Reactive Crystallization of Lithium Carbonate Nanoparticles by Microwave Irradiation of Aqueous Solution Containing CO\textsubscript{2} Microbubbles

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Keywords: Reactive Crystallization, Microbubbles, Microwaves, Lithium Carbonate, Nanoparticles

In this study, we used minute gas-liquid interfaces around CO\textsubscript{2} microbubbles activated by microwave irradiation as new reaction fields and developed a crystallization technique to produce lithium carbonate (Li\textsubscript{2}CO\textsubscript{3}) nanoparticles. At the minute gas-liquid interfaces, nucleation occurs predominantly because of the formation of numerous local supersaturation regions at higher temperatures; hence, fine-sized Li\textsubscript{2}CO\textsubscript{3} particles with a narrow size distribution are crystallized, as the Li\textsubscript{2}CO\textsubscript{3} solubility decreases sharply with an increase in temperature. Microwaves (2.45 GHz) were used to irradiate an aqueous solution containing lithium ions and CO\textsubscript{2} microbubbles in a waveguide-type microwave apparatus. The heating method, rate of temperature increase (r\textsubscript{T}) and average bubble size (d\textsubscript{32}) were considered as the operation parameters and varied; the combined effects of CO\textsubscript{2} microbubble formation and microwave irradiation on the reactive crystallization of Li\textsubscript{2}CO\textsubscript{3} nanoparticles were examined. Consequently, during microwave irradiation of the solution containing CO\textsubscript{2} microbubbles, the crystallization of Li\textsubscript{2}CO\textsubscript{3} nanoparticles was significantly accelerated with an increase in r\textsubscript{T} and a decrease in d\textsubscript{32}.

Introduction

Carbon dioxide (CO\textsubscript{2}) is one of the important greenhouse effect gases that cause global environmental problems. Researchers around the world have been carrying out studies for reducing the CO\textsubscript{2} concentration in the atmosphere (Alpert and Maulbetsch, 1996; Audus and Oonk, 1997; Fujii, 2001). One of the effective countermeasures for the aforementioned problem is CO\textsubscript{2} fixation, in which useful ions in waste brine after sodium carbonization with exhaust CO\textsubscript{2} gas (Tsuge et al., 2002). Calcium, magnesium, and lithium carbonates are obtained as the products. Recently, the demand for lithium carbonate (Li\textsubscript{2}CO\textsubscript{3}) has remarkably increased, as it is used in lithium-ion batteries, heat-resistant glassware, and medicines, as well as in the manufacture of other lithium salts. To improve the dissolubility of this salt for better Li\textsubscript{2}CO\textsubscript{3} utilization, the following must be achieved: fine particle size, narrow size distribution, uniform morphology, and high surface area. Therefore, downsizing and control of the size distribution of Li\textsubscript{2}CO\textsubscript{3} particles are very important during Li\textsubscript{2}CO\textsubscript{3} crystallization. Studies on the kinetics of the reactive crystallization of calcium carbonate and magnesium carbonate show that high supersaturation results in the crystallization of small particles, as the nucleation process is more sensitive to supersaturation than to crystal growth (Garside and Shah, 1980; Swinney et al., 1982). However, it is difficult to achieve high supersaturation during Li\textsubscript{2}CO\textsubscript{3} crystallization because the solubility product of Li\textsubscript{2}CO\textsubscript{3} at a specified temperature is almost 1,000 times that of calcium carbonate. Therefore, fine particles of Li\textsubscript{2}CO\textsubscript{3} are not easily crystallized. With the development of the microscale bubble generation technique to obtain bubbles whose size is ≪50 µm, considerable attention has been paid to the utilization of the so-called “microbubbles”. Minimizing bubble formation in gas–liquid systems helps achieve the following: i) acceleration of mass transfer and reactive absorption with an increase in the gas–liquid interfacial area, ii) increase in the average residence time of the bubbles with a decrease in buoyancy, and iii) occurrence of interactions at the gas–liquid interface (Onoe et al., 2002; Matsumoto et al., 2004). Thus, by increasing the residence time of bubbles in the liquid phase, a quasi-homogeneous gas–liquid system can be obtained. Furthermore, when external energy is supplied to an aqueous solution con-
taining microbubbles, unique mass-transfer patterns and reaction phenomena are expected to occur (Onoe et al., 2007; Onoe and Matsumoto, 2008). In the present study, microwave irradiation is used as the source of external energy. During microwave irradiation, local high-temperature regions (hot-spots) are formed because of the vibration of polar molecules and ions, and thus, rapid and efficient internal heating is achieved. Microwave irradiation has been recently employed in the solid-phase synthesis of oxides and sulfides and fine metal powders, fabrication of superconductors and semiconductors, pyrolysis of metal-organic precursors for powder synthesis, and crystallization of inorganic compounds from solution (Wada et al., 2001; Guo et al., 2006; Heuser et al., 2007). In this study, for developing a crystallization technique that enables the control of the crystal properties of carbonates with high insolubility by the generation of local supersaturation regions, we studied the reactive crystallization of Li$_2$CO$_3$ using minute gas–liquid interfaces around CO$_2$ microbubbles activated by microwave irradiation. The solubility of Li$_2$CO$_3$ decreases sharply with an increase in temperature. Therefore, when such minute gas–liquid interfaces are considered as new reaction fields, fine crystals with a narrow size distribution can be obtained by inhibiting crystal growth in the liquid phase. This inhibition is due to the progress of nucleation, which in turn is because of the formation of numerous local supersaturation regions at a specific temperature and concentration. In this paper, we report a technique that combines microwave-irradiated CO$_2$ microbubble formation, which helps control the particle size distribution of Li$_2$CO$_3$, and nanoparticle crystallization.

