CO₂ Absorption and Desorption Abilities of Li₂O–TiO₂ Compounds

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As an initial stage of the creation of a new solid material for carbon dioxide capture and storage (CCS), the behaviors of CO₂ absorption and desorption were investigated in terms of Li₂O–TiO₂ compounds. The Li₄TiO₄ specimen began to absorb CO₂ at 250°C with the formation of Li₂TiO₃ and Li₂CO₃ phases. The absorption rate was significantly enhanced at 710°C by the formation of the Li₂CO₃-based liquid phase. Decomposition of Li₂CO₃ was observed above 960°C in CO₂ atmosphere and above 900°C in Ar-10%CO₂ atmosphere. In the formation of solid Li₄CO₃ after Li₄TiO₄/CO₂ reaction below 700°C, the reaction rate of CO₂ absorption increased with the decreasing diameter of Li₄TiO₄ particles. The area ratio of the Li₄TiO₄ phase decreased and that of the Li₂TiO₃ phase increased in the Li₄TiO₄ sample after repeating the reaction path of CO₂ absorption and desorption.

KEY WORDS: CO₂ capture; solid CO₂ absorption material; CO₂ absorption and desorption; Li₂O–TiO₂ compound; Li₂CO₃ decomposition.

1. Introduction

In order to decrease greenhouse gas emissions, technological advances in CO₂ capture and storage (CCS) are essential.¹) Because the solid CO₂ absorption method has a large capacity of CO₂ separation per unit weight and is advantageous in terms of handling, solid absorption material is considered to be more suitable for CCS. In a previous study,²) the adaptability of alkaline metal oxide, alkaline earth metal oxide, and their compounds for CO₂ absorption material was discussed from a thermodynamic point of view. It was found that alkaline metal oxide and alkaline earth metal oxide are reactive with CO₂ in the order of K₂O, Na₂O, BaO, Li₂O, and CaO. The experimental results revealed that BaO, LiOH, and CaO were effective for CO₂ absorption. CaCO₃, which was formed by the reaction between CaO and CO₂, decomposed at around 900°C, whereas the carbonated BaO and LiOH had to be heated to a higher temperature for CO₂ desorption. KOH and NaOH absorbed CO₂ easily, but CO₂ desorption from them was difficult even at high temperature. Moreover, alkaline metal oxides were too deliquescent to be used as CO₂ absorption materials. It was suggested from thermodynamical considerations that the formation of double oxide compounds of BaO, CaO, and Li₂O with SiO₂, TiO₂, and Al₂O₃ decreased the temperature of CO₂ decomposition. The compounds of alkaline metal carbonate and alkaline earth metal carbonate became lower by the formation of compound with SiO₂, ZrO₂, TiO₂, and Al₂O₃. In the present study, in order to use the Li₂O–TiO₂ compound as a CO₂ absorption material, the behavior of CO₂ absorption and desorption of Li₄TiO₄ was investigated in various controlled atmospheres.

2. Experimental

2.1. Specimen Preparation

A mixture of Li₂CO₃ and TiO₂ reagents with stoichiometric proportions of Li₄TiO₄ or Li₂TiO₃ was melted in a Pt crucible at 1540°C in air atmosphere. Next, the Pt crucible was withdrawn from the furnace, and the Li₂O–TiO₂ sample in the crucible was poured on a water-cooled copper mold with flowing He gas. The obtained sample was immediately stocked in a vacuum desiccator. Immediately before the CO₂ absorption and desorption experiment, the sample was ground and screened in a glove box, which was purged with dry N₂ gas.
change of the Li$_4$TiO$_4$ carbonation represented by Eq. (1). The weight change of Li$_4$TiO$_4$ begins to increase at approximately 250°C and the increment in the sample is 8% at 660°C. The weight increases drastically at 710°C, becomes 27% in weight change at 900°C, which is 85% in reaction ratio of Li$_4$TiO$_4$, and decreases above 900°C. In contrast, the weight of Li$_2$TiO$_3$ changes minimally.

