



## Preparation of pure vaterite by simple mechanical mixing of two aqueous salt solutions

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### ABSTRACT

Vaterite-type calcium carbonate particles have some unique properties such as high hydrophilicity, large surface areas, and hierarchical structures consisting of primary vaterite particles in comparison with calcite- or aragonite-type polymorphs. In this paper, preparation conditions of vaterite by mixing treatment of two salt solutions,  $\text{CaCl}_2$  and  $\text{K}_2\text{CO}_3$ , were studied in terms of the presence of surfactant, agitation method of the solutions and other conditions. A double-cylinder-type homogenizer or ultrasonic homogenizer was used for agitation of the solutions. When suitable mixing conditions were adopted, pure vaterite was obtained as fine powders quantitatively by mixing the two salt solutions at room temperature without any surfactant using any types of homogenizers. When a polyoxyethylene sorbitan monofatty acid ester was present as a surfactant in the mixing solutions, pure vaterite but different morphologies or particle sizes were obtained, depending on the chemical structure of the surfactant used. The obtained results revealed that homogeneous, high-shear and constant agitation of the mixing solutions around 1 M salt concentration was necessary to prepare pure vaterite under the conditions used in this study.

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### 1. Introduction

Synthesized and natural calcium carbonates have been widely used as fillers, pigments and other functional materials for paper, foods, cosmetics, medical materials and commodities produced at industrial level. Three polymorphs of calcium carbonate ( $\text{CaCO}_3$ ) have been known: calcite, aragonite and vaterite. Vaterite-type  $\text{CaCO}_3$  particles are meta-stable, and have secondary spheres consisting of primary particles approximately 100 nm in diameter. Thus, vaterite particles have large specific surface areas with porous structures and to be more hydrophilic than other two types. These properties of vaterite  $\text{CaCO}_3$  particles are promising as pigments in coating colors for high-grade ink-jet papers, because rapid absorption of extremely small and water-based ink droplets into the coated layer without spreading to the in-plane direction is the most significant for photo-grade ink-jet printing. Silica has been generally used as a coating pigment for ink-jet paper, since silica gel particles are highly hydrophilic and have large surface areas of 200–400  $\text{m}^2/\text{g}$  [1]. If  $\text{CaCO}_3$  particles in place of silica can be used as the pigment for ink-jet coating, it is more advantageous in terms of production cost, handlings and others. Hence, vaterite-type  $\text{CaCO}_3$  is one of the alternative candidates for the coating pigments of ink-jet paper.

Because vaterite is hydrophilic, it has been studied as a starting material of hydroxylapatite formation to prepare artificial bones or tooth [2,3].

For this purpose, it is necessary to establish a production procedure of pure vaterite-type  $\text{CaCO}_3$  whose properties are controllable for end uses, because vaterite is hardly present in nature. Many papers have been reported so far to prepare vaterite-type  $\text{CaCO}_3$  particles in high yields and to characterize them. Generally,  $\text{CaCO}_3$  particles are prepared by mixing two salt solutions, e.g.  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$ . The presence of glycine, L-alanine or L-aspartic acid in the mixing solutions enhances the vaterite ratios in the  $\text{CaCO}_3$  precipitates formed [4–7]. Addition of a surface active agent such as sodium dodecylbenzenesulfonate improves the formation of vaterite-type  $\text{CaCO}_3$  particles, while that of sodium dodecylsulfonate does the formation of calcite [8,9]. When trichloroacetic acid and hydroxyethylidene-1,1-phosphonic acid are present in the sonically mixing solutions at 95 °C, vaterite is stably formed [10]. Other methods using membranes or spin-coaters have been also proposed to prepare vaterite-type  $\text{CaCO}_3$  [11,12]. Weight ratios of vaterite in the  $\text{CaCO}_3$  mixtures can be determined from their X-ray diffraction patterns or FT-IR spectra [13–15]. As to the vaterite formation in the mixing treatments, aggregation or crystal growth mechanism has been proposed so far [16,17].

In this study, we investigated some conditions to prepare pure vaterite by mixing aqueous  $\text{CaCl}_2$  and  $\text{K}_2\text{CO}_3$  solutions using a double-cylinder-type or ultrasonic homogenizer with or without a surfactant. The ratios of vaterite in the  $\text{CaCO}_3$  precipitates thus formed were determined by X-ray diffraction method, and morphologies of the

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CaCO<sub>3</sub> particles were observed by scanning electron microscopy (SEM).

