Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Yi, Kwang Bok and Eriksen, Dag Øistein(2006) 'Low Temperature Liquid State Synthesis of Lithium Zirconate and its Characteristics as a CO_2 Sorbent', Separation Science and Technology, 41: 2, 283 — 296
To link to this Article: DOI: 10.1080/01496390500496884
URL: http://dx.doi.org/10.1080/01496390500496884

Separation Science and Technology, 41: 283–296, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500496884

Low Temperature Liquid State Synthesis of Lithium Zirconate and its Characteristics as a CO_2 Sorbent

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Abstract: In this study, a new preparation method providing greatly improved CO_2 sorption is introduced. Li_2ZrO_3 sorbent was prepared by low temperature co-precipitation and compared in CO_2 sorption performance with a sorbent prepared by the conventional high temperature solid-state reaction method. The two sorbents were characterized using scanning electron microscopy, X-ray diffraction and thermo-gravimetric analysis. The Li_2ZrO_3 powder prepared by the relatively simple co-precipitation method showed significantly better performance than the one prepared by solid-state reaction with respect to both kinetics and CO_2 sorption capacity. Extensive study of the powder prepared by co-precipitation has been performed at various conditions.

Keywords: Lithium zirconate, high temperature CO_2 absorbent, co-precipitation, CO_2 reduction

INTRODUCTION

Carbon dioxide (CO_2) emitted from fossil fuel combustion is the main cause of climate change on earth. Many researchers are currently working on the reduction of CO_2-emissions using various approaches. CO_2 reduction technology has received even more attention since the Kyoto protocol was adopted at COP 3 in Kyoto, Japan, on 11 December, 1997. Capture of CO_2 from existing processes producing substantial amounts of CO_2 such as coal-burning power

Received 3 August 2005, Accepted 15 November 2005
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plants and steam-fuel reforming provides an instant reduction. In both power plants and fuel reforming processes flue gas or product gas containing CO_2 is present at high temperature (over 400°C). A broad range of cyclic concepts can be used to separate CO_2 from a flue gas (post-combustion capture) or fuel gas (pre-combustion capture). These include commercially available amine processes and both physical and chemical sorbents. In order to obtain a proper economic evaluation of processes, sorbent properties should be obtained accounting for the unit cost of the sorbent (1).

Recently CO_2 sorption has been studied in the steam-fuel (methane) reforming process in order to simultaneously increase H_2 yield and remove carbon oxides (2, 3). The sorbent properties are very important if the processes are to become economically viable. The sorbent must be heat tolerant, possess high CO_2 sorption capacity, and fast kinetics. Satisfactory heat tolerance and high capacity in multi-cycle operation are seldom provided with currently available sorbents (4).

Nakagawa and Ohashi reported that lithium zirconate (Li_2ZrO_3) can react with CO_2 over a temperature range from 450°C to 550°C based on the following reaction (5):

$$Li_2ZrO_3 + CO_2 = Li_2CO_3 + ZrO_2 \tag{A}$$

The stoichiometric capacity is 28.7% CO_2 by weight. Currently around 20% CO_2 capture by weight has been achieved with Li_2ZrO_3 in other studies and this value is higher than the sorption capacity of most other sorbents (4). It has been reported that the reaction rate is accelerated when lithium zirconate is doped with sodium carbonate and/or potassium carbonate. The doping produces an eutectic of molten carbonate that reduces CO_2 diffusion resistance (6, 7).

Wang et al. (8) and Nair et al. (9) compared the performance of lithium zirconate prepared using tetragonal and monoclinic zirconia and reported that tetragonal lithium zirconate reacted with CO_2 significantly faster. Xiong et al. (4) reported that particle size and starting material size control the CO_2 sorption rate. Ida et al. (7) developed a double shell model to identify the reaction mechanism of Li_2ZrO_3 prepared by powder mixing method based on the following reactions:

$$Li_2ZrO_3 = ZrO_2 + 2Li+ + O^{2-} \tag{B}$$

$$CO_2 + 2Li+ + O^{2-} = Li_2CO_3 \tag{C}$$

According to the double shell model, Li_2CO_3 forms an outer shell on the particle leaving the layer of ZrO_2 behind. As a consequence, the inner core of Li_2ZrO_3 shrinks as ZrO_2 and Li_2CO_3 layers grow. Lithium and oxygen ions diffuse through ZrO_2 and Li_2CO_3 layers for further reaction. Because reaction (C) is very fast, the rate-limiting step is the diffusion of lithium and oxygen ions through the ZrO_2 and Li_2CO_3 layers.

Despite several attractive characteristics of lithium zirconate, its sorption rate has been too slow. Reports claim that approximately 250 minutes are required to reach maximum sorption capacity (4, 5). Most lithium zirconates studied to date were prepared by high temperature (850 to 1000°C) solid-state reaction. These materials required a carbonate additive to achieve a reasonable reaction rate. Even with the additive the reaction rate strongly depends on particle size. The solid-state preparation method is energy intensive, requires long reaction times, and it is difficult to control the product particle size (7, 10, 11). In addition, the introduction of carbonate additives will reduce the CO_2 capacity of the sorbent. Therefore, the development of simple and effective preparation method for lithium zirconate is needed.

