Original Paper

CO₂ Absorption/Release Properties of Lithium Zirconate Powder Prepared by the Sol-Gel ProcessFei WANG¹, Yoshinori YOSHIMURA², Shinji HIRAI^{1*}
and Toshihiro KUZUYA²¹Division of Engineering for Composite Functions, Muroran Institute of Technology²Division of Materials Science and Engineering, Muroran Institute of Technology**Abstract**

The sol-gel synthesized powder was a single phase Li₂ZrO₃. This synthesized powder reacted with CO₂ at temperatures from the ambient temperature to a high temperature. The reaction products reacted reversibly to form Li₂ZrO₃ at temperatures above 925 K. The degree of absorption was defined as the value obtained by dividing the fractional mass gain of Li₂ZrO₃ after absorption by the fractional mass gain corresponding to a 100% reaction. Consequently, the degree of absorption was determined to be 95.2% under the absorption condition of 773 K and 7.2 ks. When CO₂ absorption at 773 K and release at 993 K were repeated five times to examine the cyclic behavior, the degree of absorption was almost the same as the initial amount. The degree of absorption of commercial powder prepared by a solid-solid reaction of Li₂CO₃ and ZrO₂ was 10.6% under the same absorption condition. The degrees of absorption with the sol-gel synthesized powder were determined to be 26, 31 and 43% under the absorption conditions of 293, 313 and 333 K for an exposure time of 115.2 ks. The absorption behavior could be best explained by an intraparticle diffusion mechanism. The diffusion of CO₂ gas through the reaction product with an apparent activation energy of 24 kJ·mol⁻¹ was a rate-determining step of the absorption reaction.

Key words: Li₂ZrO₃, CO₂ absorption, Sol-Gel process, Ambient temperature, Rate-determining process

1. Introduction

Regarding to the CO₂ sequestrations based on a chemical reaction, an efflorescence by using a silicate, which is an abundant natural resource¹, the chemical reactions using an amine aqueous solution that produces carbamate ion², dolomite pyrolysis products³ and lithium complex oxides such as Li₂ZrO₃⁴⁻⁷ and lithium silicate (Li₄SiO₄)^{5,8} were investigated. In particular, CO₂ sequestration using Li₂ZrO₃ and Li₄SiO₄ has advantages over the recovery of CO₂. Li₂ZrO₃ reacts immediately with CO₂ at temperatures from 723 to 923 K. The products react reversibly to form Li₂ZrO₃ at temperatures above 873 K. In the case of Li₄SiO₄, it has been confirmed that Li₄SiO₄ reacts with CO₂ at the temperatures of up to 973 K, and the products release CO₂ completely at 1123 K, and are reconvert-

ed to Li₄SiO₄. These lithium complex oxides are prepared by heating a mixture of lithium carbonate and each metal oxide or each metal hydroxide at 1273 K⁴⁻⁸. Furthermore, the addition of potassium carbonate (K₂CO₃) has been reported to promote CO₂ absorption due to the intervention of the liquid phase. Based on the assumption that the penetration of CO₂ gas through the Li₂CO₃ layer formed around the Li₂ZrO₃ particles may be suppressed by the resistance of the Li₂CO₃ layer, the intervention of the liquid phase in the Li₂CO₃ layer formed by the eutectic reaction between Li₂CO₃ and K₂CO₃ facilitates the penetration of CO₂ gas. As a result, it has been reported that the degree of absorption is 76.3% under the absorption condition at 773 K in a 20 vol% CO₂ atmosphere balanced by N₂⁴.

Sol-gel processing allows greater control over the formation of a particular phase, higher purity of the formed phases, and lower processing temperature. Moreover, it is convenient to prepare fine powders by using a simple procedure and

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simple equipment^{9,10}. The sol-gel process has already been performed using lithium methoxide and zirconium ethoxide under an acid catalysis regime, and only the Li₂ZrO₃ crystalline phase has been formed by calcinations at 1073 K for 14.4 ks¹¹.

