Synthesis of Single Phase Aragonite Precipitated Calcium Carbonate in $Ca(OH)_2$-Na_2CO_3-NaOH Reaction System

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Abstract−The formation behavior of precipitated calcium carbonate polymorphs was investigated in three different supersaturation levels. Because the most easily adjustable and influential variable determining supersaturation is the ion concentration of the major reactants - Ca^{2+} and CO_3^{2-} - the supersaturation can be adjusted by changing the ion concentration of these two ions. At high supersaturation, free energy is necessary for a decrease in nucleation, promoting the formation of a sphere-shaped vaterite, while aragonite and calcite were seen to co-exist at medium supersaturation. At low supersaturation, aragonite was mainly formed by mixing with some calcite. Hence, we considered that lower supersaturation was necessary to obtain a single phase aragonite. Furthermore, we found that the solubility of $Ca(OH)_2$ was decreased with the addition of NaOH by a common ion effect. Thus, it is possible to perform an experiment at a lower Ca^{2+} concentration. The aragonite was synthesized by adding the Na_2CO_3 solution to the $Ca(OH)_2$ slurry containing several concentrations of NaOH solution at 75 °C and under the addition rate of Na_2CO_3 at 3 ml/min. The formation yield of calcite decreased when the NaOH concentration was increased. In conclusion, in the case of the reaction of the 2.5 M NaOH solution over 210 minutes, single-phase aragonite with an aspect ratio of 20 was obtained.

Key words: Precipitated Calcium Carbonate, Aragonite, Solution Process, Supersaturation, NaOH

INTRODUCTION

Precipitated calcium carbonate (PCC) is fine particles that are synthesized either by carbonation and/or solution process after calcination and hydration reaction of limestone [Arai and Yasue, 1990; Tanaka, 1990]. Generally, commercially available PCC is synthesized by a carbonation process in which hydrated lime is reacted with pure CO_2 or CO_2 containing gas. However, it is difficult to control precisely the phase, shape, and aspect ratio of the crystal. An alternative synthetic method for PCC is a solution process by which Na_2CO_3 is reacted with hydrated lime. PCC is obtained as the main product and recyclable NaOH is produced as a by-product of the solution process. In this solution process the phase and morphology can be controlled more easily by controlling supersaturation than in the carbonation process [Kim et al., 2004]. Calcium carbonate is used in various industrial fields as an additive in medical supplies, foods, paper, plastics, printing ink, etc [Wang et al., 1999]. In particular, aragonite has a slightly greater average index of refraction than calcite, and possesses a needle-like characteristic shape. Hence, aragonite is expected to have higher performance properties as a filler in the paper and plastics industries when compared with calcite [Dalas et al., 1988; Konno et al., 2002]. Furthermore, aragonite has a needle-like shape with a very large aspect ratio [Sohnel and Mullin, 1982], so it can be used in various high-tech industrial fields as a new inorganic material with high functionality and high added value. Recently, many studies have been conducted on the synthesis of aragonite precipitated calcium carbonate used in many

industries; however, its synthesis mechanism has not been clearly understood. In most cases, there was a problem in realizing the same result even under the same experimental conditions since the studies focused on experimental variables. Konno et al. reported that the precipitation of aragonite increased as the $Ca(OH)_2$ suspension was increased, occurring predominantly in the presence of NaOH [Konno et al., 2003]. Kitamura et al. reported that highly alkaline solutions are advantageous for the nucleation of aragonite, and that at a pH larger than about 13.5 the nucleation of aragonite begins [Kitamura et al., 2002]. Hu and Deng demonstrated that magnesium ions increase the aragonite fraction but slightly decrease the aspect ratio, and that a high synthesis temperature is favorable to both the aragonite fraction and its aspect ratio [Hu and Deng, 2004]. Kawano et al. reported a method of producing sediment selectively by maintaining the components in a solution higher than the solubility of the products [Kawano et al., 2002]. Since these studies were performed within a narrow boundary of supersaturation, they are insufficient for an understanding of the comprehensive trends of the three polymorphs of calcium carbonate.

