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Doped lithium orthosilicate for absorption of carbon dioxide

C. GAUER*, W. HESCHEL
Department of Energy Process and Chemical Engineering, TU Bergakademie Freiberg, Freiberg 09596, Germany
E-mail: cornelius.gauer@chem.ethz.ch

Solid absorption is regarded as an option to separate CO_2 from high temperature gases. At present, suitable sorbents are limited to calcium or lithium containing oxides. Among the latter, lithium orthosilicate (Li_4SiO_4) might be preferred due to its high reactivity for CO_2 absorption. Improved sorption properties are obtained by appropriate doping of Li_4SiO_4. Especially, doping of vacancies into the lattice of crystalline Li_4SiO_4 seems to be advantageous. This is concluded from sorption experiments of Al- and Fe-doped Li_4SiO_4 that are presented in this article. In addition, a comparison to eutectic doping by use of potassium is provided. For the investigation of practical applicability, cyclic absorption/desorption was performed on selected samples. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

High temperature absorption of carbon dioxide (CO_2) by solid oxides might become an important alternative to low temperature separation technologies. Its applicability to remove CO_2 from hot gas streams, as in fossil fired power stations and related industries, is of special value. Because of thermal resistance, solid absorption allows *in situ* capture of CO_2 from fuel reforming processes. Reaction enhancement has been reported for methane reforming and water gas shift reaction due to integrated CO_2 withdrawal by use of calcium based absorbents [1–3]. Among those, calcined dolomite is the preferred absorbent, owing to its superior cyclic stability [4]; however, the highly energy intensive regeneration is a substantial disadvantage of this group of materials. Aside from calcium based absorbents, lithium containing oxides have been established to reversibly absorb CO_2. Among them, lithium orthosilicate (Li_4SiO_4) and lithium zirconate (Li_2ZrO_3) are the most reactive species [5]. According to the reaction

$$Li_4SiO_4 + CO_2 \rightleftarrows Li_2CO_3 + Li_2SiO_3 \qquad (1)$$

Li_4SiO_4 can absorb CO_2 up to 36.7% of its own weight, whereas the theoretical capacity of Li_2ZrO_3 is limited to 28.7wt%. This is not as much as the maximum capacity of e.g. calcined dolomite (46 wt%). However, the less energy requiring sorbent regeneration of Li_4SiO_4 ($\Delta H_{r,298} = +142.8$ kJ/mol) compared to calcium oxide ($\Delta H_{r,298} = +178.1$kJ/mol) and lower temperatures for CO_2 emission qualify Li_4SiO_4 as a very promising absorbent material. For application of solid absorption e.g. in water gas shift reaction, high reactivity is demanded at moderate temperatures e.g. 500°C. At that temperature Li_4SiO_4 absorbs CO_2 already much faster than Li_2ZrO_3 [6] but there are several options of doping Li_4SiO_4 to enhance its reactivity.

Our study is aimed to investigate doping of Li_4SiO_4 with hetero elements such as aluminum (Al) or iron (Fe) to improve ion mobility as it can be derived from the design approaches of solid state ionic conductors [7–9]. Since the reaction of Li_4SiO_4 with CO_2 is assumed to occur at the outer surface of the crystal grain, it is related to ion diffusion of Li^+ and O^{2-} which react with CO_2 to form lithium carbonate (Li_2CO_3) [10]. Thus, inserting defects into crystalline Li_4SiO_4 by appropriate doping of foreign elements is likely to improve its reactivity. This can be concluded from studies where interstitial Li^+ are created due to substitution of Si^{4+} by Al^{3+} or where vacancies originate from replacement of Li^+ by Al^{3+}. In both cases, Li^+-mobility and conductivity are increased compared to non-modified Li_4SiO_4 [7, 8]. However, since Li^+ is much smaller compared to O^{2-}, diffusion of the latter one should be the limiting part of ion availability at the reaction surface. Hence doping vacancies into the Li_4SiO_4 lattice, which is assumed to facilitate O^{2-} hopping, is intended to improve reactivity substantially. For the choice

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*Author to whom all correspondence should be addressed.