In the present study, the Li₂ZrO₃ powders are synthesized by a sol-gel process at a low temperature. Since the porous powder is synthesized by a sol-gel process, it is expected that the promotion of CO₂ occurs due to the penetration of CO₂ gas through the pore formed in xerogel. Further, CO₂ absorption and the release properties associated with the reaction between Li₂ZrO₃ and CO₂ are evaluated at temperatures ranging from the ambient temperature to a high temperature by using a thermogravimetric (TG) method.

2. Experimental Procedure

The preparation of sols was conducted in a dry N₂ atmosphere because sols are extremely sensitive to moisture in air. The sol was prepared by the following procedure. Guaranteed-grade reagents of zirconium tetra-n-butoxide, lithium ethoxide, anhydrous ethanol, and diethylene glycol were used as starting materials. Zirconium tetra-n-butoxide was dissolved in a mixture containing diethylene glycol and a quarter of the total amount of anhydrous ethanol by stirring for 1.8 ks. Then, a quarter of the total amount of anhydrous ethanol containing distilled water was gradually added to the above solution by stirring for 10.8 ks. On the other hand, lithium ethoxide was dissolved in a quarter of the total amount of anhydrous ethanol by stirring for 10.8 ks. Finally, this solution was gradually added to the above total solution, which was then stirred for 1.9 ks and aged for 28.8 ks at ambient temperature. The final composition of zirconium tetra-n-butoxide, lithium ethoxide, anhydrous ethanol, diethylene glycol, and water is represented by the molar ratios of 1 : 2 : 240 : X : 6, where X was varied from 3 to 30. Sols with different compositions were prepared to investigate the effects of the molar ratio of water on the sols.

The gels were obtained by drying the sol in a Petri dish in a vacuum for three days. The wet gels obtained were fired at 973 K for 1.8 ks under a flow of O₂. For evaluating the absorption property, commercial Li₂ZrO₃ powder prepared by the heat treatment of Li₂CO₃ and ZrO₂ was also used.

X-ray diffractometry (XRD: Rint-Ultima+, Rigaku Corp., Tokyo, Japan) using monochromatic CuKα radiation was used to identify the synthetic powders. The specific surface areas of the synthetic powders were determined by a surface

Fig. 1 Temperature dependences (T) of standard free-energy changes (ΔG°) for reactions of lithium containing complex oxides with CO₂ gas.

area and pore size analyzer (AUTOSORB-1, QUANTACHROME INSTRUMENTS, Florida, USA) using the BET method. Furthermore, the surface and fracture sections of the synthetic powders were observed by field-emission-type high-resolution scanning electron microscopy (SEM: S-5000, Hitachi, Tokyo, Japan). The CO₂ absorption and release properties were evaluated using a thermogravimetric instrument (TG: TG-DTA2000S, MAC Science Co., Ltd., Kanagawa, Japan) by the following two procedures. First, the synthesized powder was heated to 1373 K at a constant rate of 10 K·min⁻¹ in dry pure CO₂ gas flowing at the rate of 300 ml·min⁻¹ to examine the reaction temperature. Second, after heating under the same condition, the samples were maintained at a temperature at which the mass change in CO₂ absorption was observed in the TG curve. The degree of absorption was defined as the value obtained by dividing the fractional mass gain of Li₂ZrO₃ after absorption by the fractional mass gain corresponding to a 100% reaction.

3. Results and Discussion

(1) Synthesis of Li₂ZrO₃ powders

Figure 1 illustrates the temperature dependences of the standard free-energy changes (ΔG°) for the reactions of lithium-containing complex oxides with CO₂ gas; the (ΔG°) values have been calculated from the thermodynamic data collected by Barin *et al.*^{12,13}. The figure indicates that Li₂ZrO₃ reacts immediately with CO₂ at temperatures from the ambient temperature to high temperatures. Moreover, the products react reversibly to form lithium complex oxides at high temperatures. It is

Fig. 2 TG curves for synthetic powder (Li_2ZrO_3) in CO_2 and Ar atmospheres. ((a): CO_2 atmosphere; (b): Ar atmosphere).

expected that Li_2ZrO_3 absorbs CO_2 in a wide range of temperatures and releases CO_2 at or above 1000 K.