## 2. Experimental procedures

Calcium carbonate was synthesized by pouring a 1 M calcium chloride solution (20 mL) with or without 0.5 wt.% surfactant into a 1 M potassium carbonate solution (20 mL), which was being agitated in an Erlenmeyer flask using a double-cylinder-type homogenizer at 5000 rpm (20 mm  $\phi$ , Phycotron, Nippon Seimitsu Kogyo Co., Japan) or an ultrasonic homogenizer at 19.5 kHz and 300 W output power (26 mm in the probe tip diameter, US-300T, Nihonseiki, Japan). When the double-cylinder-type homogenizer was used, one of the two salt solutions was added slowly using a disposable pipette to another solution agitated using the homogenizer. On the other hand, one of the two salt solutions was added at once to another solution agitated using the ultrasonic homogenizer. All experiments were carried out at room temperature, and the concentration and volume of the salt solutions before mixing were changed to 0.1 M and 100 mL, respectively, in some cases. Tween 20, 40, 60 or 80 (Wako Pure Chemicals Co., Japan) was dissolved in the 1 M CaCl<sub>2</sub> solution, and used for the mixing treatment. Tween 20, 40, 60 and 80 have chemical structures of polyoxyethylene sorbitan mono-fatty acid ester, and the fatty acid components are lauric, palmitic, stearic and oleic acid, respectively.

White fine powder of CaCO<sub>3</sub> was formed as the precipitate during mixing the two salt solutions. The flask was appropriately moved by hand to agitate the mixture homogeneously. After agitation for 2–3 min, the CaCO<sub>3</sub> precipitate was separated from the mixture by centrifugation at 1000 g for 5 min. The supernatant was removed by decantation, and the precipitate was washed thoroughly with water by repeated centrifugation. The CaCO<sub>3</sub> precipitate was washed with ethanol and

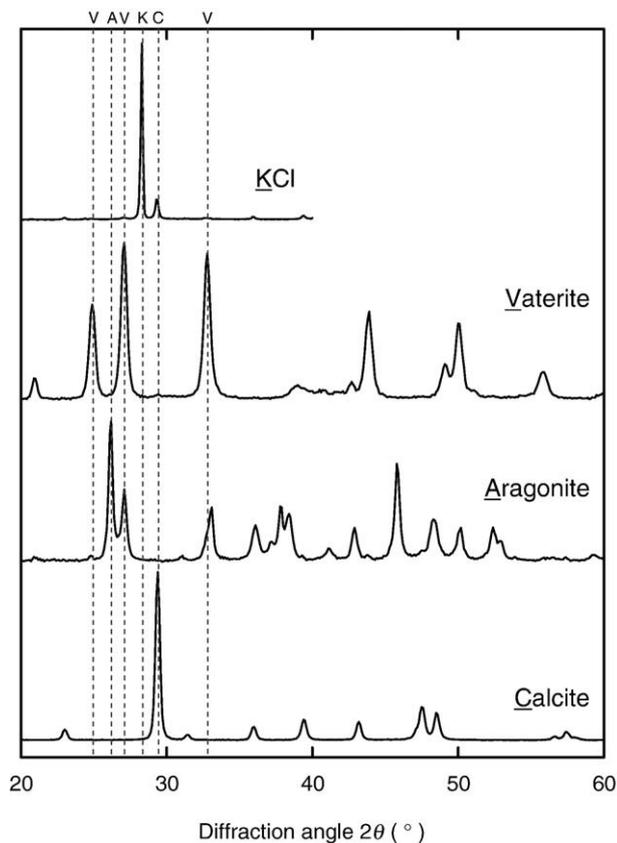


Fig. 1. Typical X-ray diffraction patterns of CaCO<sub>3</sub> polymorphs and KCl.