1. Experimental

1.1 Source gas and materials

Commercial-grade CO$_2$ and nitrogen (N$_2$) gases were selected as feed sources for bubbles. CO$_2$ gas was used to generate carbonate ions (CO$_3^{2-}$), and N$_2$ gas was added to control the feed molar fraction and bubble size. Lithium nitrate (LiNO$_3$, 99 wt% purity, Wako Pure Chemical Industries, Ltd.) was dissolved in ion-exchanged water and used as a source of Li$^+$ ions. The solution of sodium hydroxide (NaOH, 99 wt% purity, Wako Pure Chemical Industries, Ltd.) was maintained at a constant pH of 13.5 by adding 8.0 mol/l solution (volume: 2000 ml). The initial concentration: 1000 mmol/l) and F$_{CO_2}$ of 4.46 mmol/l by using a propeller-type mixer with four blades. Bubbles with different d$_{bbl}$ values are obtained by changing the hole size (65–300 µm) on the dispersing plate at a constant F$_{N_2}$ of 22.0 mmol/l (min) and F$_{CO_2}$ of 4.46 mmol/l (min). d$_{bbl}$ is determined from the bubble size distribution measured using a laser particle size analyzer (LA920, HORIBA, Ltd.).

1.2.2 Waveguide-type microwave apparatus

Figure 1 shows the schematic of the waveguide-type microwave apparatus comprising a 1.5-kW generator (magnetron), rectangular waveguide (cross sectional area: 109.2 × 54.6 mm$^2$), and an irradiated field including a flask-type quartz vessel (internal volume: 500 ml) as a crystallizer. Microwaves with a frequency of 2.45 GHz generated from the magnetron are adjusted by the tuner and made incident on the quartz vessel after passing through a horizontal waveguide.