Therefore, the purpose of this study was to synthesize single phase aragonite PCC by a solution process using $Ca(OH)_2$ slurry and Na_2CO_3 solution as the main reactants. First, the formation mechanism of the PCC polymorphs was investigated from the kinetic point of view; then, based on the formation mechanism of the PCC polymorphs and the role of NaOH in the bulk solution, the optimum synthetic condition of single-phase aragonite PCC was intensively investigated.

EXPERIMENTAL

The reactor used a cylinder made of Pyrex glass with a diameter

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of 10 cm and a volume of 1.0 L, with a 4 cm long impeller attached. The temperature in the reactor was maintained constantly with a water bath (Jeio Tech, WB02). In order to adjust the concentration of the CO_3^{2-} ions, 0.5M Na_2CO_3 solution (150 ml) was added at a rate of 3 ml/min to the $Ca(OH)_2$ slurry (50 ml) at the same time for a lower concentration. All of the experiments were conducted at 75 °C under a constant agitation speed of 400 rpm. The $Ca(OH)_2$ solutions were divided into three parts following the concentration of Ca^{2+}: a high-concentration the Ca^{2+} solution was prepared by adding HNO_3 to 1.5 M $Ca(OH)_2$ slurry and dissolving it completely; the medium-concentration Ca^{2+} solution consisted of 1.5 M slurry only, and the low-concentration Ca^{2+} solution was prepared by adding NaOH to $Ca(OH)_2$ slurry. In order to adjust the concentration of the CO_3^{2-} ions, changes were made to the method of adding the

0.5 M Na_2CO_3 solution. To maintain a high CO_3^{2-} ion concentration, the 1.5 M Na_2CO_3 solution was simultaneously added to the $Ca(OH)_2$; for a lower concentration, it was injected gradually at the rate of 3 ml/min. The synthesized samples were washed with ethanol two to three times to remove any residual ion components, then filtered and dried in an oven at 80 °C. The dry precipitates were characterized by XRD (MacScience Co. M18XHF-SRA) using CuKα₁ radiation, and the shapes of the particles were observed by SEM. A schematic diagram and a flow chart for this experiment are shown in Fig. 1.

RESULTS AND DISCUSSION

In general, supersaturation is directly related to formation behav-
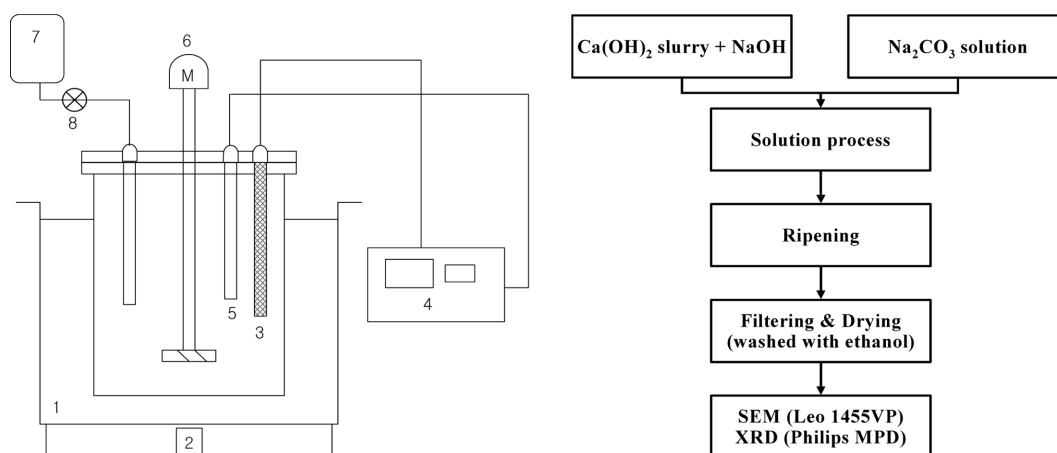

