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Synthesis of calcium carbonate in ethanol-ethylene glycol solvent

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Calcium carbonate has been synthesized from $Ca(OH)_2$ in ethanol-ethylene glycol solvent by carbonation and aging process. Carbonation in organic solvent caused $Ca(OH)_2$ to form a white gelatinous $CaCO_3$ product, which was then destroyed by aging process. The calcium carbonate precipitated and agglomerated in these steps was composed of stable calcite, and meta-stable aragonite and vaterite. These meta-stable particles were shaped either peanut-like or sphere. When a little amount of distilled water was added to organic solvent, the meta-stable phases remarkably decreased, whereas stable calcite increased. When $Ca(OH)_2$ was carbonated with water addition increased to 2 vol% of the total organic solvent and aged at 40°C, only rhombic calcite was synthesized.

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1. Introduction

Calcium carbonate is used commercially in various industrial applications such as fillers for plastics, rubber, paper, glass manufacture, and sulfur dioxide scrubbing.[1)] The possible applications of $CaCO_3$ products should be determined by specific properties such as particle size, morphology, specific surface area, brightness, and chemical purity.[2),3)] Morphological property is a decisive factor for some applications. Hence the careful control of particle shape should be required in particular case.[4)] Toward this end, morphological modification and formation mechanism have been investigated extensively.[5)–7)]

The shape of $CaCO_3$ particles changes, depending on additive, solvent, and reaction conditions such as temperature, pH, and induction time. Some uncommon shapes formed by liquid–liquid or liquid–gas reactions through the selection of adequate synthesis conditions were reported.[8)–12)] Calcium carbonate is known to have three phases, namely stable calcite, and meta-stable aragonite and vaterite at room temperature and normal pressure. The particle shape of these phases differs from each other. The morphology of calcite, aragonite and vaterite are known to be rhombohedral, needle- or spindle-shaped and spherical, respectively. The meta-stable phases, however, are dissolved well in aqueous solution compared to stable calcite, so that it is hard to get these meta-stable aragonite and vaterite. Calcite can be synthesized through the phase transformation of the meta-stable phases.[13)] The meta-stable phases are transformed to stable calcite when the solubility of calcium carbonate in solvent is high. It means that meta-stable phases can be obtained if a suitable solvent in which calcium carbonate has a low solubility is chosen.

Synthesis processing of calcium carbonate in ethanol-ethylene glycol solutions is almost similar to that in general aqueous solution. CO_2 and $Ca(OH)_2$ don't directly react each other. Rather, $Ca(OH)_2$ and CO_2 gas are dissolved in aqueous solutions and ionized and then $CaCO_3$ is precipitated according to the following reactions:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

$$\text{Overall reaction: } Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

In this work, calcium carbonate was synthesized in ethanol-ethylene glycol solvent by carbonation. After carbonation, $CaCO_3$ suspension changed into a white gelatinous product, which was destroyed by aging process. Ethanol is known to stabilize vaterite and hider its transformation into calcite.[8)] Ethylene glycol has been used to modify the morphology of calcium carbonate.[14)] The phase and shape of calcium carbonate synthesized in organic solvent which has a low solubility were investigated. When a little amount of distilled water was added to solvent in order to increase solubility, it was investigated how the phase and shape of particles changed.

2. Experimental

2.1 Synthesis of calcium carbonate

20 g of $Ca(OH)_2$ was added to a mixture containing 450 ml of ethanol and 50 ml of ethylene glycol at room temperature. The resulting solution was then stirred using a mechanical stirrer at 600 rpm. After the pH was stabilized at 12, CO_2 gas was injected into a reactor at a velocity of 500 ml/min to form an amorphous $CaCO_3$ gel. The gel obtained was then transferred to a Pyrex bottle and aged at 3 different temperatures, i.e. 40°C, 60°C, and 100°C. After 3 d at these temperatures, the solid product was separated and collected by centrifugation, washed with ethanol and dried at room temperature in a desiccator.

For the synthesis of calcium carbonate with water addition, distilled water in 4 different volumes, 1, 5, 10, and 20 ml which are equivalent to 0.2, 1, 2 and 4 vol% of the total solvent was added to each mixture of 450 ml of ethanol and 50 ml of ethylene glycol with 20 g of $Ca(OH)_2$. The carbonation reaction then occurred. The resulting gelatinous product was aged at 40°C for 3 days. The final product was collected in the same separation procedure mentioned above.

