

Synthesis of Precipitated Calcium Carbonate in $\text{Ca(OH)}_2\text{-CO}_2\text{-H}_2\text{O}$ System by the Continuous Drop Method of Ca(OH)_2 Slurry

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ABSTRACT

Experiments were conducted to investigate the synthesis characteristics of Precipitated Calcium Carbonate (for short PCC) in $\text{Ca(OH)}_2\text{-CO}_2\text{-H}_2\text{O}$ system by the continuous drop method of Ca(OH)_2 slurry into the solution containing $\text{CO}_2(\text{aq})$. When the flow rate of $\text{CO}_2(\text{g})$ increases and the concentration of Ca(OH)_2 slurry become low, the absorption rate of $\text{CO}_2(\text{g})$ become faster than the dissolution rate of Ca(OH)_2 . Consequently, the growth of the calcite crystal plane is facilitated resulting in synthesis of $1.0\ \mu\text{m}$ of rhombohedral calcite. On the other hand, when the flow rate of $\text{CO}_2(\text{g})$ decreases and the concentration of Ca(OH)_2 slurry become high, new nuclei is created along with the crystal growth resulting in synthesis of $1.0\ \mu\text{m}$ of prismatic calcite. Maintaining 1.0 wt% of Ca(OH)_2 slurry, 120 drops/min of drop rate and 25°C of temperature, the shape of PCC shows colloidal and spherical agglomerate at 100 mL/min of the flow rate of $\text{CO}_2(\text{g})$; the mixture of rhombohedral and plate-shaped calcite, at 200~500 mL/min. Therefore, as the flow rate of $\text{CO}_2(\text{g})$ increases, the shape of PCC changes from colloidal and rhombohedral calcite to plate-shaped calcite. Maintaining 500 mL/min of the flow rate of $\text{CO}_2(\text{g})$, 120 drops/min of the drop rate of Ca(OH)_2 slurry, and 25°C of temperature, the shape of PCC shows the plate-shaped calcite at 1.0~3.0 wt% of Ca(OH)_2 slurry; the hexagonal plate-shape calcite of the thickness of $0.1\ \mu\text{m}$ and the width of $1.0\ \mu\text{m}$, at 4.0 wt%.

Key words : PCC, Continuous drop method, Calcite, $\text{Ca(OH)}_2\text{-CO}_2\text{-H}_2\text{O}$

1. Introduction

Calcium carbonate has been widely used as inorganic filler for rubber, plastics, paper, paints, adhesive and etc. for its low price, high whiteness, inactivity and nonflammability.^{1,2)} In the paper industry, PCC have been used as the filler of paper^{3,4)} because its whiteness is higher than that of kaolin and its morphology and particle size can be easily controlled by synthesizing method.

In the carbonation process, PCC are synthesized by the reaction of Ca(OH)_2 with $\text{CO}_2(\text{g})$ which is generated from the thermal decomposition of limestone and their particle size or shape can be controlled according to synthesis conditions. Thus, in recent, most of PCC is synthesized by the carbonation process. In particular, CMSMPR (Continuous Mixture Suspension Mixed Product Removal) is used⁵⁻⁷⁾ for industrial purpose.

Recently, to synthesize rhombohedral PCC which is high-priced and used as a functional material, new technologies are being developed and various kinds of factors such as the concentration of reactants, reaction temperature, contact methods, and use of additives, etc. are being tested. If the

concentration of Ca(OH)_2 slurry is lower and the feeding rate of $\text{CO}_2(\text{g})$ is high, the colloidal PCC is synthesized. In order to control the homogeneity and size of PCC particles, the phosphate, boride, soluble metallic chloride or sulfate and zinc sulfide, etc. are added.⁸⁻¹¹⁾ Sometimes, their size and morphology is changed by the shape of reaction bowl, the size of bubble, the shape of impeller, and the smooth contact of reactants.¹²⁻¹⁴⁾

Therefore, in this study, the properties of PCC synthesized by the new the carbonation process, the dropping Ca(OH)_2 slurry into the solution containing $\text{CO}_2(\text{g})$, were examined according to the concentration of Ca(OH)_2 slurry, the flow rate of $\text{CO}_2(\text{g})$, the feeding rate of Ca(OH)_2 slurry, and the length of magnetic bar.

2. Experimental Procedure

As starting materials for an experiment, 95.0% of Ca(OH)_2 [SIGMA] and 99.0% of $\text{CO}_2(\text{g})$ were employed. First, the Ca(OH)_2 slurry was dropped at the constant rate in an apparatus of feeding Ca(OH)_2 slurry [capacity 250 mL, pyrex] that $\text{CO}_2(\text{g})$ is dissolved in 150 mL of distilled water [the initial electric conductivity is $0.32\ \text{mS/cm}$] as shown in Fig. 1. The concentration of Ca(OH)_2 slurry was controlled in 1.0~4.0 wt%; the flow rate of $\text{CO}_2(\text{g})$,

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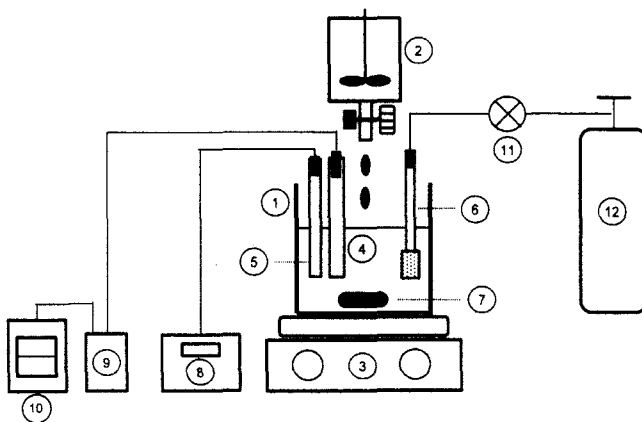


Fig. 1. Diagram of experimental apparatus; ① reactor, ② slurry vessel, ③ hot plate, ④ conductivity electrode, ⑤ pH electrode, ⑥ bubbler, ⑦ magnetic bar, ⑧ pH meter, ⑨ conductivity meter, ⑩ recorder, ⑪ $\text{CO}_2(\text{g})$ regulator and ⑫ $\text{CO}_2(\text{g})$ bombe.