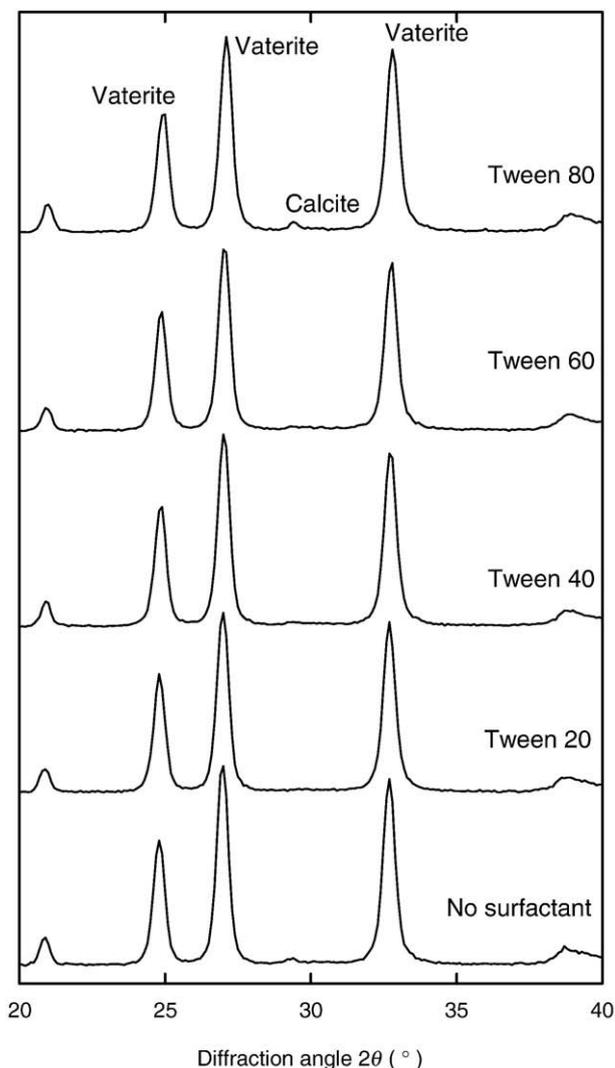


Fig. 2. X-ray diffraction patterns of CaCO<sub>3</sub> particles prepared by mixing 1 M K<sub>2</sub>CO<sub>3</sub> and 1 M CaCl<sub>2</sub> solutions (20 mL each) with or without 0.5 wt.% surfactant using a double-cylinder-type homogenizer at room temperature. Tween (0.5 wt.%) was dissolved beforehand in the CaCl<sub>2</sub> solution, which was then poured into the agitated K<sub>2</sub>CO<sub>3</sub> solution in the flask.

then acetone by centrifugation, and dried in air at room temperature for 12 h. The powder-like CaCO<sub>3</sub> was stored at room temperature in a sample bottle with a screw cap before use. Yields of CaCO<sub>3</sub> were in the range of 90–95%, and the yield losses were mostly caused by handling during the recovery and washing processes.

The CaCO<sub>3</sub> powders thus obtained were subjected to X-ray diffraction measurement by the reflection mode using a Rigaku RINT 2000 with monochromatic CuK $\alpha$  radiation at 40 kV and 40 mA. The weight ratios of vaterite in the CaCO<sub>3</sub> powders were calculated from the X-ray diffraction intensities due to vaterite and calcite according to the equation proposed by Rao [13,14]. Morphologies of CaCO<sub>3</sub> powders were observed by means of a field-emission-type scanning electron microscope at 10 kV (SEM; S-4000, Hitachi Co., Japan) after platinum-sputtering for 120 s.

## 3. Results and discussion

Crystal forms of CaCO<sub>3</sub> particles are distinguishable by X-ray diffraction patterns [4]. Especially, the strong diffraction peak at 29.4° is typical for calcite, and those at 24.8°, 27.1° and 32.8° are for vaterite (Fig. 1). These X-ray diffraction peaks are appropriate indicators for

qualitative and quantitative determination of calcite/vaterite ratios in the obtained  $\text{CaCO}_3$  [13,14].

In the first experiment, the two salt solutions,  $\text{K}_2\text{CO}_3$  and  $\text{CaCl}_2$ , whose concentration and volume were set to be 1 M and 20 mL, respectively, were mixed in a flask at room temperature using the double-cylinder-type homogenizer to prepare vaterite-type  $\text{CaCO}_3$  in high ratios. Some researchers have already reported that the presence of a surfactant in the mixing solution often enhanced the formation of vaterite rather than calcite [8–10]. Thus, the influence of a surfactant dissolved in the 1 M  $\text{CaCl}_2$  solution on the vaterite formation was also studied.

