Chemical Engineering Science 63 (2008) 3632 – 3642

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Particle morphology, habit, and size control of $CaCO_3$ using reverse microemulsion technique

Clifford Y. Tai*, Chih-kuang Chen

Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

ARTICLE INFO

Article history:
Received 12 March 2007
Received in revised form 22 November 2007
Accepted 11 April 2008
Available online 22 April 2008

Keywords:
Particle morphology
Particle habit
Particle size
Reverse microemulsion technique
Additives
Calcium carbonate

ABSTRACT

The particle morphology, habit and size of calcium carbonate were controlled simultaneously via reverse microemulsion technique. Several important operating variables in AOT/isooctane/water reverse microemulsion system, such as ω values (water/surfactant molar ratio), S values (water/oil molar ratio), R values (molar ratio of $CaCl_2$ to Na_2CO_3) and type and concentration of additives, were systematically investigated. Among which, the R value is the most important factor affecting particle habit and polymorph of calcium carbonate. On the other hand, the addition of additive strongly influences the particle morphology, size and habit of calcium carbonate. As a result nano-sized spherule and micro-sized hexagonal-plate, disk, doughnut and spindle particles of calcium carbonate were successfully synthesized in this study. These products with distinctive morphology, size, and habit are expected to be applicable in various industrial fields.

1. Introduction

Particles have distinctive properties when their crystalline sizes are reduced to submicron range with respect to corresponding bulk materials (Gleiter, 2000), including prominent mechanical/optical properties, high specific surface area and chemical activity, and superior barrier effects especially in polymer matrix. Among the numerous nano-sized materials synthesized within the past decade, calcium carbonate is one of the most useful and abundant materials. Calcium carbonate nucleates in three crystal morphologies—calcite, aragonite, and vaterite. Calcite, easy to find in nature, is more stable than other polymorphs at ambient temperature and atmospheric pressure whereas vaterite is most unstable. Aragonite is less stable than calcite and commonly found in marine organisms (Tai and Chen, 1998; Kato et al., 2002). One of the common applications of $CaCO_3$ is used as inorganic filler for various industries, such as plastic, rubber, paper and pharmacy. Thus, the nano-sized calcium carbonate can find a myriad of applications. For example, as in plastic products, Guo et al. (2005) found that nano-sized calcium carbonate was able to improve the modulus of polypropylene. Meanwhile, it also strengthened the stiffness and heat resistance of polymer matrix. Also, Jiang et al. (2005) showed that nano-sized calcium carbonate increased modulus of acrylonitrile–butadine–styrene copolymer and even increased its impact strength under a certain loading range. In paper application, paper coated with submicron-sized aragonite, compared with traditional use of micron calcite particles, was demonstrated to improve gloss, brightness and opacity effectively by Dimmick and Mueller (2006). Doughherty et al. (2005) applied calcium carbonate of 40 nm in size as filler in a paper manufacturing process. They proved that paper sheets coated with nano-sized calcium carbonate showed an increase in cross-direction stiffness and a decrease in void count. In other industries, Liu (2005) showed that when spherical vaterite of 0.2–3 μm size was added within the toothpaste or dentifrice, the cleaning and abrasiveness characteristics of the toothpaste were obviously improved. Thus $CaCO_3$ fine particle with distinct morphology has its specific application.

Because of the wide application of nano/micro-sized calcium carbonate, the technique to synthesize calcium carbonate with particle size below 1 μm became an interesting research topic. There are several methods for producing nano/micro-sized calcium carbonate, among which the carbonation process to prepare precipitated calcium carbonate is an economical one (Chen et al., 2000). Thus, a number of researchers have tried to modify this process aiming at commercialization. For example, Chen et al. (2000) synthesized calcium carbonate with particle size ranging from 17 to

* Corresponding author. Tel./fax: +886 2 2362 0832.
E-mail address: cytai@ntu.edu.tw (C.Y. Tai).

0009-2509/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2008.04.022

36 nm by using a new process called high-gravity reactive precipitation. Under the high-gravity field, micromixing and mass-transfer enhancement were achieved so that the particle size distribution was well controlled. However, this novel technique is only able to synthesize calcium carbonate with spherical habit. Vacassy et al. (2000) also synthesized calcium carbonate via a novel apparatus called segmented flow tubular reactor. Using this method, micro-sized calcium carbonate particles with spherical and brick-like shape were synthesized. Although this modified carbonation process reduced the particle size of $CaCO_3$ to micro even nano range, it is difficult to control crystal habit even with such a complicated technique.

At the present time new methods via template concepts to control the particle habit of calcium carbonate are being developed, including two-reverse-microemulsion technique (Rock et al., 1997; Tai et al., 2001, 2004; Viravaidya et al., 2004; Kang et al., 2005; Rauscher et al., 2005), microemulsion-based method (Li and Mann, 2002), pseudovesicular double emulsion synthesis (Hirai et al., 1997), emulsion liquid membrane process (Sun and Deng, 2004), biomimetic synthesis under templates of double-hydrophilic block copolymers and Langmuir monolayer (Mann et al., 1988; Qi et al., 2002). A variety of particle habits such as plate, rhombohedron, spindle, needle, filament and porous sponge have been reported, while particle size down to nano-sized range can be achieved by some methods. Among the methods mentioned above, the two-reverse-microemulsion technique has many advantages, such as easy control of particle size even down to micro- or nano-sized range, monodisperse characteristics, uncomplicated equipment and procedure, and mild operating conditions. Various materials such as copper, silver, CdS and TiO_2 were successfully synthesized by the two-reverse-microemulsion technique (Hirai et al., 1994; Pileni, 1997; Li and Wang, 1999; Bagwe and Khilar, 2000) and the particle formation model of this technique has been thoroughly discussed by Kumar et al. (2004).

The two-reverse-microemulsion technique has been applied to synthesize calcium carbonate. For instance, a reverse microemulsion system, CTAB/hexane/water, was studied by Rock et al. (1997). The water phases of the two-emulsion system were $(NH_4)_2CO_3$ and $CaCl_2$ aqueous solution. They found that the amount of water content in emulsion and ratio of calcium to carbonate were crucial factors affecting the particle size and particle habit. However, the particle size of the produced particle did not reach submicron. Besides, Rauscher et al. (2005) applied Marlipal O13-40/hexane/water as two-reverse-microemulsion system to synthesize calcium carbonate, where the Na_2CO_3 and $CaCl_2$ aqueous solution were used as the two water phases. They found that microemulsion composition as well as initial reactant concentration showed a weak effect on the particle size of $CaCO_3$ and only spherical particle was precipitated by controlling these two factors. In addition, the concentration ratio of Na_2CO_3 solution to $CaCl_2$ solution also had no significant influence on the particle size and habit. In their study, spherical calcium carbonate of 4 nm size was synthesized and needle-like calcium carbonate was prepared by extending the reaction time from 30 min to 24 h. Moreover (Viravaidya et al., 2004) mixing carbonate-containing NaAOT microemulsion with reverse micelles of calcium dodecylbenzenesulfonate successfully synthesized calcium carbonate composed of stacked arrays of 20 nm-thick plate-like calcite crystals with pseudo-hexagonal particle habit. Recently, Kang et al. (2005) investigated the influence of surfactants on the polymorphism and crystal size of $CaCO_3$ produced in microemulsion. The effect of SDS was more noticeable than that of AOT. Two polymorphs of $CaCO_3$, i.e., calcite and vaterite, of micron size were reported.

Although the two-reverse-microemulsion technique used to synthesize calcium carbonate has advantages in controlling particle size down to nanometer range, particle morphology and habit control by using this technique were not thoroughly investigated in the literature. In this study, we used the two-reverse-microemulsion technique to synthesize nano/micro-sized calcium carbonate, aiming at the control of particle habit and crystal polymorphism simultaneously. The effects of several operating variables, including ω values (molar ratio of water/surfactant), S values (molar ratio of water/oil), type and concentration of additives and R values (molar ratio of $CaCl_2$ to Na_2CO_3) on the particle size and morphology of calcium carbonate were investigated.