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2.2 Characterizations

X-ray diffraction (XRD) patterns were obtained with a diffractometer (MAC Science M18XHF-SRA) using Cu Kα radiation at a scanning speed of 0.08° in 2θ per second. Microstructural observation was made using a scanning electron microscope (SEM, JEOL 6630) and a field-emission scanning electron microscope (FE-SEM, JEOL 6360F) at an accelerating voltage of 15 kV.

3. Results and discussion

3.1 pH and temperature as a function of carbonation time, and product characterization

Figure 1 shows the curves of pH and temperature variation during the carbonation in ethanol-ethylene glycol. These curves are almost same as those of reacting solution when the carbonation occurs in aqueous solution. However, the ionization of CO_2 gas in organic solvent was slower than that in aqueous solution because H_2O was not involved in it. H_2O molecules seem to be supplied by the reaction of $Ca(OH)_2$ which might act as a self catalyst. Though the solvent does not have H_2O molecules, but it can be supplied from $Ca(OH)_2$. When 20 g of $Ca(OH)_2$ is dissociated by itself, 0.27 mol of H_2O can be obtained. The 0.27 mol of H_2O can dissolve CO_2 gas, and carbonation occurs. The amount of water formed from the $Ca(OH)_2$ is so small that it takes more time to start and complete the carbonation. Therefore, the reaction pH was kept at about 12 for the initial few minutes.

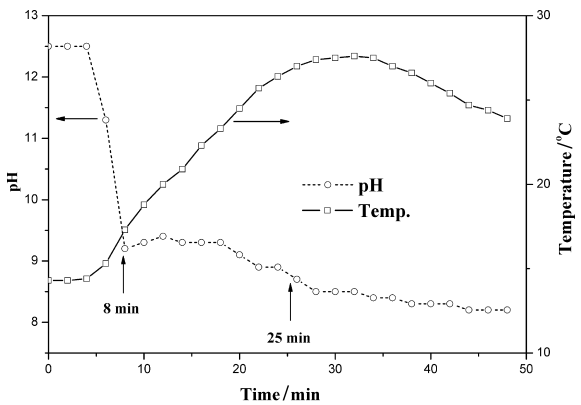

Fig. 1. pH and temperature profiles with time during the carbonation.

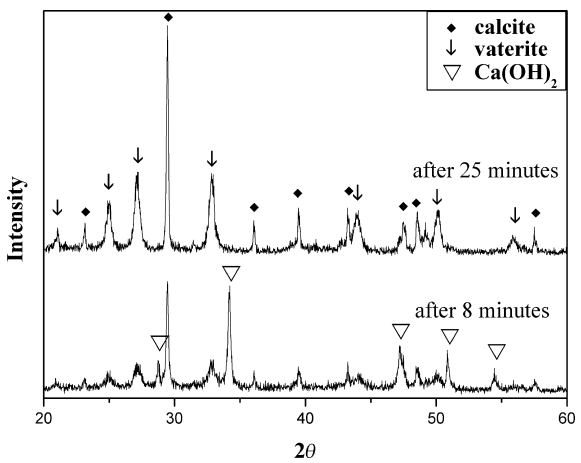

Fig. 2. XRD patterns of particle collected from reaction solution during carbonation.

After injecting CO_2 gas for 5 min, the pH decreased drastically. From this state, the injected CO_2 gas was ionized into CO_3^{2-} and then calcium carbonate started to be precipitated.

The temperature of the solvent was found to increase from 14°C to 27°C in 32 min by the exothermic nature of the carbonation. This indicates that about 30 min is enough to complete the carbonation of $Ca(OH)_2$ in the organic solvent.

The XRD patterns of calcium hydroxide carbonated for 8 and 25 mins in ethanol-ethylene glycol are shown in **Fig. 2**. When the pH of the reacting solution was dropped to about 9 in 8 mins, the particles in suspension are found to be composed of calcite and vaterite as well as unreacted $Ca(OH)_2$. However, in 25 mins, all the $Ca(OH)_2$ feed was completely transformed to calcium carbonate precipitating as stable calcite and meta-stable vaterite. This confirms that the carbonation has already been completed in 25 mins.

The morphology of the calcium carbonate particles carbonated for 8 mins and 25 min is shown in **Fig. 3**. The shape of the individual particles carbonated for 25 min is still similar to that for 8 mins though it is heavily agglomerated.