Based on the results of preliminary experiments, it was visually confirmed that the mixture became a viscous gel in quite short time just after the mixing the two salt solutions (within 5 s), and then turned to a white slurry due to the formation of the  $\text{CaCO}_3$  precipitate. When the  $\text{CaCl}_2$  solution containing 0.5 wt.% Tween was agitated in the flask, into which the  $\text{K}_2\text{CO}_3$  solution was poured, many bubbles were formed during the homogenizer treatment. Hence, homogeneous agitation of the mixing solution could not be achieved, resulting

in high calcite ratios in the precipitates. Moreover, when the  $\text{K}_2\text{CO}_3$  solution was quickly added to the  $\text{CaCl}_2$  solution at once, a gel-like mixture was formed in the flask. Homogeneous stirring of the mixing solution could not be carried out also in this case, and the precipitates formed contained calcite in high ratios. These results indicate that homogeneous and continuous agitation of the mixing solution by the homogenizer was necessary to prepare vaterite in high ratios. On the basis of the above preliminary results, the following mixing sequence was adopted; the 1 M  $\text{CaCl}_2$  solution containing 0% or 0.5 wt.% Tween was slowly but continuously poured into the 1 M  $\text{K}_2\text{CO}_3$  solution, which was being agitated using the homogenizer. A series of Tween were used, and all experiments were carried out at room temperature.

X-ray diffraction patterns of the obtained  $\text{CaCO}_3$  precipitates are shown in Fig. 2. Interestingly, almost pure vaterite was obtained in all cases with and without the surfactant in the 1 M  $\text{CaCl}_2$  solution. These results revealed that homogeneous and constant agitation with high shear force is one of the significant factors to prepare pure vaterite. The surfactant addition to the mixing solution is, therefore, not necessary. When no surfactant was used, pure vaterite was also obtained by

