on CO_2 absorption capacity was investigated. The results showed that CO_2 absorption capacity was dependent on the raw material ratio. When the raw material ratio was 2.6:1, the CO_2 absorption capacity reached 30.32 wt% (83% of the theoretical absorption capacity) in the atmosphere (50 mL/min N_2 and 50 mL/min CO_2). Meanwhile, it was found that the as-prepared Li_4SiO_4-based sorbents from diatomite exhibited good absorption–desorption performance.

Keywords: Diatomite; Lithium silicate; Carbon dioxide; Absorption

1. Introduction

With use of fossil fuels, CO_2 becomes a major greenhouse gas that is released into air. The separation, recovery and storage/utilization of CO_2 have attracted considerable attention in recent years owing to the growing problem of global warming and other hazards. CO_2 can be removed from flue gas and waste gas streams by various methods such as membrane separation, absorption with a solvent, and absorption using molecular sieves [1–6]. However, these methods are expensive or consume a lot of energy. Hence, the materials with high CO_2 capture capacity at high temperature are desirable.

In recent years, CO_2 capture at high temperatures (450–750 °C) based on regenerable sorbent materials has received increasing attention as an alternative to low-temperature CO_2 capture sorbents [7–10]. In the last few years, some researchers have reported some new sorbents for CO_2 capture. The use of these high temperature sorbents provides both high CO_2 absorption capacity and CO_2 selectivity at temperatures between 450 and 700 °C. Specifically, lithium and sodium-based ceramics seem to present adequate conditions for CO_2 capture. Among all these ceramics, Li_4SiO_4 seems to have excellent properties for CO_2 capture. Compared with other lithium-based ceramics such as Li_2ZrO_3, $LiFeO_2$, $LiNiO_2$ and Li_2TiO_3, Li_4SiO_4 has better CO_2 absorption properties (higher absorption capacity, faster absorption rate, and better cyclability properties) over a wide range of temperature and CO_2 concentration [11–13]. The solid phase reaction is the most common synthesis route of Li_4SiO_4. By this method, some researchers usually prepared Li_4SiO_4 sorbents with high absorption properties with analytically pure SiO_2 as silicon source, which needs harder preparation conditions (900–1000 °C) [14,15]. According to the double sorption mechanism [7,10,13], the diffusion process, as one of the limiting steps, may be avoided or at least reduced by the synthesis of small particles. Marin et al. [16] reported that pure Li_4SiO_4

*Corresponding authors at: School of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Bailong Temple 293, Kunming 650093, China. Tel.: +86 871 5191046.
E-mail addresses: shansy411@163.com (S. Shan), jhpeng@kmust.edu.cn (J. Peng).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.12.051

sorbents with SiO_2 nanopowders as silicon source had high absorption capacity, which increased the preparation cost.

Taking into account the significant content of SiO_2 on diatomite and in order to increase its use, this work has focused on the solid-phase preparation of novel Li_4SiO_4-based sorbents from cheap porous diatomite (with ~1 μm pore size) for high temperature CO_2 capture at lower temperature (700 °C). The influence of raw material ratios on the absorption capacity was investigated. Additionally, the absorption–desorption performances of Li_4SiO_4-based sorbents from diatomite were investigated by thermogravimetric analysis.

2. Experimental

Diatomite (about 75% SiO_2, C.R., Shanghai Fengxian Reagent Co.Ltd., China) and Li_2CO_3 (97%, A.R., Tianjin Fengchuan Chemical Reagent Co.Ltd., China) were used as the starting powders. The compositions for diatomite are shown in Table 1. Li_4SiO_4-based sorbents were synthesized by calcining the starting powder mixture with different molar ratios (nLi$_2$CO$_3$:nSiO$_2$=2–2.8) at 700 °C for 4 h. The synthesizing reaction is as follows:

$$2Li_2CO_3+SiO_2=Li_4SiO_4+2CO_2$$

Table 1
Diatomite composition analysis.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Loss	others
Content (wt%)	75.26	14.33	2.31	1.02	1.56	4.35	1.17

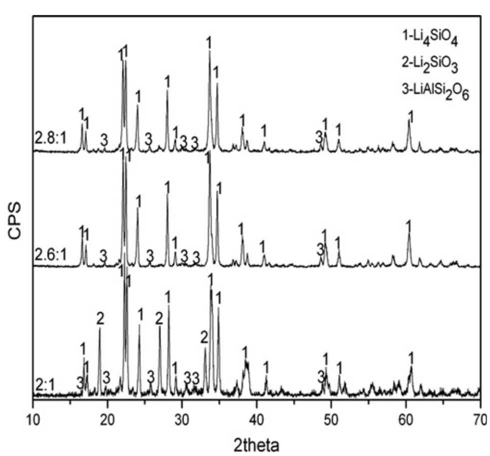

Fig. 1. XRD pattern of Li_4SiO_4-based sorbents with different raw material ratios at 700 °C for 4 h.

