

Research Article

Morphological Investigation of Calcium Carbonate during Ammonification-Carbonization Process of Low Concentration Calcium Solution

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Ultrafine calcium carbonate is a widely used cheap additive. The research is conducted in low degree supersaturation solution in order to study the polymorphic phases' change and its factors of the calcium carbonate precipitate in the ammonification-carbonization process of the solution with calcium. Fine particles of calcium carbonate are made in the solution containing 0.015 mol/L of Ca^{2+} . Over 98% of the calcium carbonate precipitate without ammonification resembles the morphology of calcite, while the introduction of ammonia can benefit the formation of vaterite. It was inferred that the main cause should be serious partial oversaturation or steric effects. Ammonia also helps to form the twin spherical calcium carbonate. However, particles formed in the process of ammonification-carbonization in solution with low concentration degree of calcium are not even with a scale of the particle diameter from 5 to 12 μm . Inorganic salts, alcohol, or organic acid salts have significant controlling effect on the particle diameter of calcium carbonate and can help to decrease the particle diameter to about 3 μm . Anionic surfactants can prevent the agglomeration of calcium carbonate particles and shrink its diameter to 500 nm–1 μm .

1. Introduction

Ultrafine calcium carbonate of nano- and submicron size is widely used as cheap additive in manufacturing plastic, rubber, varnish, ink, paper, paint, medicine, and other fields [1, 2]. Calcium carbonate and inorganic oxide have good affinity; therefore, it can be used as the model material [3, 4] to make inorganic hollow microsphere such as SiO_2 and TiO_2 . The reason why calcium carbonate can be so widely used is that it has a unique crystal structure and particle size.

Calcium carbonate has three kinds of crystal polymorphs [5], namely, spherical vaterite, aragonite in the shape of a needle, and rhomboidal calcite. The energy level decreases according to this order, while the stability increases. Calcium carbonate of calcite type can stay stable at room temperature, while those of vaterite and aragonite type with metastability are easier to be transformed into the calcite type. Spherical calcium carbonate is commonly used for its smoothness and fluidity. Usually, it is a porous structure and resembles

the clustering with microcrystal of nanosize (25–35 nm). Large amounts of expensive biological macromolecules, dendronized polymers, or compound additives as crystalline controller are used to form spherical calcium carbonate, and less cheap acid, alkali, and salt are used to control the crystal shape.

There are many ways to compose calcium carbonate including carbonization, precipitate method, and high gravity method. Carbonization refers to the method of adding CO_2 gas to suspension with Ca^{2+} and adding morph regulator to control the growing rate of each face of the crystal to achieve morphology control. Precipitate method is to mix the solution of Ca^{2+} and CO_3^{2-} to make calcium carbonate particles. High gravity method is to create the condition for the intensive mixing of liquid and raise the reaction rate of calcium carbonate with centrifugal force. Ultrafine calcium carbonate is mainly synthesized in liquid. Controlling the operation conditions, like temperature, pH, and

supersaturation, or adding crystalline regulator, it can influence nucleation, formation, and the final polymorph of calcium carbonate [6]. Commonly used crystalline regulators include chelating agent [7], organic compound [8, 9], inorganic salt, minerals, organic acid [10], alcohol, amino acid [11], and chitosan. The morphology of calcium carbonate can also be induced by biological factors [12]. From the dynamics perspective, mixed solution can help to form the crystal of metastability, for example, the mixture of alcohol and water. With ammonia, hexagonal calcium carbonate crystal can be formed by the self-assembly of vaterite nanoparticles. While in the reaction of CO₂ gas and CaCl₂ solution, ammonia can function to shape the CaCO₃ into spherical vaterite of metastability [13]. In addition, the spherical CaCO₃ after thermal decomposition becomes spherical CaO which can be used as catalyst in biodiesel or to manufacture the organic light-emitting diode. Magnesium also plays an important role in the precipitation of calcium carbonate. When the Mg²⁺ concentration degree is low, calcite is formed; when it is high, aragonite is formed.