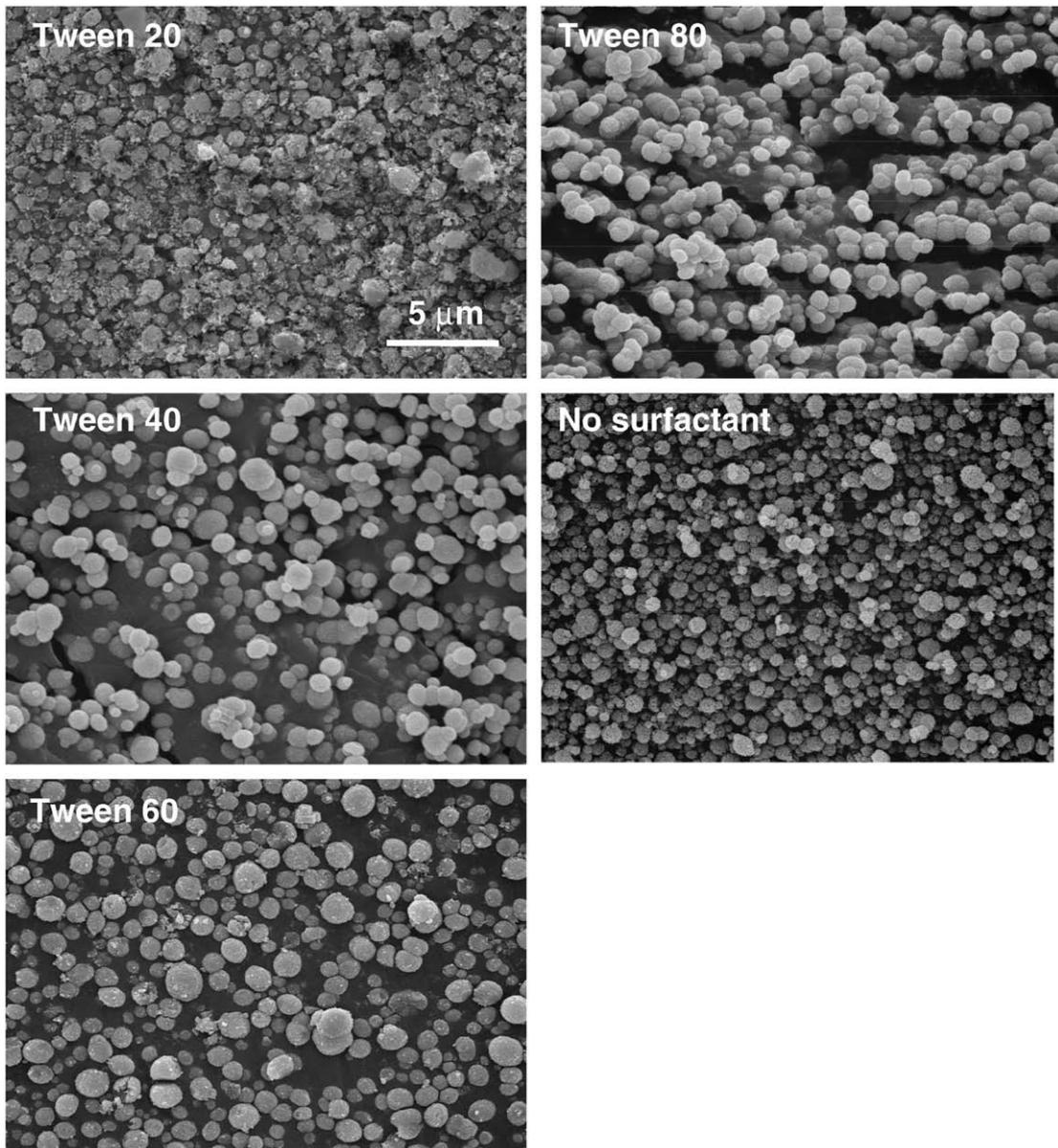


Fig. 3. SEM images of  $\text{CaCO}_3$  particles prepared under the conditions in Fig. 2.