According to the phase diagram for the Li$_2$O–TiO$_2$ system, Li$_4$TiO$_4$, Li$_2$TiO$_3$, and Li$_4$Ti$_5$O$_{12}$ exist as the Li$_2$O–TiO$_2$ compound below 1000°C. Therefore, the reactions presented in Eqs. (1)–(3) can be considered in the carbonation reaction of each Li$_2$O–TiO$_2$ compound.

\[
\text{Li}_4\text{TiO}_4 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{Li}_2\text{TiO}_3 \quad \ldots \ldots (1)
\]

The weight of Li$_4$TiO$_4$ begins to increase at approximately 250°C, and the increment in the sample is 8% at 660°C. The weight increases drastically at 710°C, becomes 27% in weight change at 900°C, which is 85% in reaction ratio of Li$_4$TiO$_4$, and decreases above 900°C. In contrast, the weight of Li$_2$TiO$_3$ changes minimally.

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\[
5\text{Li}_4\text{TiO}_4 + 3\text{CO}_2 = 3\text{Li}_2\text{CO}_3 + \text{Li}_4\text{Ti}_5\text{O}_{12} \quad \ldots \ldots (2)
\]

\[
\text{Li}_2\text{Ti}_5\text{O}_{12} + 2\text{CO}_2 = 2\text{Li}_2\text{CO}_3 + 5\text{TiO}_2 \quad \ldots \ldots (3)
\]

Because the weight of Li$_4$TiO$_4$ varies and that of Li$_2$TiO$_3$ does not vary in Fig. 1, it is considered that only the reaction of Eq. (1) progresses in the carbonation of Li$_2$O–TiO$_2$ compounds. Though it is suggested that the generation of liquid Li$_2$CO$_3$ enhances Li$_4$TiO$_4$ carbonation at 710°C in Fig. 1, the melting point of Li$_2$CO$_3$ reported is in the range from 724°C to 735°C. A possible explanation for this discrepancy is as follows: when the generated Li$_2$CO$_3$ phase is saturated with Li$_2$TiO$_3$ and Li$_4$TiO$_4$, a liquid phase of the Li$_2$CO$_3$–Li$_2$O–TiO$_2$ system, whose liquidus temperature can be expected as 710°C based on a previous report that the eutectic point of Li$_2$CO$_3$–Li$_2$O system is 705°C, might be formed.

From Fig. 1, the following two stages are suggested in CO$_2$ absorption:

Stage 1: 250–660°C: adsorption or absorption on the surface

\[
\text{Li}_4\text{TiO}_4(s) + \text{CO}_2(g) = \text{Li}_2\text{CO}_3(s) + \text{Li}_2\text{TiO}_3(s) \quad \ldots \ldots (4)
\]

Stage 2: 710–900°C: chemical reaction

\[
\text{Li}_2\text{Ti}_5\text{O}_{12}(s) + \text{CO}_2(g) = \text{Li}_2\text{CO}_3(l) + 5\text{TiO}_2 \quad \ldots \ldots (5)
\]

According to the standard free energy change of Li$_2$CO$_3$ decomposition, it is understood that Li$_2$CO$_3$ is stable in CO$_2$ atmosphere below 1611°C.

\[
\Delta G^\circ(650) = 150,000 – 79.6T \text{ J/mol} \]

Therefore, the decrease in weight above 900°C depicted in Fig. 1 is explained not by Eq. (6) but by the reverse reaction of Eq. (4). It is concluded that the reverse formation of Li$_4$TiO$_4$ can decrease the Li$_2$CO$_3$ decomposition temperature.

3.2. Carbonation Reaction of Li$_4$TiO$_4$

SEM images of the sample surface before heating and after heating to 600 and 800°C in CO$_2$ atmosphere are presented in Fig. 2(a), (b) and (c), respectively. Because the surface of the specimen heated to 600°C is covered with small particles with a diameter of approximately 1 μm in Fig. 2(b), it is considered that the increase in the sample weight below 600°C might be caused by the reaction presented in Eq. (4) proceeding on the surface of the specimen. Larger particles of 10 μm in diameter (but no small particles) are observed along with sintered small particles on the surface of the sample heated to 800°C, as shown in Fig. 2(c). The smooth surface suggests the formation of the liquid phase, which is the Li$_2$CO$_3$–Li$_2$O–TiO$_2$ system mentioned in Sec. 3.1.