EXPERIMENTAL SECTION

Synthesis of Li_2ZrO_3

Lithium zirconates were prepared by two different methods. The first method used the conventional high temperature solid-state reaction, and is designated as LiZr-HS. Starting materials were lithium carbonate (Li_2CO_3, 99%, Fluka), zirconia (ZrO_2, 99%, Aldrich), and potassium carbonate (K_2CO_3, 99%, Fluka). The molar ratio of the starting materials was adjusted to $Li_2CO_3 : ZrO_2 : K_2CO_3 = 1.1 : 1.0 : 0.1$. Each material was weighed, mixed, and ground in an agate mortar. Then the mixture was heat treated at 1000°C for 10 hours. The calcined material was quenched in air and ground again in an agate mortar before testing.

The second method used a low temperature liquid phase co-precipitation method, and is designated as LiZr-LL. Starting materials were zirconium oxynitrate ($ZrO(NO_3)_2 \cdot 2H_2O$, Merck), and lithium nitrate ($LiNO_3 \cdot xH_2O$, ca 78% $LiNO_3$, Merck). Sufficient starting materials to produce a Li/Zr molar ratio of 2 were dissolved in double distilled water at 70°C using separate beakers. $LiNO_3 \cdot xH_2O$ dissolved instantly while $ZrO(NO_3)_2 \cdot 2H_2O$ needed more time to dissolve and produced a cloudy solution. The solutions were then mixed and the final mixture was stirred using a magnetic bar for 30 minutes. The mixed oxide was then precipitated by a dropwise addition of an aqueous ammonia solution (NH_3, 25% solution, Merck). The addition of ammonia solution was continued until no more precipitation occurred. Stirring was stopped and the precipitate was filtered using ash-free paper filter (Schleicher & Schüll) using a hydraulic vacuum funnel. The filter cake was dried overnight in air at 150°C and then calcined at 500°C for 2 hours.

Characterization

The XRD spectra of the sorbents were obtained using an Inel XRG 3000 diffractometer with CuKα radiation. XRD test results were retrieved and stored using commercial software (Inel Acquisition). Crystal sizes were calculated based on resolved peaks using the Scherrer equation (12). Sample surface morphology was investigated by scanning electron microscopy (SEM, Hithachi S-4800 Field Emission).

Reaction Kinetics and Sorption Capacity

CO_2 sorption kinetics and capacity were studied using a thermogravimetric analyzer (TGA, CI electronics). The TGA test was initiated in a N_2 atmosphere with temperature increased to the desired reaction temperature at a rate of 10°C/min. CO_2 and/or H_2O were introduced after 20 minutes at the desired temperature. The N_2/CO_2 ratio was controlled by mass flow controllers (Bronkhorst, EL-FLOW Digital series). The steam flow was controlled using a liquid flow controller (Bronkhorst, Liquid flow). The separate flows were combined using a controlled evaporation mixing system (Bronkhorst, CEM). The reverse reaction was studied at each temperature by turning off the CO_2 and H_2O flows after carbonation was complete. The effects of CO_2 and steam partial pressures on the carbonation of Li_2ZrO_3 were investigated.

RESULTS AND DISCUSSION

XRD

XRD results of LiZr-HS and LiZr-LL are shown in Fig. 1. The major component of LiZr-HS is monoclinic Li_2ZrO_3 while that of LiZr-LL is tetragonal Li_2ZrO_3. The diffraction peaks of LiZr-LL are much lower and wider than those of LiZr-HS, indicating that the crystallite size of LiZr-LL is much smaller than LiZr-HS. Crystallite sizes of LiZr-HS and LiZr-LL, calculated using the Scherrer equation, are 40 and 5 nm, respectively.

SEM

Figure 2 shows scanning electron micrographs of LiZr-LL and LiZr-HS at the same magnification. These two materials have completely different particle morphology. It is clear that LiZr-LL particles are much smaller than those of LiZr-HS and have relatively uniform particle sizes. The LiZr-HS particles have a smooth, dense surface with no indication of cracks or agglomeration of small particles. This suggests that it may be difficult for CO_2 to penetrate inside individual particles, and, as a consequence, the reaction rate with CO_2 is expected to be slower than that of LiZr-LL. The average particle size of LiZr-HS is around 2.5 μm.