Crystalline phases were identified by XRD (D8ADVANCE, German) analysis. The morphologies were characterized by SEM (JSM-35C, JEOL Ltd., Japan). The absorption properties of Li_4SiO_4-based sorbents were investigated at the absorption condition (the absorption temperature is 620 °C, retaining time is 30 min, and the atmosphere is the gas mixture (50 mL/min N_2 and 50 mL/min CO_2)) by TG–DSC (STA 449 F3, Netch Co. Ltd., German). The absorption reaction is as follows:

$$Li_4SiO_4+CO_2=Li_2SiO_3+Li_2CO_3$$

As seen from reaction (2), the theoretical absorption capacity of Li_4SiO_4 is 36.7 wt%.

3. Results and discussion

3.1. Phase composition of Li_4SiO_4 sorbents

Fig. 1 shows the XRD patterns of Li_4SiO_4-based sorbents with different raw material molar ratios prepared at 700 °C for 4 h. As shown in Fig. 1, when the raw material molar ratio is 2:1, Li_4SiO_4 and Li_2SiO_3 were the main phases, and only small quantities of SiO_2 (not marked) and $LiAlSi_2O_6$ phases were observed. Based on Scherrer's formula [17], the fractions of Li_4SiO_4, Li_2SiO_3, $LiAlSi_2O_6$ and SiO_2 phases were evaluated to be about 68.9%, 22.1%, 4.7% and 3.7%, respectively. The occurrence of $LiAlSi_2O_6$ phase resulted from the reaction between Al_2O_3 phase coming from diatomite and Li_2CO_3. And the presence of Li_2SiO_3 and SiO_2 phases indicated that the lower synthesis temperature and shorter calcination time were not enough to complete the reaction [18]. With increasing raw material molar ratios(2.6:1 or 2.8:1), Li_2SiO_3 phase disappeared. Kato and Nakagawa [19] tested Li_2SiO_3 material for the CO_2 capture, and they did not observe any weight increment due to kinetics factors. It is obviously seen from Fig. 1 that higher raw material molar ratio is helpful for the production of Li_4SiO_4 phase, which is probably because the existence of impurities needs a greater amount of Li for the Li_4SiO_4 formation.

3.2. Effect of raw material ratios on absorption capacity

Table 2 shows the effect of different raw material ratios on CO_2 absorption capacity. As seen from Table 2, with increasing raw material ratio, CO_2 absorption capacity increased at first, then decreased. When the raw material ratio is 2.6:1, the CO_2 absorption capacity reached the largest value (30.32 wt%), which is 83% of the theoretical absorption capacity. In fact, the largest absorption capacity

Table 2
Effect of raw material ratios on absorption capacity.

Raw material ratio	2:1	2.1:1	2.2:1	2.3:1	2.4:1	2.6:1	2.8:1
Absorption capacity(%)	15.86%	22.32%	24.47%	28.62%	29.40%	30.32%	16.34%