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of dopant thermodynamic considerations might be taken into account [9]. Doping of cations with less negative Gibbs energy of formation of the corresponding metal oxide, compared to the parent oxide, should decrease the strength of oxygen bonding. This might facilitate the mobility of O^{2-} and therefore lead to additionally increased reactivity of Li_4SiO_4 for CO_2 sorption.

With progressing absorption the silicate crystal is depleted of Li^+ and O^{2-} and Li_2CO_3 is accumulating at the outer crystal surface. The successive build up of a product layer is increasingly restricting CO_2 in approaching the reaction surface which limits the progress of absorption. According to suggested shell models [5, 10, 11] this resistance might be overcome by doping potassium (K) to Li_4SiO_4. Since Li_2CO_3 forms an eutectic melt with potassium carbonate (K_2CO_3) at elevated temperatures, the resulting liquid phase is proposed to facilitate CO_2 diffusion through the product layer.

Both kinds of doping Li_4SiO_4 are compared by sorption experiments in this study. Additionally, the durability to withstand several absorption/desorption cycles was investigated for selected samples.

2. Experimental

2.1. Synthesis of Li_4SiO_4 material

Solid-state synthesis of analytical grade lithium carbonate and highly dispersed silicon dioxide (SiO_2) (both from Merck) was performed by adjusting a molar ratio of 2:1 to obtain Li_4SiO_4 powder. After homogenization in a vibrating disc mill for a minute the initial mixture was calcined in air at 850°C for at least 8 h.

Synthesis of Al- and Fe-doped Li_4SiO_4 followed the above mentioned procedure. To prepare Li_4SiO_4 with interstitial ions, Li_2CO_3, SiO_2 and Al_2O_3 (Laborchemie Apolda) were initially mixed according to a molar ratio of 2.05 : 0.9 : 0.05. For doping vacancies Li_2CO_3, SiO_2 and Al_2O_3 or Fe_2O_3 (Riedel de Haën) were joined in a molar ratio of 1.85 : 1.0 : 0.05.

For eutectic doping, Li_2CO_3 and K_2CO_3 (Chemapol) were added to previously synthesized Li_4SiO_4 meeting a molar ratio of 0.2 : 0.2 : 1.0. After short homogenization (1 min in a vibrating disc mill) the mixture was tempered at 550°C in air for 30 min.

The synthesis products were checked by powder X-ray diffraction (XRD) employing a Phillips PW3710.

2.2. Investigation of general sorption behavior

The sorption behavior was investigated using a thermogravimetric (TG) instrument (Netzsch STA 409C) that recorded differential thermal analysis (DTA) simultaneously. Prior to deployment, the synthesized materials were ground in a mortar for a minute to break down agglomeration. Applying an atmosphere of 100% CO_2 and atmospheric pressure the samples were heated from 25 to 850°C with 1 K/min and cooled down with 2 K/min subsequently.

2.3. Study of cyclic behavior

To examine the absorbent durability, samples of Fe-doped and non-doped Li_4SiO_4 were ground in a vibrating disc mill for a minute. Afterwards they were heated in helium to 650°C and kept at those conditions for 30 min. Absorption of CO_2 was performed at 650°C in 100% CO_2 (atmospheric pressure) for 60 min. Desorption was carried out in an atmosphere of 100% helium at 650°C for 60 min in a first approach and at 750°C for 30 min in a second one. In the second experiment the atmosphere was switched from CO_2 to helium after reaching 750°C and turned back after approaching 650°C again. By alternating the reaction conditions five absorption/desorption cycles were realized in the above mentioned TG instrument.

3. Results and discussion

3.1. CO_2 sorption by Li_4SiO_4 material

Mass changes as indicated by Figs. 1 and 2 are considered to be due to absorption and desorption of CO_2 according to Equation 1. This was confirmed by analyzing samples before and after CO_2 uptake as well as after CO_2 emission by powder XRD. Regarding Al- and Fe-doped Li_4SiO_4, significant phases with aluminum or iron were not detected – which suggests formation of known solid solutions. On the one hand, Li_5AlO_4 is incorporated into Li_4SiO_4 to form e.g. $Li_{4.1}Al_{0.1}Si_{0.9}O_4$, which contains interstitial Li^+. This can be related to the Kröger-Vink notation

$$Li_5AlO_4 \xrightarrow{Li_4SiO_4} 4Li_{Li}^{x} + Li_i^{\bullet} + Al_{Si}' + 4O_O^{x}\,. \qquad (2)$$

