New Series of Lithium Containing Complex Oxides, Lithium Silicates, for Application as a High Temperature CO₂ Absorbent

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Lithium zirconate (Li₂ZrO₃) has been developed for application as a novel CO₂ absorbent. This material reacts immediately with CO₂ in the temperature range of 450 to 550°C. Moreover, the products react and revert reversibly to Li₂ZrO₃ at temperatures above 650°C. The possibility of a CO₂ separation system utilizing this reaction and operating at around 500°C is suggested. The absorption is ascribed to the mechanism whereby lithium oxide in the Li₂ZrO₃ crystal structure reacts reversibly with CO₂. However, this material has the disadvantages of heavy weight and high cost due to the use of ZrO₂. On the basis of the above mechanism, a series of lithium silicates were considered as candidates for new CO₂ absorbents, and their CO₂ absorption properties were evaluated by TG analysis. Furthermore, in order to confirm the reaction, phase analysis was conducted by XRD.

Key-words: CO₂, Absorbent, Separation lithium, Silicate

1. Introduction

In recent years, it is anticipated that the average temperature of the earth increases due to the increase in greenhouse gases such as the carbon dioxide (CO₂), in the atmosphere. The Kyoto protocol adopted in 1997 requires a reduction in the release of such gases.

In order to achieve the above goal, practical methods such as saving energy, improvement of conversion efficiency and development of alternative energy sources are required. Moreover, separation of CO₂ from the exhaust gas of power plants and factories and the absorption of CO₂ by forests and oceans are needed.

Regarding the separation methods for CO₂, many works have been done under the support by government.¹⁻⁴ Our group has developed a CO₂ separation technology based on the chemical reaction using lithium zirconate (Li₂ZrO₃).⁵⁻⁶ Since this method is available in the temperature range of 450°C to 700°C, it has some advantages over separation of CO₂ from power plants without lowering temperature, and it can be used with catalysts for CO shift reaction or methane reforming reaction.⁷

The absorption is ascribed to the mechanism whereby lithium oxide (Li₂O) in the Li₂ZrO₃ crystal structure reacts reversibly with CO₂. However, this material has the disadvantages of heavy weight and high cost due to the use of ZrO₂. Therefore, if an oxide with lighter molecular weight than ZrO₂ were available, the molecular weights of absorbents would also decrease. Moreover, when an absorbent contains more than 2 mol of Li₂O in the crystal, it can absorb more than 2 mol of CO₂. Consequently, the weight of an absorbent becomes much lighter.

In this work, therefore, we studied a series of lithium silicates instead of the previously studied lithium zirconate. Since silicon dioxide (SiO₂) is abundant, and is a material with a light molecular weight, lithium silicates are expected to be promising absorbents from the viewpoints of weight and cost. Furthermore, chemical formulae of lithium silicates vary with respect to lithium stoichiometry. We tried to synthesize stable phases of lithium silicates and evaluate their CO₂ absorbent properties.

2. Experimental procedures

2.1 Sample preparation

From a series of lithium silicates, we attempted to fabricate lithium metasilicate (Li₂SiO₃) and lithium orthosilicate (Li₄SiO₄) since they are stable phases.

Li₂CO₃ (average grain size: 0.5 μm, purity: 99.5%, Wako Pure Chemicals Co., Ltd.) and SiO₂ (quartz type, average grain size: 4 μm, High Purity Chemicals Co., Ltd.) were mixed by agate mortar and pestle in a molar ratio of 1 : 1 or 2 : 1. The mixed powders were put into alumina crucibles and heat treated in a box furnace at 1000°C for 8 h. The heat-treated powders were lightly ground by agate mortar and pestle again to break down agglomeration before the following evaluations were performed.