When the injection of CO_2 gas was kept for 60 min, the $CaCO_3$ suspension became highly viscous and then was suddenly changed into a gelatinous product. Carmona et al.[15] reported this gelatinous product formed in the $Ca(OH)_2$–CO_2–H_2O system by the strong hydration trapping of OH^- and other solution components at the amorphous $CaCO_3$–$Ca(OH)_2$ interface. In our study, the XRD patterns of particles before gel formation as shown in Fig. 2 reveal broad peaks of vaterite. With these broad peaks, we may conclude the gelatinous product includes a large portion of amorphous calcium carbonate.[16]

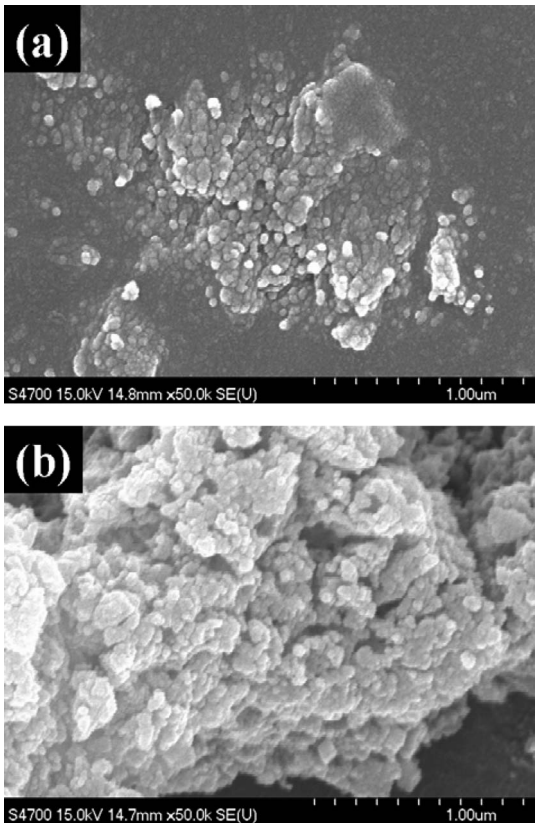

Fig. 3. FE-SEM images of precipitates carbonated for (a) 8 min and (b) 25 min.

3.2 Aging of calcium carbonate gel at different temperatures

A gel was collected after 1 h carbonation and aged for 3 d at 3 different temperatures, 40°C, 60°C and 100°C. The X-ray pattern and morphology of calcium carbonate aged at 40°C are shown in **Fig. 4**. The crystals in the precipitate are identified as three phases, i.e. stable calcite, and meta-stable aragonite and vaterite. Meta-stable aragonite can not be detected during the carbonation alone as shown in Fig. 2. After aging at 40°C, however, an appreciable amount of aragonite was produced by the transformation of amorphous calcium carbonate as a gelatinoid though the calcite is still the major phase as shown in Fig. 4(a). We can find same particles shaped like a peanut in Fig. 4(b). The calcium carbonate aged at 40°C is composed of rhombic calcite and peanut-like particles though the particles are agglomerated during the carbonation alone.

The XRD pattern and morphology of the precipitate aged at 60°C are shown in **Fig. 5**. As the aging temperature increases, the X-ray diffraction intensity of aragonite becomes stronger than that of calcite. Aragonite and vaterite exist as the major phases which are meta-stable, while a small amount of stable calcite still remains. The two meta-stable phases in Fig. 5(a) are not separated clearly and the highest peaks of aragonite and vaterite are nearly overlapped each other. It indicates that these two phases are poorly crystallized. The morphology of the calcium carbonate in Fig. 5(b) is mostly spherical and partly columnar, which is quite different from that aged at 40°C.

The XRD pattern and morphology of the precipitate aged at 100°C are also shown in **Fig. 6**. The calcium carbonate aged at 100°C is composed of mostly meta-stable phases and partly calcite. The amount of each phase seems to be almost the same as that aged at 60°C. As seen in Fig. 6(a), however, the highest peaks of aragonite and vaterite are almost separated each other. In other words, the meta-stable calcium carbonate is well crystallized, consisting of mainly spherical and partly spindle-like particles.

3.3 Addition of different water amount in solvent

When distilled water was added to ethanol-ethylene glycol solvent and $Ca(OH)_2$ began to react with CO_2 gas, $CaCO_3$ suspension was first formed and then changed into a gel. But it took a shorter time to form a gel compared with that without water and the gel structure was destroyed very readily by aging. As the amount of the water addition was increased to 4 vol% of the total organic solvent, the gel was destroyed in a few minutes at room temperature even before aging. During carbonation, CO_2 gas readily reacts with H_2O molecules. In ethanol-ethylene glycol solvent alone, however, the rate of carbonation is very slow because of no H_2O present in the solvent. When water is added in organic solvent, the rate of carbonation increases remarkably since CO_2 reacts with H_2O molecules at a faster rate compared to that without water. The X-ray patterns of the calcium carbonate formed with 4 different amounts of water, 0.2, 1, 2 and 4 vol% during carbonation and aged for 3 d at 40°C are shown in **Fig. 7**.