In contrast vacancies are generated by combination of $LiAlSiO_4$ with Li_4SiO_4 (e.g. $Li_{3.7}Al_{0.1}SiO_4$) as might be illustrated by

$$LiAlSiO_4 \xrightarrow{Li_4SiO_4} Li_{Li}^{x} + Al_{Li}^{\bullet\bullet} + 2V_{Li}' + Si_{Si}^{x} + 4O_O^{x}. \qquad (3)$$

Similarly, incorporation of $LiFeSiO_4$ into Li_4SiO_4 to obtain e.g. $Li_{3.7}Fe_{0.1}SiO_4$ should follow this scheme [7, 8].

In case of pure Li_4SiO_4 the sorbent mass increased by up to 36.3 wt% at 700°C which is very close to the

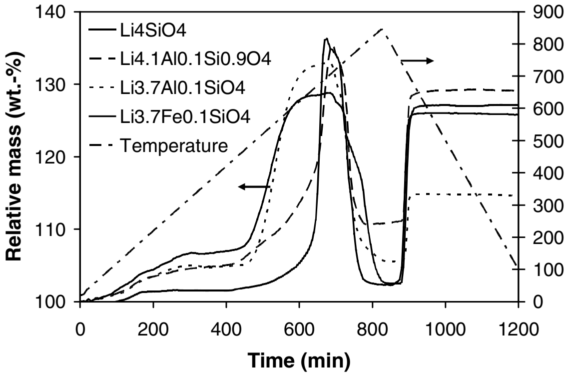

Figure 1 Mass changes due to CO_2 sorption by different types of Li_4SiO_4 (doped with hetero elements), in 100% CO_2 at atmospheric pressure.

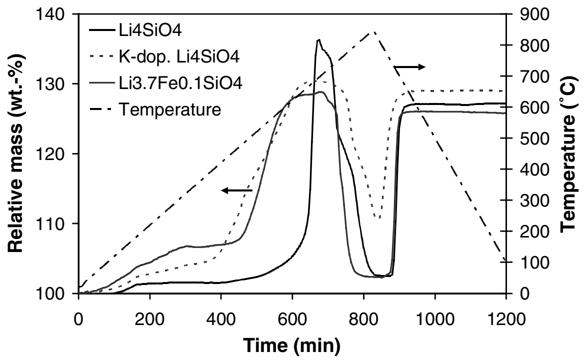

Figure 2 Comparison of sorption behavior of eutectic and vacancy doped Li_4SiO_4.

theoretical maximum capacity of 36.7 wt%. However, the sorption rate is relatively little below 650°C.

In particular, doping Li_4SiO_4 with hetero elements changes sorption properties as shown in Fig. 1. $Li_{4.1}Al_{0.1}Si_{0.9}O_4$, which is intended to have interstitial Li^+, reacts quite similarly to non-doped material even if CO_2 absorption below 650°C is slightly enhanced. Despite addition of aluminum, the maximum capacity of 35.4 wt% is close to the one of pure Li_4SiO_4 due to surplus Li^+. The other modifications exhibit significantly lower maximum loads because additional components reduce the active mass (likewise Li-concentration). A comparison is given in Table I. Vacancy doped material ($Li_{3.7}Al_{0.1}SiO_4$ and $Li_{3.7}Fe_{0.1}SiO_4$) comes up with increased CO_2 uptake from about 500°C. Significantly higher reactivity might be concluded, comparing the weight increase at that temperature. The absorption rate is approximately one order of magnitude superior to pure Li_4SiO_4 and four times above $Li_{4.1}Al_{0.1}Si_{0.9}O_4$ (Table I).

Regardless of different Li_4SiO_4 modifications, absorption and desorption are on equilibrium at about 700°C, but differences in CO_2 emission become obvious with increased heat. Previously absorbed CO_2 is emitted almost completely from $Li_{3.7}Fe_{0.1}SiO_4$ at 800°C and from pure Li_4SiO_4 at 850°C whereas desorption from both Al-doped Li_4SiO_4 remains incomplete during the experiment.