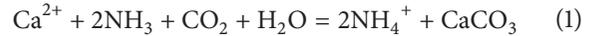
Making ultrafine calcium carbonate, mix solution with Ca²⁺ and solution with CO₃²⁻ or add organic substance to regulate the mass transfer of Ca²⁺ and CO₃²⁻ to control nucleation and formation of crystal. What is more, CO₂ gas can be added to Ca(OH)₂ solution [14]. The method of the reaction of Ca(OH)₂ solution and CO₂ gas [15] is the major way for industrial ultrafine calcium carbonate making considering the production cost. However, in this method, Ca(OH)₂ solution can also be replaced by other solutions with Ca²⁺, such as CaCl₂ solution. The solution should be changed to alkaline in order to make the reaction with CO₂ happen faster, and the process of alkalization is usually achieved by using ammonia solution. Also, the method of adding ammonia and CO₂ gas to gypsum serum to make ammonia sulfate is to recycle the gypsum to solid wastes and has produced calcium carbonate as well. The common method of making calcium carbonate in existing findings is basically using solution with high concentration of Ca²⁺ as source of calcium, through which enough calcium carbonate can be obtained. However, solution with low concentration of Ca²⁺ is also worth being studied [16, 17]. The supersaturation degree will remain at a low level. Theoretically, in the system with low degree of supersaturation, the control of the morphology of calcium carbonate particles will be easier. In the process of formation and precipitation of crystal, the solution becomes supersaturated and the crystal nucleus is formed with the clashes of ions. Then the ions that constructed the crystal in the solution diffuse and precipitate on the surface of crystal nucleus, which is called the crystal nucleus growth. Crystal nuclei form crystal particles gradually, and particles concentrate and form crystal with orientation arrangement. If the supersaturation degree is too high, it is easy to form amorphous precipitate. With a low supersaturation degree, the growth velocity of crystal is slow, and the surface of crystal is well formed. When the supersaturation degree is too high, the reaction of Ca²⁺ and CO₃²⁻ will be too quick to control the crystal morphology. Thus, the control of reaction speed is usually achieved by controlling the concentration

of participating substances [18, 19]; for example, in the formation process of biological mineralization (such as the formation of shell), semipermeable membrane is used to control the release of Ca²⁺ or CO₃²⁻. It will function to control the crystal morphology of calcium carbonate.

The focus of this paper is to analyze the morphology of the calcium carbonate precipitate of low concentration degree and the way to control its morphology to infer the formation mechanism of calcium carbonate materials. It is of great importance to research on making nano- and submicron calcium carbonate materials in solutions with Ca²⁺, such as CaCl₂. It can also explain how solutions with low concentration of Ca²⁺, such as calcium sulfate, can form the calcium carbonate materials with unique morphology.

2. Experimental Details

Calcium carbonate precipitate is made by adding CO₂ gas to solution with Ca²⁺. Calcium sulfate saturated solution with about 0.015 mol/L of Ca²⁺ is used since it will be a proper concentration for the calcium carbonate precipitating. If we need a higher concentration of Ca²⁺, CaCl₂ solution is used. Since calcium sulfate or CaCl₂ solution is neutral, Ca²⁺ and CO₂ will not react. Thus, ammonia liquid is added to the solution as follows:



The reagents and additives used in this experiment include calcium sulfate, calcium chloride, sodium carbonate, sodium chloride, ammonia, alcohol, and sodium acetate, which are all analytical reagents (BOLT Tianjin Chemical Co., Ltd., China). A CO₂ cylinder (99.5% in purity) is used to provide carbon source. The anionic surfactant (Nafine Chemical Industry Group Co., Ltd., China) including sodium alkane sulfonate and poly(oxy-1,2-ethanediyl),a-sulfo-w-(dodecyloxy)-, sodium salt (1:1) which is usually used as a detergent is used to control the crystal morphology.

Scanning electron microscope (SEM, JEOL JSM-6701F, Japan) is applied to inspect the morphology of the formed calcium carbonate and X-ray powder diffraction (XRD, Bruker D2 Advance Phaser, Germany) to analyze its crystalline phase. When XRD is used to analyze the crystal morphology, lattice planes 104, 113, 202, 024, 116, 221, and 122 correspond to the diffraction peaks of crystal planes of the calcite, while 110, 112, 114, and 300 correspond to the diffraction peaks of crystal plane of vaterite. According to the literature [20], the proportion of vaterite (f_v) can be calculated as follows:

$$f_v = \frac{(I_{110v} + I_{112v} + I_{114v})}{(I_{110v} + I_{112v} + I_{114v} + I_{104c})}, \quad (2)$$

where I is the intensity of diffraction peak, the subscript v represents the vaterite, and c represents calcite.

3. Results and Discussion

3.1. Influence of Ammonia on the Crystal Phase of Calcium Carbonate. To investigate the influence of ammonia on

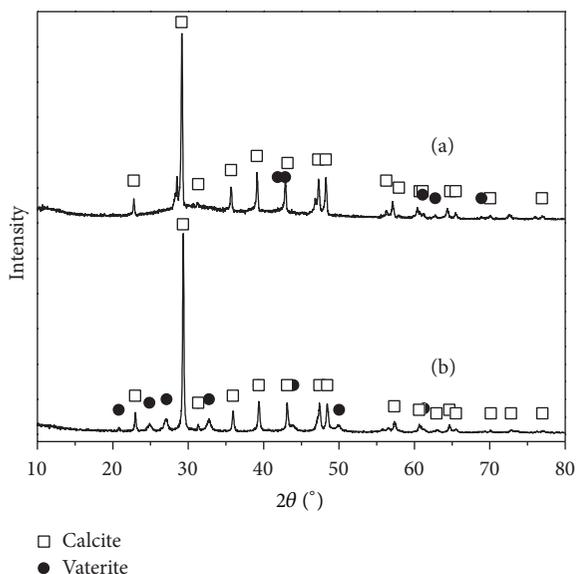


FIGURE 1: Crystal phase of calcium carbonate precipitate. (a) Solutions: CaCl_2 , 0.18 mol/L; Na_2CO_3 , 0.18 mol/L. (b) Solutions: CaCl_2 , 0.13 mol/L; NH_3 , 0.74 mol/L. CO_2 gas: 60 ml/min \times 20 min.