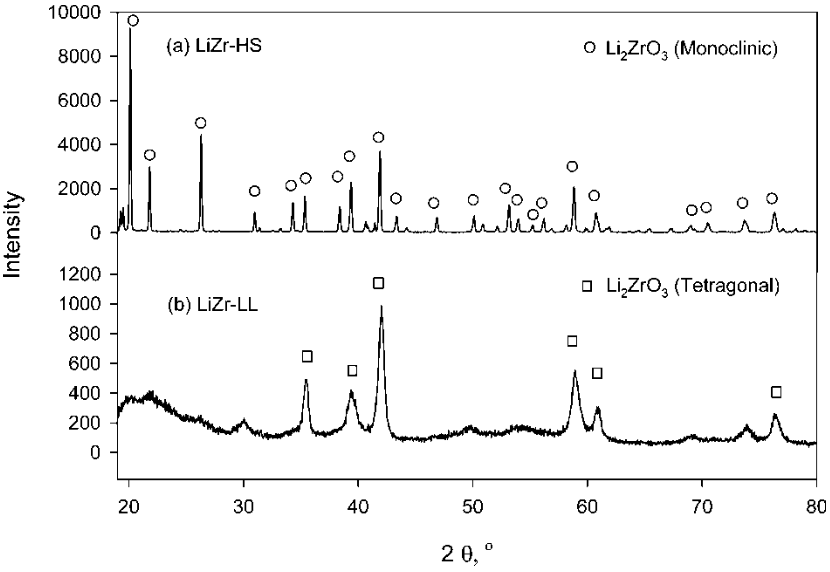

Figure 1. XRD spectra of Li_2ZrO_3.

At larger magnification the particle size of LiZr-LL is determined to be around 40 nm as shown in Fig. 3. This particle size is almost the same as the LiZr-LL crystallites (4).

CO_2 Sorption Properties of LiZr-LL

Figure 4 compares TGA test results of LiZr-HS and LiZr-LL. The tests were carried out in pure CO_2 at 500°C. The CO_2 uptake rate of LiZr-LL was much faster than that of LiZr-HS. Less than 6 minutes were required to reach 20%

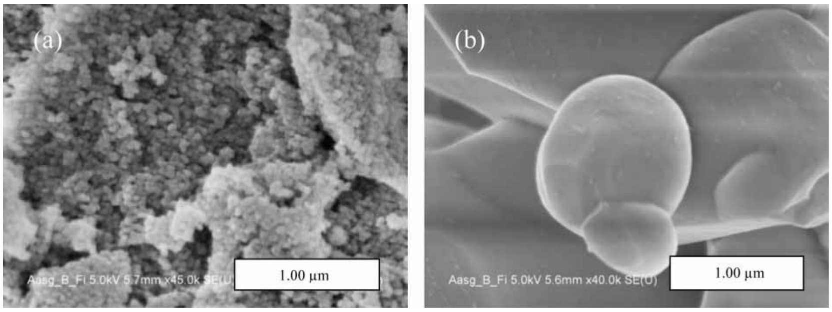

Figure 2. SEM images of (a) LiZr-LL and (b) LiZr-HS.

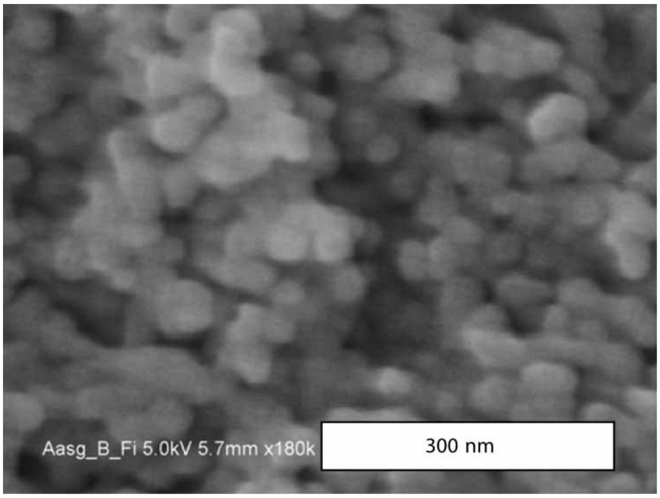

Figure 3. SEM images of LiZr-LL.

weight change. The sorption rate then decreased rapidly after reaching 23% weight change and flattened out. The ultimate weight gain of 26% was about 90% of the stoichiometric capacity (the dashed line in Fig. 4) of Li_2ZrO_3. The rate of CO_2 sorption was calculated using the Excel spread sheet regression function in the range of 2 to 18% weight gain and was

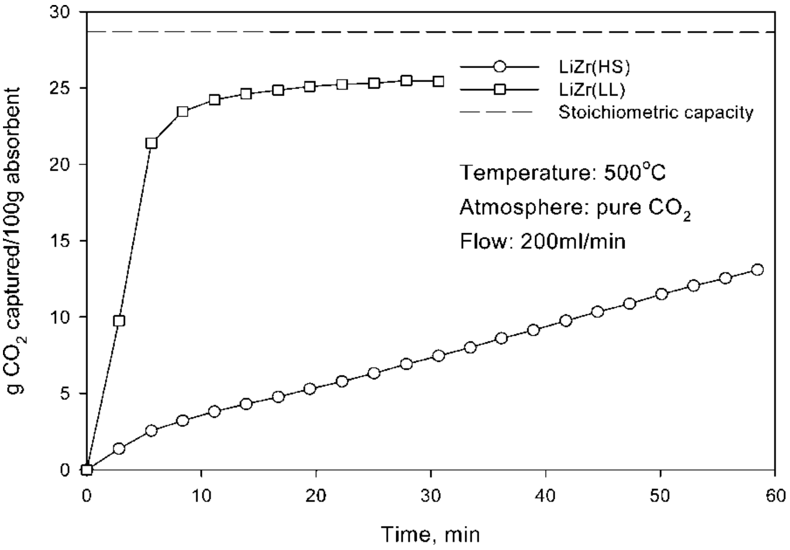

Figure 4. Comparison of LiZr-LL with LiZr-HS.