1.3 Experimental procedures

1.3.1 Reactive crystallization of Li$_2$CO$_3$ by CO$_2$ microbubble generation (constant temperature: 313 K)

CO$_2$/N$_2$ bubbles with d$_{bbl}$ values of 25, 600, or 2000 µm were continuously supplied to an aqueous LiNO$_3$ solution (volume: 2000 ml; initial concentration: 1000 mmol/l), and reactive crystallization of Li$_2$CO$_3$ was carried out. The solution temperature (T$_s$) was maintained at 313 K, and the bubble supply time (t$_b$) was controlled within 60 min. The solution pH during crystallization was maintained constant at 13.5 by adding 8.0 mol/l NaOH solution. After the bubbles were supplied for a specified length of time, the suspension was filtered and dried at 343 K for 60 min under reduced pressure. The physical properties (crystal structure, morphology, and particle size distribution) of the reaction products were measured by X-ray diffraction (XRD, RINT2100, Rigaku Co.) and scanning electron microscopy (SEM, JSM-6300, JEOL, Ltd.) and by using a laser particle size analyzer (LA920, HORIBA, Ltd.).
1.3.2 Reactive crystallization of Li$_2$CO$_3$ by microwave irradiation of a solution with/without CO$_2$ microbubbles (temperature is increased from 289 to 313 K)

CO$_2$/N$_2$ microbubbles with a $d_{	ext{bbl}}$ of 25 µm were continuously supplied to 2000 ml of an aqueous LiNO$_3$ (1000 mmol/l) solution. $T_s$ was maintained constant at 289 K, and $t_b$ was set at 40 min. The solution pH during the bubble supply was maintained at 13.5 by adding 8.0 mol/l NaOH solution. When $T_s$ was 289 K, no crystallization of Li$_2$CO$_3$ was observed even after supplying bubbles for 240 min. After the bubble supply was stopped, 200 ml of the prepared solution was rapidly transferred to the flask-type quartz vessel and used as the solution containing CO$_2$ microbubbles. A solution free of CO$_2$ microbubbles was obtained 240 min after the bubble supply was ceased. The presence of microbubbles in the solution was confirmed by estimating the bubble size distribution. The solutions with and without CO$_2$ microbubbles were subjected to microwave irradiation, and reactive crystallization of Li$_2$CO$_3$ was carried out. $T_s$ during crystallization was measured using a thermocouple. The rate of temperature increase ($r_T$) was varied in the range of 9.0–23.0 K/min by adjusting the incident irradiation power ($P_W$) to 200–400 W. For comparison, conventional heating using a thermostat bath was carried out at the same $r_T$ mentioned above. The irradiation time or heating time ($t_h$) was maintained within 150 s. After increasing $T_s$ to 313 K, microwave irradiation (or heating of the thermostat bath) was stopped, and the suspension was filtered. The physical properties of the solid products obtained were analyzed by the same techniques mentioned in Section 1.3.1. Furthermore, to examine the effect of minimizing CO$_2$ bubble formation, microwave irradiation of the bubble-free solution was carried out when supplying CO$_2$/N$_2$ bubbles with a $d_{	ext{bbl}}$ of 250, 800, or 2000 µm, and Li$_2$CO$_3$ crystallization was achieved.