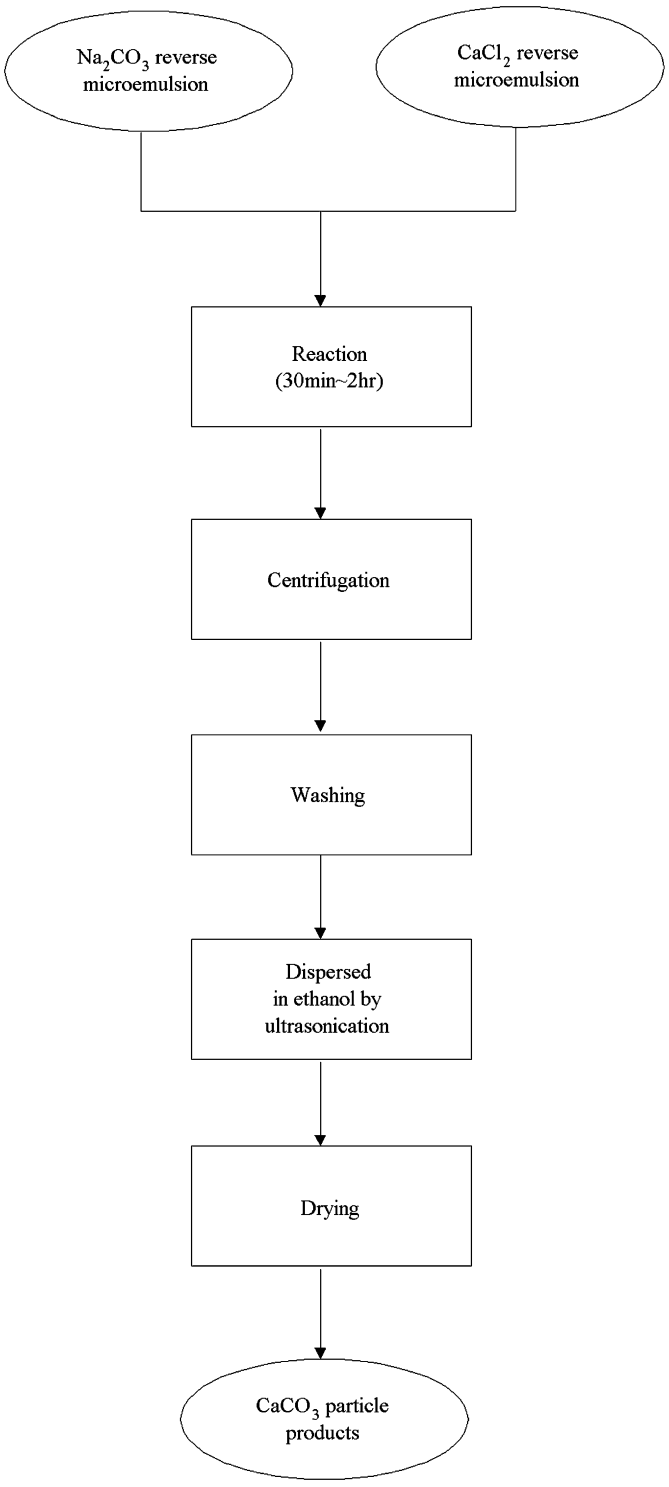

Fig. 1. The flowchart for preparing calcium carbonate particles using the two-reverse-microemulsion technique.

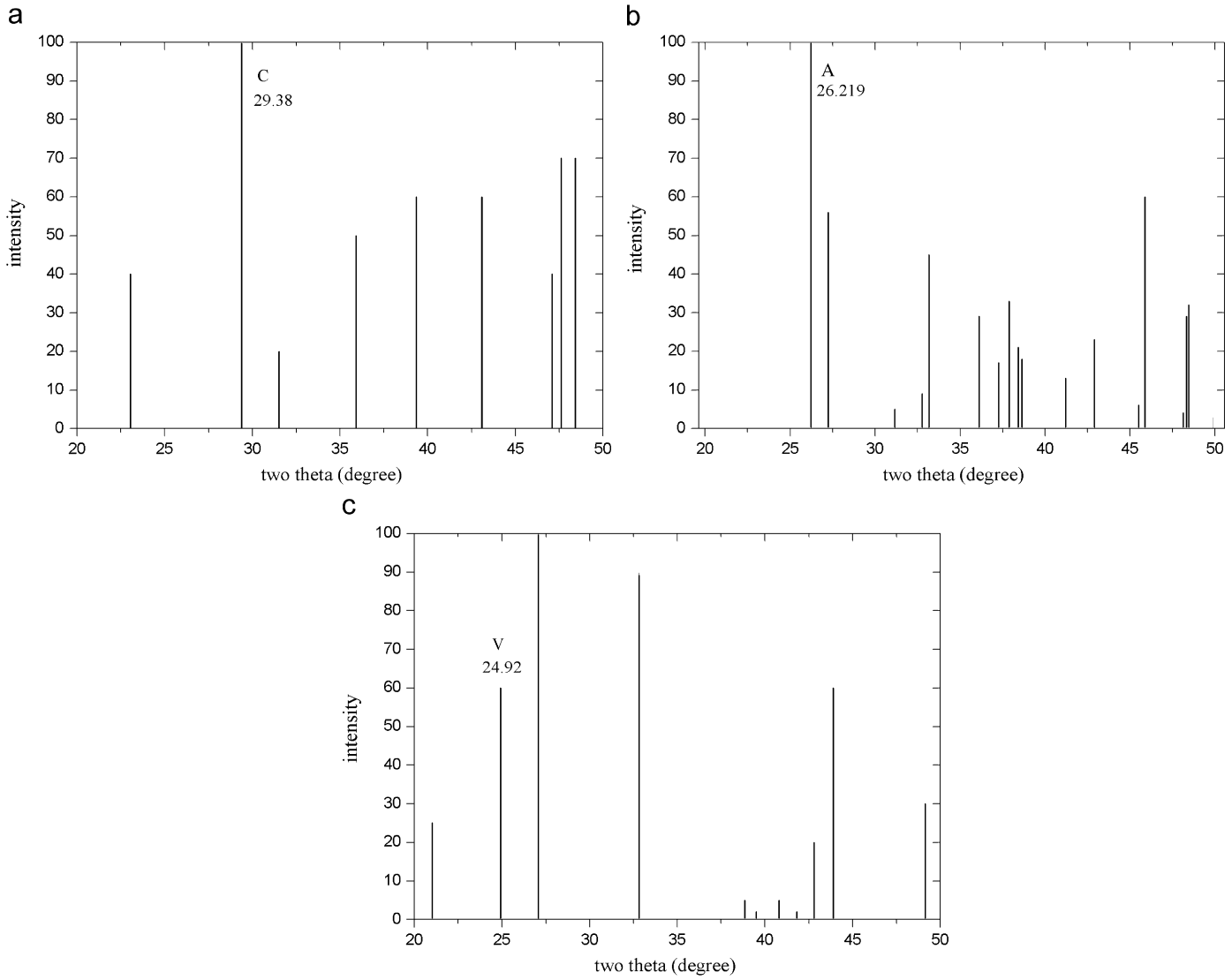

Fig. 2. XRD characteristic peaks for three calcium carbonate polymorphs: (a) calcite; (b) aragonite; and (c) vaterite from JCPDS card database.

2. Experimental

A reverse microemulsion system of AOT/isooctane/water was selected for this study due to its wide stable-region (Kunieda and Shinoda, 1979). Chemicals used in this experiment were from different sources: calcium chloride and sodium carbonate from Nacalai Tesque, surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) from Aldrich, and isooctane from J.T. Baker as oil phase. All the chemicals were used without further purification. The flow chart for preparing calcium carbonate powder via the two-reverse-microemulsion technique is shown in Fig. 1.

The first step was to prepare two reverse microemulsions of $CaCl_2$ and Na_2CO_3 solutions by mixing isooctane, surfactant and a certain amount of aqueous $CaCl_2$ or Na_2CO_3 solutions in two 500 ml beakers agitated by a magnetic stirrer at ambient temperature. For the experimental runs to study the effect of additive, a specified amount of additive by weighting was added to the $CaCl_2$ or Na_2CO_3 aqueous solution. Then, the aqueous solution containing additive was mixed with isooctane and surfactant to form a microemulsion. After 2-h mixing, the two mixture solutions became optically transparent. Then the two reverse microemulsions of $CaCl_2$ and Na_2CO_3

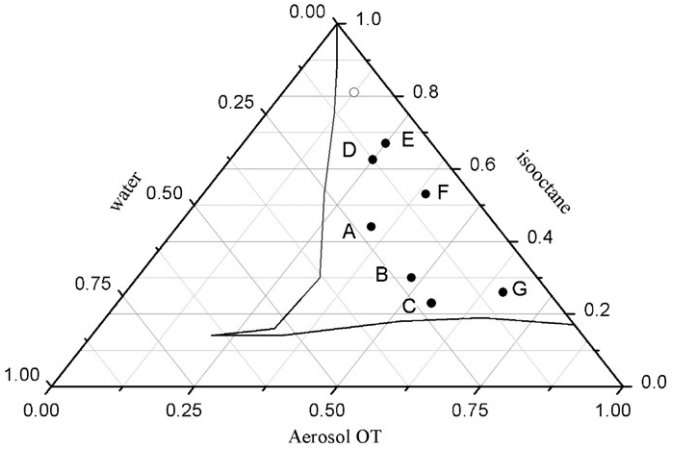

Fig. 3. Stable region for AOT/isooctane/water system (Kunieda and Shinoda, 1979) and the selected compositions of reverse microemulsion in which water was replaced by 0.05 M $CaCl_2$ or Na_2CO_3 aqueous solution for this study. The hollow point indicates the unstable composition of 0.05 M $CaCl_2$ reverse microemulsion.