In order to confirm the equilibrated phases formed at 600 and 800°C, Li$_4$TiO$_4$ was maintained at specific temperatures for 4 h in CO$_2$ atmosphere. The results of the XRD analysis are shown in Fig. 3(a), (b) and (c); these correspond to those of the sample before heating and after heating to 600 and 800°C, respectively. The XRD pattern of Fig. 3(a) is almost the same as that of Li$_4$TiO$_4$. In Fig. 3(b), Li$_4$TiO$_4$, Li$_2$TiO$_3$, and Li$_2$CO$_3$ are detected in the sample maintained at 600°C. Therefore, Eq. (4) proceeds at 600°C. The Li$_4$TiO$_4$ phase is not observed but the Li$_2$TiO$_3$ and Li$_2$CO$_3$ phases coexist in the sample heated to 800°C, as shown in Fig. 3(c). On the basis of these experimental findings, it is easily recognized that all Li$_4$TiO$_4$ reacts with CO$_2$ following Eq. (5). Togashi et al. reported that Li$_2$TiO$_3$ (x = 2–2.5) is formed by Eq. (7) under a condition similar to that of the present study, but this phase was not observed.
Li$_4$TiO$_4$ + 1.5CO$_2$ = LiTiO$_x$ + 1.5Li$_2$CO$_3$
+ (2.5-x)/2O$_2$ (x = 2–2.5)...................... (7)

3.3 Influence of Initial Size of Particles on Carbonation Rate

The reaction between Li$_4$TiO$_4$ and CO$_2$ at 600°C is a solid-gas reaction that does not generate the liquid phase and is slower than that above the melting point of Li$_2$CO$_3$, as illustrated in Fig. 1. Because the surface reaction area increases with decreasing Li$_4$TiO$_4$ particle size, the CO$_2$ absorption rate is expected to be accelerated in the case of smaller particles. The Li$_4$TiO$_4$ was crushed and sieved to the three diameter ranges of -53, 100–200, and 200–250 μm. The weight change ratios of these classified Li$_4$TiO$_4$ heated in CO$_2$ flow are presented in Fig. 4, where the heating rate was 5°C/min. An initial increase in the weight of all samples begins at approximately 250°C. The weight change ratios of samples with the diameter ranges of -53, 100–200, and 200–250 μm are approximately 10, 3, and 2% at 400°C, respectively. Because the reaction rate increases with the specific surface area, the rate-limiting step of CO$_2$ absorption is considered to be the chemical reaction. The rate of increase in sample weight slows in the temperature range from 400 to 600°C. A rapid increase is observed at 710°C as a result of the formation of the eutectic liquid phase of the Li$_2$CO$_3$–Li$_2$O–TiO$_2$ system, as mentioned in Sec. 3.1. The influence of particle size becomes unclear above 710°C because of the high reactability of the eutectic liquid phase. Though the sample weight starts to decrease at 910°C, most CO$_2$ remains in the sample up to 1100°C.

Figure 5 presents the SEM images of the samples with various particle sizes heated to 1100°C in Fig. 4. Sintered lumps with a diameter of 2–3 mm are observed for all samples. The morphology of the lumps differ depending on the initial particle size, but the morphology of the sample surface is similar among samples. The small precipitates on the surface of the solid particles are considered to be the...
Li₂CO₃–Li₂O–TiO₂ liquid phase, which increases the CO₂ absorption rate. The behavior of the liquid phase formation is independent of the particle size and the increase rate of the weight of all samples becomes similar above 710°C. The liquid phase is also observed in the slit among grains.

The liquid phase initially forms on the surface of the solid particles. Subsequently, it is supposed that some part of the liquid phase remains on the solid surface and the remaining part moves to the slit among grains and penetrates the cracks in the solid surface through the capillary effect. This will be discussed in next section. When the reverse reaction of Eq. (5) does not proceed because of the lack of liquid Li₂CO₃ on the surface of Li₂TiO₃, the amount of CO₂ absorbent (Li₄TiO₄) decreases.