about 58 mg/(g · min), which is at least 5 to 20 times faster than reported rates (4, 9, 13) for other Li_2ZrO_3 sorbents.

Figure 5 shows further comparison of CO_2 uptake of LiZr-LL with results from the literature including LiZr-HS. All were carried out in an atmosphere of 100% CO_2. Reference 1 and 2 represent CO_2 uptakes using 1 micron and 45 micron ZrO_2 derived lithium zirconates, respectively (4). Both were prepared using solid-solid reaction. These two samples were tested at 650°C with a flow rate of 160 ml/min. Reference 3 and 4 represent CO_2 uptake using Li_2ZrO_3 prepared using a solid-solid reaction (9) and using a sol-gel method (9). These tests were performed at 450°C with a flow rate of 300 ml/min. While it may be difficult to make a direct comparison because reaction temperatures and flow rates are different from the LiZr-LL test, the sorption rate of LiZr-LL was surely much faster than the other references. CO_2 uptake rate using LiZr-HS falls close to the reference 2 and 4. The small particle size of LiZr-LL seems to be the main factor contributing to the increase in CO_2 uptake rate. During carbonation, the layers of Li_2CO_3 and ZrO_2 formed outside of the Li_2ZrO_3 core should be extremely thin. Before those layers reach sufficient thickness to limit diffusion of CO_2, most of the Li_2ZrO_3 would be already reacted. This argument is consistent with the model developed by Xiong et al. (14).

Figure 6 shows the effect of temperature on CO_2 uptake. Tests were carried out in a pure CO_2 atmosphere at temperatures ranging from 450°C to 600°C. As temperature increased from 450°C to 500°C the CO_2 uptake

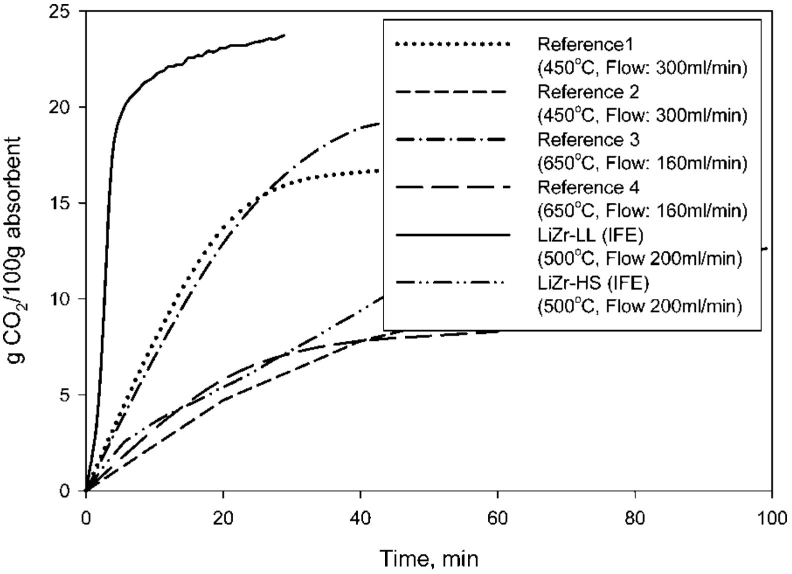

Figure 5. Comparison of LiZr-LL with other literature references.

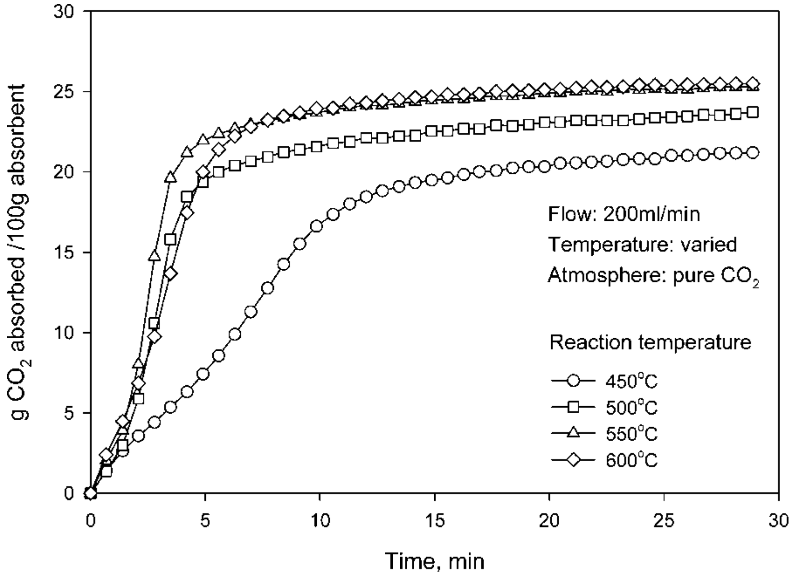

Figure 6. Temperature effect.