Cooling down the samples in CO_2, absorption starts again at 740°C with absorption rates above 1wt%/min at 720°C indicating almost equal reactivity at that temperature. The only exception is $Li_{3.7}Al_{0.1}SiO_4$. Formation of little reactive lithium aluminate ($LiAlO_2$) [12] might be presumed to cause the lower absorption rate as well as the strongly reduced capacity. However, fast absorption lasts as long as the absorption product Li_2CO_3 is in liquid state. Since Li_2CO_3 transforms into solid state between 700 and 670°C, re-absorption of CO_2 slows down due to increased diffusion resistance of the solid product layer. Below 670°C CO_2 absorption is not observed any more. The phase change of Li_2CO_3 is proved by a sharp exothermic DTA peak at about 680°C.

The results demonstrate an increased reactivity for absorption of CO_2 if Li_4SiO_4 is doped with hetero elements. Introduction of vacancies into the crystal lattice seems to be especially advantageous. It is assumed to gain (n-1) vacancies by replacement of n Li^+ by one n-valent metal ion (M^{n+}) according to

$$n\,Li^+ \rightleftarrows M^{n+}\,. \tag{4}$$

This can also be reproduced from Equation 3. Vacancies in Li_4SiO_4 are supposed to improve ion mobility in general and to facilitate O^{2-} diffusion by offering more sites for ion hopping in particular. Li^+ is subjected to move easily by interstitial diffusion in any case. The strongly improved CO_2 uptake by $Li_{3.7}Al_{0.1}SiO_4$ and $Li_{3.7}Fe_{0.1}SiO_4$ at e.g. 500°C seems to prove this idea. On the other hand, hetero elements might be used to modify Li_4SiO_4 with interstitial ions. By exchanging Si^{4+} with M^{n+} (4–n) Li^+ are needed to balance the electrical charge as might be comprehended from Equation 2 or

$$Si^{4+} \rightleftarrows M^{n+} + (4-n)\,Li^+\,. \tag{5}$$

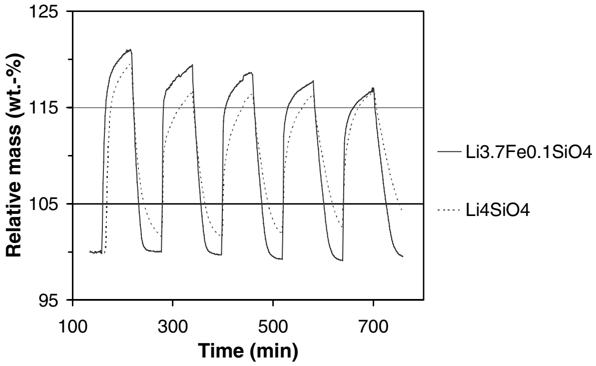

Figure 3 Cyclic performance of Li_4SiO_4 and $Li_{3.7}Fe_{0.1}SiO_4$ in alternating atmosphere of CO_2 and He at 650°C.

TABLE I Sorption properties during heat up with 1 K/min in 100% CO_2

Material	Absorption rate (wt%/min) at 500°C	Max. absorption rate (wt%/min)	Max. CO_2 load (wt%)	Max. CO_2 emission (wt%)
Li_4SiO_4	0.01	1.42 at 675°C	36.3	33.8
$Li_{4.1}Al_{0.1}Si_{0.9}O_4$	0.04	0.58 at 685°C	35.5	24.9
$Li_{3.7}Al_{0.1}SiO_4$	0.12	0.29 at 555°C	33.0	27.5
$Li_{3.7}Fe_{0.1}SiO_4$	0.15	0.21 at 540°C	28.8	26.5
K-doped Li_4SiO_4	0.1	0.18 at 480°C	30.4	19.9

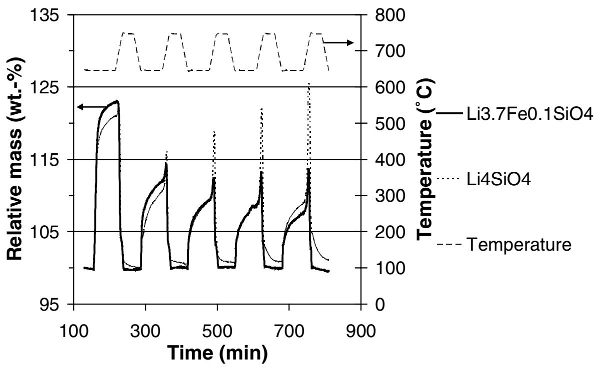

Figure 4 Cyclic performance of Li_4SiO_4 and $Li_{3.7}Fe_{0.1}SiO_4$ carrying out absorption in CO_2 at 650°C and desorption in He at 750°C.