Fig. 1. Schematic diagram and a flow chart for this experiment : (1) Reactor (2) Water bath (3) pH electrode (4) pH meter (5) Thermometer (6) Stirrer (7) Na₂CO₃ solution (8) Valve.
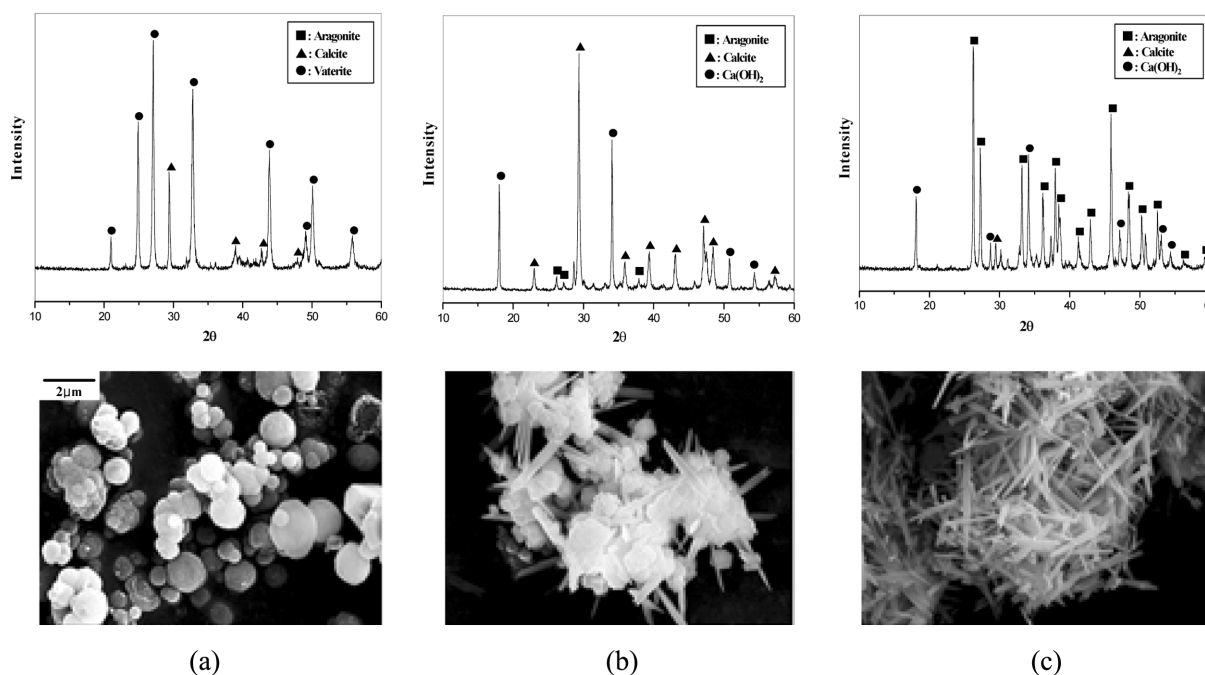

(a)   (b)   (c)

Fig. 2. XRD patterns and SEM photographs of precipitated calcium carbonate synthesized in the three reaction systems; Reaction systems for the supersaturation levels (a) High, (b) Medium, (c) Low.

ior of PCC polymorphs, and supersaturation in precipitation reaction depends on the ion concentration of the reactants present in the solution. The range of supersaturation was adjusted to three different levels: high, medium and low. Formation properties of PCC synthesized in the three reaction systems are shown Fig. 2. At high supersaturation, both Ca^{2+} and CO_3^{2-} had a high concentration (Fig. 2a), the nucleation rate increased, and the size of the critical nuclei then became smaller. This result occurs because vaterite has the smallest particle size among PCC polymorphs and it has spherical shapes which free energy necessary for critical nucleation is the smallest. Fig. 2b shows the result for medium supersaturation. In this reaction, calcite was mainly formed and some aragonite was mixed with it. In particular, the existence of $Ca(OH)_2$ peaks should be noted. This suggests that the dissolution rate of $Ca(OH)_2$ is slower than the formation rate of calcium carbonate, and that the dissolution reaction of $Ca(OH)_2$ is the rate-limiting step of the overall reaction. Fig. 2c shows the results of the reaction at low supersaturation; the supersaturation of this reaction was lowered by adding Na_2CO_3 solution to 1.5 M $Ca(OH)_2$ slurry without HNO_3 at 3 ml/min. In this case, aragonite was mainly formed, mixed with some calcite.