Table 1
Operating conditions and experimental results for the preliminary test on $CaCO_3$ synthesis[a]

Run no.	Composition of reverse microemulsion (wt%)			ω	S	RXN time (min)	Particle size (μm)	Particle habit
	AOT	Isooctane	Aqueous solution					
A	34	44	22	15.96	3.16	30	Length: 1–2, Width: 0.4	Rod
B	48	30	22	11.30	4.65	30	1–3	Irregular shape
C	55	23	22	9.87	6.07	30	1–3	Irregular shape
D	25	63	12	12.34	1.27	75	1–2	Spherule
E	25	67	8	7.90	0.76	80	1–3	Doughnut
F	39	53	8	5.06	0.95	900	1–2	Spherule

[a]Operating variables kept constant were: $[CaCl_2]=[Na_2CO_3]=0.05$ M, $R=1$, and $T=25\,^{\circ}C$. The R value is defined as the molar ratio of $CaCl_2$ to Na_2CO_3. The amounts of 0.05 M $CaCl_2$ and 0.05 M Na_2CO_3 microemulsion solutions were 100 g, respectively, indicating that the R value was set at 1.

aqueous solutions were mixed together in a jacked reactor where the temperature was kept at 25 °C. As the two reverse microemulsions were mixed together under agitation, the mixed solution was initially transparent and then became milky gradually in 30 min for most runs or in a few hours for some cases. After the suspension was turbid enough to reach opacity state, we stopped the reaction. Then, the calcium carbonate particles were separated by centrifugation with the rotating speed and operating time being set at 8000 rpm and 10 min, respectively. After the decantation process with most of the impurity removed, the precipitates were reslurried by an ultrasonic device for 5 min, using an ethanol/water (80/20 volume ratio) mixture as washing solvent, to ensure that the particles were suspended completely before next centrifugation. The washing process was repeated again using ethanol as solvent.

Finally, the collected calcium carbonate particles were redispersed in a small amount of ethanol to form a suspension, followed by a drying process to obtain calcium carbonate particles. The drying process was conducted under hot air environment and the ethanol was rapidly evaporated in about 30 min.

The particle size and shape of resultant calcium carbonate particles were examined by a scanning electron microscope (SEM, JEOL J-5600). The crystal polymorphism of the product powder was determined by an X-ray diffractometer (Mac Science, MXP-3 TXT-7266). The operating conditions of the XRD instrument such as the step range and the scanning speed were set at 0.02° and 4 degree/min, respectively, in the scanning range from 10° to 50°. The polymorphs of calcium carbonate were identified qualitatively from the JCPDS card. The characteristic peaks of calcite, aragonite and vaterite, which were cited from No. 04-0636, 24-0025 and 33-0268 in the JCPDS card database, are shown in Fig. 2. The droplet size of reverse microemulsion was measured by a high-concentration particle size analyzer (Malvern, Zatasizer Nano ZS). The droplet concentration is allowed to operate between 0.01 ppm and 40 wt% by using this model.

3. Results and discussion

3.1. Stability of reverse microemulsion

The stable region of AOT/isooctane/water reverse microemulsion system has been reported by Kunieda and Shinoda (1979), as shown in Fig. 3. In the stable region, specified compositions were selected to examine the reverse microemulsion stability when pure water was replaced by Na_2CO_3 or $CaCl_2$ aqueous solution. All the composition points in Fig. 3 were stable as the concentrations of Na_2CO_3 and $CaCl_2$ aqueous solutions were 0.05 M, except for the hollow point of the $CaCl_2$ solution. At point F of low aqueous phase loading (8 wt% of aqueous phase) in Fig. 3, the reverse microemulsion system was still stable as the concentrations of Na_2CO_3 and $CaCl_2$ aqueous solutions increased to 0.5 M. However, at point A of high aqueous phase loading (22 wt% of aqueous phase), both reverse microemulsions were unstable when the concentrations of Na_2CO_3 and $CaCl_2$ aqueous solutions were higher than 0.5 and 0.2 M, respectively.

From the stability test, we knew that the reverse microemulsion system of the Na_2CO_3 solution was more stable than that of the $CaCl_2$ solution. This can be explained by the neutralization between the dissociated ions (such as Na^+ and Ca^{+2}) and the polar heads of surfactant (Hatton, 1989). The neutralization causes the repulsion force between polar heads of surfactant to decrease so that stable micelles are unable to form. The decrease in repulsion force results in the separation of aqueous and oil phases in the microemulsion system. As the ionic strength of dissociated ions in aqueous solution increases, more surfactant or lower ω value is required to form a stable micelle. Thus, $CaCl_2$ reverse microemulsion is less stable than Na_2CO_3 microemulsion because the neutralization ability of Ca^{+2} ion is much stronger than Na^+ ion.

3.2. Preliminary test of calcium carbonate synthesis

After the stability study, experiments of calcium carbonate synthesis were conducted at the selected compositions shown in Fig. 3 of different values of ω (molar ratio of water/surfactant) and S (molar ratio of water/oil) which were reported to affect crystal morphology (Rock et al., 1997; Kang et al., 2005; Rauscher et al., 2005). The concentrations of aqueous Na_2CO_3 and $CaCl_2$ solutions were both kept at 0.05 M. When the two reverse microemulsions of equal amount were mixed together under agitation, the mixed solution was initially transparent and then became milky gradually in 30 min to hours, depending on the operating conditions. The particle sizes of precipitates obtained in this preliminary study were a few micrometers as indicated in Table 1. However, various particle habits, including rod-like (run A), spherule (runs D and F) and doughnut shape (run E), were observed, as shown in Fig. 4. In addition, one experiment was conducted by increasing the reactant concentrations to 0.2 M while keeping other operating variables the same as run A in Table 1. Intriguingly, the particle habit changed from rod-like to doughnut shape as shown in Fig. 5(a). In order to produce $CaCO_3$ submicron particles, various attempts were made to reduce the particle size by changing the reactant concentration, varying the relative amount of the two reverse microemulsions or introducing small amount of additive. The introducing of additive turned out to be an effective way to reduce the particle size. In addition the particle habit was also altered. For example, the addition of sodium triphosphate ($Na_5P_3O_{10}$) reduced the particle size from 1–2 μm to 100–200 nm, and the particle habit changed from rod-like to spherical shape as shown in Fig. 5(b).

3.3. Effect of additives

From previous discussion, we found that the introduction of additive in the reverse microemulsion system was an effective method for controlling particle size and habit of calcium carbonate, such as