3.4. Influence of CO₂ Partial Pressure on CO₂ Absorption and Desorption

The desorption of CO₂ from Li₂CO₃ did not occur completely in CO₂ atmosphere, as illustrated in Figs. 1 and 4. Considering the reverse reaction of Eq. (5), the decomposition of Li₂CO₃ will proceed in lower CO₂ pressure.

The Li₄TiO₄ sample of diameter -53, 100–200, or 200–250 μm was heated at a rate of 5°C/min in Ar-10%CO₂ flow. The weight change ratios are shown in Fig. 6. An initial increase in the weight at 250°C, which is shown in Fig. 4, is also observed in Ar-10%CO₂. The weight change ratios of samples with the diameter ranges of -53, 100–200, and 200–250 μm are approximately 5, 2, and 2% at 400°C, respectively. The weight change ratio increased rapidly at 710°C, however, maximum weight change rates are slightly lower than those in CO₂ atmosphere. Though the CO₂ desorption barely proceeded in CO₂ atmosphere, as indicated in Fig. 4, the desorption starts at approximately 900°C in Ar-10%CO₂ atmosphere with no dependence on the particle size. The complete CO₂ desorption from the sample of diameter -53 μm is observed at 1100°C. The weight change ratio of 5% is obtained at 1100°C for samples with diameter greater than 100 μm.

Figure 7 depicts the SEM images of the samples heated to 1100°C in Ar-10%CO₂. A mesh structure is observed on the surface of all samples in Fig. 7(d)–(f). This structure is not observed after heating in CO₂ atmosphere (Fig. 5) where
CO₂ did not desorb at 1100°C. Therefore, the mesh structure is considered to be formed by CO₂ desorption. Because the Li content cannot be determined by electron probe microanalysis (EPMA), it is assumed that the dark grains in Fig. 7 are Li₂TiO₃ and the mesh is Li₄TiO₄. According to the reverse reaction of Eq. (5), Li₄TiO₄ phase is produced by Li₂TiO₃ and Li₂CO₃. The Li₂CO₃ mesh is considered to result from the reaction between Li₂TiO₃ grain and the Li₂CO₃–Li₂O–TiO₂ liquid phase that did not seep into the slit between the particles but precipitated on the Li₂TiO₃ surface during CO₂ absorption.

The Li₄TiO₄ sample of diameter 100–200 μm was heated to 1200°C, maintained at that temperature for 30 min, and cooled to 800°C in CO₂ or Ar-30%CO₂ atmosphere. The rates of heating and cooling were both 5°C/min. The variations in sample weights are plotted against temperature in Fig. 8. The weight decrease begins at approximately 900°C for each sample. Above 900°C, the amount of weight decrease in Ar-30%CO₂ is larger than that in CO₂ atmosphere. Therefore, it is considered that the reverse reaction of Eq. (5) readily proceeds in the Ar-CO₂ atmosphere than in CO₂. The experimental findings that the sample weight becomes lower than the original at 1200°C and is lower during decreasing temperature from 1200°C than that during increasing temperature to 1200°C might be explained by Li₂O evaporation, as follows. Figure 9 presents a schematic phase diagram of the Li₂O–TiO₂–CO₂ system. The composition of liquid phase A double-saturated with Li₂TiO₃ and Li₄TiO₄ moves gradually toward B, which is located on the line between A and C, by Li₂O evaporation above 900°C.
The point C is on the border of $\text{Li}_2\text{TiO}_3$–CO$_2$. This composition change of the liquid phase causes the weight loss of the sample as well as the decrease in the amount of $\text{Li}_4\text{TiO}_4$ produced by the reverse reaction of Eq. (5). When the sample weight starts to increase with decreasing temperature from 1200°C, the composition of liquid phase B moves toward the CO$_2$ corner by CO$_2$ absorption. However, the amount of Li$_2$O in the liquid phase is smaller than that before Li$_2$O evaporation. The composition of the liquid phase cannot return to A after CO$_2$ desorption.