2. Results and Discussion

2.1 Reactive crystallization of Li$_2$CO$_3$ using via CO$_2$ microbubble formation

Extensive research has been carried out to identify the factors that affect the reactive crystallization of Li$_2$CO$_3$ in a gas–liquid–solid system, such as solution temperature, initial solution composition, and mixing rate. During reactive crystallization in a gas–liquid–solid system with an mixed-suspension, mixed-product-removal (MSMPR) crystallizer, the nucleation rate of Li$_2$CO$_3$ increases with the initial concentration of lithium hydroxide and the reaction temperature and a decrease in the impeller speed (Fujii et al., 2003; Tsuge et al., 2004). However, the effects of bubble size on the reactive crystallization of Li$_2$CO$_3$ have not been investigated yet. The time changes in $T_s$ and the produced moles of Li$_2$CO$_3$ based on unit volume ($Q_{L_2CO_3}$) when CO$_2$/N$_2$ bubbles with a $d_{	ext{bbl}}$ of $25\,\mu m$, $600\,\mu m$, or $2000\,\mu m$ are supplied to the 1000 mmol/l LiNO$_3$ solution are shown in Figure 2. The dotted line shows the supplied moles of CO$_2$ based on unit volume ($Q_{CO_2}$). $Q_{L_2CO_3}$ is determined from the weight of the solid products and the selectivity of Li$_2$CO$_3$ calculated by XRD. Under these experimental conditions, Li$_2$CO$_3$ crystals with high selectivity (almost 100%) are obtained. $T_s$ is independent of $t_b$ and $d_{	ext{bbl}}$ and remains almost constant at 313 K. $Q_{L_2CO_3}$ is higher at a $d_{	ext{bbl}}$ of 25 µm than at a $d_{	ext{bbl}}$ of 600 µm or 2000 µm for all values of $t_b$. The induction period for nucleation, that is, the time between the bubble supply and the formation of crystal nuclei, decreases with $d_{	ext{bbl}}$. This is probably due to the increase in supersaturation, which acts as the driving force for crystallization, with the concentration of dissolved CO$_2$ caused by minimizing bubble formation. Figure 3 shows the comparison of the volume frequency of the particle size distribution of the crystallized Li$_2$CO$_3$. Immediately after nucleation, particles with a $d_{	ext{bbl}}$ of 25 µm are converted to nanosized particles (200 to 800 nm) and micron-sized particles (10 to 100 µm), while a few nanoparticles whose sizes are less than 1 µm are crystallized. At a $d_{	ext{bbl}}$ of 600 or 2000 µm, the particles with sizes of approximately 35 µm were crystallized, and nanoparticle crystallization was hardly observed. Furthermore, the increase in the particle size with $t_b$ is more inhibited at a $d_{	ext{bbl}}$ of 25 µm than at a $d_{	ext{bbl}}$ of 600 or 2000 µm. From these results, we conclude nucleation progresses predominantly at the minute gas–liquid interfaces when $d_{	ext{bbl}}$ is decreased.

Investigation of the fundamental properties of microbubbles revealed that the flotation rate at a $d_{	ext{bbl}}$ of 50 µm was 30 times smaller than that of 500 µm, and the CO$_2$ absorption rate at a $d_{	ext{bbl}}$ of 50 µm was twice

![Figure 2](image-url)
that at a $d_{bbl}$ of 2000 µm (Matsumoto et al., 2004). Further, electrification of the bubbles was measured to clarify the occurrence of interactions at the gas–liquid interfaces when bubble formation was minimized. The results confirmed that the zeta potential of the microbubbles was negative, from $-20$ to $-100$ mV, at a $d_{bbl}$ of 10–30 µm, and the negative value increased with the solution pH (Matsumoto et al., 2004, 2006). Takahashi (2005) studied the effect of the presence of an inorganic electrolyte (NaCl or MgCl₂) on the zeta potential of microbubbles and found that an increase in the electrolyte concentration resulted in a reduction in the zeta potential. These findings indicated that the increase in the Li⁺ concentration in the gas–liquid interfacial area was caused by increasing the electric charge on the bubble surface because of minimization of bubble formation. Thus, minimization of CO₂ bubble formation caused accumulation of Li⁺ and CO₃²⁻ ions in the region around the gas–liquid interface. Therefore, nucleation occurred easily in the vicinity of the gas–liquid interfaces, where large local supersaturation areas existed and a large number of particles were nucleated. After nucleation, particle growth commenced in the bulk liquid, and hence, particle size became relatively small.

2.2 Reactive crystallization of Li₂CO₃ by microwave irradiation of the solution without CO₂ microbubbles

In order to examine the effects of increase in the temperature caused by microwave irradiation on the particle size distribution of Li₂CO₃, reactive crystallization of Li₂CO₃ was carried out by microwave irradiation or thermostat bath heating of the solution without CO₂ microbubbles. Figure 4 shows the time changes in $T_s$ under the microwave irradiation when $P_w$ is varied in the range of 200–400 W.