Consequently, we confirmed that aragonite was mainly formed in low supersaturation. From these results, the formation mechanism of PCC polymorphs was investigated from a kinetic point of view. The critical free energy necessary for stabile nucleation can be expressed by the following Eq. (1) [Langerak et al., 1999].

$$\Delta G_{cr} = \frac{\beta v^2 \gamma^3}{(k T \ln S)^2} \qquad (1)$$

(β : shape factor, v : molecular volume, γ : surface tension, k : Boltzmann's constant, T : temperature, S : supersaturation)

In this equation, nucleation energy depends on the shape factor and supersaturation at a fixed temperature. To begin with, regarding the three polymorphs of calcium carbonate - vaterite, calcite, and aragonite - their representative shapes are spherical, cubic and needle-like, and their shape factors are 16.75, 32.00 and 109.76, respectively (Fig. 3) [Nyvlt, 1985].

Next, assuming that the temperature remains constant, a variable to consider is supersaturation, which can be expressed by Eq. (2) [Kitamura et al., 2002],

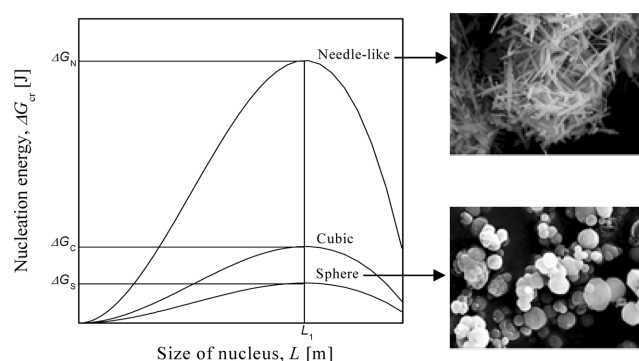$$S = \left(\frac{a^{Ca^{2+}} a^{CO_3^{2-}}}{K_{sp}} \right)^{1/2} \qquad (2)$$

Fig. 4. Critical free energy for nucleation having size of L_1 for the polymorphs of precipitated calcium carbonate.

($a^{Ca^{2+}}$: activity of a calcium ion, $a^{CO_3^{2-}}$: activity of carbonate, K_{sp} : solubility product of calcium carbonate)

Ion activity is expressed as the product of the activity coefficient and ion concentration in the solution. Fig. 4 shows the plotting of the critical energy necessary for nucleation by using these values. The free energy necessary for the formation of a spherical, cubic, and needle-like nucleus with the size of the characterization dimension L_1 is G_s, G_c, and G_n respectively. Thus, we can see that the free energy needed for the formation of calcium carbonate polymorphs increases for vaterite, calcite, and aragonite.

Based on these results and the relevant theoretical background, it was considered that lower supersaturation was necessary to obtain a single-phase aragonite. As can be seen from Eq. (2),