Figure 2(a) shows the TG curves for the synthetic powders. The molar ratio of water in the sol was fixed as 6. In CO_2 atmosphere, TG increased gradually with temperature up to about 500 K and subsequently increased for a shorter period of time after a slight decrease in TG. At a higher temperature, TG decreased immediately for a shorter period of time. The remarkable increase and decrease in mass were observed at 780 K and 925 K, respectively. These suggest that the increase and decrease in mass correspond to the absorption and release of CO_2 . The difference in the amount of CO_2 before absorption and after release can be attributed to the preparation of the powders by the sol-gel process. When residual organic components in wet gels are decomposed by heat treatment, it is considered that a carbonated phase is formed¹⁴. In Ar atmosphere, as shown in Figure 2(b), a mass loss at about 925 K is very small. The mass loss may presumably correspond to the release of CO_2 generated by the dissociation of the original residual organic component. The xerogel obtained from the sol, which was prepared by mixing zirconium tetra-*n*-butoxide, anhydrous ethanol, diethylene glycol and water in the molar ratio of 1 : 50 : 2 : 2, also indicated a mass loss in the TG curve, a broad exothermic peak in the DSC curve and a densification due to the decomposition of organic components at similar temperatures¹⁵. Based on the above findings, heating was performed in Ar atmosphere to bring about release; this process involved heating up to 993 K and cooling down to the ambient temperature. Subsequently, the atmosphere was changed to CO_2 , and heating was performed to evaluate the CO_2 absorption and release properties.

The representative XRD pattern for sol-gel synthesized powder that has been heated to 993 K in Ar atmosphere for bringing about release is shown in Figure 3(a). The molar ratio of water in the sol

Fig. 3 XRD patterns for sol-gel synthesized powder before and after CO_2 absorption. (Sol-gel synthesized powder was heated to 993 K in Ar atmosphere for release. (a): Before CO_2 absorption; (b): After CO_2 absorption).

was also fixed as 4. Diffraction peaks corresponding to Li_2ZrO_3 have been observed, and the sol-gel synthesized powder could be considered to be single phase Li_2ZrO_3 . Although the crystallization temperature depends on the composition of the sol, it was considered that the sol-gel synthesized powder composed of amorphous materials was crystallized by heating at a temperature of 993 K. Figure 3(b) shows the XRD pattern for sol-gel synthesized powder with the degree of absorption of 95.2% of CO_2 . The diffraction peaks of Li_2CO_3 and ZrO_2 , which was explained by the reaction of synthetic Li_2ZrO_3 and CO_2 , and a few weak and unknown diffraction peaks were observed.

(2) CO_2 absorption at high temperatures

Figure 4 shows the comparison between the TG curve of sol-gel synthesized powder and that of commercial Li_2ZrO_3 powder. Synthetic powder was prepared by using sol containing water with a molar ratio of 6. After heating at a constant rate up to 790 K, the samples were maintained at this temperature. The degree of CO_2 absorption of the synthetic powder was determined to be 95.2% under the absorption condition at 790 K for 7.2 ks. On the other hand, the degree of absorption of the commercial Li_2ZrO_3 powder was 10.6% under the same absorption condition. A remarkable improvement in the CO_2 absorption property of the sol-gel synthesized powder was confirmed. Since the specific surface areas of the synthetic and commercial powders were $12.25 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.54 \text{ m}^2 \cdot \text{g}^{-1}$, respectively; this improvement may presumably be due to the large surface area of the sol-gel synthesized powder. The specific surface area of synthetic powder also depends on the molar ratio of water in the sols. The specific surface area at water molar ratios of 3, 6, 9, 12 and 30 were determined to be 15.94, 12.25, 7.13, 6.76 and $4.72 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. These specific surface areas decreased slightly as the molar ratio of water in the sol increased, whereas the degree of CO_2 absorption was independent of the specific surface

Fig. 4 TG curves for synthetic and reagent-grade Li_2ZrO_3 powder in CO_2 atmosphere.

area in this region.