2.2 Evaluation

Phase analysis was conducted by means of an X-ray diffraction machine (XRD: RINT1200, Rigaku Co., Ltd.) for the powders before and after CO₂ absorption. CO₂ absorption properties were evaluated using a thermogravimetric instrument (TG: TG-DTA2500, MAC Science Co., Ltd.). TG measurements were performed for the powders under two types of heating procedures. In the case of absorbing CO₂ from the exhaust gases of power plants, H₂O or other gases, such as NOₓ and SOₓ, were expected to have a great influence on the absorption of CO₂. However, in this case, dry pure gases were used to examine the pure reaction between lithium silicate and CO₂. First, in order to examine the reaction temperature, samples were heated to 900°C at a constant rate of 5°C/min in dry pure CO₂ gas with a flow rate of 300 ml/min. In this case, CO₂ can be absorbed during the cooling procedure and the crystalline phases are not the same as those after release. Next, in order to clarify the type of reaction between lithium silicate and CO₂, samples were kept at the temperatures at which clear weight changes were observed in the TG curve. After keeping the samples for 1 h for CO₂ absorption, the atmosphere was changed to N₂ and heated to 850°C and kept for 0.5 h for release. In this case, crystalline phases after release can be maintained because CO₂ is not absorbed during the cooling procedures.
3. Results and discussion

3.1 Equilibrium temperature

The following equations represent reactions between lithium silicates and CO₂.

\[ \text{Li}_2\text{SiO}_3(s) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) + \text{SiO}_2(s) \quad (3.1) \]
\[ \text{Li}_4\text{SiO}_4(s) + 2\text{CO}_2(g) \rightarrow 2\text{Li}_2\text{CO}_3(s) + \text{SiO}_2(s) \quad (3.2) \]

s means solid and g means gas.

Before experiments, we tried to ascertain in what temperature ranges lithium silicates absorb CO₂. The equilibrium temperature, at which reaction of CO₂ absorption apparently stops, was calculated from thermodynamics. That is, it is the temperature at which Gibbs free energy changes (\( \Delta G \)) for the above reactions become zero.

In order to calculate the \( \Delta G \) of each reaction, standard free energies for each substance are needed, and can be calculated using the following reactions.

\[ 2\text{Li}(s) + \text{Si}(s) + 3/2\text{O}_2(g) \rightarrow \text{Li}_2\text{SiO}_3(s) \quad (3.3) \]
\[ 4\text{Li}(s) + \text{Si}(s) + 2\text{O}_2(g) \rightarrow \text{Li}_4\text{SiO}_4(s) \quad (3.4) \]
\[ 2\text{Li}(s) + \text{C}(s) + 3/2\text{O}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) \quad (3.5) \]
\[ \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad (3.6) \]
\[ \text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) \quad (3.7) \]

The standard free energies at various temperatures of each substance were calculated using the "Thermochemical Data of Pure Substances." As a result, the equilibrium temperatures of Li₂SiO₃ and Li₄SiO₄ were calculated to be 250°C and 445°C, respectively. The results are listed in Table 1 with the molecular weight, density and maximum amount of CO₂ absorption. It was found that replacing ZrO₂ with SiO₂ enabled the weight of the absorbent to be reduced by 42% for Li₂SiO₃ and by 23% for Li₄SiO₄. Moreover, the absorption temperatures are reduced at the same time.

3.2 Crystalline phases

Figures 1 and 2 show the XRD patterns for the mixed powders after heat treatment. In both cases, although a few unknown peaks were detected, all other peaks were indexed to Li₂SiO₃ and Li₄SiO₄, respectively. Therefore, it was confirmed that almost single phases from XRD level were obtained under the above conditions.

3.3 CO₂ absorbent properties

Figure 3 shows the TG curves for Li₂SiO₃ and Li₄SiO₄. In the case of Li₂SiO₃, no weight increase was observed at temperatures up to 900°C. The reason is thought to be that Li₂SiO₃ can absorb CO₂ at temperatures of less than 250°C, but the absorption rate is very slow in this temperature range from the viewpoint of kinetics. In the case of Li₄SiO₄, clear weight increase and decrease were observed at about 720°C and 770°C, respectively, also as shown in Fig. 3. The weight change was about 35 mass%, which was 50% larger than that for Li₂ZrO₃. Weight increase and decrease correspond to the amount of CO₂ absorption and release, respectively. Therefore, it was thought that Li₂SiO₃ absorbed CO₂ reversibly. In order to examine the cyclic behavior, absorption at 700°C and release at 850°C were repeated 5 times as shown in Fig. 4. As a result, it was found that absorption amounts were almost the same as initial amount.