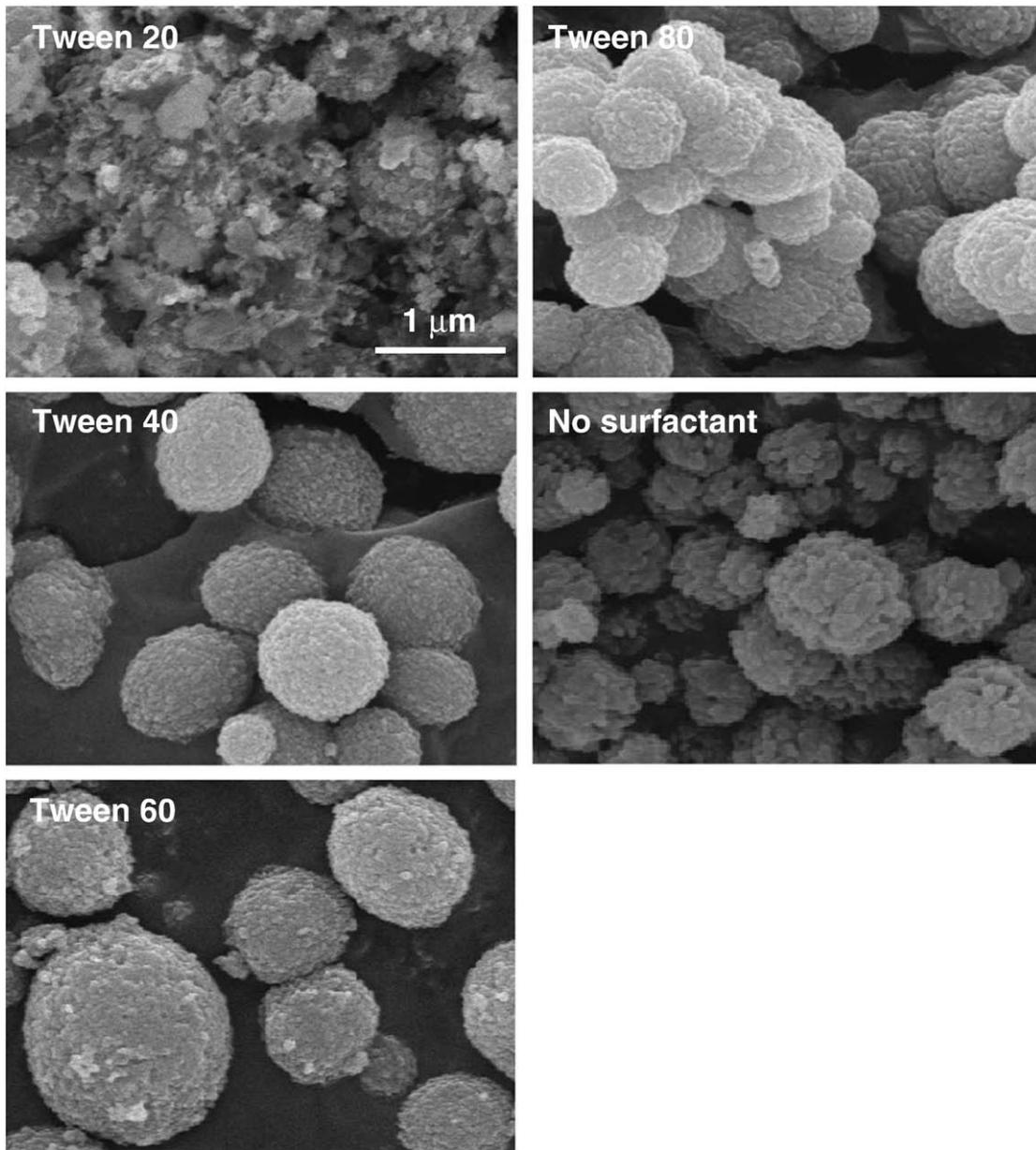


Fig. 4. The same as those in Fig. 3 but with different magnification.

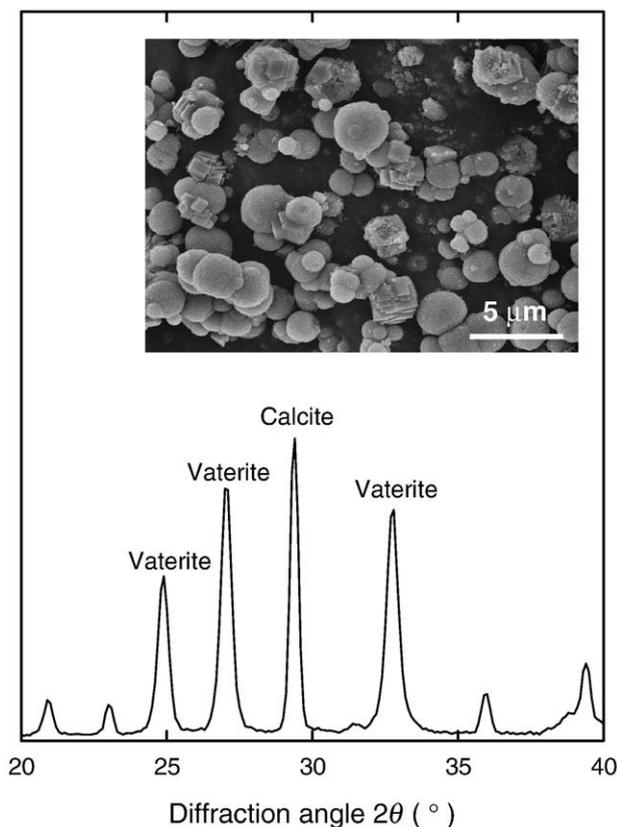
adding 1 M  $K_2CO_3$  solution into 1 M  $CaCl_2$  solution being agitated using the homogenizer, *i.e.* the inverse addition sequence.

Morphologies of the  $CaCO_3$  particles prepared with various surfactants are depicted as SEM images in Figs. 3 and 4 with different magnifications, respectively. Although all  $CaCO_3$  particles consist of almost pure vaterite (Fig. 2), their morphologies vary depending on the chemical structure of the surfactant used. When no surfactant was used, the  $CaCO_3$  particles had spherical shapes smaller than 1  $\mu m$  and the surfaces were relatively rough; the primary particles had rather heterogeneous shapes and formed the spherical secondary particles with many pores. The addition of Tween 20, on the other hand, brought about the formation of many fine and anomalous particles of vaterite with heterogeneous shapes, and the particle sizes varied from a few tens nm to 1  $\mu m$ . Spherical vaterite particles are not common in this case. Probably the presence of Tween 20 strongly restricts the secondary aggregation of the primary vaterite particles formed at the initial stage.