Since CO_2 absorption and release are brought about by chemical reactions, the following reaction model of Li_2ZrO_3 particles during the CO_2 absorption is considered. The formation of a dense Li_2CO_3 shell on the outer surface and a dense ZrO_2 shell in the middle region covering the unreacted Li_2ZrO_3 core was reported⁶. CO_2 can diffuse through the solid Li_2CO_3 shell and reacts with Li^+ and O^{2-} on the outer surface of the ZrO_2 shell. It is considered that both Li^+ and O^{2-} are generated on the surface of the unreacted Li_2ZrO_3 core. It is reported that the reaction of Li_2ZrO_3 particles, as shown in Figure 1, is limited by the solid state transport of CO_2 , Li^+ and O^{2-} in the Li_2CO_3 and ZrO_2 shells. Since the diffusion of CO_2 in the solid Li_2CO_3 layer is significantly slower than that of Li^+ and O^{2-} ions in the ZrO_2 shell, it is considered that the diffusion of CO_2 in the solid Li_2CO_3 layer is the rate-determining step. Based on the assumption that the diffusion of CO_2 through the Li_2CO_3 shell may be suppressed by the resistance of the Li_2CO_3 layer, the intervention of the liquid phase in the Li_2CO_3 layer is formed by the eutectic reaction between Li_2CO_3 and K_2CO_3 . Consequently, a degree of CO_2 absorption of 76.3% under the condition of 773 K and 20 vol% CO_2 atmosphere balanced by N_2 has been reported⁷. The high degree of reaction is considered to be caused by the porosity and the generated cracking^{9,16}, independent of the specific surface area in the sol-gel synthesized powder. The penetration of CO_2 gas through the Li_2CO_3 layer may be accelerated by the porosity and the cracking.

In order to examine the cyclic behavior, CO_2 absorption at 773 K and release at 993 K were repeated five times. Figure 5 shows the dependence of the number of repetitions on the degree of reac-

Fig. 5 Cyclic absorption with synthetic Li_2ZrO_3 powder.

Fig. 6 CO_2 absorption with synthetic Li_2ZrO_3 powder at ambient temperature.

tion. It was found that CO_2 absorption was almost the same as the initial absorption.

(3) CO_2 absorption at ambient temperatures

Figure 6 shows the degree of the CO_2 absorption reaction at each temperature. Synthetic powder was prepared by using sol containing water with a molar ratio of 6. The degree of CO_2 absorption was determined to be 26, 31 and 43% under the conditions of 293, 313 and 333 K, respectively, for an exposure time of 115.2 ks. That is, it was confirmed that the sol-gel synthetic powder absorbs CO_2 even near ambient temperatures.

The XRD pattern for sol-gel synthetic powder with the degree of CO_2 absorption of 26% is shown in Figure 7. The diffraction peaks of the remaining Li_2ZrO_3 were observed along with a few weak diffraction peaks of ZrO_2 , which are explained by the reaction of synthetic Li_2ZrO_3 with CO_2 (See Figure 1).

Figure 8 shows the typical microstructures of the sol-gel synthesized powder with degrees of CO_2 absorption of 18.3 and 44.3% at 333 K for 20.6 and 123.1 ks. The specific surface areas were determined to be 8.38, 13.46, 26.57 and

Fig. 7 XRD pattern of synthetic Li_2ZrO_3 powder after CO_2 absorption.

Fig. 8 SEM patterns of synthetic Li_2ZrO_3 powder under different conditions. ((a): Synthetic Li_2ZrO_3 powder; (b): Li_2ZrO_3 after CO_2 absorption, 18.3%; (c): Fracture of synthetic Li_2ZrO_3 powder; (d): Li_2ZrO_3 after CO_2 absorption, 44.3%).

$29.96 \text{ m}^2 \cdot \text{g}^{-1}$ under the degrees of CO_2 absorption of 26.3, 29.7, 34.3 and 44.3%, respectively. The specific surface area slightly increased as the reaction proceeded. The reaction products were board-like powder particles comprising many grains. The morphology of the grains differed from the degree of reaction and the size of the grains increased as the degree of reaction increased. In the case where the degree of CO_2 absorption is 18.3%, it is presumed that there are few interstices between the grains. When the degree of CO_2 absorption is 44.3%, it is presumed that there are many and large interstices between the grown grains. As shown in a fracture section of board-like powder particles, the interstices were in fact observed on the outer surface of the board-like powder particle.