Ion concentration in this solution should be low because supersaturation greatly depends on the ion concentration of the reactants present in the solution. In the first place, NaOH was added to the solution to adjust the Ca^{2+} ion concentration. If NaOH is added to $Ca(OH)_2$ slurry, the solubility of $Ca(OH)_2$ is significantly decreased by a common ion effect; thus, it is possible to perform an experiment at a lower Ca^{2+} concentration. We added 2.5 to 6.0 M NaOH to the $Ca(OH)_2$ slurry to confirm whether single-phase is created in some Ca^{2+} ion concentration (Fig. 5). In this reaction, the formation yield of aragonite was increased with the increasing of NaOH up to 4.5 M, and it shows a tendency to decrease in concentrations above 4.5 M NaOH; whereas calcite decreased with increases in the NaOH concentration and disappeared altogether at 6.0 M. Un-reacted Ca $(OH)_2$ showed a tendency to increase with an increase in the NaOH concentration. The reason why a quantity of Ca $(OH)_2$ remaining un-reacted increases as the addition of NaOH is increased may be attributed to the fact that the quantity of $Ca(OH)_2$ that can be dissolved for 30 minutes falls owing to a decrease in solubility.

Formation behavior of PCC polymorphs can be controlled by controlling the calcium and carbonate ions, and that aragonite is synthesized at low supersaturation. The addition rate of Na_2CO_3 had to be fixed at 3 ml/min to decrease the of CO_3^{2-} ions concentration (Fig. 6). In the same way, in this reaction, the un-reacted Ca $(OH)_2$ was increased with the increase in NaOH. The reason why is that the quantity of Ca^{2+} ion by solubility decrease in $Ca(OH)_2$ is decreased with the increasing in NaOH concentration. So, the formation yield of calcite decreased continually, disappearing altogether at 2.5 M. With the increase of NaOH, the aspect ratio of aragonite
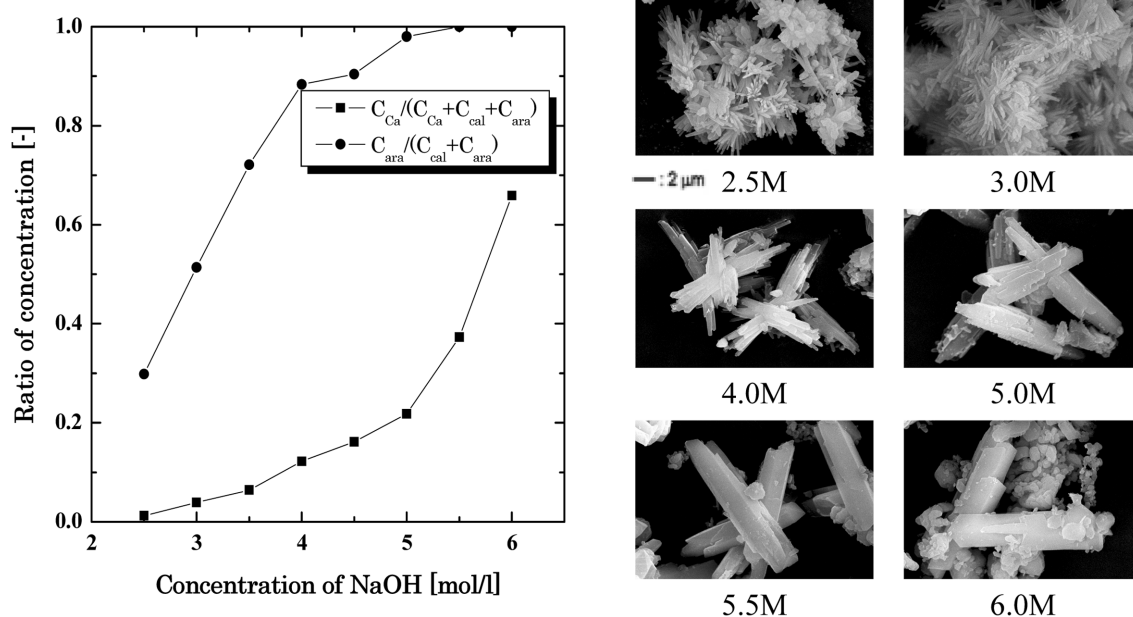
Body	a	b	β (4b3/27a2)
Tetrahedron	0.182	2.309	-
Sphere	0.524	3.142	16.75
Octahedron	0.471	3.464	-
Six-sided prism	2.60	11.2	-
Cube	1.0	6.00	32.00
Prism	10.0	2.00	-
Platelet	0.2	2.80	-
Needle-like	10.0	42.00	109.76

Vaterite

Calcite

Aragonite

Fig. 3. Shape factors for various geometries.