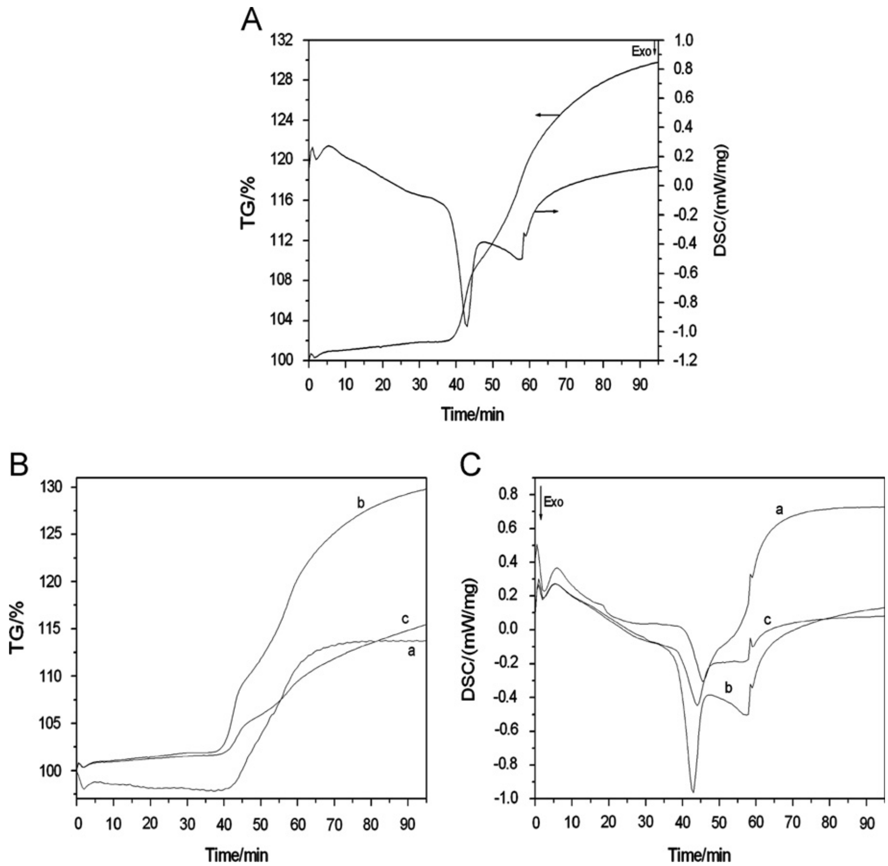

Fig. 2. TG–DSC curves of Li_4SiO_4-based sorbents (700 °C, 4 h) with different raw material ratios (a: 2:1, b: 2.6:1, and c: 2.8:1).

was more than 30.32 wt%, which was because diatomite contains 25 wt% impurities except for SiO_2. TG–DSC curves of Li_4SiO_4-based sorbent at 2.6:1 was shown in Fig. 2A. As shown in Fig. 2A, two different weight increments for TG curve and two obvious exothermic peaks in the DSC curve were observed between 200 and 450 °C, and 480 and 620 °C, respectively. This kind of thermal trend had been observed for other ceramics [20], which may be explained by the absorption mechanism of lithium-based sorbents [7]. The whole chemisorption process is divided into two steps: first, a superficial reaction is produced at low temperatures (200–450 °C). At this moment, a Li_2CO_3 external shell is formed at the particle surface. Then, the lithium diffusion is activated with increasing temperature (480–620 °C), and the reaction continues through the bulk material, completing the CO_2 chemisorption.

TG and DSC curves comparisons of Li_4SiO_4-based sorbents with three raw material ratios are shown in Fig. 2B and C. When the raw material ratio was less than 2.6:1, the CO_2 absorption capacity increased with increasing raw material ratio (seen from Table 2, Fig. 2B(a) and (b)). As shown in Fig. 2C, the sample (b) has two sharper peaks appearing at lower temperatures than those of the sample (c). At the same time, the sample (b) showed a larger absorption rate in Fig. 2B. This showed that the reaction happened quickly at lower temperatures for the

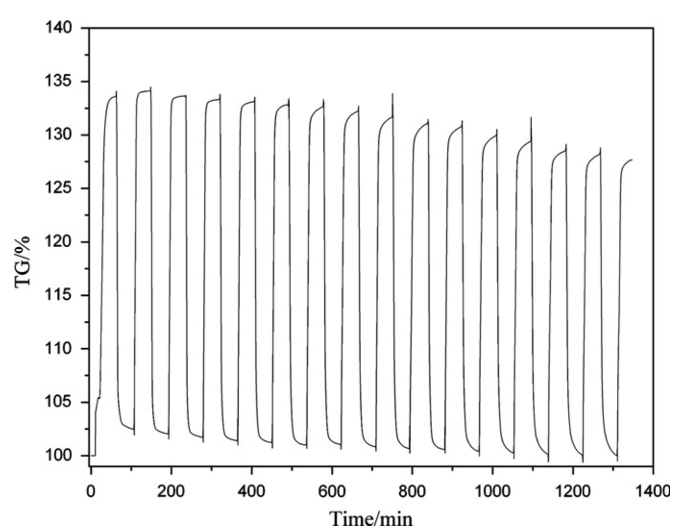

Fig. 3. Absorption–desorption performance of Li_4SiO_4-based sorbents from diatomite.

sample (b), resulting in larger absorption capacity. On the other hand, this is probably because the formation of $(K_2/Li)CO_3$ eutectic melt at higher raw material ratio promotes the sorption kinetics on Li_4SiO_4 [21,22]. When the raw material ratio increased from 2.6:1 to 2.8:1, the absorption capacity decreased from 30.32 wt% to 16.34 wt%