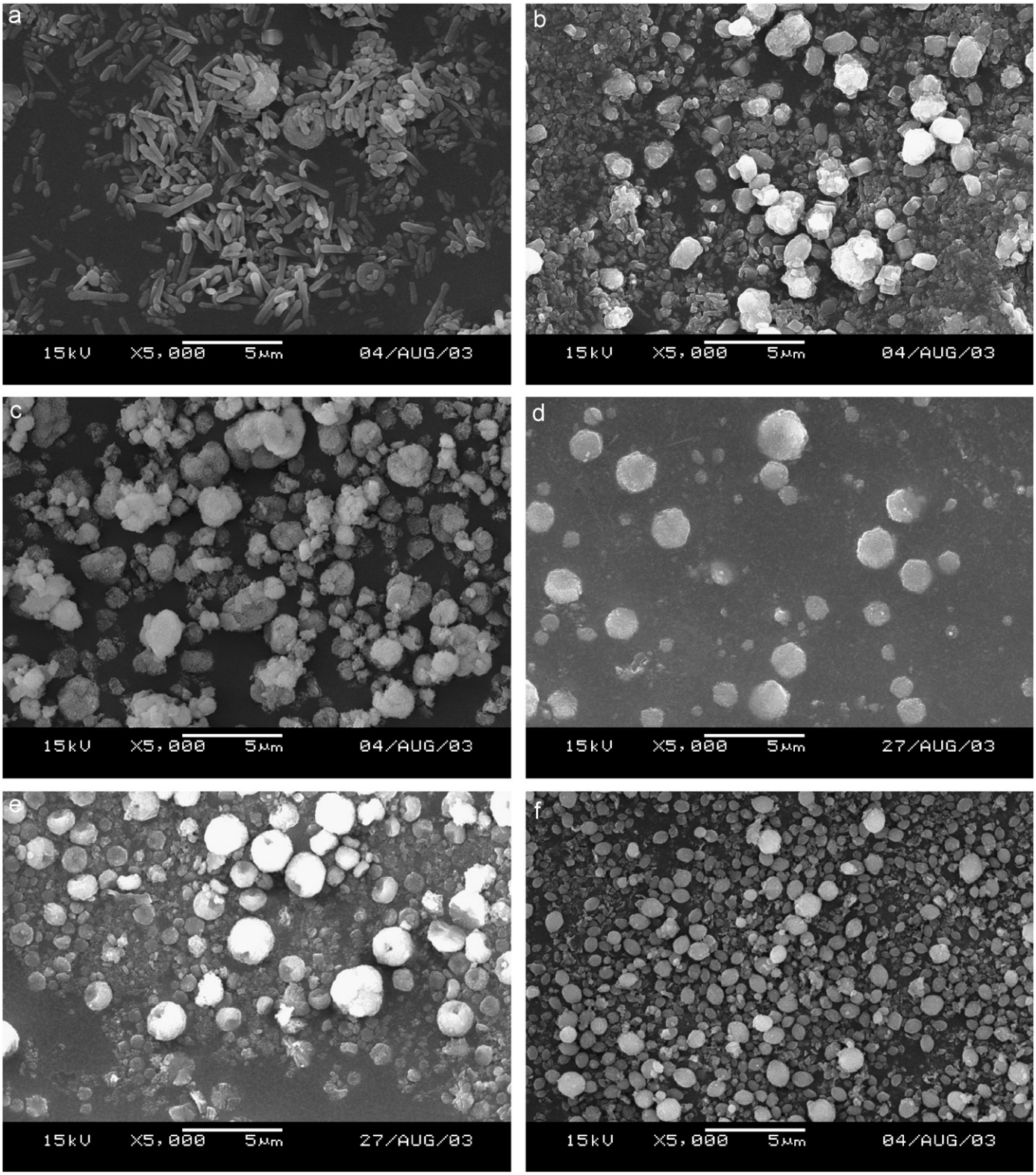

Fig. 4. SEM photographs of calcium carbonate synthesized under conditions as shown in Table 1: (a) run A; (b) run B; (c) run C; (d) run D; (e) run E; and (f) run F.

the effect of sodium tripolyphosphate ($Na_5P_3O_{10}$) in the preliminary study. In the literature, various additives have been applied by several researchers to control the particle habit in different synthetic methods (Pach et al., 1996; Sugihara et al., 1996; Yu et al., 2004), including carbonation and bulk liquid–liquid precipitation. Therefore, it is interesting to see how the additives would affect the particle characteristics of calcium carbonate in the reverse microemulsion process.

Three types of additive were tested in the aqueous phase of our reverse microemulsion system, including phosphorous salts, metal ions and organic compounds of low and high molecular weight. Compared with the results with no additive added, the introducing

of additive definitely influenced the particle morphology, size and habit of calcium carbonate, as shown in Table 2 and Fig. 6. As far as the morphology is concerned, all the tested impurities changed the morphology from aragonite to calcite under the specific conditions: $\omega = 15.96$, $S = 3.16$, $R = 4$ and $T = 25\,^{\circ}C$. Disk-like particles were obtained in the presence of Fe^{+3}, Cu^{+2}, EDA and DETA. Furthermore, as far as particle size was concerned, Cu^{+2} was the most effective one, as shown in Fig. 6(b), in which the particle size was down to 200–300 nm. The addition of organic compounds such as ethylenediamine (run 0309) and diethylenetriamine (run 0330) favored the formation of disk-like particles with high aspect ratio (diameter/thickness) ranging from 3 to 8, as shown in Fig. 6(c) and (d). Besides, the additions of sodium triphosphate and potato starch produced spherical and irregular particles as shown in Fig. 6(e) and (f), respectively.

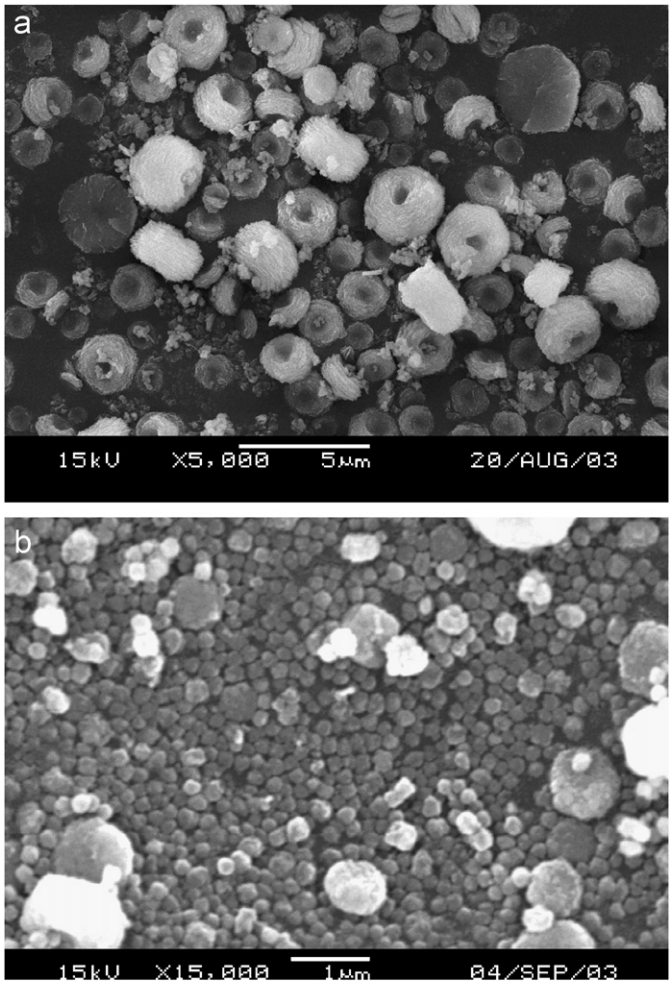

Fig. 5. SEM photographs of calcium carbonate synthesized under the same conditions of run A in Table 1 but (a) changing both reactant concentrations to 0.2 M and (b) adding 135 ppm sodium triphosphate in the Na_2CO_3 aqueous phase.

3.4. Effect of microemulsion composition

In the reverse microemulsion system, several crucial factors such as surfactant fraction, oil fraction and concentration of reactants in aqueous phase were reported to affect the droplet size, the exchanging rate between reactants and the aggregation behavior of the surfactant (Kang et al., 2005; Rauscher et al., 2005), among which the droplet size was the most important factor to affect the particle size of the precipitated particle (Kang et al., 2005; Rauscher et al., 2005). Therefore, the effect of molar ratio of water/surfactant and molar ratio of water/oil on the particle size and habit of calcium carbonate were discussed under specific conditions in our reverse microemulsion system. Sodium triphosphate ($Na_5P_3O_{10}$) was chosen as the additive because it had a profound effect on the particle size, which was down to 100–200 nm, as shown in Fig. 5(b).

As shown in Table 3, it was found that the ω value had a greater influence than the S value on the particle size and habit of calcium carbonate. For example, for all S values, submicron-sized particles with spherical shape were produced at $\omega = 12.3$ and micron-sized particles with irregular shape were obtained at $\omega = 20$. On the other hand, the particle shape changed from spherule to disk and then to irregular shape when ω varied from 12.3 to 20 for $S = 3.16$. For the experimental runs of $\omega = 20.0$, the weight fractions of surfactant in the emulsion system, ranging from 17 to 28 wt% as S varied from 1.26 to 3.16, were rather low as compared with other runs of different ω values. The amount of surfactant may not be sufficient or barely enough to form stable micelles. Thus, phase separation between water and oil phase may occur, causing coarse particles to be produced.