$T_s$ increases linearly with $t_h$, and $r_T$ is 9.0, 14.5, and 23.0 K/min when $P_w$ is maintained at 200, 300, and 400 W, respectively. This increase in $r_T$ results from the strong vibration of water molecules and ions that selectively absorb the microwave energy (Wada, 2004). The results for the conventional method of heating in a thermostat bath are shown in Figure 4 for comparison. The
time courses of $T_s$ and $r_T$ observed when heating in the thermostat bath are approximately similar to those obtained during microwave irradiation. Figure 5 shows the particle size distribution of Li$_2$CO$_3$ at $T_s = 313$ K when $r_T$ is varied from 9.0 to 23.0 K/min. Under these experimental conditions, the particle size distribution plot shows two peaks, one in the 230–770 nm range, and the other in the 3–30 µm range. The peak in the micrometer range probably results from the agglomeration of some nanoparticles. Moreover, the produced moles of Li$_2$CO$_3$ based on unit volume at $T_s = 313$ K is constant at around 4.0 mmol/l under all the experimental conditions considered. At all values of $r_T$, the ratio of the volume of nanosized particles (size less than 1 µm) to the total volume of all the particles produced ($V_{np}/(V_p)_{0}$) gradually increases during microwave irradiation; however, this increase is not prominent during thermostat bath heating. This is probably because of the rapid nucleation caused by the hot spots generated during microwave irradiation (Rodriguez-Clemente and Gomez-Morales 1996; Torrent-Burgues et al., 1999; Guo et al., 2006).

2.3 Reactive crystallization of Li$_2$CO$_3$ by microwave irradiation of the solution containing CO$_2$ microbubbles

2.3.1 Effect of $r_T$ on particle size distribution of Li$_2$CO$_3$ at a constant $d_{bbl} = 25$ µm To investigate the combined effects of CO$_2$ microbubble formation and microwave irradiation on the crystallization of Li$_2$CO$_3$ nanoparticles, Li$_2$CO$_3$ was crystallized at $T_s = 313$ K by microwave irradiation of the solution containing CO$_2$ microbubbles with a $d_{bbl}$ of 25 µm. The $r_T$ values obtained for the solution containing CO$_2$ microbubbles were approximately identical to those obtained for the solution without microbubbles. The influence of energy absorption by the bubbles on the increase in the solution temperature was comparatively small. Figure 6 shows the particle size distributions of Li$_2$CO$_3$ observed in the case of microwave irradiation when $r_T$ was in the range of 9.0–23.0 K/min. With an increase in $r_T$, $V_{np}/(V_p)_{0}$ increased remarkably and reached 0.95 at an $r_T$ value of 23.0 K/min. The dependence of $V_{np}/(V_p)_{0}$ on $r_T$ was more pronounced in the solution containing microbubbles than that in the solution without microbubbles (Figure 5). The results obtained for thermostat bath heating are also shown in Figure 6. From Figure 5, it was seen that the increase in $V_{np}/(V_p)_{0}$ caused by microbubble formation during thermostat bath heating was smaller than during microwave irradiation.

2.3.2 Effect of $d_{bbl}$ on particle size distribution of Li$_2$CO$_3$ at a constant $r_T$ of 23.0 K/min The results presented in Section 2.3.1 show that CO$_2$ microbubble formation for $d_{bbl} = 25$ µm and microwave irradiation are interdependent during the crystallization of Li$_2$CO$_3$ nanoparticles. Therefore, $d_{bbl}$ is varied as an operating parameter, and the effects of minimization of bubble formation are examined in detail. Figure 7 shows the particle size distributions of Li$_2$CO$_3$ at various $d_{bbl}$ values when $r_T$ is fixed at 23.0 K/min ($P_{in} = 400$ W).

Because of the minimization of bubble formation, the rate of nanoparticle crystallization was significantly enhanced during microwave irradiation than during thermostat bath heating. Furthermore, the increase in $V_{np}/(V_p)_{0}$ with a decrease in $d_{bbl}$ during microwave irradiation...
diation of the solution with CO$_2$ microbubbles was more pronounced than that in only the CO$_2$ microbubble formation (Figure 3).