Fig. 5. Ratio of concentration and SEM images of samples obtained by simultaneous reaction in various concentrations of NaOH for 30 minutes.
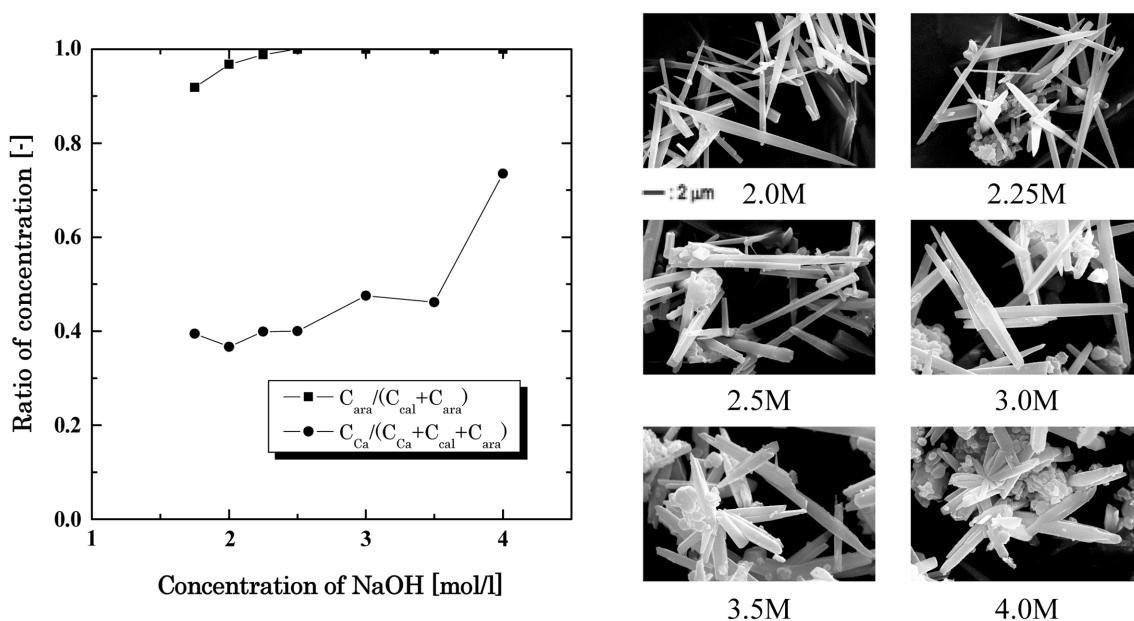

Fig. 6. Ratio of concentration and SEM images of samples obtained in several concentrations of NaOH.

decreased with the increase in thickness. Therefore, based on these results, we confirmed the changes of formation yield of the samples obtained in 2.5 M NaOH solution as a function of the reaction time (Fig. 7).

In this reaction, calcite did not appear and the aragonite nuclei were formed about 10 minutes after the start of the reaction. Subsequently, single-phase aragonite with an aspect ratio of 20 was obtained with a concentration of 2.5 M NaOH and the addition rate of Na₂CO₃ at 3 ml/min over 210 minutes. In addition, there is a tendency for the particle size and aspect ratio to increase with the reaction time. However, it was considered that the dissolution reaction