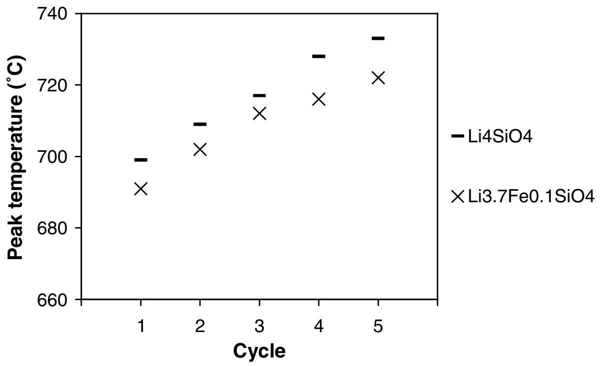

Figure 5 Increase of peak temperature with cycle number, indicating a shift of the absorption/desorption equilibrium.

These Li^+ are thought to occupy interstitial sites in Li_4SiO_4. Even if ion mobility is enhanced in general, this way of doping seems to be less favorable as might be concluded from the less significant enhancement of CO_2 absorption by $Li_{4.1}Al_{0.1}Si_{0.9}O_4$. The less enhanced reactivity is attributed to the lack of additional sites for O^{2-} hopping which apparently approves O^{2-} diffusion as the main resistance for CO_2 absorption as long as the product layer resistance by Li_2CO_3 is not limiting.

According to thermodynamic considerations to design solid state ion conductors [9], iron might be preferred for doping vacancies into Li_4SiO_4. Since Gibbs energy of formation ($\Delta G_{f,298}$) of Fe_2O_3 (−742 kJ/mol) is less negative compared to SiO_2 (−856 kJ/mol), oxygen bondings in Li_4SiO_4 might be weakened and therefore the detachment of O^{2-} is eased. In contrast, oxygen bondings might be strengthened by Al doping because of higher negative Gibbs energy of formation of Al_2O_3 (−1582 kJ/mol). In fact, absorption performance of $Li_{3.7}Al_{0.1}SiO_4$ and $Li_{3.7}Fe_{0.1}SiO_4$ is too similar to clarify the effect of the doped cation. However, emission behavior of the latter is much superior to all other samples. Even though it is hard to state a reason, an influence of dopant might be considered.

Doping of vacancies by introduction of hetero elements to Li_4SiO_4, needs to be compared to doping of additives e.g. K_2CO_3 (or Na_2CO_3) which form eutectic melts with Li_2CO_3 at elevated temperatures. Sorption properties of such K-doped Li_4SiO_4 are depicted in Fig. 2, which allows a good comparison to pure and Fe-doped Li_4SiO_4. An enhanced mass increase is evident for K-doped Li_4SiO_4 from about 400°C which is supposedly reasoned by the formation of an eutectic melt. This liquid phase would facilitate CO_2 diffusion to the grain boundaries of crystalline Li_4SiO_4. In fact a solid-liquid transformation was not indicated by a considerable endothermic DTA peak until 480°C. On the other hand, calculation with thermodynamic software (FactSage 5.2) revealed an eutectic temperature of 391°C for the system Li_2CO_3 – K_2CO_3. However, since pure and Fe-doped Li_4SiO_4 absorb CO_2 scarcely at temperatures well below 500°C, formation of a finely distributed liquid phase, even if it might be little, seems to be reasonable to explain the enhanced CO_2 uptake.

Above 700°C, CO_2 is emitted from K doped Li_4SiO_4 but desorption is still fairly incomplete when re absorption starts again at 800°C during cool down. Consequently, higher temperatures are implied to regenerate K doped Li_4SiO_4. Another disadvantage is the risk of glass forming from potassium and silica which might impair sorption properties.