Moreover, a plateau was observed at around 800°C in Fig. 3. The appearance of the plateau was explained as follows. The velocity of CO₂ release became lower because the velocity of absorption became higher with the surrounding CO₂ content due to the sudden CO₂ release beginning at 770°C, and the release velocity became higher again as the temperature became higher.

In the case of applying this material to power plants as a CO₂ absorbent, the influence of steam is thought to be one of the important factors. Then TG measurement was conducted in wet atmosphere. The CO₂ was introduced to the bubbling unit with water heated at 80°C. Figure 5 shows the TG

Table 1. Molecular Weight, Density, Maximum Absorption Amount and Equilibrium Temperature of Absorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular weight</th>
<th>Density g/cm³</th>
<th>Maximum absorption amount mass%</th>
<th>Equilibrium temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂SiO₃</td>
<td>90.0</td>
<td>2.5</td>
<td>48.8</td>
<td>243</td>
</tr>
<tr>
<td>Li₄SiO₄</td>
<td>119.9</td>
<td>2.4</td>
<td>73.4</td>
<td>445</td>
</tr>
<tr>
<td>Li₂ZrO₃</td>
<td>155.1</td>
<td>3.6</td>
<td>28.7</td>
<td>715</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern for powder mixture of Li₂CO₃ + SiO₂ heat-treated at 1000°C for 8 h.

Fig. 2. XRD pattern for powder mixture of 2Li₂CO₃ + SiO₂ heat-treated at 1000°C for 8 h.

Fig. 3. TG curves for Li₂SiO₃ and Li₄SiO₄.
curves for Li$_4$SiO$_4$ in dry and wet atmosphere. Although slight difference was observed at the beginning of absorption, almost the same absorption amount was obtained after about 20 min. Therefore, the influence of steam is thought to be small. However, further investigations are needed to clarify the influence of steam, especially on the long-term life.

3.4 Reaction mechanism

In order to clarify the type of reaction between Li$_4$SiO$_4$ and CO$_2$, crystalline phases were identified by high-temperature XRD at various temperatures during TG measurement using the heating procedure shown in Fig. 6. Inflection points were observed both in absorption and release. Since absorption and release are performed by chemical reaction, the velocities become larger when temperature is apart from the equilibrium point according to the thermodynamics, and when temperature is higher from the viewpoint of kinetics. That is why the maximum values of absorption and release exist and the inflection points were observed. Figures 7 and 8 show the XRD patterns for samples kept at 700°C for 1 h in CO$_2$ and at 850°C for 1 h in N$_2$, respectively. The results revealed that Li$_4$SiO$_4$ decomposed to Li$_2$CO$_3$ and Li$_2$SiO$_3$ by absorbing CO$_2$, and the products reverted to the original state during release at 850°C.

When the Reaction (3.2) occurs, the weight ought to increase by 74%, and Li$_2$CO$_3$ and SiO$_2$ should be formed. However, in this case the weight increase was about half of the theoretical maximum, and Li$_4$SiO$_4$ was formed instead of SiO$_2$. Considering the amount of weight change and phase transition, the following reaction is thought to have occurred.

\[ \text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3 \]  

(3.8)

The equilibrium temperature of this reaction was calculated to be 710°C. This temperature was very similar to the experimental value. Therefore, it was thought that the reaction between Li$_4$SiO$_4$ and CO$_2$ proceeded firstly by Eq. (3.8) followed by Eq. (3.1). In this case, it is necessary for CO$_2$ to be absorbed at a temperature of less than 250°C due to the kinetic limit of Eq. (3.1).

4. Conclusion

From the results of XRD and TG analysis, the following conclusions were reached.

(1) Lithium methasilicate (Li$_2$SiO$_2$) hardly absorbed CO$_2$ up to 900°C.

(2) Lithium orthosilicate (Li$_4$SiO$_4$) absorbed CO$_2$ at around 35% in weight up to 700°C and decomposed to
Li₂SiO₃ and Li₂CO₃.
(3) The products released CO₂ absolutely at 850°C and reconverted to Li₂SiO₃.
(4) Replacing SiO₂ with ZrO₂ resulted in reducing the absorbent weight by 23% and improved the CO₂ absorption amount by about 50%.

References