3.5. Repeatability of CO$_2$ Absorption and Desorption

The long-term stability of the cycle of CO$_2$ absorption and desorption is essential for CO$_2$ absorbent. The repeatability of CO$_2$ absorption and desorption of $\text{Li}_4\text{TiO}_4$ was investigated by the thermal cycle test between 900 and 1100°C, which was carried out in Ar-10%CO$_2$ atmosphere using the $\text{Li}_4\text{TiO}_4$ sample with a diameter of 53 μm. The sample was heated to 900°C at a rate of 25°C/min and to 1100°C at a rate of 10°C/min. After being maintained at 1100°C for 20 min, the sample was cooled to 900°C at a rate of 10°C/min. After being maintained at 900°C for 20 min, the sample was again heated to 1100°C. This thermal cycle between 900 and 1100°C was repeated three times. The experimental result is shown in Fig. 10, where solid and broken lines denote the weight change ratio and temperature, respectively. The sample weight starts to increase at 380°C. After this first variation in the weight change ratio, the decrease and increase in sample weight begins at approximately 1000°C during heating and cooling, respectively. The maximum and minimum values of the weight change ratio in each cycle decrease gradually when the heat cycle is repeated. In addition, the difference in the weight change ratio between the maximum value and the minimum value also decreases. After the third CO$_2$ desorption, the sample weight decreases by approximately 5%. The decrease in the maximum value in Fig. 10 is thought to be caused by the decrease in the reactive surface area and the crystal growth of the oxide compound, as described in Sec.3.4. The decrease in the minimum value might be caused not by the vaporization of solid $\text{Li}_2\text{TiO}_4$ and $\text{Li}_2\text{TiO}_3$, but by that of Li$_2$O from the Li$_2$CO$_3$–Li$_2$O–TiO$_2$ melt.

The XRD patterns of specimen after one and three thermal cycles are presented in Fig. 11. The specimen before the reaction is identified as $\text{Li}_4\text{TiO}_4$ in Fig. 11(a). After the first (Fig. 11(b)) and third ((c)) thermal cycle, $\text{Li}_4\text{TiO}_4$, $\text{Li}_2\text{TiO}_3$, and $\text{Li}_2\text{CO}_3$ phases are detected. Because the peak heights of $\text{Li}_2\text{TiO}_3$ and $\text{Li}_2\text{CO}_3$ increase and that of $\text{Li}_4\text{TiO}_4$ decreases with the carbonation cycle, the $\text{Li}_4\text{TiO}_4$ does not begin to form because of the non-coexistence of $\text{Li}_2\text{CO}_3$ and $\text{Li}_2\text{TiO}_3$. The SEM images of the specimen after the first and third thermal cycle are presented in Fig. 12. As shown in Fig. 12(a), sintered particles of 1 μm in diameter contain many cracks. After three thermal cycles, the grain size increases as a result of the sintering of grains. The concentrations of Ti and C in the grains observed in Fig. 12(a), which were determined by FE-SEM-EDX, were approximately 20% and
10\textdegree}–15\% whereas those in Fig. 12(b) were 30–45\% and less than 10\%, respectively. The latter could be considered Li$_2$TiO$_3$ because of the higher Ti concentration, and the small particles on Li$_2$TiO$_3$ could be considered Li$_2$CO$_3$. After the cycle test, the amount of Li$_4$TiO$_4$ decreases, because the reaction zone of Li$_2$TiO$_3$ with Li$_2$CO$_3$, which is located at the slit among grains, decreases with increasing Li$_2$TiO$_3$ grain size. The Li$_2$O evaporation described in Sec.3.4 is also the reason for the decrease in the amount of Li$_2$TiO$_3$.

3.6. Evaluation of Free Energy Change of Li$_4$TiO$_4$ Carbonation Reaction

The equilibrium constant $K$ and free energy change $\Delta G^0$ of Eq. (1) are expressed by Eqs. (8) and (9), respectively.