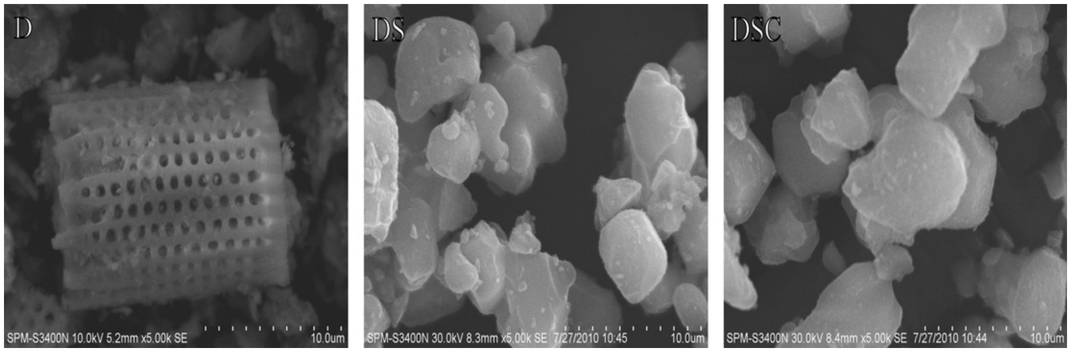

Fig. 4. Morphologies of diatomite (D), Li_4SiO_4-based sorbents (DS) and Li_4SiO_4-based sorbents after 16 cycles (DSC).

(see Fig. 2B). As seen from Fig. 2B and C, the sample (c) showed two more moderate peaks and lower absorption rate than the sample (b), resulting in lower absorption capacity. This could be attributed to the presence of more secondary phases or impurities not absorbing CO_2 with higher raw material ratio (2.8:1).

3.3. *Absorption–desorption performance measurement*

A Netzsch thermogravimetric analyzer was used to screen the performance of Li_4SiO_4-based sorbents. The absorption–desorption test was carried out at a fixed temperature, 700 °C. During the test, a mixture gas (50 mL/min N_2 and 50 mL/min CO_2) for absorption and (100 mL/min N_2) for desorption was introduced into the system alternatively via an automated switch valve every 30 min. The purpose of the test is to carry out the uptake and regeneration cycles. Fig. 3 shows the absorption–desorption cycle number of Li_4SiO_4-based sorbents from diatomite. As shown in Fig. 3, with increasing cycle number, the absorption capacity decreased by 6.44 wt% from the first cycle (34.14 wt%) to the 16th cycle (27.70 wt%). This is because Li_4SiO_4-based sorbents from diatomite have specific morphologies, which refrained Li_4SiO_4-based sorbents from sintering in multinumber cycles (see Fig. 4). Seen from Fig. 4D, diatomite has rich pore structure and uniform pore distribution with the pore size of 0.5–1.0 μm. The as-prepared sorbents do not inherit the morphologies of diatomite. It is noticeable that the morphologies of Li_4SiO_4-based sorbents after 16 cycles (Fig. 4DSC) are similar to those of fresh Li_4SiO_4-based sorbents (Fig. 4DS), which resulted in better cyclic absorption stability of Li_4SiO_4-based sorbents. Compared with the lithium-based sorbents prepared by Marin et al. [16], the as-prepared Li_4SiO_4-based sorbents have a higher CO_2 absorption capacity and better cyclic properties. Therefore, Li_4SiO_4-based sorbents from diatomite should have a potential application prospect for high temperature CO_2 capture.

4. Conclusions

Novel Li_4SiO_4-based sorbents from diatomite for high temperature CO_2 capture were developed at lower temperatures (700 °C). From the results of this work, the following conclusions were obtained:

1) Effect of different raw material ratios on CO_2 absorption capacity was investigated. With increasing raw material ratio, CO_2 absorption capacity increased first, then decreased. When the raw material ratio is 2.6:1, the CO_2 absorption capacity reached the largest value (30.32 wt%) in a mixture gas (50 mL/min N_2 and 50 mL/min CO_2), which is 83% of the theoretical absorption capacity.
2) The absorption–desorption performance of Li_4SiO_4-based sorbents from diatomite was investigated. The absorption capacity decreased by 6.44 wt% from the first cycle (34.14 wt%) to the 16th cycle (27.70 wt%), which resulted from the unchanged morphologies in multinumber cycles.

Acknowledgments

This work has been sponsored by National Natural Science Foundations of China (51104075, 50963004 and 31160146).