As the amount of water addition increases, both the crystallinity of calcium carbonate and fraction of calcite formed also increase. When 1 ml of water is added to 500 ml of ethanol-

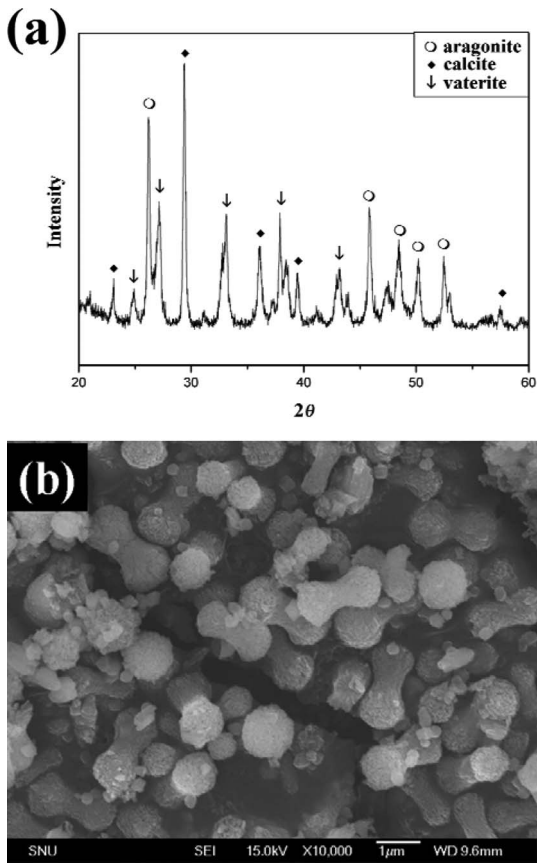

Fig. 4. Phase and morphology analysis of calcium carbonate aged at 40°C for 3 d. (a) X-ray diffraction pattern (b) FE-SEM image.

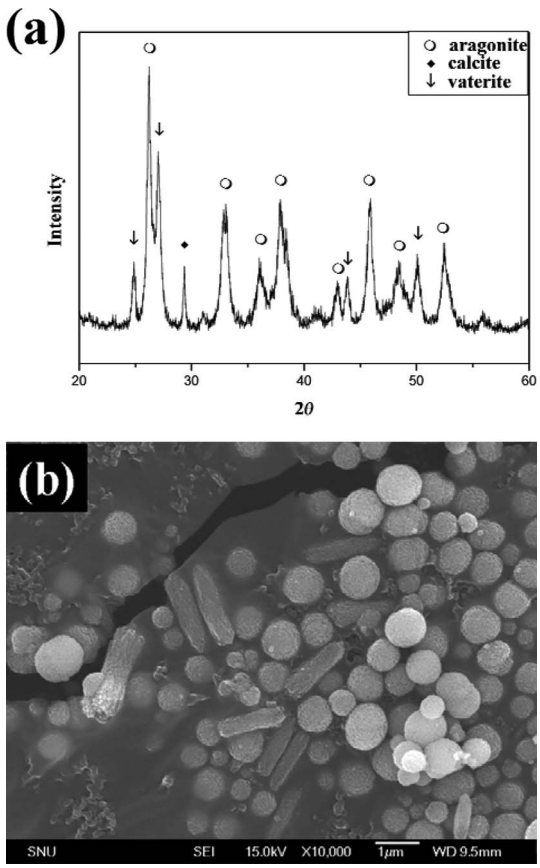

Fig. 5. Phase and morphology analysis of calcium carbonate aged at 60°C for 3 d. (a) X-ray diffraction pattern (b) FE-SEM image.