rate increased significantly. However, the rate decreased at 600°C and was similar to that at 500°C. Xiong et al. (4) explained this behavior based on the effect of temperature on CO_2 equilibrium partial pressure. Increasing temperature will result in an increase in both the reaction rate constant and the equilibrium partial pressure of CO_2. This is a very important point to be considered when effective CO_2 removal is desired. In pure CO_2, the reaction driving force, which is characterized by the difference between experimental and equilibrium CO_2 pressure, does not change by a large amount because the experimental partial pressure of CO_2 is significantly higher than the equilibrium CO_2 partial pressure. However, this partial pressure driving force will be more dependent on temperature when lower experimental concentrations of CO_2 are tested. Lower temperature would be required to achieve lower CO_2 concentration in the product. However, this positive effect of lower temperature on equilibrium CO_2 partial pressure will be canceled by slow kinetics at some point.

Since LiZr-LL was synthesized at lower temperature than actual carbonation or calcination temperature, it is very important to check its thermal stability. The multi-cycle test result is shown in Fig. 7. Temperature was increased to 550°C at a rate of 10°C/min in N_2 atmosphere. After 10 minutes of stabilization, the atmosphere was switched to CO_2 (200 ml/min, 25°C) and 20 minutes of reaction time was allowed. Then the temperature was increased to 690°C and the atmosphere was switched to N_2 for regeneration. After 10 minutes at 690°C, the temperature was decreased to 550°C at a rate of 3°C/min for another CO_2 uptake cycle. The same manipulations

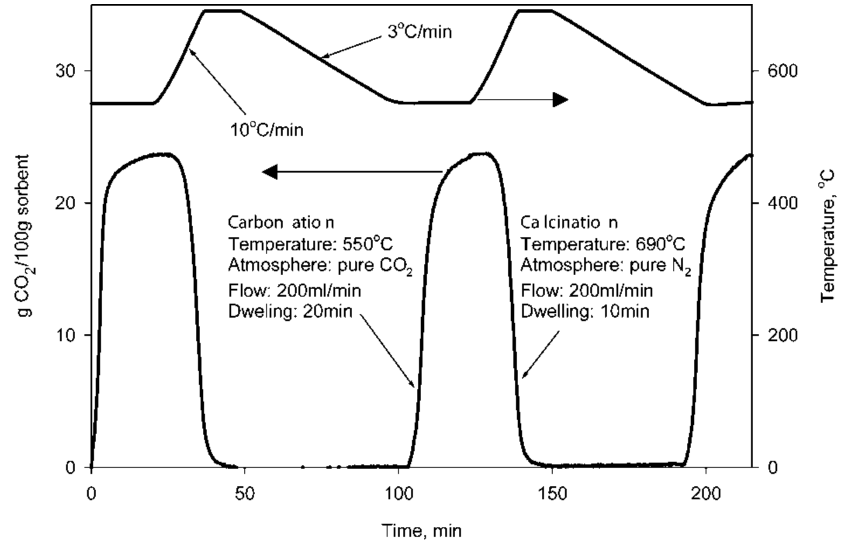

Figure 7. Multi-cycle test of LiZr-LL.

were done to obtain the second and third CO_2 uptakes. As shown in Fig. 7, the CO_2 capacity of the sorbent was not reduced after two cycles of carbonation and regeneration. The CO_2 uptake rate of the second cycle, however, was slightly slower than that of the first cycle. The third CO_2 uptake rate remained the same as the second. As previously described, maximum CO_2 uptake rates were calculated using the Excel spread sheet regression function in the range of 2 to 18% CO_2 uptake. The first-cycle CO_2 uptake rate was 57.0 mg/g · min, while the second- and third-cycle rates were 34.9 mg/g · min and 34.8 mg/g · min, respectively. Even though LiZr-LL was prepared at room temperature and calcined at 500°C for a short period of time, the test result showed fine thermal stability. Furthermore, in a later study of multi-cycle performance, particularly with steam addition LiZr-LL did not show any indication of degradation of its absorption ability over 30 cycles. These multi-cycle test results and steam addition effects on long-term performance of LiZr-LL and other new absorbents will be presented in next publication.