$$K = \frac{a_{LiCO_3} \cdot a_{Li_2TiO_3}}{a_{Li_4TiO_4} \cdot P_{CO_2}} \quad \text{(8)}$$

$$\Delta G^0 = -RT \ln K = -RT \ln \frac{a_{LiCO_3} \cdot a_{Li_2TiO_3}}{a_{Li_4TiO_4} \cdot P_{CO_2}} \quad \text{(9)}$$

where $a$, $P$, and $R$ denote activity, partial pressure, and the gas constant, respectively. Activities of Li$_4$TiO$_4$ and Li$_2$TiO$_3$ are considered to be unity. Though Li$_2$CO$_3$ contains Li$_2$O and is saturated with both Li$_4$TiO$_4$ and Li$_2$TiO$_3$ in the present experimental condition, Eq. (9) can be rewritten as Eq. (10) by assuming that the Li$_2$CO$_3$ activity is unity.

$$\ln P_{CO_2} = \frac{\Delta G^0}{RT} \quad \text{(10)}$$

To clarify the influence of CO$_2$ partial pressure, the Li$_4$TiO$_4$ sample was heated and cooled in Ar-50, 30, 5, or 3\%CO$_2$ at a rate of 5\°C/min. The temperature at the beginning of the weight decrease and that at the beginning of the weight increase are listed in Table 1. Both temperatures decrease with decreasing CO$_2$ partial pressure.

$$\ln P_{CO_2} = -41,700 \cdot \frac{1}{T} + 30.0 \quad \text{from 930 to 1020°C} \ldots (11)$$

Finally, the free energy change $\Delta G^0$ of Eq. (5) is expressed by Eq. (12).

$$\Delta G^0 = -347,000 + 250T \ J/\text{mol} \quad \text{from 930 to 1020°C} \ldots (12)$$

Relationship between decomposition temperature and partial pressure of CO$_2$ can be derived from Eq. 11. CO$_2$ desorption temperature of Li$_2$CO$_3$–Li$_4$TiO$_4$–Li$_2$TiO$_3$ system is lower than that of Li$_2$CO$_3$–Li$_2$O system. Since reaction absorption of CO$_2$ progresses with generation of liquid phase, the reaction rates of absorption and desorption are high enough. Decomposition temperature of Li$_2$CO$_2$ in the present system is higher than that of CaO or BaO, absorption material of the present system would be used between 1000 to 1200\°C.

4. Conclusions

In order to clarify the ability of the Li$_2$O–TiO$_2$ compound as a CO$_2$ absorption material, the behavior of the absorption and desorption of CO$_2$ by Li$_4$TiO$_4$ of various grain sizes was investigated under various CO$_2$ partial pressures. The conclusions obtained are as follows:

(1) Absorption of CO$_2$ by Li$_4$TiO$_4$ was expressed as Li$_4$TiO$_4(s)$ + CO$_2(g)$ = Li$_2$CO$_3(s, l)$ + Li$_2$TiO$_3(s)$.

(2) Li$_4$TiO$_4$ rapidly reacted with CO$_2$ above 710\°C, where the eutectic liquid phase of the Li$_2$CO$_3$–Li$_2$O–TiO$_2$ system was formed.

(3) The initial size of Li$_4$TiO$_4$ affects the reactivity below 700\°C. The reactivity increased with decreasing grain size.

(4) After repeating CO$_2$ absorption and desorption, the ratio of Li$_4$TiO$_4$ and Li$_2$TiO$_3$ phases decreased.

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Table 1. Temperature of beginning of weight decrement and increment.

| $P_{CO_2}$ | Temperature at weight change [°C] |
|------------|---------------------------------|
|            | Decrement | Increment |
| 1          | 925       | 1202      |
| 0.5        | 891       | 1100      |
| 0.3        | 888       | 1104      |
| 0.1        | 885       | 1022      |
| 0.05       | 879       | 971       |
| 0.03       | 832       | 937       |

Fig. 13. Equilibrium CO$_2$ pressure at the coexistence of Li$_2$TiO$_3$, Li$_2$CO$_3$ and Li$_4$TiO$_4$. 

| Temperature [°C] | $\ln P_{CO_2}$ [atm] |
|-----------------|----------------------|
| 1200            | -3                   |
| 1100            | -2                   |
| 1000            | -1                   |
| 910             | 0                    |

Fig. 13. Equilibrium CO$_2$ pressure at the coexistence of Li$_2$TiO$_3$, Li$_2$CO$_3$ and Li$_4$TiO$_4$. 

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