Fig. 9 Plot of $1 - 3(1 - R)^{2/3} + 2(1 - R)$ and reaction time for data given in Figure 6.

Although the outer surface cannot be clearly divided into a dense Li_2CO_3 shell on the outer surface and a dense ZrO_2 shell in the middle, which is already reported, it can be divided into a reaction product and an unreacted Li_2ZrO_3 on account of the existence of interstices.

It is estimated that CO_2 can diffuse through the intraparticle pores within the reaction products. Since it was found that the flow rate of the gas mixture had little effect on the rates of reaction, the resistance to gas transfer through the gas film on the surface of the Li_2ZrO_3 powder particles can be ignored. This process proceeds topochemically by the formation of a reaction interface from the surface of the Li_2ZrO_3 powder particle to the inner side, so that the reaction rate may be expressed by the unreacted core model. In the present study, kinetic analysis was conducted by the kinetic equation which includes only the resistance of intraparticle diffusion, based on the assumption that gas diffusion through the reaction product may be the primary rate-determining process. The equation¹⁷ is given below:

$$1 - 3(1 - R)^{2/3} + 2(1 - R) = \frac{(2MDC/\alpha\rho r_0^2)t}{k't} \quad (1)$$

Where, R represents the degree of absorption ($-$), M is the molecular weight of the reactant, D is the effective intraparticle effective diffusivity ($\text{cm}^2 \cdot \text{s}^{-1}$), C denotes the reagent concentration, α is the stoichiometry factor, ρ is the density of the reactant, r_0 means the original radius of the reactant particle (cm), t is the reaction time (s) and k' is a constant.

The data illustrated in Figure 6 were plotted according to the above equation. The results are shown in Figure 9. A satisfactory linear behavior

Fig. 10 Temperature dependence of $\ln k'$.

was observed for relatively high degrees of CO₂ absorption; therefore, the above mentioned assumption regarding the rate-determining process may be considered to be valid. The values of constants k' are illustrated in an Arrhenius plot shown in Figure 10. Consequently, a satisfactory linear behavior was observed and the apparent activation energy (ΔE) was determined to be 24 kJ·mol⁻¹. The apparent activation energy for the diffusion of CO₂ through zeolite pores with a diameter of approximately 0.4 nm is around 20 kJ·mol⁻¹¹⁸. As in the case of zeolite, the rate-determining process for the CO₂ absorption by Li₂ZrO₃ is presumed to be gas diffusion in the reaction product layer.

Summary

We attempted to prepare Li₂ZrO₃ powder by a sol-gel process. The CO₂ absorption and release properties were evaluated using a TG method. Since CO₂ was previously included in the sol-gel synthesized powders due to the dissociation of the original residual organic component, heating in Ar atmosphere was performed to bring about CO₂ release; this process involved heating up to 993 K and cooling down to the ambient temperature before evaluation. After heating to bring CO₂ release, the preparation of a single phase Li₂ZrO₃ powder was confirmed. This material reacted with CO₂ at temperatures from the ambient temperature to 780 K. The products reacted reversibly to form Li₂ZrO₃ at temperatures of above 925 K. The CO₂ absorption of Li₂ZrO₃ powder with specific surface area of 12.25 m²·g⁻¹ was determined to be 95.2% under the absorption condition of 773 K and 7.2 ks. By repeating the CO₂ absorption at 773 K and release at 993 K five times to examine

the cyclic behavior, it was found that the amount of absorption was almost the same as the initial amount. The CO₂ absorption with the Li₂ZrO₃ powder was determined to be 26, 31 and 43% under the absorption conditions of 293, 313 and 333 K, respectively, for an exposure time of 115.2 ks. The absorption behavior could be best explained by an intraparticle diffusion mechanism; the diffusion of CO₂ gas through the reaction product was a rate-determining step of the CO₂ absorption reaction with an apparent activation energy of 24 kJ·mol⁻¹.

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