100~500 mL/min; and the feeding rates of $\text{Ca}(\text{OH})_2$ slurry, 60 to 120 drops/min. And the length of magnetic bar(stirring bar) was changed to identify the effects of stirring. After the carbonation reaction is over, the synthesized PCC was filtered and dried in vacuum oven at 60°C for 24 h.

The phase, shape and pyrolysis characteristic of synthe-

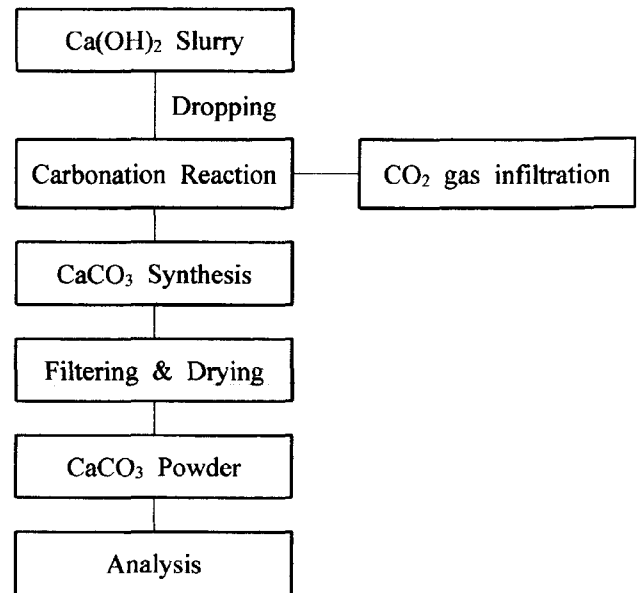


Fig. 2. Flow sheet for the synthesis of precipitated calcium carbonate.

sized PCC powder were analyzed using XRD(Philips, X'pert), SEM(JEOL, JSM-6400 scanning microscope) and TG-DTA (NETZSCH, STA 409), respectively. The particle size was measured with a particle analyzer (Malvern. Co.,

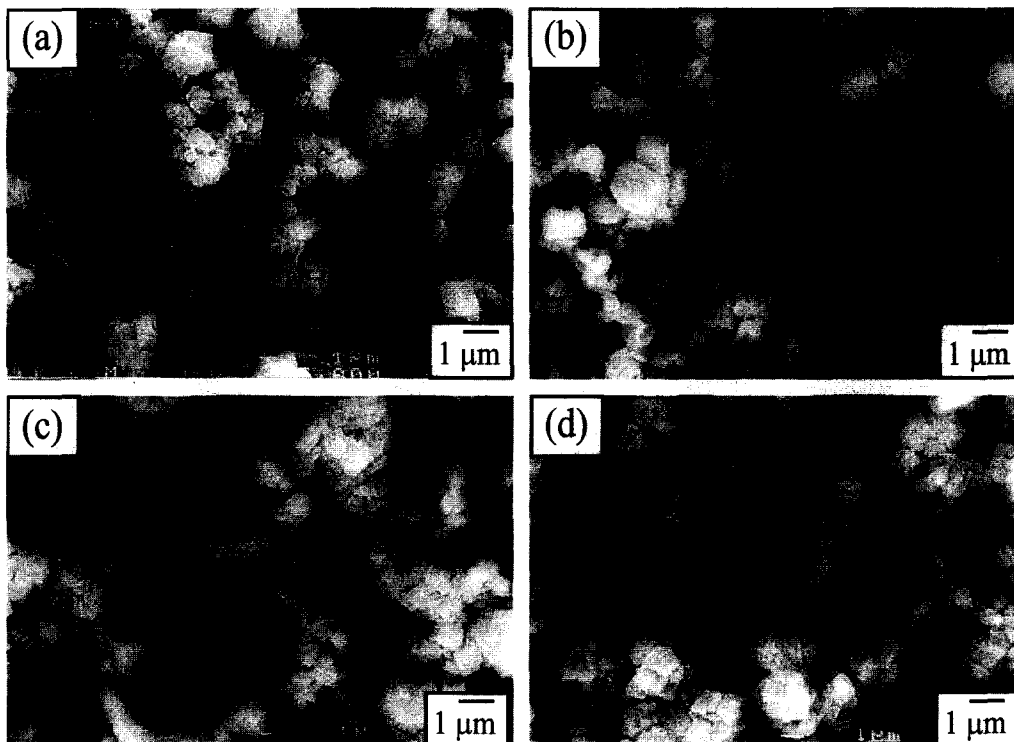


Fig. 3. SEM photographs of PCC synthesized at $\text{Ca}(\text{OH})_2$ slurry of 1.0 wt% according to the flow rates of $\text{CO}_2(\text{g})$; (a) 100 mL/min, (b) 200 mL/min, (c) 300 mL/min and (d) 400 mL/min. (feeding rate : 60 drops/min, reaction temperature : 25°C , length of magnetic bar : 2.5 cm).

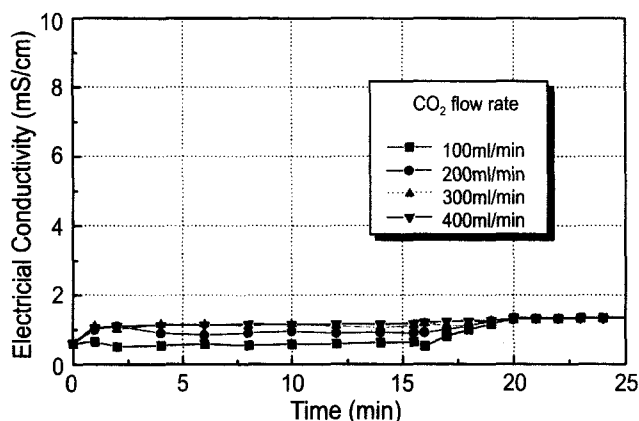


Fig. 4. The change of electrical conductivity according to the flow rates of $\text{CO}_2(\text{g})$ under $\text{Ca}(\text{OH})_2$ slurry of 1.0 wt% and feeding rate of 60 drops/min.

