Preparation of CO_2 Absorbent by Spray Pyrolysis

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Li_2ZrO_3 particles were prepared by spray pyrolysis and solid state reaction to compare their CO_2 absorption capacity and rate. The former method provided much higher CO_2 absorption capacity and rate than those by the latter. Spherical particles of rather small and uniform size allow the faster diffusion of Li to the surface for higher CO_2 absorption capacity and regeneration of absorption through CO_2 recovery.

CO_2 abatement to protect the global ecosystem has been urgently appealed because of global warming by CO_2. Currently, waste CO_2 from the combustion of CH_4 is attempted to react with the fuel above 500 °C to recover the waste heat. For this, high temperature CO_2 must be separated from the flue gas for the reaction with CH_4.[1]

Li_2ZrO_3 was proposed for a CO_2 absorbent at high temperature.[2–5] It has been reported to absorb CO_2 at 450–550 °C and release it above 650 °C. Lithium ion is believed to diffuse to the surface to react with CO_2 into lithium carbonate and to release it through its thermal transformation into lithium metazirconate.

Spray pyrolysis has been known as a simple procedure to produce spherical particles of uniform size through the optimization.[6] The product has uniform distribution of constituting elements within its particle because each particle produced from each droplets has the same concentration and thermal history. In contrast, traditional solid state method of mixing, calcining, milling, washing, post-calcining, milling, and sieving must result in the broad distribution in the composition, size, and shape of the final product.

Thus, Li_2ZrO_3 was prepared by spray pyrolysis method (SP-Li_2ZrO_3) to evaluate its performances in high temperature CO_2 recovery, to be compared with those prepared by traditional solid state method (SS-Li_2ZrO_3).

Physically mixed ZrO_2 (Kyoritsu Ceramic Material Co., 0.2–8 um) and Li_2CO_3 (WAKO Chem.) in molar ratio of 1:1 by ball milling for 24 h was calcined to prepare SS-Li_2ZrO_3 at 800 °C (-C8) and 1000 °C (-C10) for 8 h in air, followed by dry ball-milling for 6 h. Spray pyrolysis was performed by using ultrasonic nebulizer (1.7 MHz) as aerosol generator, quartz tube and filter. Two quartz reactors were connected serially to achieve the preheating at 200 °C and main decomposition at 750 °C. Air (3 L/min) was used as a carrier gas and total residence time in reactors was calculated as 16 s. Precursor solution for spray pyrolysis was prepared by dissolving Li_2CO_3 (WAKO Chem.) and $ZrO(NO_3)_2{\cdot}2H_2O$ (WAKO Chem.) into distilled water. Total concentration of lithium and zirconium in solution was 0.25 M. Spray pyrolyzed powder (SP-Li_2ZrO_3-P, as-prepared) was post-calcined at 800 °C (-C8) and 1000 °C (-C10) for 8 h in air. SP-Li_2ZrO_3-T8 was prepared by post-calcining SP-Li_2ZrO_3-P at 800 °C without dwelling time.

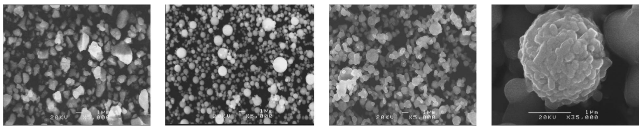
CO_2 absorption capacity was examined by thermogravimetry (TG) and its rate was defined as weight increase (wt %) per min. X-ray diffractometer (XRD), X-ray photoelectron spectrometer (XPS) and scanning electron microscope (SEM) were used to characterize Li_2ZrO_3.

SP-Li_2ZrO_3-C8 and -C10 consisted of spherical particles of ca. 0.5–1 um, which were sintered together by the calcination, while the as-prepared product showed separated spherical particles as shown in Figure 1. In contrast, SS-Li_2ZrO_3-C8 and -C10, showed the aggregates of irregular particles with ca. 1-um diameter.

SS-Li_2ZrO_3-C8 and -C10 had almost the same diffraction patterns with the standard one. While SP-Li_2ZrO_3-P and SP-Li_2ZrO_3-T8 showed much broad peaks on diffractogram as shown in Figure 2, whereas calcined SP-Li_2ZrO_3-C8 and -C10 had the almost same patterns with those of solid state method. The peaks attributable to pure ZrO_2 were observed in SS- or SP-Li_2ZrO_3-C8 and -C10 indicating that Li_2ZrO_3 from spray pyrolysis must have some amount of free lithium, which is not bound to Li_2ZrO_3 structure. Very small peak attributable to Li_2CO_3 was found in the spray pyrolyzed products.

Electron binding energies of Zr $3d_{5/2}$ were 181.2 and 181.6 eV for SS-Li_2ZrO_3-C10 and SP-Li_2ZrO_3-C10, respectively, although it was reported as 182.2 eV[7] for ZrO_2 meaning the presence of ZrO_2 which didn't interact with Li.

Figure 3 shows TG profiles of Li_2ZrO_3s under CO_2 flow (200 mL/min) from 30 °C to 800 °C in the rate of 5 °C/min. SP-Li_2ZrO_3-T8 showed the maximum weight increase of 13.8 wt % at 683 °C while SP-Li_2ZrO_3-C8 and C10 reached



(A) (B) (C) (D)

Figure 1. SEM images of (A) SS-Li_2ZrO_3-C8, (B) SP-Li_2ZrO_3-P, (C) and (D) SP-Li_2ZrO_3-C8.