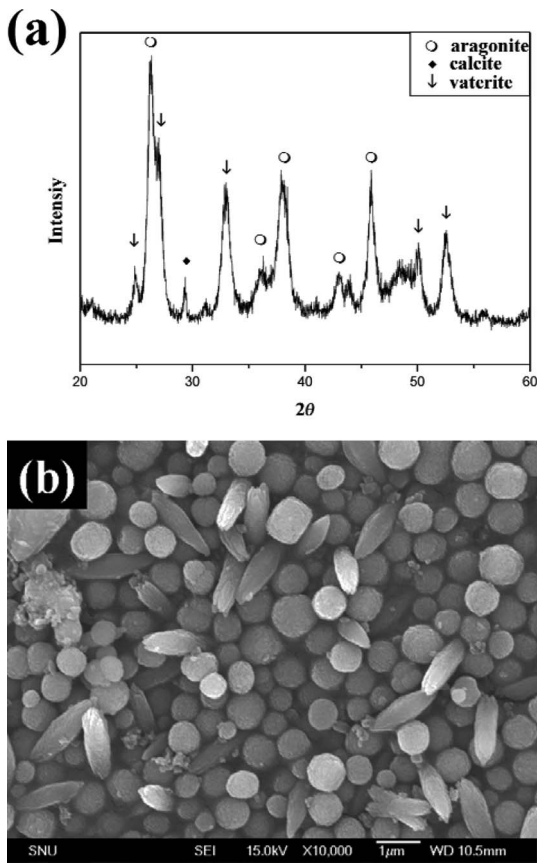

Fig. 6. Phase and morphology analysis of calcium carbonate aged at 100°C for 3 d. (a) X-ray diffraction pattern (b) FE-SEM image.

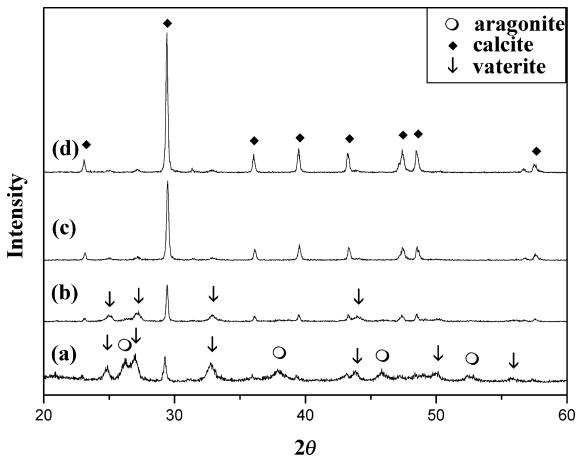

Fig. 7. XRD curves of calcium carbonate precipitated and aged with an addition of (a) 0.2 vol% water, (b) 1 vol% water, (c) 2 vol% water and (d) 4 vol% water.

ethylene glycol solvent to obtain 0.2 vol%, the XRD pattern in Fig. 7(a) is almost the same as that in Fig. 4(a), showing the diffraction pattern of the particles aged at 40°C without water addition. The diffraction pattern in Fig. 7(a) indicates that the calcium carbonate is composed of three phases, calcite, aragonite and vaterite. The diffraction peaks of aragonite and vaterite are broad, which means these crystals are poorly crystallized.

The aragonite content decreases significantly as the water addition increases, and disappears completely at 1 vol% of water