3.5. Effect of total molar ratio

Rock et al. (1997) reported that the total molar ratio, which was defined as the molar ratio of initial moles of $CaCl_2$ to moles of $(NH_4)_2CO_3$, was an important factor that affected the particle size and habit of calcium carbonate in the oil-in-water microemulsion system. In their system cationic-type surfactant (CTAB) was used to form small oil droplets. It was found that 2 mm spherical-like particles were transferred to 2 μm spherical-like particles as calcium to carbonate molar ratio was changed from 1:1 to 10:1. However, the

Table 2
Effects of additives on particle size and habit of calcium carbonate under the conditions: $\omega = 15.96$, $S = 3.16$, $R = 4$, $T = 25\,^{\circ}C$[a]

Run no.	Additives and its conc. (ppm)[b]	Particle habit	Crystal polymorphism[c]	Particle size
0225	Without additive	Irregular shape	A(V,C)	1–2 μm
1230	Fe ions (10)	Disk	C	400–500 nm
0106	Cu ions (10)	Disk	C	200–300 nm
1221	$Na_5P_3O_{10}$ (200)	Spherule	C	200–800 nm
0309	EDA (3000)	Disk	C	500–600 nm
0330	DETA (3000)	Disk	C	700–800 nm
0407	Potato starch (1000)	Irregular shape	C(A)	1–2 μm

[a]The amount of 0.1 M $CaCl_2$ and 0.05 M Na_2CO_3 used were 22 and 11 g, respectively.

[b]EDA and DETA are abbreviations of ethylenediamine and diethylenetriamine.

[c]C, A and V represent calcite, aragonite and vaterite, respectively. Polymorph in parenthesis indicates a small amount in the product.

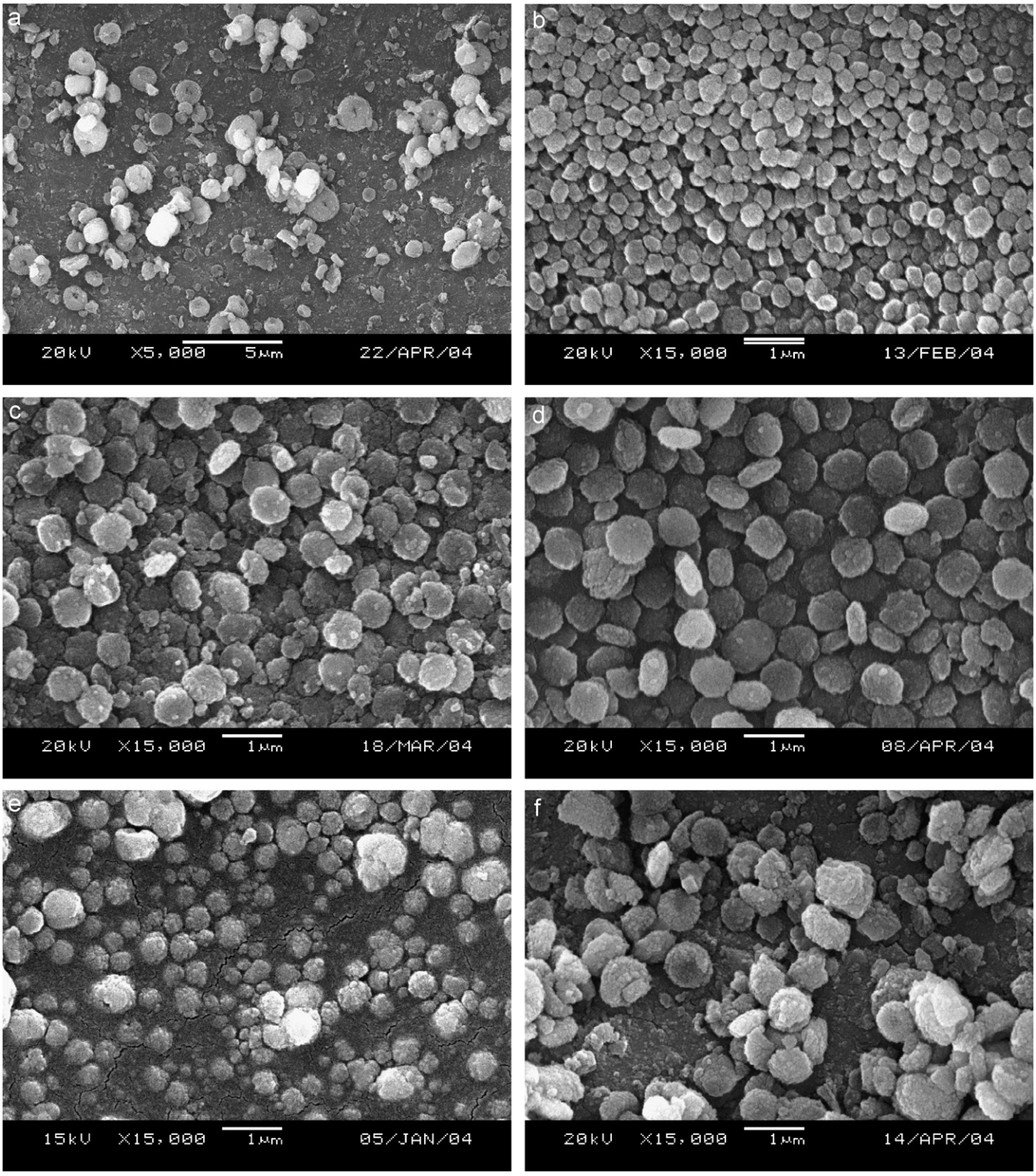

Fig. 6. SEM photographs of calcium carbonate synthesized in the presence of various additives under the conditions listed in Table 2: (a) without additive; (b) Cu ion 10 ppm; (c) EDA 3000 ppm; (d) DETA 3000 ppm; (e) $Na_5P_3O_{10}$ 200 ppm; and (f) potato starch 1000 ppm.

total molar ratio did not have significant influence on the particle size and habit of calcium carbonate in Rauscher's study (2005) when non-ionic-type surfactant (Marlipal O13-40) was used.

In this study, we first investigated the effects of total molar ratio, *R*, on the particle size and habit of calcium carbonate by keeping other operating conditions the same. As shown in Table 4, the

Table 3
The effects of ω (molar ratio of water/surfactant) and S (molar ratio of water/oil) on particle size and habit of calcium carbonate under the conditions: $R = 4$, $T = 25\,^{\circ}C$, $[Na_5P_3O_{10}] = 135$ ppm in Na_2CO_3 aqueous phase, and the amount of 0.1 M $CaCl_2$ and 0.05 M Na_2CO_3 aqueous solutions being 22 g and 11 g, respectively

ω	12.3	14.0	16.0	20.0
S				
3.16	Sphere 400–500 nm	Disk 200–600 nm	Disk 400–500 nm	Irregular shape 1 μm
2.0	Sphere 100–200 nm	Irregular shape 1 μm	Disk 400–500 nm	Irregular shape 1 μm
1.26	Sphere 100–200 nm	Irregular shape 1 μm	Sample amount produced not enough for observation	Irregular shape 1 μm

Table 4
The effects of total molar ratio on the particle size and habit of calcium carbonate under the conditions: ω=15.96, S=3.16, T=25 °C, water content=22 wt%, $[Na_5P_3O_{10}]$=135 ppm in Na_2CO_3 water phase

Run no.	$CaCl_2$ emulsion		Na_2CO_3 emulsion		R values	Particle habit and size	Crystal polymorphism[a]
	Weight (g)	Conc. of aqueous phase (M)	Weight (g)	Conc. of aqueous phase (M)			
A	100	0.05	50	0.2	$\frac{1}{2}$	Hexagonal-plate (1–3 μm)	A(C)
B	100	0.05	100	0.2	$\frac{1}{4}$	Spindle (500–600 nm)	C(A)
C	50	0.05	100	0.2	$\frac{1}{8}$	Irregular (3–5 μm)	No sufficient amount for analysis

[a]C and A indicate calcite and aragonite, respectively. The symbol in the parenthesis indicates the minor form of $CaCO_3$ in the product.