References

[1] D.P. Hagewiesche, S.S. Ashour, H.A. Al-Ghawas, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of monoethanolamine and N-methyldiethanolamine, Chemical Engieering Science 50 (1995) 1071–1079.
[2] M. Mavroudi, S.P. Kaldis, G.P. Sakellaropoulos, Reduction of CO_2 emissions by a membrane contacting process, Fuel 82 (2003) 2153–2159.
[3] S.W. Park, B.S. Choi, S.S. Kim, J.W. Lee, Mass transfer of carbon dioxide in aqueous polyacrylamide solution with methyldiethanolamine, Korean Journal of Chemical Engineering 21 (2004) 1205–1211.
[4] W.K. Choi, T.I. Kwon, Y.K. Yeo, H. Lee, H.K. Song, B.K. Na, Optimal operation of the pressure swing adsorption (PSA) process for CO_2 recovery, Korean Journal of Chemical Engineering 20 (2003) 617–623.
[5] Y. Takamura, S. Narita, J. Aoki, S. Hironaka, S. Uchida, Evaluation of dual-bed pressure swing adsorption for CO_2 recovery from boiler exhaust gas, Separation and Purification Technology 24 (2001) 519–528.

[6] M. Wilson, P. Tontiwachwuthikul, A. Chakma, R. Idem, A. Veawab, A. Aroonwilas, D. Gelowitz, J. Barrie, C. Mariz, Test results from a CO_2 extraction pilot plant at boundary dam coal-fired power station, Energy 29 (2004) 1259–1267.
[7] H.A. Mosqueda, C. Vazquez, P. Bosch, H. Pfeiffer, Chemical sorption of carbon dioxide on lithium oxide, Chemistry of Materials 18 (2006) 2307–2310.
[8] H. Pfeiffer, P. Bosch, Thermal stability and high-temperature carbon dioxide sorption on hexa-lithium zirconate($Li_6Zr_2O_7$), Chemistry of Materials 17 (2005) 1704–1710.
[9] H. Pfeiffer, E. Lima, P. Bosch, Lithium–sodium metazirconate solid solutions, $Li_{2-x}Na_xZrO_3(0 \leq X \leq 2)$, a hierarchical architecture, Chemistry of Materials 18 (2006) 2642–2647.
[10] J.I. Ida, R. Xiong, Y.S. Lin, Synthesis and CO_2 sorption properties of pure and modified lithium zirconate, Separation and Purification Technology 36 (2004) 41–51.
[11] M. Kato, CO_2 separation techniques using lithium containing oxide, in: Proceedings of the Sixth Workshop on the International Test Network for CO_2 Capture, Trondheim, 2004.
[12] C. Gauer, W. Heschel, Doped lithium orthosilicate for absorption of carbon dioxide, Journal of Materials Science 41 (2006) 2405–2409.
[13] K. Essaki, K. Nakagawa, M. Kato, H. Uemoto, CO_2 absorption by lithium silicate at room temperature, Journal of Chemical Engineering of Japan 37 (2004) 772–777.
[14] M.E. Bretado, V.G. Velderrain, D.L. Gutierrez, V.C. Martinez, A.L. Ortiz, A new synthesis route to Li_4SiO_4 as CO_2 catalytic/sorbent, Catalysis Today 107–108 (2005) 863–867.
[15] M. Kato, S. Yoshikawa, K. Nakagawa, Absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations, Journal of Materials Science Letters 21 (2002) 485–487.
[16] M.O. Marin, T.C. Drage, M.M. Maroto-Valer, Novel lithium-based sorbents from fly ashes for CO_2 capture at high temperatures, International Journal of Greenhouse Gas Control 4 (2010) 623–629.
[17] T. Nutz, U. Felde, M. Haase, Wet-chemical synthesis of doped nanoparticles: blue-colored colloids of n-doped SnO_2: Sb, Journal of Chemical Physics 110 (1999) 12142–12150.
[18] M.G. Venegas, E. Fregoso-Israel, R. Escamilla, H. Pfeiffer, Kinetic and reaction mechanism of CO_2 sorption on Li_4SiO_4: study of the particle size effect, Industrial and Engineering Chemistry Research 46 (2007) 2407–2412.
[19] M. Kato, K. Nakagawa, Application as a high temperature CO_2 absorbent, Journal of the Ceramic Society of Japan 109 (2001) 911–914.
[20] L.M. Palacios-Romero, H. Pfeiffer, Lithium cuprarte (Li_2CuO_2): a new possible ceramic material for CO_2 chemisorption, Chemistry Letters 37 (2008) 862–863.
[21] K. Essaki, M. Kato, H. Uemoto, Influence of temperature and CO_2 concentration on the CO_2 absorption properties of lithium silicate pellets, Journal of Materials Science 21 (2005) 5017–5019.
[22] J. Ida, Y.S. Lin, Mechanism of high-temperature CO_2 sorption on lithium zirconate, Environmental Science and Technology 37 (2003) 1999–2004.