Model Mastersizer) and electric conductivity was measured to examine the behavior of Ca ion during the process. Fig. 2 shows the flow sheet for the synthesis of PCC in this study.

3. Results and Discussion

Fig. 3 shows the shape of PCC synthesized in the carbonation process according to the flow rate of $\text{CO}_2(\text{g})$ when the

reaction temperature, the concentration, the feeding rate of $\text{Ca}(\text{OH})_2$ slurry and the length of magnetic bar were fixed at 25°C , 1.0 wt% and 60 drops/min and 2.5 cm, respectively. As shown in this figure, the synthesized PCC is $0.5\text{--}1.0\ \mu\text{m}$ of rhombohedral calcite and their particle size showed the decreasing tendency to some extent as the flow rate of $\text{CO}_2(\text{g})$ increases. However, in general carbonation process, the pH of $\text{Ca}(\text{OH})_2$ keeps pH 12~13 and the colloidal calcite below $0.1\ \mu\text{m}$ or the prismatic calcite over $1.0\ \mu\text{m}$ is formed because of difficulty in regulating supersaturation.^{15,16)}

Fig. 4 shows the change in electric conductivity measured in Fig. 3. As shown in the figure, the electric conductivity is $0.7\ \text{mS/cm}$ at the initial stage of carbonation process, but it increased as the flow rate of $\text{CO}_2(\text{g})$ increase by $1.0\ \text{mS/cm}$. When the carbonation process was completed, that is, after the feeding of $\text{Ca}(\text{OH})_2$ slurry was stopped, the electric conductivity was maintained as $1.5\ \text{mS/cm}$ regardless of the flow rate of $\text{CO}_2(\text{g})$ after 20 min.

Fig. 5 shows the shape of PCC synthesized in the carbonation process according to the flow rate of $\text{CO}_2(\text{g})$ when the reaction temperature, the concentration, the feeding rate of $\text{Ca}(\text{OH})_2$ slurry, and the length of magnetic bar were fixed at 25°C , 1.0 wt%, 120 drops/min, and 2.5 cm, respectively. When the flow rate of $\text{CO}_2(\text{g})$ was 100 mL/min, $0.1\ \mu\text{m}$ of prismatic calcite was synthesized. But when the flow rate of $\text{CO}_2(\text{g})$ was 200 to 400 mL/min, $0.5\text{--}1.0\ \mu\text{m}$ of rhombohedral

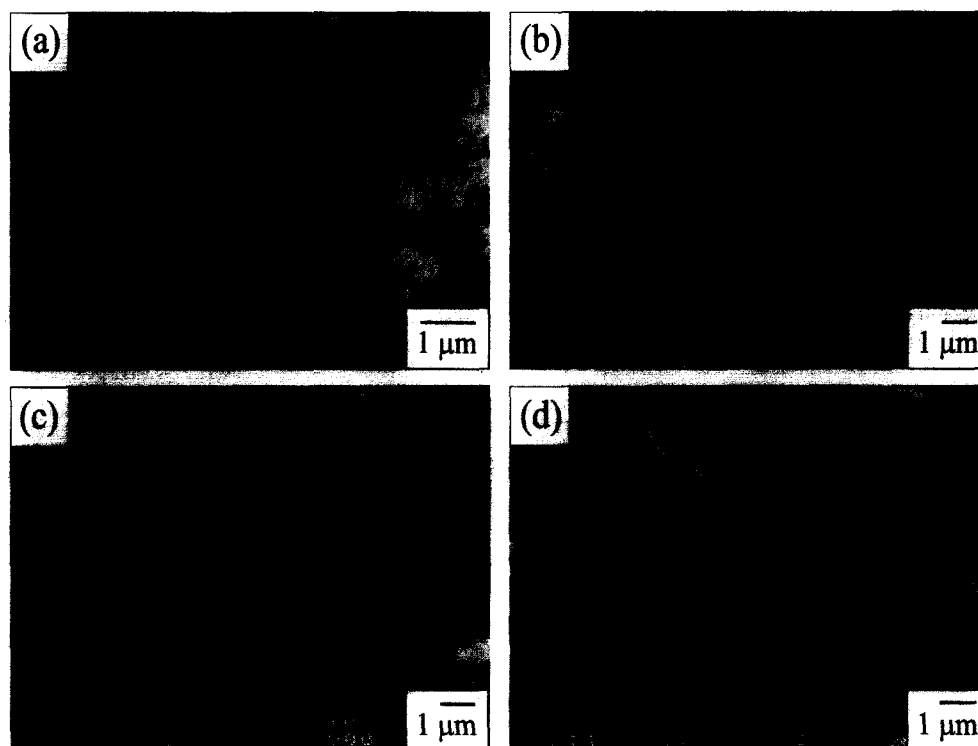


Fig. 5. SEM photographs of PCC synthesized at $\text{Ca}(\text{OH})_2$ slurry of 1.0 wt% according to the flow rates of $\text{CO}_2(\text{g})$; (a) 100 mL/min, (b) 200 mL/min, (c) 300 mL/min and (d) 400 mL/min. (feeding rate : 120 drops/min, reaction temperature : 25°C , length of magnetic bar : 2.5 cm).

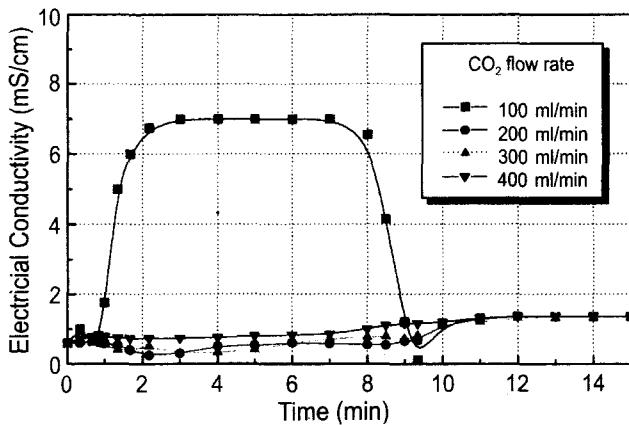


Fig. 6. The change of electrical conductivity according to the flow rates of $\text{CO}_2(\text{g})$ under the $\text{Ca}(\text{OH})_2$ slurry concentration of 1.0 wt% and feeding rate of 120 drops/min.

calcite was synthesized. However, as shown in Fig. 6, when the flow rate of $\text{CO}_2(\text{g})$ was 200~400 mL/min, the electric conductivity was 1.5 mS/cm; when the flow rate of $\text{CO}_2(\text{g})$ was 100 mL/min, the electric conductivity increased by 7.0 mS/cm.