Table 5
Calcium carbonate synthesized under the conditions: $R = \frac{1}{2}$, $\omega = 15.96$, $S = 3.16$, $T = 25\,^{\circ}C$ and without additive

Run no.	$CaCl_2$ aqueous reactant		Na_2CO_3 aqueous reactant		Crystal polymorphism[a]	Particle habit	Particle size (μm)
	Weight (g)	Conc. of aqueous phase (M)	Weight (g)	Conc. of aqueous phase (M)			
0519	22	0.05	11	0.2	A	Hexagonal plate	2–2.5
0722	11	0.1	22	0.1	A(C)	Hexagonal plate	1.5–3
0729	16.5	0.067	16.5	0.133	A(C)	Hexagonal plate	1.5
0731	5	0.2	27.5	0.08	A(C)	Hexagonal plate	1.5–2

[a]C and A indicate calcite and aragonite, respectively. The symbol in the parenthesis indicates the minor form of $CaCO_3$ in the product.

value of R varied by changing the relative amount of the two reverse microemulsions. The particle size and habit of calcium carbonate were strongly affected by the R value. Hexagonal-plate particle was transferred to spindle-like particle when the R value changed from $\frac{1}{2}$ to $\frac{1}{4}$. Besides, the crystal polymorph also changed from aragonite to calcite. Then, irregular particle formed as R value was set to $\frac{1}{8}$.

Further, four runs were conducted with the same R value ($\frac{1}{2}$), which was designed by using different amounts and initial concentration of aqueous solution. As shown in Table 5, $CaCO_3$ sustained the same particle habit (hexagonal plate) and polymorph (aragonite) for all runs regardless of the variation of initial weight and concentration of the two reactants. Fig. 7 shows the SEM photographs of $CaCO_3$ which were synthesized under the same R value. The particle shape looks similar, but with a small difference in particle size, ranging from 1.5 to 3 μm.

Furthermore, a high value of R (4) was set by mixing aqueous solutions of different amounts and concentrations of $CaCl_2$ and Na_2CO_3 solutions. As shown in Table 6 and Fig. 8, calcite of disk-shaped particles was obtained for all runs. However, the particle size varied by a factor of 4, ranging from 0.2 to 0.8 μm.

The mixed solution of all experimental runs in this section was initially transparent for about 10 min and then became milky. This is very different from the bulk liquid–liquid reaction by direct mixing of $CaCl_2$ and Na_2CO_3 aqueous solutions, resulting in rapid precipitation of calcium carbonate. The effect of R value on the characteristics of $CaCO_3$ precipitates can be explained by the induction period of $CaCO_3$ nucleation and intermicellar exchange rate of reactants. It is supposed that the anionic heads of AOT had strong interaction with positive-charged reactant ions to cause a longer induction period and higher local supersaturation near the surfactant and water interface as compared with the case of bulk aqueous reaction (Kang et al., 2005). When the two microemulsion solutions were mixed together, the Brownian motion of the micelles led to intermicellar collisions and sufficiently energetic collisions led to a mixing of micellar contents via a fusion–fusion process (Kumar et al., 2004). Before the mixed emulsion solution became milky, which meant the onset of $CaCO_3$ nucleation, the reactant concentrations and pH in the micelles became almost identical, i.e., the mixing time of microemulsion to reach constant composition was shorter than the induction time of $CaCO_3$ crystals. Thus, the total molar ratio of the reactants was an important factor for determining the morphology, habit and particle size and its distribution. The identical composition when nucleation occurs can also be used to explain the uniform morphology, habit and size distribution of the product produced from the microemulsion technique.

3.6. Droplet size of reverse microemulsion

The droplet sizes of reverse microemulsion of different compositions listed in Table 3 were measured by a high-concentration particle size analyzer (Model Zetasizer Nano ZS, Malvern), which is claimed to be suitable for the droplet concentration ranging from 0.01 ppm to 40 wt%. This range covers the water content from 12 to 24 wt% investigated in this study. To estimate the droplet size distribution, two parameters, i.e., refractive index and viscosity of oil and

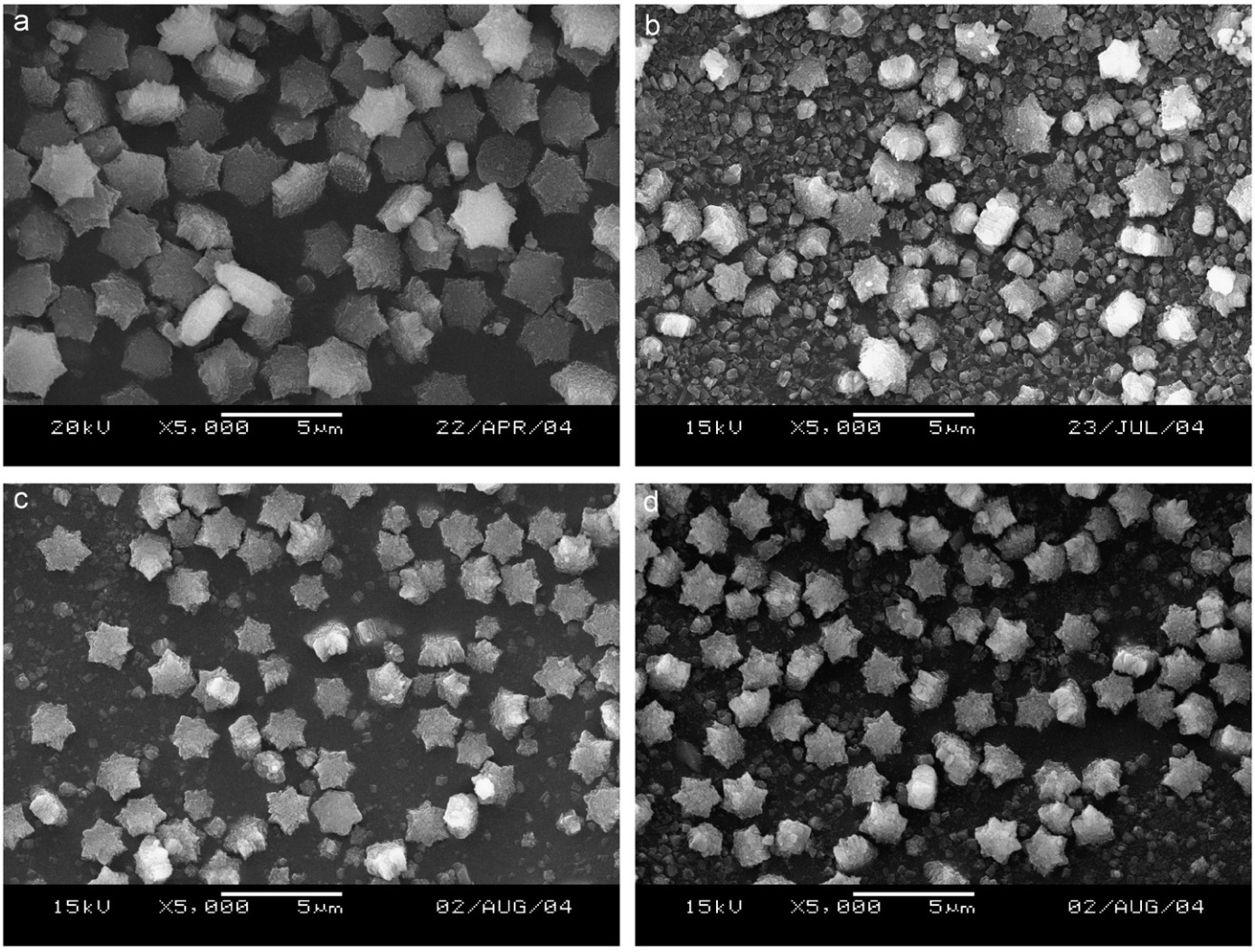

Fig. 7. SEM photographs of hexagonal plate $CaCO_3$ synthesized under a same R value ($\frac{1}{2}$) with other experimental conditions listed in Table 5: (a) run 0519; (b) run 0722; (c) run 0729; and (d) run 0731.