2.3.3 Relation between $d_{\text{blb}}$, $r_T$, and production rate of Li$_2$CO$_3$ nanoparticles

From the above results obtained by varying $r_T$ and $d_{\text{blb}}$, the production rate of Li$_2$CO$_3$ nanoparticles with diameters less than 1 mm ($r_{np}$) and the rate of production of micron-sized particles ($r_{mp}$) are determined. The obtained values are plotted against $d_{\text{blb}}$ and $r_T$, as shown in Figure 8.

$r_{np}$ and $r_{mp}$ were calculated from the total production rate of the Li$_2$CO$_3$ particles and the particle size distribution of Li$_2$CO$_3$. At all values of $r_T$, the total production rate increased slightly when bubble size was minimized. Under microwave irradiation, $r_{np}$ increased remarkably with an increase in $r_T$ and a decrease in $d_{\text{blb}}$. On the contrary, during thermostat bath heating, the increase in $r_{np}$ was relatively smaller than that under microwave irradiation. Furthermore, using the experimental results obtained for the solution containing CO$_2$ microbubbles, $r_{np}$ was determined by multiple regression analysis. Consequently, the empirical formulae for $r_{np}$ [mmol/(l-min)] in the case of microwave irradiation ($r_{np}$) and thermostat bath heating ($r_{np(TS)}$) could be expressed as shown in Eqs. (1) and (2), respectively.

$$\ln(r_{np})_{\text{MW}} = -0.40 \cdot \ln(d_{\text{blb}}) + 1.82 \ln(r_T) - 3.00 \quad (1)$$
$$\ln(r_{np})_{\text{TS}} = -0.20 \cdot \ln(d_{\text{blb}}) + 1.15 \ln(r_T) - 3.00 \quad (2)$$

The coefficient of $\ln(d_{\text{blb}})$ and $\ln(r_T)$ under microwave irradiation is about 2.0 and 1.5 times that during thermostat bath heating. Figure 9 shows the comparison of $r_{np}$ obtained using the empirical formula and that obtained experimentally. In either case, the tendency of $r_{np}$ to increase with a decrease in $d_{\text{blb}}$ observed in the experimental results are well consistent with that observed in the calculated curves. This confirms that the obtained equations can be used to simulate the experimental results. From these experimental results and empirical formulae, it is apparent that nanoparticle crystallization under microwave irradiation in the solution containing CO$_2$ microbubbles is accelerated when bubble size is minimized under high incident irradiation power. From discussions presented in Section 2.1, it is clear that minimization of CO$_2$ bubble size leads to the generation of regions with high concentrations of Li$^+$ and CO$_3^{2-}$ ions in the area around gas–liquid interfaces. Generally, the overall heat output to the liquid phase under microwave irradiation is defined as dielectric loss. The dielectric loss of the solution containing an electrolyte increases with the electrolyte concentration; for example, the dielectric loss of a 0.5 mol/l NaOH solution is 41.9, which is 3.5 times that of water (12.0). Therefore, when microwave irradiation is used as a source of external energy supplied to the aqueous solution containing CO$_2$ microbubbles, vibration of polar molecules and ions and energy absorption occur in the regions with high Li$^+$ and CO$_3^{2-}$ ion concentrations near the CO$_2$ microbubbles. Nucleation proceeds predominantly because of the increase in the number of local supersaturation regions near the gas–liquid interfaces at higher temperature. Furthermore, agglomeration of the nucleated particles is suppressed. This suppression probably results from the decrease in the contact frequency between the particles and supersaturation around the particle surface. The contact between the particles is prevented owing to the high residence time of microbubbles. Supersaturation in the vicinity of the solid–liquid interfaces decreases because of the diffusion of the nucleated particles in the bulk liquid with low Li$^+$ concentration and temperature. Thus, it can be stated that the crystallization of Li$_2$CO$_3$ nanoparticles is accelerated under these conditions.