The addition of Tween 40 and Tween 60 gave similar and typical vaterite particles with spherical shapes 0.5–1  $\mu m$  in diameter. Each

vaterite sphere is recognized to consist of primary particles of less than 100 nm in diameter. Some spherical vaterite particles prepared with Tween 80 were fused to each other and film-like materials were also observed below the particles, although each spherical particle had the surface morphology similar to that prepared with Tween 40 or Tween 60. Thus, almost pure vaterite can be prepared by the simple mixing method of the two salt solutions using the double-cylinder-type homogenizer around room temperature irrespective of the addition of surfactant. Even though almost pure vaterite can be prepared by this method, morphologies and sizes of the  $CaCO_3$  particles vary, depending on the surfactant used. Moreover, the addition of the surfactant is not necessary, but homogeneous and constant agitation of the mixing solution with high shear force might be the most significant factor to prepare pure vaterite.

When the volume of the two salt solutions were increased from 20 mL to 100 mL, the calcite ratio increased and spherical vaterite particles were present together with rhombohedral particles due to calcite in the SEM image (Fig. 5). The vaterite ratio in this case was 72%, when Rao's equation was adopted for calculation [13,14].

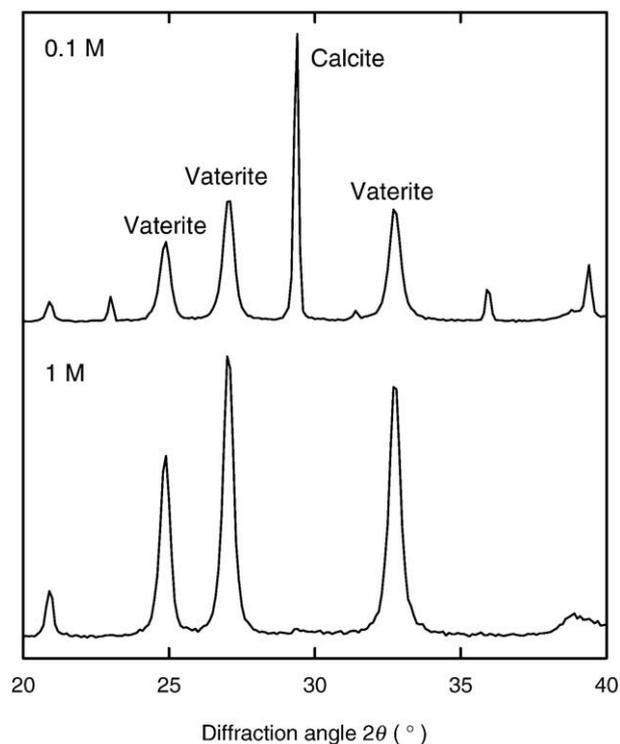


**Fig. 5.** X-ray diffraction pattern and the corresponding SEM image of  $\text{CaCO}_3$  particles prepared by mixing 1 M  $\text{CaCl}_2$  and 1 M  $\text{K}_2\text{CO}_3$  solutions (100 mL each) using a double-cylinder-type homogenizer.

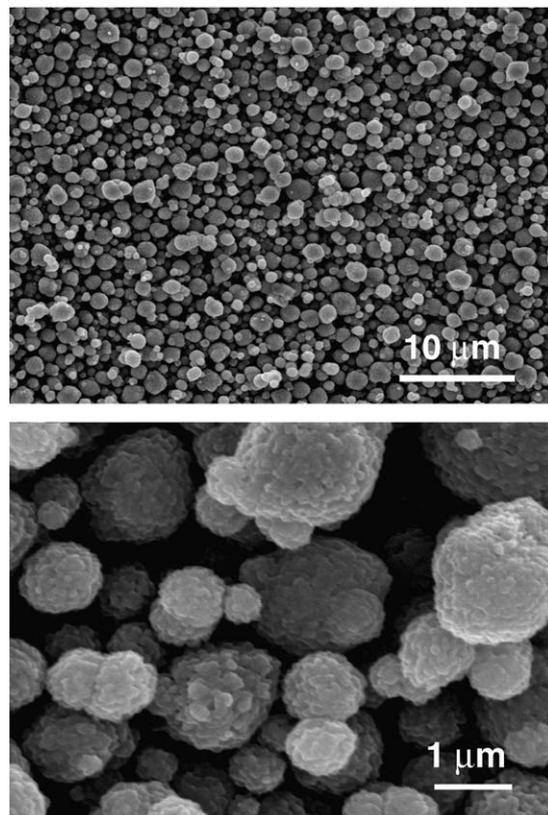
In the next experiment, an ultrasonic homogenizer was used in place of the double-cylinder-type homogenizer to prepare vaterite, because ultrasonication may transmit the agitation energy more homogeneously and entirely to the mixing solution. The concentration and volume of the two salt solutions were set to be 1 M and 20 mL, respectively, and the mixing was carried out at room temperature. No surfactant was used in this case. When the 1 M  $\text{CaCl}_2$  solution was added at once to the 1 M  $\text{K}_2\text{CO}_3$  solution, which was being sonicated in a flask, almost pure vaterite was obtained (Fig. 6). Here, the addition sequence of the salt solutions had no influence on the vaterite formation; both the  $\text{K}_2\text{CO}_3 \rightarrow \text{CaCl}_2$  and  $\text{CaCl}_2 \rightarrow \text{K}_2\text{CO}_3$  addition sequences gave the same results. Morphologies of the vaterite-type  $\text{CaCO}_3$  particles prepared are shown in Fig. 7. The spherical shapes as well as their surface morphologies are very close to, for example, those prepared using the double-cylinder-type homogenizer without surfactant in Figs. 2 and 3, which are almost pure vaterite.