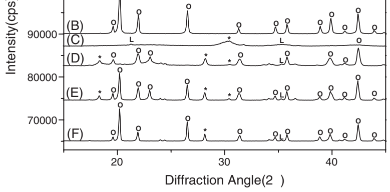


Figure 2. XRD data of (A) SS-Li_2ZrO_3-C8, (B) SS-Li_2ZrO_3-C10, (C) SP-Li_2ZrO_3-P, (D) SP-Li_2ZrO_3-T8*, (E) SP-Li_2ZrO_3-C8, (F) SP-Li_2ZrO_3-C10. *SP-Li_2ZrO_3-P was pretreated in air at 800 °C for 0 min.

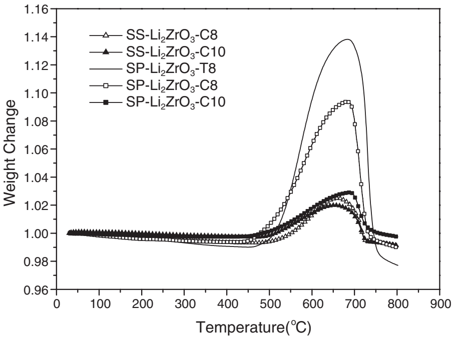


Figure 3. TG Profiles of Li_2ZrO_3 under CO_2 (200 mL/min) flow from 30 to 800 °C in the rate of 5 °C/min.

those to 9.4 and 2.9 wt % at 683 and 688 °C, respectively. SS-Li_2ZrO_3-C8 and -C10 showed much lower weight increase of 3.2 wt % at 663 °C and 2.3 wt % at 658 °C, respectively, than the spray pyrolyzed Li_2ZrO_3.

In order to evaluate the CO_2 absorption capacity and regenerability, Li_2ZrO_3 samples were exposed to CO_2 (200 mL/min) at 500 °C for 1 h and then to N_2 (200 mL/min) at 680 °C for 30 min. Absorption and regeneration were repeated twice. Li_2ZrO_3 was heated to 800 °C in N_2 flow (200 mL/min) before the CO_2 absorption to remove adsorbed CO_2 and H_2O although their amounts were negligible. As shown in Figure 4, CO_2 absorption was not saturated within 1 h at this temperature. SP-Li_2ZrO_3-P showed much larger CO_2 absorption capacity of about 16 wt % and absorption rate of 0.0041 wt %/min, than the other Li_2ZrO_3s. SP-Li_2ZrO_3-C8 gave also larger CO_2 absorption capacity of about 5 wt % and absorption rate of 0.0010 wt %/min. In contrast, maximum amounts of CO_2 absorption of SP-Li_2ZrO_3-C10, SS-Li_2ZrO_3-C8, and SP-Li_2ZrO_3-C10 were only about 1.5, 2.1, 2.1 wt %, respectively, although SP-Li_2ZrO_3-C10 showed much faster absorption than SS-Li_2ZrO_3-C8 and -C10. CO_2 absorption capability of such Li_2ZrO_3s was completely regenerated by heating at 680 °C for 30 min. The second CO_2 absorption showed slightly higher capacity than those in the first absorption over all Li_2ZrO_3.

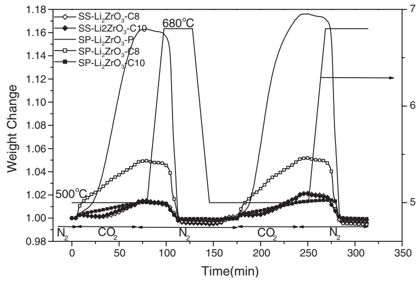


Figure 4. TG Profiles of Li_2ZrO_3 under CO_2(200 mL/min) flow at 500 °C and N_2 (200 mL/min) flow at 680 °C. All Li_2ZrO_3 samples were pre-heated at 800 °C for 0 min.

Spray pyrolysis was confirmed to be an excellent preparation procedure of Li_2ZrO_3 powder as CO_2 absorbent. CO_2 absorption process is suggested to consist of diffusion of Li ion through Li_2ZrO_3 particle and reaction with CO_2 on the surface to form Li_2CO_3. Thus, rate determining step was proposed as Li diffusion from the bulk to the surface.[8] Hence, primary particle of smaller grain size is favorable to capture CO_2 faster than that of the larger size. As shown in Figure 1, the apparent secondary particle size of SP-Li_2ZrO_3 is not much different with that of the SS-Li_2ZrO_3. However, SP-Li_2ZrO_3 was consisted of very fine particles of ca. 10 nm as shown in Figure 1. Furthermore, XRD peaks of SP-Li_2ZrO_3 were broader than that of SS-Li_2ZrO_3. Higher calcination temperature (1000 °C) for SP-Li_2ZrO_3 reduces the CO_2 absorption capacity as shown in Figures 2 and 3 due to larger particle size and higher crystallinity. Structural defects distribution within particles of low crystallinity may be also favorable for diffusion of Li.[8,9]

It should be also noted that spray pyrolyzed Li_2ZrO_3 had some kinds of "free" Li, such as Li_2CO_3, as indicated by XRD and XPS. Such "free" Li species appears to be amorphous or glassy solids since very small peak identified to Li_2CO_3 is on the diffractogram.

SP- and SS-Li_2ZrO_3 were successfully regenerated as shown in Figure 4. Absorption capacity was restored to their initial level.

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