In case of $\text{CO}_2(\text{g})$ be injecting into $\text{Ca}(\text{OH})_2$ slurry (general carbonation process), as shown in Fig. 7.¹⁶⁾ For the primary electric conductivity to decrease shows because the amorphous calcium carbonate is formed in the surface of $\text{Ca}(\text{OH})_2$ at the initial stage of process, which prevents the dissolu-

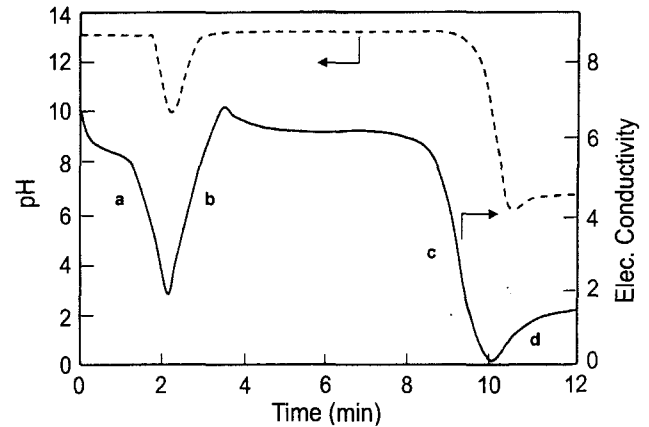


Fig. 7. The change of electrical conductivity and pH $\text{Ca}(\text{OH})_2$ - H_2O - CO_2 system at 25°C by Yamada *et al.*

tion of $\text{Ca}(\text{OH})_2$. As the carbonation process progresses, the electric conductivity increases because the amorphous calcium carbonate is changed into chain-type calcium carbonate and $\text{Ca}(\text{OH})_2$ begins to redissolve again. And, it is assumed that it showed the final decrease in electric conductivity and the crystal of colloidal or rhombohedral calcite is grown consuming the starting materials, $\text{Ca}(\text{OH})_2$, through continuous reaction. Juvekar *et al.*¹⁷⁾ insisted that the electric conductivity is affected by Ca^{2+} ions in an aqueous solution. Therefore, when the feeding rate of $\text{Ca}(\text{OH})_2$

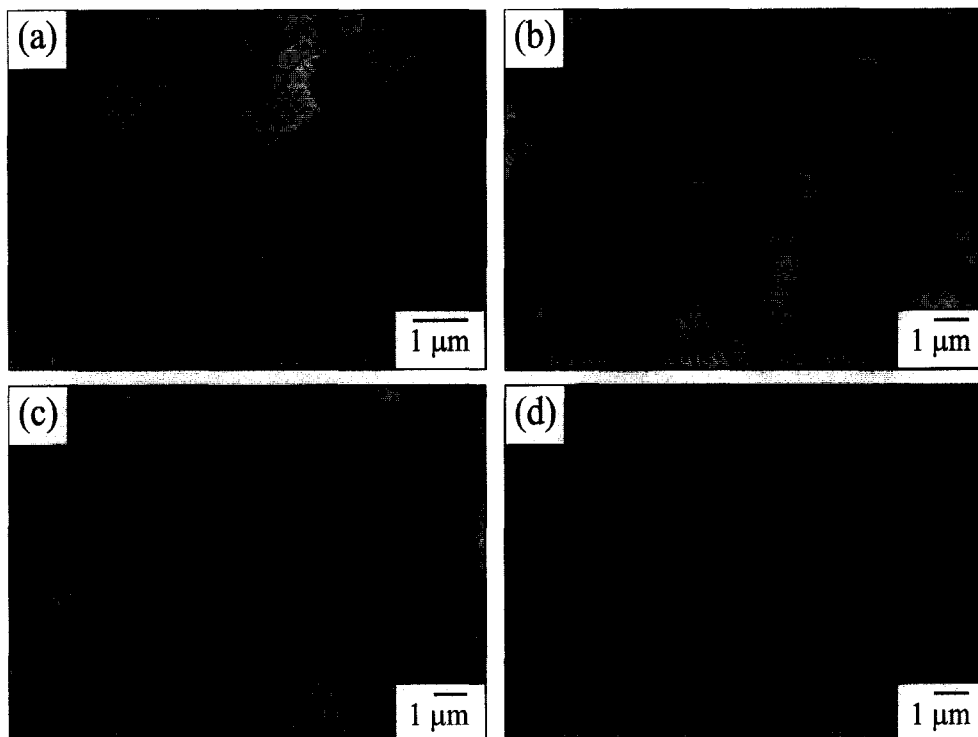


Fig. 8. SEM photographs of PCC synthesized at $\text{Ca}(\text{OH})_2$ slurry of 2.0 wt% according to the flow rates of $\text{CO}_2(\text{g})$; (a) 100 mL/min, (b) 200 mL/min, (c) 300 mL/min and (d) 400 mL/min. (feeding rate : 60 drops/min, reaction temperature : 25°C, length of magnetic bar : 2.5 cm).

slurry is low, the dissolution rate of $\text{Ca}(\text{OH})_2$ became higher by enlarging the interface area of solid and liquid or reducing the dispersed raw materials compared to a liquid. Furthermore, the $\text{CO}_2(\text{g})$ absorption rate gets higher by increasing the partial pressure of gas or enlarging the interface area of solid and liquid. Consequently, it is thought that the low electric conductivity is maintained during the carbonation process because Ca^{2+} ions in solution react with CO_3^{2-} ions to form rhombohedral calcite rapidly.