Conclusions

Using the minute gas–liquid interfaces around CO$_2$ microbubbles activated by microwave irradiation, reactive crystallization of Li$_2$CO$_3$ was carried out to gener-
ate $\text{Li}_2\text{CO}_3$ nanoparticles. The following results were obtained: 1) during $\text{CO}_2$ microbubble formation, $\text{Li}_2\text{CO}_3$ nanoparticles were crystalized to a small extent with a decrease in $d_{\text{bbl}}$; 2) during microwave irradiation of a solution without $\text{CO}_2$ microbubbles, the number of nanoparticles crystalized was greater than that crystal-
lized in thermostat bath heating; 3) during microwave ir-
radiation of the solution with $\text{CO}_2$ microbubbles ($d_{\text{bbl}} = 25 \, \mu\text{m}$), $V_{\text{np}}(V_p)_{\text{bbl}}$ increased to a greater extent than in the solution without microbubbles; 4) during thermostat bath heating, the increase in $V_{\text{np}}(V_p)_{\text{bbl}}$ because of $\text{CO}_2$ microbubble formation ($d_{\text{bbl}} = 25 \, \mu\text{m}$) was smaller than that observed in microwave irradiation; 5) reactive crystal-
lization of nanoparticles proceeded rapidly with an in-
crease in $r_T$ and a decrease in $d_{\text{bbl}}$ during microwave ir-
radiation of the solution containing $\text{CO}_2$ microbubbles.

**Nomenclature**

- $d_{\text{bbl}}$: average bubble size [µm]
- $d_p$: particle size of $\text{Li}_2\text{CO}_3$ [µm]
- $F_{\text{CO}_2}$: $\text{CO}_2$ flow rate based on unit volume [mmol/(l·min)]
- $F_{\text{N}_2}$: $\text{N}_2$ flow rate based on unit volume [mmol/(l·min)]
- $P_{\text{W}}$: incident irradiation power [W]
- $Q_{\text{CO}_2}$: supplied moles of $\text{CO}_2$ based on unit volume [mmol/l]
- $Q_{\text{Li}_2\text{CO}_3}$: produced moles of $\text{Li}_2\text{CO}_3$ based on unit volume [mmol/l]
- $r_{\text{np}}$: production rate of $\text{Li}_2\text{CO}_3$ micron-sized particles based on unit volume [mmol/(l·min)]
- $r_{\text{np}}$: production rate of $\text{Li}_2\text{CO}_3$ nanoparticles based on unit volume [mmol/(l·min)]
- $r_T$: rate of temperature increase [K/min]
- $T_{\text{s}}$: solution temperature [K]
- $t_{\text{b}}$: bubble supply time [min]
- $t_{\text{i}}$: irradiation or heating time [min]
- $V_{\text{np}}$: volume of distributed particles in nanometer range [$\mu\text{m}^3$]
- $V_p$: volume of distributed particles of each size [$\mu\text{m}^3$]
- $(V_p)_{\text{bbl}}$: total volume of all generated particles [$\mu\text{m}^3$]

**Literature Cited**


Audus, H. and H. Oonk: “An Assesment Procedure for Chemical Uti-
lization Schemes Intended to Reduce $\text{CO}_2$ Emissions to Atmo-


Fujii, K., I. Kuze and H. Tsuge; “Production of Lithium Carbonate Par-


Guo, L., H. Luo, J. Gao, L. Guo and J. Yang: “Microwave Hydrother-
3014 (2006)

Exchanged Zeolite Using Microwave Radiation,” *J. Mater. Sci.*, 42,
9057–9062 (2007)


Matsumoto, M., T. Fukunaga and K. Onoe: “Effects of $\text{CO}_2$/NH$_3$/N$_2$ Bubble Size on Reactive Crystallization of CaCO$_3$ Fine Parti-


Rodriguez-Clemente, R. and J. Gomez-Morales; “Microwave Precipi-


Wada, Y.: “Synthesis of Inorganic Nanocrystallites by Microwave Irra-