CO_2 release rates from carbonated sorbents are presented in Fig. 8 at different temperatures from 500°C to 650°C. 70 mg of LiZr-LL was reacted with 200 ml/min (25°C, 1bar) of pure CO_2 for one hour. Then, the CO_2 atmosphere was switched to N_2. The CO2 adsorbed at the moment when the atmospheres were shifted was considered to be 100%. 80% of the CO_2 captured during carbonation was released after 60 min at 600°C. 90% of the CO_2 was released after two hours. The CO_2 release rate was significantly smaller at 550°C, and at 500°C, effectively no CO_2 was released during the 2 hours test period. This result is consistent with the argument described above that

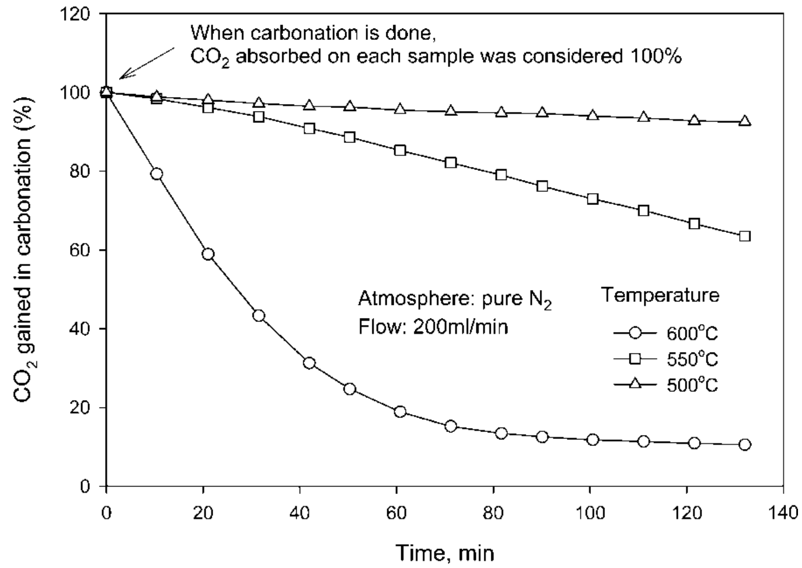

Figure 8. CO_2 releasing from completely reacted sorbent.

lower temperature is required in order to capture CO_2 at low concentrations using Li_2ZrO_3. In order to justify this argument, equilibrium partial pressures of CO_2 were calculated as a function of temperature using HSC (15) commercial thermodynamics software. The results are shown in Fig. 9. According to HSC calculations, it is theoretically possible to reduce CO_2 pressure to about 0.0027 bar at 500°C, 0.04 bar at 600°C, and to about 0.30 bar at 700°C. Therefore, it is necessary to use reaction temperature less than 500°C if CO_2 concentrations less than 3% by volume are required. However, it is not reasonable to use temperatures much less than 500°C because of the significant decrease in sorption rate at 450°C as shown in Fig. 6.

The effect of CO_2 partial pressure on CO_2 sorption using LiZr-LL at a reaction temperature of 500°C is presented in Figure 10. The flow rate of the CO_2/N_2 mixture was 300 ml/min (25°C, 1bar). CO_2 partial pressure was varied from 1 to 0.1 bar. As expected, the CO_2 uptake rate was fast at $PCO_2 = 1$ bar, and decreased slowly as PCO_2 was decreased to 0.3 bar. However, the uptake rate became quite slow when PCO_2 was decreased to 0.1 bar. Only 10% weight gain was achieved in 10% CO_2 in N_2 in 2 hours.

This result confirms that the major challenge of utilizing Li_2ZrO_3 in CO_2 capture is achieving low CO_2 concentration in the exit gas. Reduced CO_2 capacity in low partial pressure of CO_2 can be explained by associating it with diffusion and reaction rate. It is assumed that at high PCO_2, diffusion of CO_2 into the core of macro-particles and the reaction forming Li_2CO_3 occur at the same time. Therefore, the global reaction is under kinetic control. When PCO_2 is low, however, CO_2 molecules tend to react on the

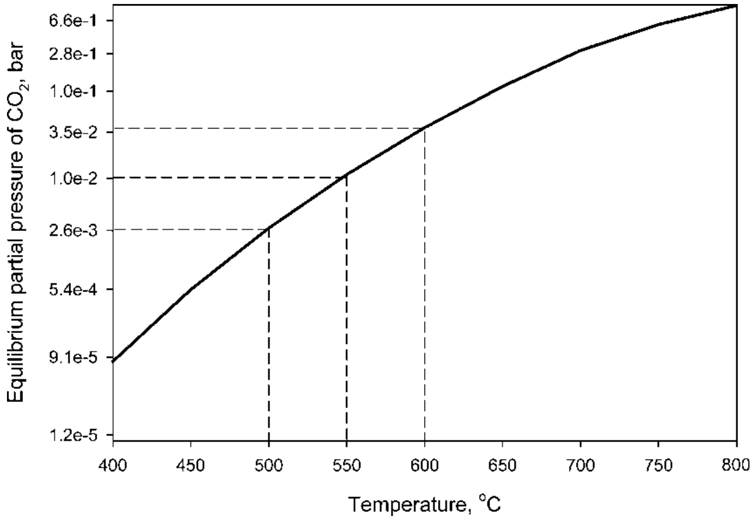

Figure 9. Equilibrium partial pressure of CO_2.

surface of the particle before they diffuse into the core. Since volumetric expansion occurs when Li_2ZrO_3 is converted to Li_2CO_3 and ZrO_2, the diffusion path becomes increasingly blocked, and the global rate becomes diffusion controlled. Considering that gas leaving the steam methane reformer (SMR) or coal-burning power plant contain 10 to 13% of CO_2, (15, 16) the challenge becomes more evident.