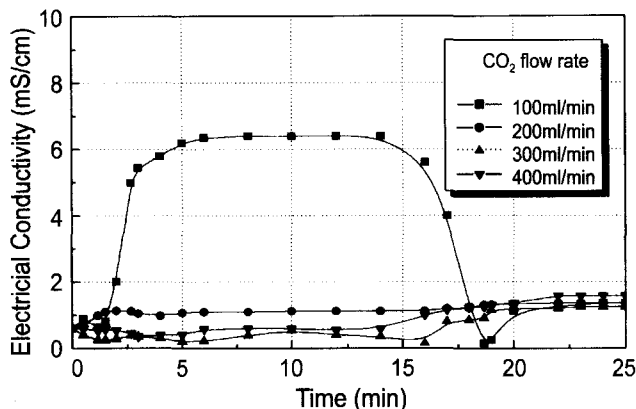


Fig. 9. The change of electrical conductivity according to the flow rates of $\text{CO}_2(\text{g})$ under $\text{Ca}(\text{OH})_2$ slurry concentration of 2.0 wt% and feeding rate of 60 drops/min.

Fig. 8 shows the shape of PCC synthesized according to the flow rate of $\text{CO}_2(\text{g})$ when the reaction temperature, the concentration and the feeding rate of $\text{Ca}(\text{OH})_2$ slurry, the length of magnetic bar were fixed at 25°C , 2.0 wt%, 60 drops/min and 2.5 cm, respectively. At $\text{CO}_2(\text{g})$ flow rate of 100 mL/min, 0.2 μm of prismatic calcite was synthesized; but the flow rate of $\text{CO}_2(\text{g})$ was 200–400 mL/min, the rhombohedral calcite was synthesized. It is assumed that the prismatic calcite is synthesized at the low flow rate of $\text{CO}_2(\text{g})$ because the amount of the dropped $\text{Ca}(\text{OH})_2$ slurry is greater than 1.0 wt%. However, as shown in Fig. 9, when the flow rate of $\text{CO}_2(\text{g})$ was 100–400 mL/min, the electric conductivity curves were the same as in Fig. 6.

Fig. 10 shows the shape of PCC synthesized according to the flow rate of $\text{CO}_2(\text{g})$ when the reaction temperature, the concentration, the feeding rate of $\text{Ca}(\text{OH})_2$ slurry and the length of magnetic bar were fixed at 25°C , 2.0 wt%, 120 drops/min and 2.5 cm, respectively. At all conditions of the carbonation process, the prismatic or the colloidal calcite was synthesized and the agglomeration of the particles appeared seriously. As shown in Fig. 10(b), when the flow rate of $\text{CO}_2(\text{g})$ is 200 mL/min, the plate-shaped calcite was synthesized. However, as shown in Fig. 11, the electric conductivity curves are quite the same as the case when the prismatic calcite was synthesized; the lower the flow rate of $\text{CO}_2(\text{g})$ is, the higher the electrical conductivity is. This result indicates that some possibility of synthe-

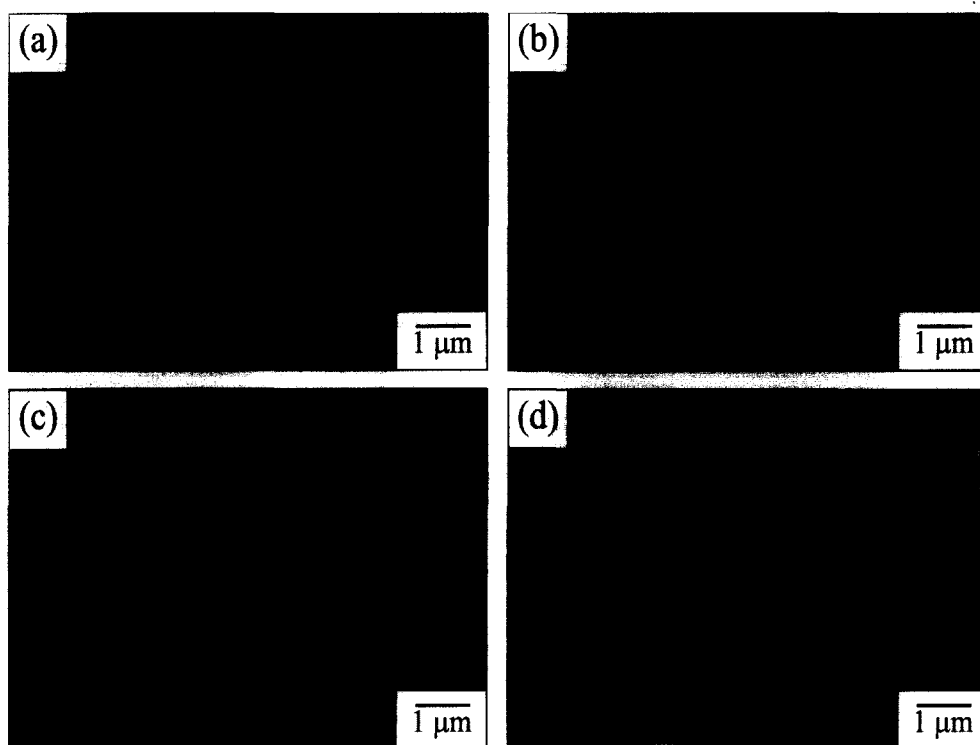


Fig. 10. SEM photographs of PCC synthesized at $\text{Ca}(\text{OH})_2$ slurry of 2.0 wt% according to the flow rates of $\text{CO}_2(\text{g})$; (a) 100 mL/min, (b) 200 mL/min, (c) 300 mL/min and (d) 400 mL/min. (feeding rate : 120 drops/min, reaction temperature : 25°C , length of magnetic bar : 2.5 cm).