Table 6
Calcium carbonate synthesized under the conditions: $R = 4$, $\omega = 15.96$, $S = 3.16$, $T = 25\,^{\circ}C$ and [diethylenetriamine] = 3000 ppm

Run no.	$CaCl_2$ aqueous reactant		Na_2CO_3 aqueous reactant		Crystal polymorphism[a]	Particle habit	Particle size (μm)
	Weight (g)	Conc. of aqueous phase (M)	Weight (g)	Conc. of aqueous phase (M)			
0330	22	0.1	11	0.05	C	Disk	0.7–0.8
0804	27.5	0.08	5.5	0.1	C	Disk	0.2–0.3
0810	16.5	0.133	16.5	0.033	C	Disk	0.4–0.6
0812	11	0.2	22	0.025	C	Disk	0.7

[a]C indicates the calcite.

water phase, should be provided. The measured parameters were used in the particle size analysis. Typical results of droplet size distribution are presented in Fig. 9 for Na_2CO_3 and $CaCl_2$ reverse microemulsion, in which intensity percent instead of volume percent was plotted against droplet size. The intensity is proportional to the sixth power of droplet size; thus a small amount of droplet of any size will appear in the plot. The stability of a system can be judged from the intensity peaks, i.e., a plot with a higher portion in larger sizes represents a less stable system. When S (molar ratio of water/oil) was increased from 1.26 (Fig. 9(a)) to 3.16 (Fig. 9(b)), and ω (molar ratio of water/surfactant) was kept at 12.3, the system became less stable. When S was kept at 3.16, the system became less stable as ω changing from 12.3 (Fig. 9(b)) to 20.0 (Fig. 9(d)). It is concluded that the higher water content yields a less stable system. Referring to Table 3, the more stable system yields smaller particles. For instance, the particle sizes were between 100 and 200 nm for the system of $\omega = 12.3$ and $S = 1.26$, which is the most stable one, and the particle sizes are larger than 1 μm for the system of

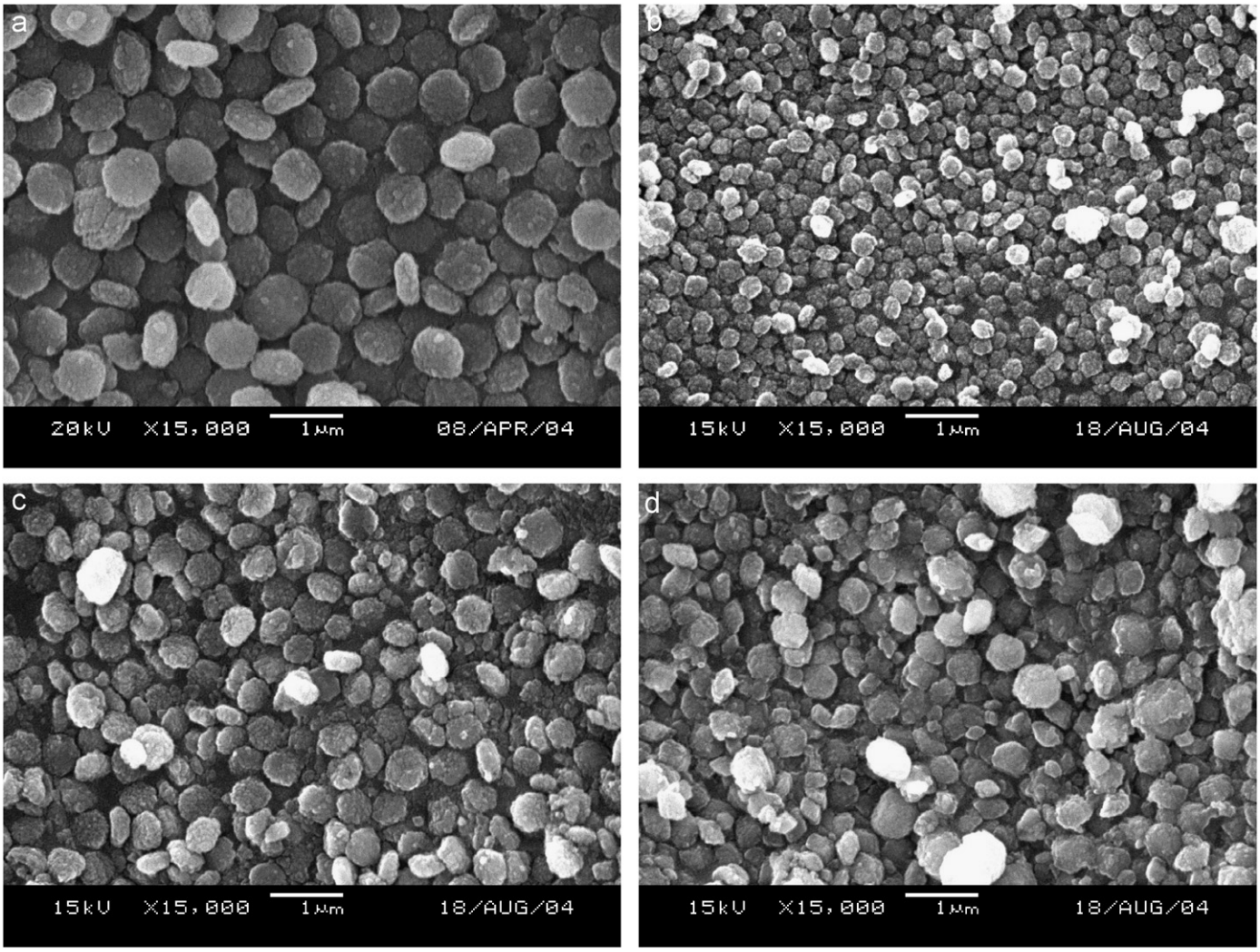

Fig. 8. SEM photographs of disk-like $CaCO_3$ synthesized under a same R value (4) with other experimental conditions listed in Table 6: (a) run 0330; (b) run 0804; (c) run 0810; and (d) run 0812.

$\omega = 20.0$ and $S = 3.16$, which is the least stable one. It should be noticed that the particle size is much larger than the droplet size; for example, the particle size is between 100 and 200 nm and the droplet size is around 3 nm for the system of $\omega = 12.3$ and $S = 1.26$. It was suspected that the droplet size became larger and larger during the induction period, i.e., the time interval between the mixing of two emulsions and the onset of nucleation. Therefore, the transient droplet-size distributions were measured for run 0106 in Table 2, which was chosen because of its long induction period. The results are presented in Fig. 10, in which the time was counted after the two emulsion solutions were mixed. The droplet size was rather small up to 21 min with the mode of distribution at 1.36 nm, and then became larger at 25 min with the mode of distribution at 535 nm. Finally, the microemulsion solution became milky after 27 min. The particle size of run 0106 is between 200 and 300 nm (see Table 2), which is close to the droplet size of emulsion right before the onset of nucleation.

4. Conclusion

The particle size, habit and morphology of calcium carbonate were controlled in the reverse microemulsion system. Several crucial operating factors such as ω, S, R and additives were discussed. The ω value had a greater influence than the S value on the particle size and habit of calcium carbonate because it strongly affected the stability and size of aqueous droplets. For example, the particle shape changed from spherule to disk and then to irregular shape when ω varied from 12.3 to 20 for $S = 3.16$. The induction period of calcium carbonate in the reverse microemulsion system was longer than that observed in bulk reaction. Thus identical concentration and pH of aqueous $CaCl_2$ and Na_2CO_3 solutions in droplets were achieved due to intermicellar exchange of reactants before calcium carbonate precipitated. Consequently, the same R values gave the same morphology and habit, and similar size. On the other hand, different R values gave completely different calcium carbonate. The relation between the droplet size of emulsion and the particle size of $CaCO_3$ product has been investigated. The droplet size of stable microemulsion was much smaller than the particle size. However, the droplet size became larger and larger during the induction period after mixing the two microemulsions and the final particle size was close to the droplet size right before the onset of nucleation. In this research, micron- and submicron-sized $CaCO_3$ particles were synthesized, and smaller particles were obtained by introducing additive. Thus, effects of additives on particle size down to nanometers and possibly on other characteristics of $CaCO_3$ particle will be further studied.

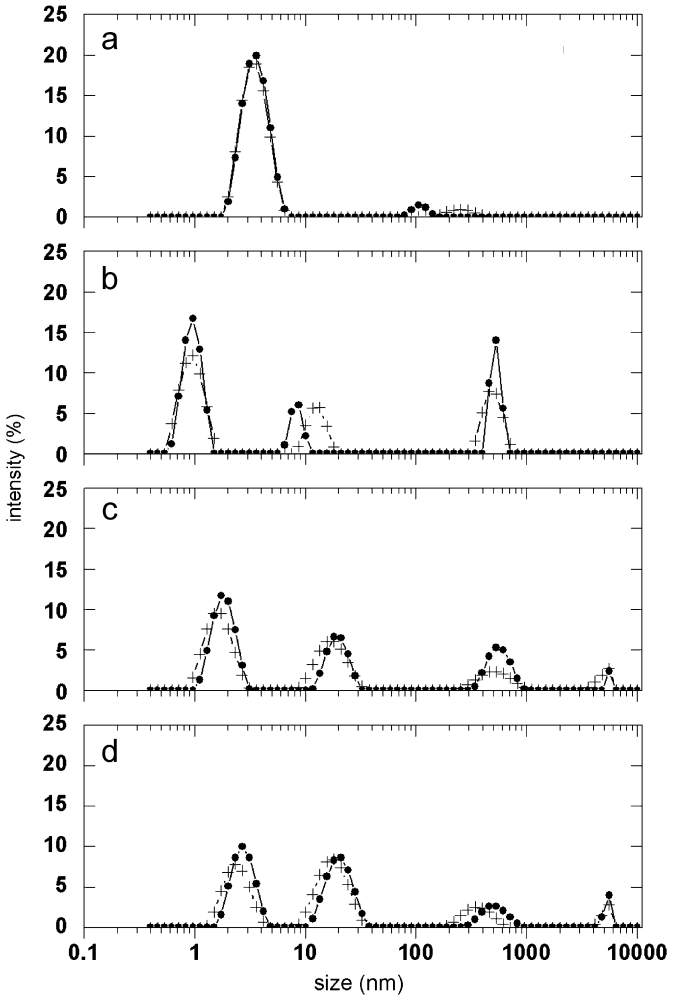

Fig. 9. Droplet size distribution by intensity of Na_2CO_3 (•) and $CaCl_2$ (+) reverse microemulsion for the systems shown in Table 3: (a) $\omega = 12.3$, $S = 1.26$; (b) $\omega = 12.3$, $S = 3.16$; (c) $\omega = 16.0$, $S = 3.16$; and (d) $\omega = 20.0$, $S = 3.16$.

