Reproducibility of CO₂ Absorption and Emission for Cylindrical Pellet Type Lithium Orthosilicate

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For the purpose of carbon dioxide (CO₂) capture at high temperature, Toshiba developed a series of novel CO₂ absorbents using lithium-containing oxides. Among these absorbents, lithium orthosilicate (Li₂SiO₃) shows the highest reaction rate of CO₂ absorption and emission, which result in weight change of up to 36%. Furthermore, the emission was performed at a much lower temperature than that of CaO. This paper is our first report regarding reproducibility of CO₂ absorption and emission using Li₂SiO₃ absorbent in the shape of cylindrical pellet. The pellets were heated at 600 °C for absorption and 800 °C for emission in a gas flowing condition of 20% CO₂ up to 50 cycles. The reproducibility was evaluated by the retention ratio of absorption rate to the initial one. In addition, the degradation mechanism of reproducibility was investigated in term of the change of microstructure.

[Received July 25, 2003; Accepted January 5, 2004]

Key-words: CO₂, absorbent, lithium silicate, reproducibility, pellet

1. Introduction

From the viewpoint of preventing global warming, there is a growing need to reduce the amount of carbon dioxide (CO₂). For that purpose, saving of energy, improvement of conversion efficiency, and development of alternative energy sources and separation of CO₂ are promising countermeasures. Regarding separation of CO₂, it is thought to be effective to remove CO₂ from the high-temperature fuel gas of power plants. However, most CO₂ removal techniques have poor heat-tolerance. The authors[1–4] have developed a novel CO₂ separation technique by employing the chemical reaction of lithium zirconate (Li₂ZrO₃) with CO₂. In this method, lithium oxide (Li₂O) in Li₂ZrO₃ reacts with CO₂ reversibly by the following reaction.

\[ \text{Li}_2\text{ZrO}_3 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{ZrO}_2 \]  (1)

This reaction immediately proceeds at around 450–700°C. Moreover, the products react and revert to Li₂ZrO₃ at higher temperature, i.e. above 700°C. Certain candidate lithium-containing oxides, which react with CO₂, were selected on the basis of thermodynamic stability. Among these absorbents, lithium orthosilicate[7–9] (Li₂SiO₃) is found to have the highest reactivity with CO₂. The absorption rate in a gas stream of 20% CO₂ is equivalent to ca. 60 mg of CO₂ uptake in a minute by 1 gram of Li₂SiO₃. Since Li₂SiO₃ is synthesized from silicon dioxide, Li₂SiO₃ is lighter in weight and lower in cost. Furthermore, the absorption also proceeds at ambient temperature in an atmospheric environment.[5] Considering the practical use as CO₂ absorbents for power plants, a pellet-type absorbent is thought to be realistic. However, in the case of pellet-type absorbents, degradation of absorption performance is of greater concern than in the case of powder-type absorbents, since sintering proceeds easily due to the small distance between particles. Furthermore, vaporization of Li₂CO₃, which is generated by absorbing CO₂, and change of crystalline phases may cause the degradation of absorption performance. In this study, reproducibility of CO₂ absorption and emission of cylindrical pellet-type lithium orthosilicate were investigated and the degradation mechanism is also discussed.

2. Experimental procedures

2.1 Sample preparations

Lithium carbonate powder (average grain size: 0.5 μm, purity: 99.5%, Wako Pure Chemicals Co., Ltd., Japan) and silicon dioxide powder (quartz type, average grain size: 4 μm, High Purity Chemicals Co., Ltd., Japan) were ball-milled mixed at a molar ratio of 2:1 with distilled water. After drying and lightly grinding, a powder mixture of raw material was obtained. This raw material powder with potassium carbonate was kneaded with distilled water and inorganic binder (SERANDER®, Yuben Industry Co., Ltd., Japan), followed by extruding to cylindrical green bodies of approximately 4 mm diameter and 5 mm length, using an extruder (FM-P20E, Miyazaki Iron Works Co., Ltd., Japan). After heat treatment at 800°C for 8 h, cylindrical pellets of lithium silicate were obtained. Furthermore, the pellets with lithium zirconate, which was added to inhibit the grain growth, were also fabricated in the same manner. Lithium zirconate was selected from the viewpoints of less reactivity with lithium silicate at a regeneration temperature and because of the expectation that it would remain at grain boundaries.

2.2 Evaluation

Cyclic tests were conducted using a cylindrical furnace. Pellets were placed on gold pans in a 20% CO₂ gas flow at a rate of 300 ml/min. Then the pellets were heated for 1 h at 600 °C for absorption and for 1 h at 800°C for regeneration. This process was repeated 1, 10, 20, and 50 times. After final regeneration, CO₂ containing gas was changed to nitrogen and pellets were cool down to a room temperature. Then weight changes of the pellets after cyclic test were measured using a thermogravimetric instrument (TG: TG–DTA2500, MAC Science Co., Ltd., Japan) at 600°C for 1 h in a 20% CO₂ atmosphere. This weight change per 1 h was defined as an absorption rate.