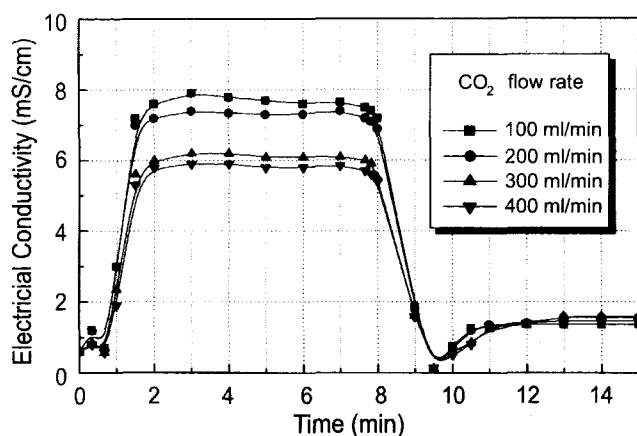


Fig. 11. The change of electrical conductivity according to the flow rates of $\text{CO}_2(\text{g})$ under $\text{Ca}(\text{OH})_2$ slurry concentration of 2.0 wt% and feeding rate of 120 drops/min.

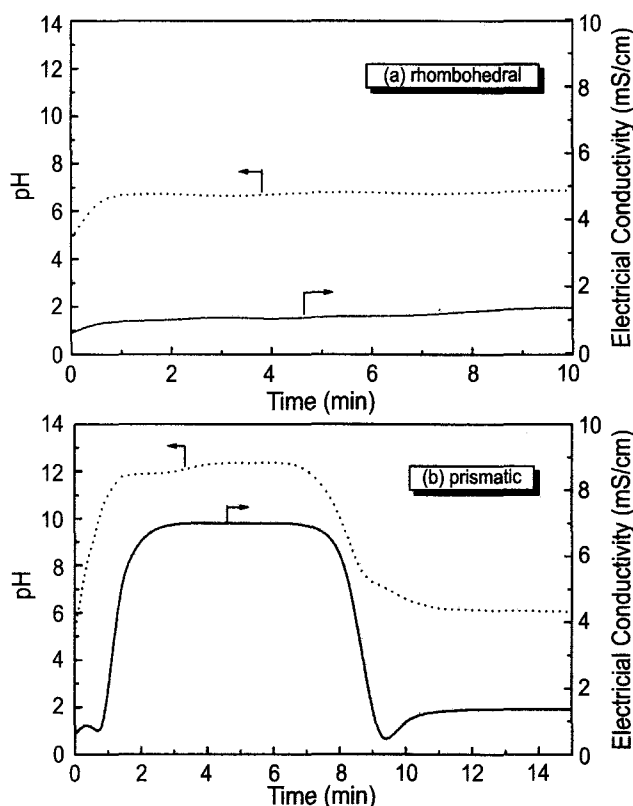


Fig. 12. Changes of pH and electric conductivity; (a) rhombohedral and (b) prismatic calcite.

sizing the plate-shaped calcite through the change in the flow rate of $\text{CO}_2(\text{g})$, the concentration of $\text{Ca}(\text{OH})_2$ slurry, and the stirring rate in $\text{Ca}(\text{OH})_2\text{-CO}_2\text{-H}_2\text{O}$ system by the continuous drop of $\text{Ca}(\text{OH})_2$ slurry into the solution containing $\text{CO}_2(\text{aq})$.

Fig. 12 shows the pH and the electric conductivity curves when the rhombohedral and prismatic calcite are synthesized. In case that the rhombohedral calcite are synthesized, the pH and the electric conductivity are

below 6.5 and 1.5 mS/cm. In case that the prismatic calcite is synthesized, the pH and the electric conductivity curves are the same with the exception of the primary descent of electric conductivity (a stage) as shown in Fig. 7 because the dropped $\text{Ca}(\text{OH})_2$ is dissolved in the solution containing $\text{CO}_2(\text{aq})$ rapidly.

Fig. 13 shows the shape of PCC synthesized according to the flow rate of $\text{CO}_2(\text{g})$ when the reaction temperature, the concentration, the feeding rate of $\text{Ca}(\text{OH})_2$ slurry, and the length of magnetic bar were fixed at 25°C , 1.0 wt%, 120 drops/min, and 5.0 cm, respectively. At $\text{CO}_2(\text{g})$ flow rate of 100 mL/min, the agglomeration of colloidal and prismatic calcite appeared. If the $\text{CO}_2(\text{g})$ flow rate increased, about $1.0\ \mu\text{m}$ of rhombohedral calcite and a very small amount of plate-shaped calcite existed together. It showed the tendency that the more the flow rate of $\text{CO}_2(\text{g})$ is supplied, the more the plate-shaped calcite is synthesized. In other words, it is thought that the changes in magnetic bar (stirring rate) and the quantity of $\text{CO}_2(\text{g})$ flow give a greater effect on the formation of plate-shaped calcite in the same conditions.

Figs. 14 and 15 shows the shape and the XRD results of PCC synthesized according to the concentration of $\text{Ca}(\text{OH})_2$ when the flow rate of $\text{CO}_2(\text{g})$, the reaction temperature, the feeding rate of $\text{Ca}(\text{OH})_2$ slurry and the length of magnetic bar were fixed at 500 mL/min, 25°C , 120 drops/min and 5.0 cm, respectively. At 1.0 wt% of $\text{Ca}(\text{OH})_2$ slurry, the angled agglomeration which grow in a scalenohedral shape from the nucleus, the agglomeration of rhombohedral calcite and a very small amount of hexagonal plate-shaped calcite appeared. On the other hand, when the concentration of $\text{Ca}(\text{OH})_2$ slurry is 2.0~3.0 wt% of $\text{Ca}(\text{OH})_2$ slurry, the shape of calcite synthesized showed plate-shaped calcite of the thickness of $0.1\ \mu\text{m}$ and the width of $1.0\ \mu\text{m}$; When the concentration of $\text{Ca}(\text{OH})_2$ slurry is 3.0 wt%, the shape of PCC synthesized shows the plate-shaped calcite with somewhat distorted particle surface; and when the concentration of $\text{Ca}(\text{OH})_2$ slurry is 4.0 wt%, the shape of PCC synthesized shows the hexagonal plate-shaped calcite of the thickness of $0.1\ \mu\text{m}$ and the width of $1.0\ \mu\text{m}$ and a very small amount of colloidal calcite with $0.1\ \mu\text{m}$. As shown in the Fig. 15, regardless of $\text{Ca}(\text{OH})_2$ slurry concentration, the synthesized powder is calcite. Furthermore, as shown in Fig. 16, the DTA curves of plate-shaped calcite is the same that of traditional calcite, because the contact area of the gas and the liquid is widened as the stirring rate is fast, in other words, the absorption rate of $\text{CO}_2(\text{g})$ is increased, which results in relatively more CO_3^{2-} than the dissolved Ca^{2+} . XRD analysis shows this phenomenon more clearly. In this case, the (110) plane in parallel with the axis *c* of the calcite crystalline has high surface energy than the (001) plane because the layers of Ca^{2+} and CO_3^{2-} are exposed to the (110) plane. The (001) plane has strong absorption and fast crystal growth rate because it is existed Ca^{2+} between CO_3^{2-} . It is known that the (001) plane develops and the plate-shaped calcite is synthesized when the saturation is low. Therefore, the plate-