When one of the two salt solutions was added slowly using a disposable pipette to another solution being agitated using the ultrasonic homogenizer, relatively large amounts of calcite were formed. Thus, in this case using the ultrasonic homogenizer, quick addition of one of the two salts solutions to another is needed to prepare pure vaterite. Probably, more homogeneous agitation of the mixture can be achieved, when the ultrasonic homogenizer is used.

Moreover, when the concentration of the two salt solutions was decreased to 0.1 M, the vaterite ratio in the  $\text{CaCO}_3$  precipitate was only 52% and a significant amount of calcite was formed (Fig. 6). Thus, aggregation of the primary particles of vaterite or growth of vaterite crystals in a short time during agitation of the mixing solution [16,17], which may be achieved around 1 M salt solutions, is also another important factor to prepare pure vaterite under the conditions especially used in this study.



**Fig. 6.** X-ray diffraction patterns of  $\text{CaCO}_3$  particles prepared by mixing  $\text{K}_2\text{CO}_3$  and  $\text{CaCl}_2$  solutions (20 mL each) at either 0.1 M or 1 M concentration without surfactant using an ultrasonic homogenizer.



**Fig. 7.** SEM images of  $\text{CaCO}_3$  particles prepared by mixing 1 M  $\text{K}_2\text{CO}_3$  and 1 M  $\text{CaCl}_2$  solutions (20 mL each) without surfactant using an ultrasonic homogenizer.

It was observed from many related preliminary experiments that the agitation of the mixing solutions using the ultrasonic homogenizer always provided pure vaterite in comparison with agitation using the double-cylinder-type homogenizer. Probably, more homogenous and stable agitation can be achieved by the ultrasonication. The results obtained in this study show that the sufficient agitation of the two salt solutions around 1 M concentration in the mixing treatment with high shear force is the most significant condition to prepare pure vaterite. It is hypothesized, therefore, that rapid and direct aggregation of primary vaterite particles with less chances for them to be surrounded with water molecules is probably necessary to grow the secondary vaterite particles.

#### 4. Conclusion

Pure vaterite can be prepared as precipitates by simple mixing method of  $K_2CO_3$  and  $CaCl_2$  solutions at room temperature without any surfactant. Homogeneous, high-shear and constant agitation of the mixing solutions around 1 M salt concentration is necessary to prepare pure vaterite under the conditions used in this study. The presence of surfactant is not necessarily required. A slow addition of one of the two salt solutions to another is required for preparation of pure vaterite, when the double-cylinder-type homogenizer is used for agitation. On the other hand, a quick addition of one solution to another is necessary for obtaining pure vaterite, when the ultrasonic homogenizer is used. The vaterite-type  $CaCO_3$  can be prepared mostly as typical spherical particles 0.1–1  $\mu m$  in diameter by this method. However, the shapes and sizes of the vaterite particles formed are controllable by selecting a surfactant present in the mixing solution. Especially, when 0.5 wt.% Tween 20 or 0.5 wt.% Tween 80 is used,

vaterite particles of unusual shapes can be obtained. Surface morphologies or shapes of primary particles of the spherical vaterite particles also vary, depending on the surfactant used.

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