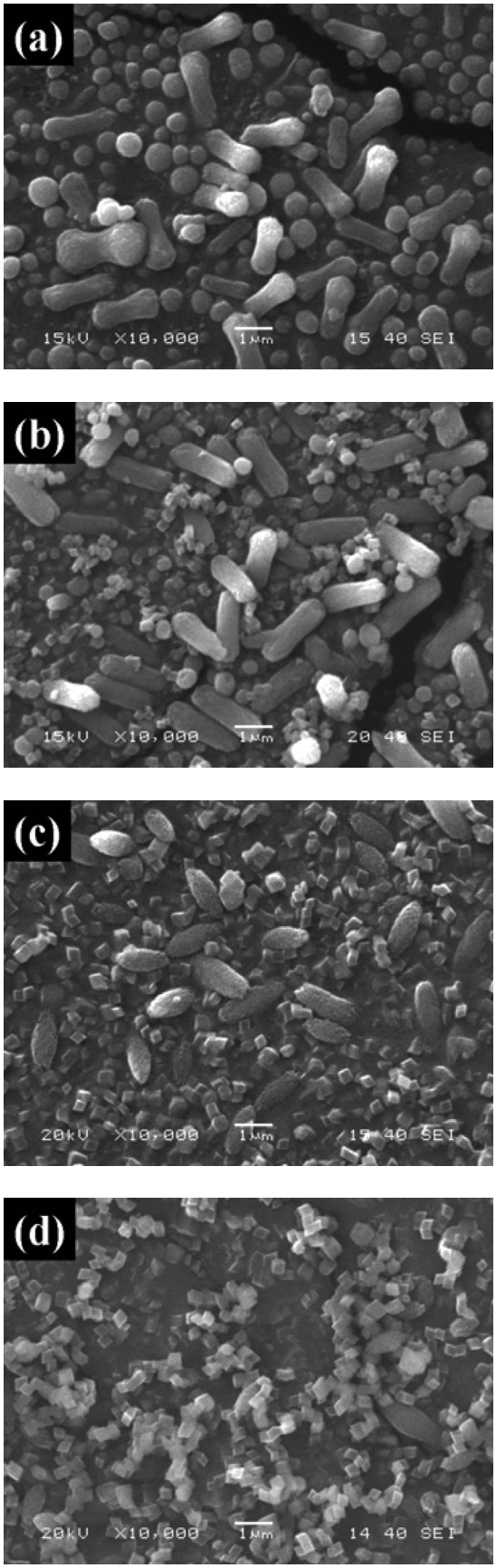

Fig. 8. SEM images of calcium carbonate precipitated and aged with an addition of (a) 0.2 vol% water, (b) 1 vol% water, (c) 2 vol% water and (d) 4 vol% water.

(Fig. 7(b)). When the water addition increases to 2 vol% of water, the diffraction intensity of vaterite decreases remarkably and that of calcite becomes strong. In the case of 4 vol% (Fig. 7(d)), the calcite peaks are intensified compared to the week vaterite peaks.

It is known that the meta-stable phases dissolve more than the stable phase in water because the solubility of the meta-stable phases is larger than that of the stable phase.[13] Ethanol inhibits the transformation of meta-stable phase vaterite into stable calcite because calcium carbonate does no dissolve in it.[8] When the water is added, however, the solubility of calcium carbonate in solvent increases and the meta-stable aragonite dissolves well and rather the precipitation of the stable calcite is favored.

When 0.2 vol% of water (0.055 mol) is added to the solvent, the reacting solution contains a total of 0.32 mol of H_2O, which dose not affects the solubility of $CaCO_3$. As the amount of water increases to 1 vol%, however, the amount of H_2O increases to 0.55 mol in the total solution which is twice as much as that without water. Finally, the water addition increases to 4 vol% which is almost 1.38 mol. The amount of water increases about 5 times, so that the solubility of $CaCO_3$ increases and only stable calcite is synthesized rather than the formation of meta-stable phases.

The morphology of the particles carbonated with different amounts of water at 0.2, 1, 2 and 4 vol% is shown in **Fig. 8**. We can find peanut-like and spherical calcium carbonate in the SEM images in Fig. 8(a) which has the same morphology of calcium carbonate precipitated in organic solvent without water. 0.2 vol% of water does not affect the morphology of precipitated calcium carbonate in this organic solvent system. In the case of 1 vol% water, the size of the spherical particles in Fig. 8(b) is found to be smaller than those in Fig. 8(a). The particle in Fig. 8(c) is a mixture of mostly rhombohedral calcite and partly spindle. As the water addition increases from 0.2 vol% to 2 vol%, calcite as a stable phase increases with decreasing aragonite and vaterite as meta-stable phases and the particles become small, changing the morphology from peanut-like to columnar and spindle ones. Most of the particles in Fig. 8(d) are calcite in rhombohedral form with a small amount of vaterite.

4. Conclusions

The results of this study could show the effects of temperature and water addition on the synthesis of calcium carbonate in ethanol-ethylene glycol solvent. We can obtain meta-stable phases because the solvent inhibits phase transformation of aragonite into stable calcite. Especially, meta-stable phases are crystallized very well as the aging temperature increases above 60°C.

A little amount of water added in ethanol-ethylene glycol solvent increases the solubility of meta-stable calcium carbonate, so that it is hard to obtain meta-stable phase like aragonite or vaterite. 2 vol% of water is enough to change the solubility of meta-stable phases, so that the particles obtained are composed of stable calcite. Consequently, we can find experimentally that the meta-stable phases are synthesized at high temperature and disappear when the solubility is high.

The calcium carbonate by carbonation in the organic solvent alone is heavily agglomerated and becomes a gel as time elapses, but the water addition shortens the gelation time. As the aging temperature increases from 40°C to 100°C after $Ca(OH)_2$ is carbonated in the organic solvent, the morphology of $CaCO_3$ has changed from peanut-shaped to spherical. As the water addition increases from 0.2 vol% to 4 vol% during the carbonation, the $CaCO_3$ product has changed from a mixture of spherical and peanut-like particles to rhombohedral ones after aging at 40°C for 3 d.

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