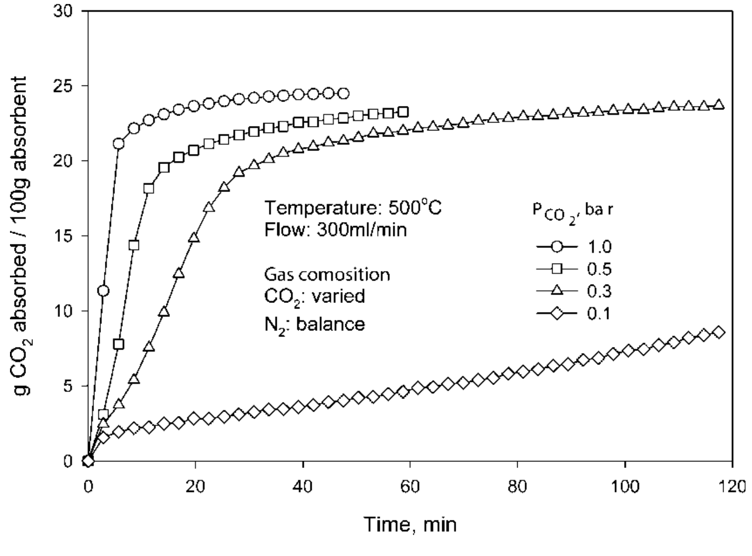

Figure 10. Partial pressure of CO_2 effect.

The gases leaving both processes also contain steam. Typical steam contents are 30% in the SMR exit gas and 10% in coal-fired power plant flue gas. Since steam often affects the kinetics of solid-gas reactions, the effect of steam addition on CO_2 sorption of LiZr-LL was also investigated and is illustrated in Fig. 11. PCO_2 was fixed at 0.1bar, temperature at 500°C, and total flow rate of the $CO_2/H_2O/N_2$ mixture was 300 ml/min (25°C, 1bar). The concentration of steam was varied from 0% to 30%. Steam clearly increased the CO_2 uptake rate, especially when the steam concentration was increased from 10% to 20%. 20% and 30% steam addition resulted in somewhat similar CO_2 uptake rates. Essaki et al. (17) reported a similar positive effect of steam on CO_2 sorption on lithium silicate at room temperature. They suggested that the Li_2CO_3 layer formed on the surface is dissolved in water. As a consequence the diffusion resistance is decreased. However, this may not be applied to Li_2ZrO_3 since its reaction temperature is over 500°C. Instead, it is thought that steam takes a role as a media to increase lithium ion mobility. Steam also increased the CO_2 uptake in TGA tests using oyher sorbents such as lithium orthosilicate and dolomite (results are not shown). The effect of steam in CO_2 removal using solid sorbents should be investigated further for clear understanding.

This positive effect of steam on CO_2 uptake suggests that Li_2ZrO_3 sorbent might be more suitable to SMR than coal-burning power plants because of its higher steam content.

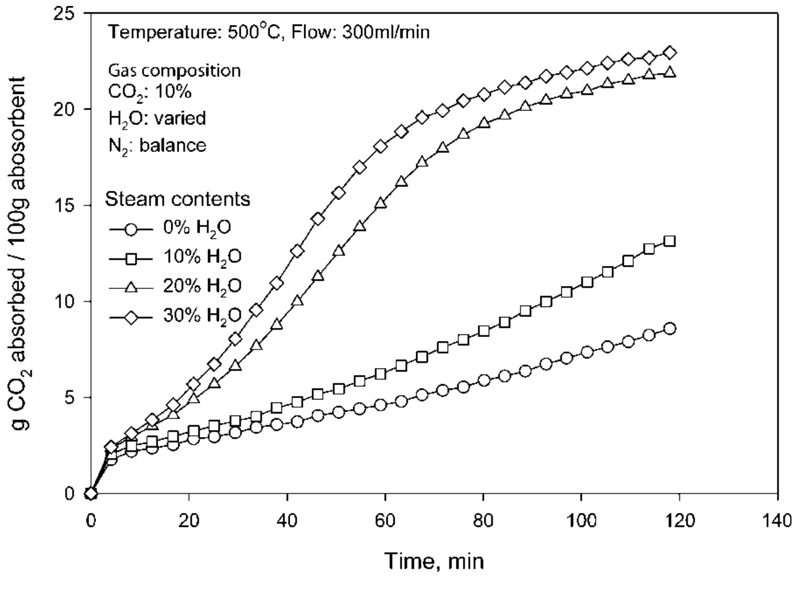

Figure 11. Steam effect on CO_2 sorption.