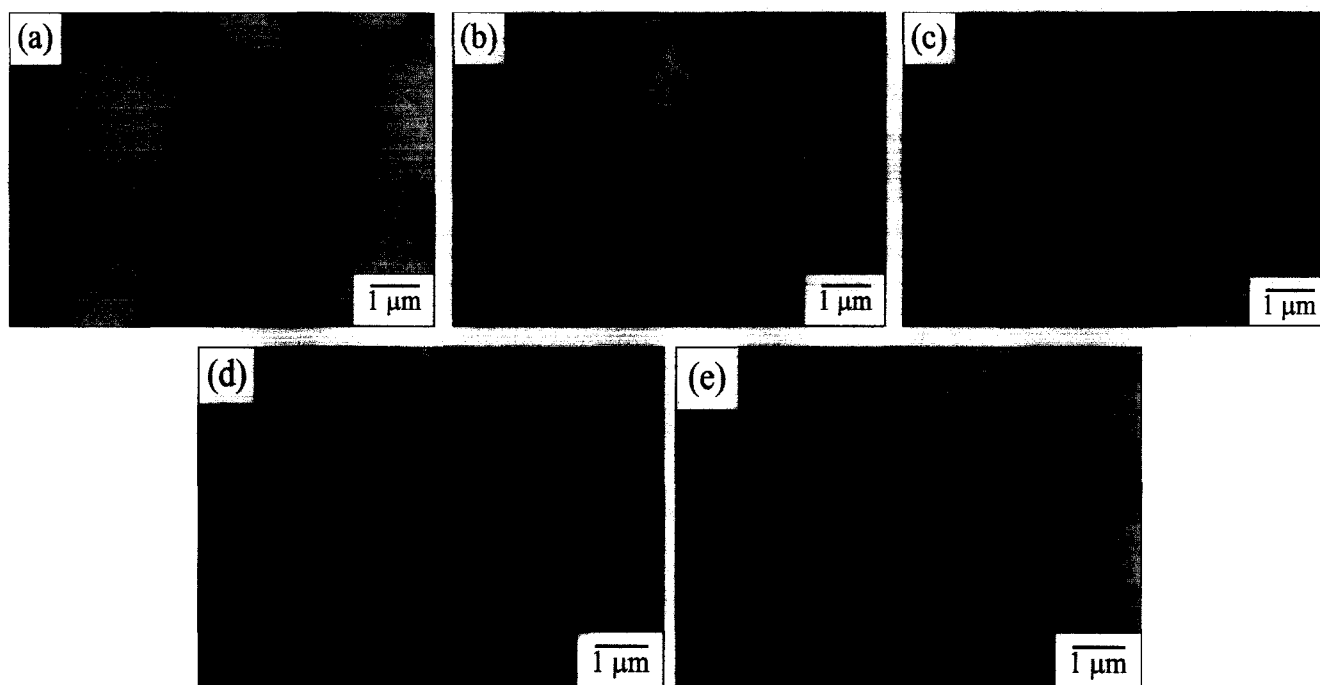


Fig. 13. SEM photographs of PCC synthesized at $\text{Ca}(\text{OH})_2$ slurry of 1.0 wt% according to the flow rates of $\text{CO}_2(\text{g})$; (a) 100 mL/min, (b) 200 mL/min, (c) 300 mL/min, (d) 400 mL/min and (e) 500 mL/min. (feeding rate : 120 drops/min, reaction temperature : 25°C, length of magnetic bar : 5.0 μm).

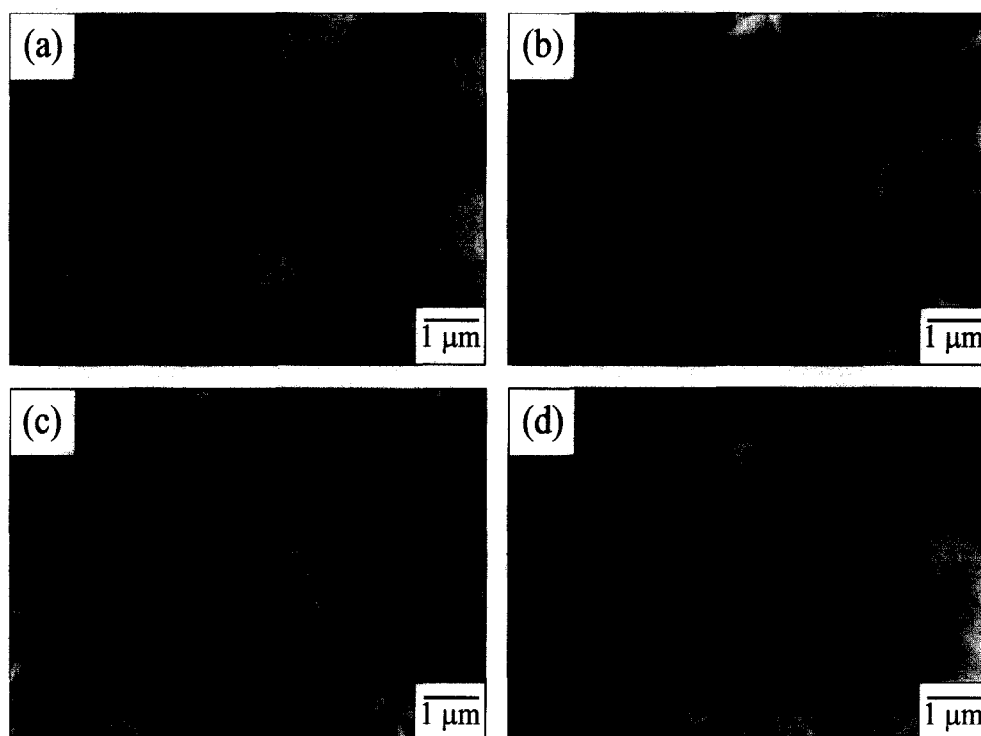


Fig. 14. SEM photographs of PCC synthesized at $\text{CO}_2(\text{g})$ flow rate of 500 mL/min according to the $\text{Ca}(\text{OH})_2$ slurry concentrations; (a) 1.0 wt%, (b) 2.0 wt%, (c) 3.0 wt% and (d) 4.0 wt%. (feeding rate : 120 drops/min, reaction temperature : 25°C, length of magnetic bar : 5.0 μm).