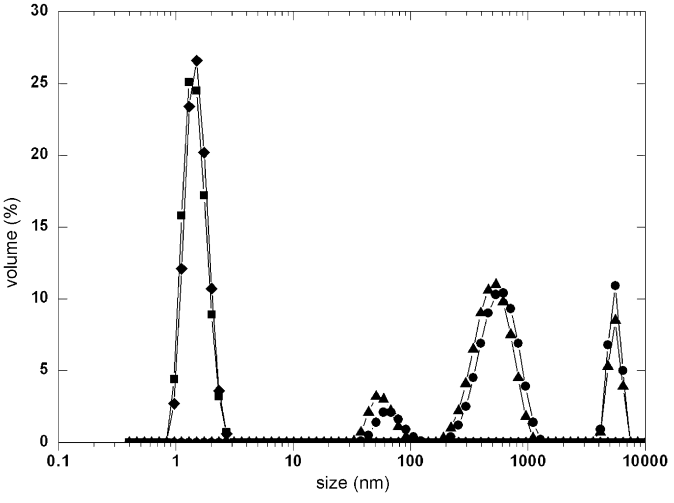

Fig. 10. Transient droplet size distribution by volume for run 0106 in Table 2: (■) 7 min; (♦) 21 min; (▲) 25 min; (•) 27 min.

Acknowledgement

The authors gratefully acknowledge the financial support of the National Science Council of the Republic of China.

References

Bagwe, R.P., Khilar, K.C., 2000. Effects of intermicellar exchange rate on the formation of silver nanoparticles in reverse microemulsions of AOT. Langmuir 16, 905–910.
Chen, J.F., Wang, Y.H., Guo, F., Wang, X.M., Zheng, C., 2000. Synthesis of nanoparticles with novel technology: high-gravity reactive precipitation. Industrial & Engineering Chemistry Research 39, 948–954.
Dimmick, A.C., Mueller, K., 2006. High gloss calcium carbonate coating compositions and coated paper and paper board manufactured from same. US Patent no. 2006/0054291.
Doughherty, M.J., Neogi, A.N., Park, D.W., 2005. Paper products and method of making. US Patent no. 2005/0133178.
Gleiter, H., 2000. Nanostructured materials: basic concepts and microstructure. Acta Materialia 48, 1–29.
Guo, T., Wang, L., Zhang, A., Cai, T., 2005. Effects of nano calcium carbonate modified by a lanthanum compound on the properties of polypropylene. Journal of Applied Polymer Science 97, 1154–1160.
Hatton, T.A., 1989. Surfactant-based Separation Process. Marcel Dekker, New York (pp. 65–68).
Hirai, T., Sato, H., Komasawa, I., 1994. Mechanism of formation of CdS and ZnS ultrafine particles in reverse micelles. Industrial & Engineering Chemistry Research 33, 3262–3266.
Hirai, T., Hariguchi, S., Davey, R.J., 1997. Biomimetic synthesis of calcium carbonate particles in a pseudovesicular double emulsion. Langmuir 13, 6650–6653.
Jiang, L., Lam, Y.C., Tam, K.C., Chua, T.H., Sim, G.W., Ang, L.S., 2005. Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate. Polymer 46, 243–252.
Kang, S.H., Hirasawa, I., Kim, W.S., Choi, C.K., 2005. Morphological control of calcium carbonate crystallized in reverse micelle system with anionic surfactants SDS and AOT. Journal of Colloid and Interface Science 288, 496–502.
Kato, T., Sugawara, A., Hosoda, N., 2002. Calcium carbonate-organic hybrid materials. Advanced Materials 14, 869–877.
Kumar, A.R., Hota, G., Mehra, A., Khilar, K.C., 2004. Modeling of nanoparticles formation by mixing of two reactive microemulsions. A.I.Ch.E. Journal 50, 1556–1567.
Kunieda, H., Shinoda, K., 1979. Solution behavior of Aerosol OT/water/oil. Journal of Colloid and Interface Science 70, 577–583.
Li, G.L., Wang, G.H., 1999. Synthesis of nanometer sized TiO_2 particles by microemulsion method. Nanostructured Materials 11, 663–668.
Li, M., Mann, S., 2002. Emergent nanostructures: water-induced mesoscale transformation of surfactant-stabilized amorphous calcium carbonate nanoparticles in reverse microemulsions. Advanced Functional Materials 12, 773–779.
Liu, S.T., 2005. Stabilized vaterite. US Patent no. 2005/0106110.
Mann, S., Heywood, B.R., Rajam, S., Birchall, J.D., 1988. Controlled crystallization of $CaCO_3$ under stearic acid monolayers. Nature 334, 692–695.
Pach, L., Duncan, S., Roy, R., Komarneni, S., 1996. Morphological control of precipitated calcium carbonates and phosphates by colloidal additives. Journal of Materials Science 31, 6565–6569.
Pileni, M.P., 1997. Nanosized particles made in colloidal assemblies. Langmuir 13, 3266–3276.
Qi, L., Li, J., Ma, J., 2002. Biomimetic morphogenesis of calcium carbonate in mixed solutions of surfactants and double-hydrophilic block copolymers. Advanced Materials 14, 300–303.
Rauscher, F., Veit, P., Sundmacher, K., 2005. Analysis of a technical-grade w/o-microemulsion and its application for the precipitation of calcium carbonate nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects 254, 183–191.
Rock, M.L., Tranchitella, L.J., Pilato, R.S., 1997. Control of calcium carbonate particle size and shape by precipitation from CTAB/alcohol/hexadecane mixtures. Colloid and Polymer Science 275, 893–896.
Sugihara, H., Ono, K.I., Adachi, K., Setoguchi, Y., Ishihara, T., Takita, Y., 1996. Synthesis of disk-like calcium carbonate (part 1): effect of various organic compounds on the carbonation of the basic calcium carbonate. Journal of the Ceramic Society of Japan 104, 832–836.
Sun, Q., Deng, Y., 2004. Synthesis of micrometer to nanometer $CaCO_3$ particles via mass restriction method in an emulsion liquid membrane process. Journal of Colloid and Interface Science 278, 376–382.
Tai, C.Y., Chen, F.B., 1998. Polymorphism of $CaCO_3$ precipitated in a constant-composition environment. A.I.Ch.E. Journal 44, 1790–1798.
Tai, C.Y., Lee, M.H., Wu, Y.C., 2001. Control of zirconia particle size by using two-emulsion precipitation technique. Chemical Engineering Science 56, 2389–2398.
Tai, C.Y., Hsiao, B.Y., Chiu, H.Y., 2004. Preparation of spherical hydrous-zirconia nanoparticles by low temperature hydrolysis in a reverse microemulsion. Colloids and Surfaces A: Physicochemical and Engineering Aspects 237, 105–111.
Vacassy, R., Lemaître, J., Hofmann, H., Gerlings, J.H., 2000. Calcium carbonate precipitation using new segmented flow tubular reactor. A.I.Ch.E. Journal 46, 1241–1252.
Viravaidya, C., Li, M., Mann, S., 2004. Microemulsion-based synthesis of stacked calcium carbonate (calcite) superstructures. Chemical Communications 19, 2182–2183.
Yu, J., Lei, M., Cheng, B., Zhao, X., 2004. Facile preparation of calcium carbonate particles with unusual morphologies by precipitation reaction. Journal of Crystal Growth 261, 566–570.