CONCLUSIONS

In this study Li_2ZrO_3 was prepared using a liquid based precipitation method and a solid-state reaction method. The CO_2 sorption kinetics and capacity were investigated in various conditions. CO_2 sorption rate of Li_2ZrO_3 prepared using the precipitation method was tens of times faster than that prepared using the solid-state reaction method. The precipitated Li_2ZrO_3 possessed an average aggregate size of 40 nm and absorbed CO_2 to 20% of the sample weight in less than 6 min at 500°C. CO_2-release tests from Li_2ZrO_3 sorbent saturated with CO_2 were carried out and the maximum temperature not to release CO_2 in CO_2-free atmosphere was 500°C. Sorption-desorption cycle tests using the Li_2ZrO_3 at 500°C and 690°C, respectively, were carried out in three cycles and the CO_2 uptake rate and capacity were almost unchanged. The CO_2 uptake rate decreased significantly as the CO_2 partial pressure decreased to less than 0.3 bar. However, the addition of more than 20% steam increased the CO_2 uptake rate substantially.

ACKNOWLEDGEMENT

This study was financially supported by the Norwegian Research Council as a part of the project "Energy for future".

REFERENCES

1. Abanades, J., Rubin, E., and Anthony, E. (2004) Sorbent cost and performance in CO_2 capture systems. *Ind. Eng. Chem. Res.*, 43 (13): 3462–3466.
2. Lopez-Ortiz, A., Rivera, N., Rojas, A., and Gutierrez, D. (2004) Novel carbon dioxide solid acceptors using sodium containing oxides. *Separ. Sci. Technol.*, 39 (15): 3559–3572.
3. Ortiz, A. and Harrison, D. (2001) Hydrogen production using sorption-enhanced reaction. *Ind. Eng. Chem. Res.*, 40 (23): 5102–5109.
4. Xiong, R., Ida, J., and Lin, Y. (2003) Kinetics of carbon dioxide sorption on potassium-doped lithium zirconate. *Chem. Eng. Sci.*, 58 (19): 4377–4385.
5. Nakagawa, K. and Ohashi, T. (1998) A novel method of CO2 capture from high temperature gases. *J. Electrochem. Soc.*, 145 (4): 1344–1346.
6. Essaki, K., Nakagawa, K., and Kato, M. (2001) Acceleration effect of ternary carbonate on CO_2 absorption rate in lithium zirconate powder. *J. Ceram. Soc. Jpn.*, 109 (10): 829–833.
7. Ida, J. and Lin, Y. (2003) Mechanism of high-temperature CO_2 sorption on lithium zirconate. *Environ. Sci. Technol.*, 37 (9): 1999–2004.
8. Wang, Y. and Qi, L. (2004) Further study on the property of absorbing CO_2 with Li_2ZrO_3 material. *Chinese. J. Inorg. Chem.*, 20 (7): 770–774.
9. Nair, B., Yamaguchi, T., Kawamura, H., Nakao, S., and Nakagawa, K. (2004) Processing of lithium zirconate for applications in carbon dioxide separation: Structure and properties of the powders. *J. Am. Ceram. Soc.*, 87 (1): 68–74.

10. Nakagawa, K. and Ohashi, T. (1999) A reversible change between lithium zirconate and zirconia in molten carbonate. *Electrochemistry*, 67 (6): 618–621.
11. Wang, Y., Qi, L., and Wang, X. (2003) The study of Li_2ZrO_3 used for absorption of CO_2 at high temperature. *Chinese. J. Inorg. Chem.*, 19 (5): 531–534.
12. Peiser, H.S., Rooksby, H.P., and Wilson, A.J.C. (1955) *X-ray diffraction by polycristalline materials*, 1st Ed.; The Institute of Physics: London.
13. Wang, Y. and Qi-Lu. (2004) The influencing factor for CO_2 absorption of Li_2ZrO_3 at high temperature. *Acta Phys-Chim Sin.*, 20 (4): 364–367.
14. Ida, J., Xiong, R., and Lin, Y. (2004) Synthesis and CO2 sorption properties of pure and modified lithium zirconate. *Sep. Purif. Technol.*, 36 (1): 41–51.
15. Roine, A. (1997) *Outokumpu HSC for Windows—Chemical Reaction Equilibrium Softward with Extensive Thermodynamic Data Base*; User's Guide, Version 5.1. Outokumpu Research Oy, Finland.
16. Eckroth, D., Grayson, M., Kirk, R.E., and Othmer, D.F. (1985) *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, 3rd Ed.; Wiley: New York.
17. Essaki, K., Nakagawa, K., Kato, M., and Uemoto, H. (2004) CO_2 absorption by lithium silicate at room temperature. *J. Chem. Eng. Jpn.*, 37 (6): 772–777.