shaped calcite(CaCO_3) can be made by the continuous $\text{Ca}(\text{OH})_2$ slurry drop in the solution containing $\text{CO}_2(\text{aq})$ like

the plate-shaped basic calcium carbonate($\text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2 \cdot \text{nH}_2\text{O}$), intermediate product, in the carbonation

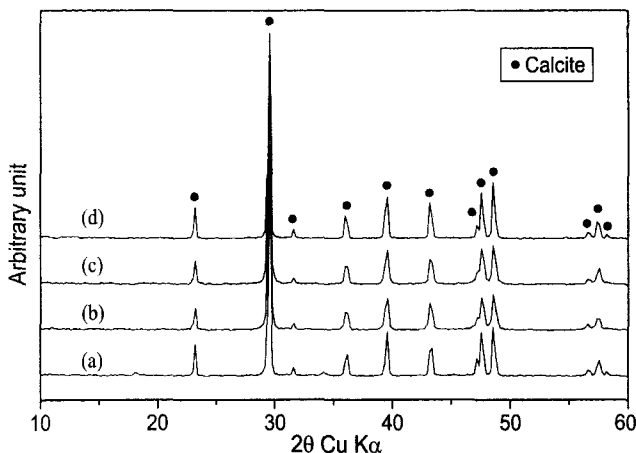


Fig. 15. XRD results of PCC synthesized at $\text{CO}_2(\text{g})$ flow rate of 500 mL/min according to the $\text{Ca}(\text{OH})_2$ slurry concentrations; (a) 1.0 wt%, (b) 2.0 wt%, (c) 3.0 wt% and (d) 4.0 wt%. (feeding rate : 120 drops/min, reaction temperature : 25°C, length of magnetic bar : 5.0 cm).

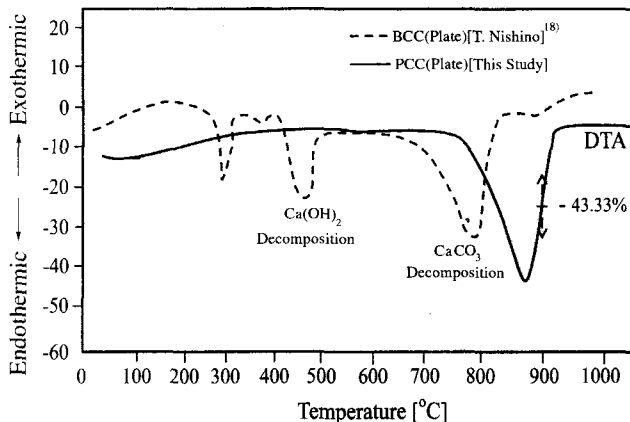


Fig. 16. DTA results of plate-shape calcium carbonate.

process by Yamada *et al.*^{14,15)} that appeared the DTA curve as shown in Fig. 16.

4. Conclusions

The PCC powders was synthesized by employing the continuous drop method of $\text{Ca}(\text{OH})_2$ slurry in the solution containing $\text{CO}_2(\text{aq})$, a new carbonation process. The following conclusions were made from according to the concentration and the feeding rate of $\text{Ca}(\text{OH})_2$ slurry, the flow rate of $\text{CO}_2(\text{g})$, and the length of magnetic bar(stirring rate).

When the absorption rate of $\text{CO}_2(\text{g})$ was higher than the dissolution rate of $\text{Ca}(\text{OH})_2$, the growth into calcite crystal plane was dominant and about 1.0 μm of the rhombohedral calcite was synthesized. Also, when the amount of the feeded $\text{Ca}(\text{OH})_2$ was greater than the absorption rate of $\text{CO}_2(\text{g})$, new nuclei were formed with the crystal growth and about 0.1 μm of the prismatic calcite was synthesized.

In case of the rhombohedral calcite is synthesized, the primary electric conductivity and pH were maintained below

1 mS/cm and 6~7 until the carbonation reaction was complete, while in case of the prismatic calcite is synthesized, the electric conductivity and pH increased in the primary stage, maintained 78 mS/cm and 12~13 in the middle stage but decreased by 1.6 mS/cm and 6.5 in the completion of reaction.

When the flow rate of $\text{CO}_2(\text{g})$ was 100 mL/min ; the concentration of $\text{Ca}(\text{OH})_2$ slurry, 1.0 wt%; the drop rate of $\text{Ca}(\text{OH})_2$ slurry, 120 drops/min; the temperature, 25°C; and the length of magnetic bar, 2.5 cm, the shape of calcite showed colloidal and spherical agglomerate. On the other hand, when the flow rate of $\text{CO}_2(\text{g})$ was 200~500 mL/min, the shapes of calcite showed the mixture of rhombohedral and plate-shaped calcite.

When the flow rate of $\text{CO}_2(\text{g})$ was 500 mL/min; the drop rate of $\text{Ca}(\text{OH})_2$ slurry, 120 drops/min; the temperature, 25°C; and the length of magnetic bar, 5.0 cm, at 1.0~3.0 wt% of $\text{Ca}(\text{OH})_2$ slurry, the shape of PCC showed plate-shaped calcite, but at 4.0 wt% of $\text{Ca}(\text{OH})_2$ slurry, the shape of PCC showed hexagonal plate-shape calcite of the thickness of 0.1 μm and the width of 1.0 μm .

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