In addition, compositional analysis by inductively coupled plasma atomic emission spectrometry (ICP–AES: SPS400, Seiko Instrument Inc., Japan), phase identification by X-ray diffractometer (XRD: RINT1200 Rigaku Co., Ltd., Japan), specific surface area measurement by BET (ASA2010, Shimadzu Corp., Japan.), and microstructure observation by sponing electron microscope (SEM: JSM–5400LV, JEOL, Japan) were conducted.
3. Results and discussion

3.1 Reproducibility of CO₂ absorption and emission

For the purpose of evaluating reproducibility of CO₂ absorption, the retention ratio was calculated using the absorption rate of the initial and the cyclic tested samples. Each initial absorption rates was around 28 wt%/h. Figure 1 shows the retention ratio of absorption rate. In the case of the sample without Li₂ZrO₃, the retention ratio of absorption ratio decreased suddenly after only 5 cycles and almost saturated to about 70% after 50 cycles. The sample with 2 mass% Li₂ZrO₃ shows almost the same behavior as the sample without Li₂ZrO₃, although the retention ratio of absorption ratio was a little higher. On the other hand, in the case of the sample with 5 mass% Li₂ZrO₃, the retention ratio of absorption ratio decreased gradually to 10 cycles and was more than 90% even after 50 cycles. From this figure, it was found that Li₂ZrO₃ addition was effective for improving the reproducibility of CO₂ absorption and emission.

3.2 Vaporization of alkali carbonate

Vaporization of alkali carbonate was thought to be one of the causes of degradation of absorption property; composition analysis was performed for the samples with and without Li₂ZrO₃ by ICP. Table 1 shows the Li/Si ratio of pellets before and after performing cyclic tests 50 times for the samples with or without Li₂ZrO₃. It was found that the Li/Si ratios of all the samples differed only slightly after cyclic tests. Therefore, evaporation of Li₂CO₃ was thought to be slight.

3.3 Constitutional phases

Phase transition was also thought to be one of the causes of degradation of absorption property since decrease of the amount of Li₂SiO₃ leads directly to lowering of the absorption amount. Then the crystalline phases were identified by XRD.

Table 1. Li/Si Ratio for the Samples Before and After 50 cycles

<table>
<thead>
<tr>
<th>Amount of Li₂ZrO₃ addition</th>
<th>Li/Si ratio /</th>
<th>Before</th>
<th>After 50 cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>3.99</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td>2 mass%</td>
<td>4.02</td>
<td>3.99</td>
<td></td>
</tr>
<tr>
<td>5 mass%</td>
<td>4.01</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 shows the XRD patterns of the sample without Li₂ZrO₃ before and after 50 cycles. It appeared that no phase change occurred. As for the other samples with Li₂ZrO₃, the same results were obtained. Therefore, the degradation of absorption property was brought about by other causes.

3.4 Specific surface area

The CO₂ absorption is ascribed to the mechanism whereby lithium oxide (Li₂O) in the lithium containing oxides reacts with CO₂ at the surface of absorbents. Therefore, contact area with CO₂ gas is expected to be the important factor. Then in order to clarify the relationship between retention ratio of absorption rate and the surface area, BET measurement was conducted. Table 2 shows the specific surface areas for the
Table 2. Specific Surface Areas for the Samples Before and After 50 cycles

<table>
<thead>
<tr>
<th>Amount of Li$_2$ZrO$_3$ addition</th>
<th>Specific surface area / m$^2$ g$^{-1}$</th>
<th>Retention ratio of surface area / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>1.525</td>
<td>27.6</td>
</tr>
<tr>
<td>2</td>
<td>0.906</td>
<td>49.2</td>
</tr>
<tr>
<td>5</td>
<td>0.669</td>
<td>87.3</td>
</tr>
</tbody>
</table>

![Before test](image1.png) ![After 50 cycle](image2.png)

Fig. 3. SEM micrographs for the samples without or with 5 mass% Li$_2$ZrO$_3$ before and after cyclic test

sample before and after cyclic test. In the case of the sample without and with 2 mass% Li$_2$ZrO$_3$, specific surface areas decreased dramatically; by more than 50%. On the other hand, in the case of the sample with 5 mass% Li$_2$ZrO$_3$, surface area was maintained at nearly 90%. This result indicated almost the same tendency as for the retention ratio of absorption rate. Therefore, decrease of contact area with CO$_2$ gas was thought to be one of the main causes of the degradation of absorption property.

3.5 Micrographs

Although the importance of contact area with CO$_2$ is mentioned above, the migration of Li$_2$O from inner parts of absorbent to the surface was also thought to be an important factor. This is because the longer distance migration caused by the grain growth lead to a decrease of the absorption rate. Then SEM observation was conducted for the samples without or with 5 mass% Li$_2$ZrO$_3$. Figure 3 shows the SEM micrographs for the samples without or with 5 mass% Li$_2$ZrO$_3$. In the case of the sample without Li$_2$ZrO$_3$, necks between primary particles grew remarkably and the aggregated particles formed large lumps of around 30 μm to 50 μm in size. The decrease of contact area with CO$_2$ due to this neck growth and longer distance caused by the grain growth was thought to degrade the absorption property notably. On the other hand, in the case of the sample with 5 mass% Li$_2$ZrO$_3$, primary particles were clearly distinguished although a certain amount of grain growth was observed. That is why only contact area and migration distance changed and higher retention ratio of absorption rate was thought to be maintained.

4. Conclusion

From the results of this study, the following conclusions were reached.

1. The absorption rate of cylindrical pellet was dramatically decreased by cyclic test.
2. Li$_2$ZrO$_3$ addition was very effective for improving the reproducibility of the pellet.
3. Evaporation of Li$_2$CO$_3$ generated as a result of CO$_2$ absorption was slight.
4. No phase transitions were observed.
5. Degradation of absorption rate was mainly caused by the decrease of contact area with CO$_2$ due to the grain growth.

References