of Ca(OH)₂ is the rate-limiting step of the overall reaction because Ca(OH)₂ remained despite the termination of the reaction. This result indicates that the dissolution rate of Ca(OH)₂ is slower than the formation rate of calcium carbonate. We can show that un-reacted Ca (OH)₂ remained despite the termination of the reaction over 50 min, and that the contents of the unreacted Ca(OH)₂ disappeared in a reaction time of 210 minutes. Therefore, it has been concluded that the dissolution rate of Ca(OH)₂ is the rate limiting step of the overall reaction. In conclusion, it was confirmed that the PCC polymorphs and the formation yield were controlled by the supersaturation following the concentration of calcium and carbonate ions.
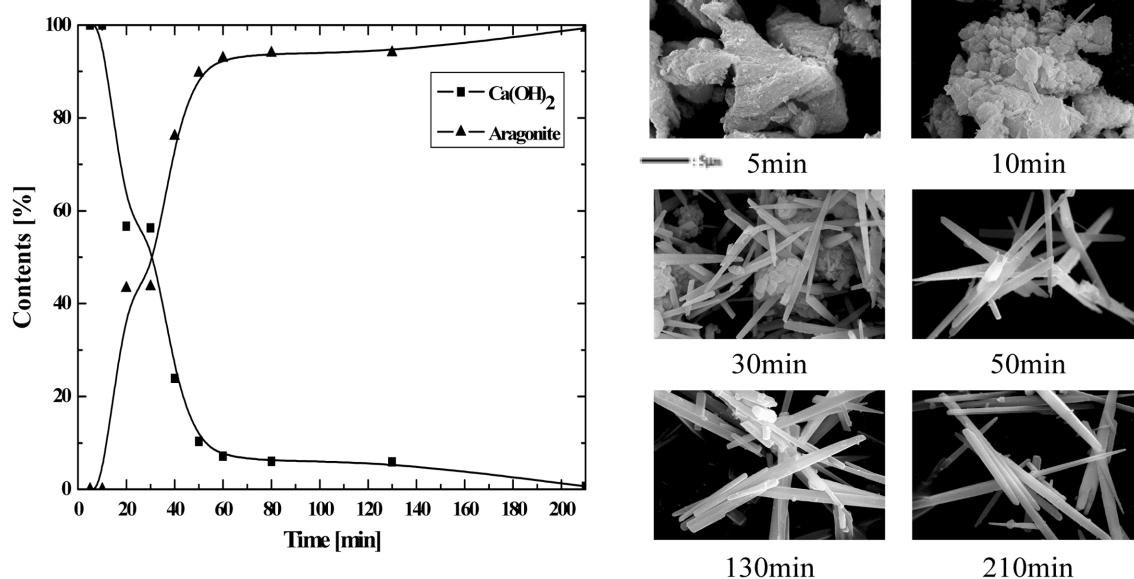
Fig. 7. Formation yield and SEM images of samples obtained in 2.5 M NaOH solution as a function of reaction time.

CONCLUSION

In this study, from results obtained by adjusting experimental variables based on the kinetics, the formation mechanism of precipitated calcium carbonate was investigated. Ranges of the supersaturation for formation of the three polymorphs were classified by considering the mechanism. At high supersaturation, vaterite was mainly synthesized even though some calcite was mixed. It was realized that vaterite was mainly synthesized in the lowest region of nucleation energy that is the highest nucleation rate among three polymorphs. Secondly, at medium supersaturation, calcite was formed primarily. This result is because that supersaturation in this reaction system was lowered together with a lowered nucleation rate, and the free energy for stable nucleation finally passed over the range of free energy for nucleation of the vaterite. Lastly, at low supersaturation, aragonite predominated. At this point, the addition of NaOH to adjust supersaturation lowers the solubility of $Ca(OH)_2$, a main reactant by common ion effect. The addition of NaOH reduced Ca^{2+} ion concentration in the solution. As the reaction continued, the formation yield of aragonite was increased, whereas that of calcite decreased continually and disappeared at 2.5 M. It is considered that lower supersaturation at the early stage of reaction and sufficient aging time would be necessary to obtain single phase aragonite. In conclusion, single phase aragonite was obtained in the 2.5 M NaOH solution for 210 minutes. Also, the rate limiting step in the calcium carbonate synthesis reaction by the solution method is the dissolution reaction of $Ca(OH)_2$; hence it is to be expected that single-phase aragonite was produced by adjusting the Ca^{2+} concentration at low concentration of CO_3^{2-}.

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