Therefore, $Li_{3.7}Fe_{0.1}SiO_4$—which is considered to be equal to K doped Li_4SiO_4 in reactivity from about 500°C and much superior in CO_2 emission — is believed to be well suitable for solid sorption of CO_2 at elevated temperatures (e.g. 500°C and above).

3.2. Cyclic behavior

Cyclic usability of Li_4SiO_4 and the favorite doping of this study ($Li_{3.7}Fe_{0.1}SiO_4$) was investigated by carrying out five cycles of CO_2 absorption/desorption at 650°C. As evident from Fig. 3, cyclic capacity is decreasing with increasing cycle number. Owing to better emission of CO_2 during regeneration cyclic capacity of $Li_{3.7}Fe_{0.1}SiO_4$ is superior to pure Li_4SiO_4. However, a reduction of the initial capacity to 85% in the fifth cycle reveals inferior durability of $Li_{3.7}Fe_{0.1}SiO_4$ compared to e.g. dolomite which is reported to come up with 1–2% capacity loss per cycle [4].

Nevertheless, CO_2 emission at 650°C has to be regarded as a mild regeneration mode. Cyclic experiments with 750°C as the regeneration temperature uncover strong sorbent deterioration as is obvious from Fig. 4. A capacity slump of 50% between the first and second cycle is especially remarkable. This substantial reduction of capacity is attributed to melting of Li_2CO_3 during heating from 650 to 750°C in CO_2 at atmospheric pressure. Liquefaction of Li_2CO_3 is suspected to affect sorbent reactivity detrimentally (e.g. surface shrinking) for absorption of CO_2 at moderate temperatures (below ca. 670°C). On the other hand, a liquid state of the product layer facilitates

CO_2 diffusion to the crystal surface. Very high reaction rates will result as is evident from the very sharp absorption/desorption peaks in Fig. 4. But taking advantage of the fast CO_2 uptake at temperatures above the melting point of Li_2CO_3 would require high CO_2 partial pressures. It might be surprising that peak capacities increase with each ongoing cycle number. Further peak temperatures also rise, as depicted in Fig. 5. This indicates a shift of the equilibrium between absorption and desorption to higher temperatures with an increasing thermal strain of sorbent. Even if a reason for the shift cannot be given at present, the delayed beginning of CO_2 emission causes an increased CO_2 uptake until its desorption becomes dominant.

4. Conclusions

Reactivity of Li_4SiO_4 for absorption of CO_2 is substantially enhanced by doping hetero elements as evident by enhanced CO_2 uptake at moderate temperatures. An obviously higher reactivity of $Li_{3.7}Al_{0.1}SiO_4$ compared to $Li_{4.1}Al_{0.1}Si_{0.9}O_4$ proves the vacancy doping to be superior to interstitial doping regarding absorption of CO_2. Facilitating O^{2-} hopping by introduction of vacancies into the crystal lattice is assumed to be the major reason. The use of iron instead of aluminum in $Li_{3.7}Fe_{0.1}SiO_4$ seems to be further advantageous since CO_2 is desorbed easier. In comparison, K-doped Li_4SiO_4 reveals problems with CO_2 emission even if absorption can be performed at slightly lower temperatures. However, Fe doped Li_4SiO_4 might be recognized as a very promising modification for improved CO_2 absorption from about 500°C. This material is suggested for *in situ* capture of CO_2 in fuel reforming processes such as the water gas shift reaction, since it exhibits additionally catalytic activity for oxidation of carbon monoxide [12, 13].

Durability tests uncover the need to stabilize the cyclic capacity of Li_4SiO_4 material. A very strong decay results if Li_2CO_3 is temporarily present in liquid state. In order to maintain high reactivity for CO_2 absorption at moderate temperatures desorption needs to be performed well below the melting point of Li_2CO_3. On the other hand, very high reaction rates as well as sustaining capacity can be presumed at temperatures that prevent Li_2CO_3 from solidification [5, 12]. This might be done at 700°C and above but is restricted to application of high CO_2 partial pressure.

Equilibrium of absorption and desorption was found to shift to higher temperatures with increased duration of thermal strain. Investigation of this surprising effect as well as combination of eutectic and vacancy doping might be of interest for further research.

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