HIGH TEMPERATURE CO₂ ABSORPTION USING LITHIUM ZIRCONATE POWDER

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ABSTRACT

In order to confirm the possibility to be a high temperature CO₂ absorbent, a reversible reaction between lithium zirconate and CO₂ was examined. Experimental results revealed that lithium zirconate powder absorbs 400 times as much CO₂ in volume preferentially at around 500°C and under high CO₂ partial pressure. Since the fuel reforming or shift conversion process in power plants is performed in a pressurized gas atmosphere at 400–700°C, the fact suggests the advantage of lithium zirconate as the absorbent in energy power plants.

INTRODUCTION

In recent years, there is a growing interest in the reduction of CO₂ exhaust from fossil fuel combustion. The Kyoto protocol adopted on December 1997 requires a definite reduction of total CO₂ emission. However, numerous CO₂ absorbents and adsorbents which have been studied for CO₂ separation 1-3 are still too costly for commercial use because of their poor CO₂ absorption capacity and large heat requirement for reusing. It is essentially difficult to segregate CO₂ from a large volume of flue gases.

On the other hand, there is a report which indicates a benefit of CO₂ segregation at a fuel reforming process of power plants ⁴. The volume of the fuel gas is much smaller and CO₂ concentration in the fuel is much higher than that of flue gas after combustion. It is naturally advantageous to segregate CO₂ in the process where the CO₂ partial pressure is high and the gas volume is small. Focusing on this benefit, we previously reported a reversible reaction between lithium zirconate and CO₂ at around 500°C ⁵. All results suggest that lithium zirconate has a certain possibility to be a novel CO₂ absorbent which is applicable to the fuel reforming process ⁶. In this study, we examined the reversible reaction, mentioned above, in order to confirm the properties of lithium zirconate as a high temperature CO₂ absorbent.

EXPERIMENTAL

Lithium zirconate powder was synthesized by the heat treatment of zirconia and lithium carbonate in the presence of a potassium carbonate additive at 900°C. In order to facilitate CO₂ absorption - emission cycle, a porous body with 61–62% porosity was fabricated from the powder by using the doctor blade technique. The reaction between
lithium zirconate and CO$_2$ was studied in controlled gas flow environments using an electric furnace and a thermogravimetric instrument in ambient pressure (TGA-50, Shimadzu) or in higher pressures (WS002, Mac Science). Atmospheric gases used in the experiment were mixtures of CO$_2$, Air, and H$_2$. We used two types of heating procedures, i.e. at constant rate heating up to 900°C to examine the reaction temperature, or at constant temperature heating with two plateaus to examine the reaction yield. After these tests, the samples were analyzed with an SEM (JSM-5400LV, JEOL) and an X-ray diffractometer (RINT-1200, Shimadzu). Pore diameter change was measured by a mercury porosimeter (Poresizer 9320, Shimadzu).

RESULTS AND DISCUSSION

We previously reported the reversible reaction between lithium zirconate and CO$_2$ [1]. Figure 1 shows the weight change of the powder during a temperature sweep up to 800°C. It is obvious that lithium zirconate absorbs CO$_2$ at around 400–550°C, and emits it above 590°C.

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

To confirm the temperature dependence of the absorption yield, a constant temperature heating test was newly performed at several temperatures. Figure 2 shows the weight change of the lithium zirconate powder in an atmosphere containing 20% CO$_2$. A large weight change due to CO$_2$ absorption was observed at around 500°C. The highest value of the reaction yield after 180 min heating is calculated to be 76.3%. On the basis of the formula weight and density, this value means that lithium zirconate absorbs 400 times as much CO$_2$ as the volume of the powder. Figure 3 summarizes the relationship between the reaction yield after 180 min heating and absorption temperature in several gas atmospheres. There is a high reaction yield region at around 450–550°C, regardless of the CO$_2$ content. It is also clear that the high reaction yield region becomes wider for the higher CO$_2$ content. This fact suggests the benefit of applying lithium zirconate in high pressure environments, since higher CO$_2$ partial pressure can be expected. In order to confirm this point, we performed pressurized thermogravimetric tests in an atmosphere containing 20% CO$_2$. Figure 4 shows the weight change of the lithium zirconate powder during temperature increase to 800°C with a constant heating rate of 10°C/min. A clear difference between atmospheric and pressurized tests can be seen. In the case of pressurized tests, the powder weights changed dramatically at around 450°C and kept a constant value up to 700°C, while in the case of the atmospheric test, the weight change was gradual and small. This difference means that (i) the reaction yield is dependent on CO$_2$ partial pressure, and (ii) the pressurized gas atmosphere is preferable for rapid CO$_2$ absorption.

Figure 5 shows X-ray diffraction patterns of the lithium zirconate porous body by the 5 h heating test in the electric furnace at 530°C. It is obvious that lithium zirconate is transformed to zirconia and lithium carbonate by the reaction with CO$_2$. After the second
heating test at 670°C, the mixture of zirconia and lithium carbonate returns to lithium zirconate, as shown in Fig. 6. The morphologic change of the porous body is shown in Fig. 7. The formation of a molten substance is confirmed after the heating test. This substance is observed as lithium carbonate in Fig. 5. Since the melting point of the lithium carbonate is 730°C, the presence of the molten substance can be attributed to the potassium carbonate additive. This feature indicates that lithium zirconate powder accumulates CO₂ in its pore structure as molten carbonate. Figure 8 shows the change of the pore structure after 20 times of the absorption - emission cycle. In comparison with the initial structure, the structure after 20 cycles showed a certain change, but it is not serious. The pore distribution change is shown in Fig. 9.

CONCLUSION

The experimental results clearly indicate that CO₂ absorption by lithium zirconate powder proceeds preferentially at around 500°C and under high CO₂ partial pressure. Since the fuel reforming or shift conversion process in the power plants is performed in a pressurized gas atmosphere at 400–700°C, the above fact suggests the advantage of lithium zirconate as the absorbent in energy power plants such as the integrated coal gasification-combined cycle (IGCC) and molten carbonate fuel cell (MCFC).

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Fig. 1 Weight change of lithium zirconate powder during a temperature sweep.  
Gas A: CO\textsubscript{2} 0%, Gas B: CO\textsubscript{2} 20%, Gas C: CO\textsubscript{2} 70%, balanced by air, atmospheric pressure.  
Initial sample weight: 24mg.  
Gas flow rate: 200 ml/min.

Fig. 2 Weight change of lithium zirconate powder during heating at two temperatures.  
Gas : CO\textsubscript{2} 20%, balanced by H\textsubscript{2}, atmospheric pressure.  
Initial sample weight: 20mg.  
Gas flow rate: 100 ml/min.

Fig. 3 Temperature dependence of the reaction yield.
Fig. 4  Weight change of lithium zirconate powder during a temperature sweep. Gas: CO₂ 20%, balanced by air, pressurized. Heating rate: 10°C/min.

Fig. 5  X-ray diffraction patterns before and after the heating test at 530°C.
Fig. 6  X-ray diffraction patterns before and after a cycle of absorption-emission test between 530°C and 670°C.

Fig. 7  SEM micrographs before and after the heating test at 530°C.
Fig. 8 SEM micrographs before and after the cycles of the absorption-emission test between 530°C and 670°C.

Fig. 9 Change of pore diameter distribution during the cycle test.