crystal polymorphs of calcium carbonate precipitate, the XRD spectra of calcium carbonate obtained in two reaction systems, one with ammonia and the other without, were compared, as shown in Figure 1. The calcium carbonate obtained by mixing calcium chloride and sodium carbonate solutions is shown in Figure 1(a). Figure 1(b) is the calcium carbonate obtained by mixing calcium sulfate solution with ammonia liquid and CO_2 gas. The concentration degrees of Ca^{2+} of two experiments are similar.

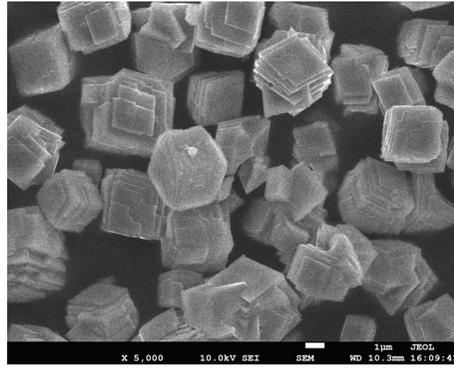
Figure 1(a) shows that when ammonia is not added, calcite is the major crystal morphology of calcium carbonate precipitate, containing a little crystal morphology of vaterite. According to (2), the proportion of calcite is 98.52%, while the remaining 1.48% is the vaterite, in terms of their total amount. When ammonia is added to the solution, the characteristic peak of vaterite is intensified, as shown in Figure 1(b). The precipitate at this time contains crystal morphology of both calcite and vaterite and a little aragonite. The calculation in (2) shows that the proportion of calcite reaches 87.83% of the total amount of calcite and vaterite, while the rest 12.17% is vaterite. It shows that adding ammonia functions to form vaterite.

When ammonia is used to form calcium carbonate precipitate, the pH is controlled between 8 and 11 [13], which is the interval to form spherical vaterite steadily. The reaction process includes CO_2 dissolving in water, ammonia and water forming NH_4^+ , and OH^- , CO_2 , and OH^- forming HCO_3^- . Finally, CO_3^{2-} is formed, and calcium carbonate is formed with Ca^{2+} and CO_3^{2-} . In this process, the speed controlling step is the formation of HCO_3^- . Supersaturation degree of calcium carbonate around the CO_2 gas bubbles is very high, which provides condition to create the new solid particles. When degree of supersaturation is maintained at a relatively high value, new vaterite will form its nucleus around the

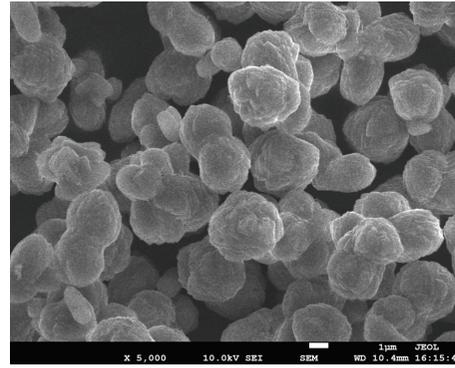
CO_2 bubbles. The dense nucleation of vaterite prevents it from dissolving and renucleation and prevents the growth of more stable calcite crystal. High degree of supersaturation can benefit to form the metastable vaterite in the dynamics perspective and stop it from transforming into calcite. The supersaturation degree can be achieved with high pH since when pH is high, the speed of dissolving CO_2 and forming CO_3^{2-} is fast, which can be achieved by adding ammonia. Thus, when ammonia exists in solution, it is easy to form calcium carbonate precipitate with crystal morphology of vaterite.

3.2. Influence of Ammonia on the Morphology of Calcium Carbonate Precipitate. Figure 2 shows, under different operation, ammonia has impact on the morphology of calcium carbonate precipitate. Figure 2(a) indicates that when solutions with Ca^{2+} and CO_3^{2-} are mixed, the calcium carbonate precipitate is cubic, which is the morphology of calcite. After ammonia is added, as shown in Figure 2(b), the precipitate embodies the rough spherical shape, ellipsoidal shape, and twin spherical shape. On the one hand, the reason can be that ammonia raised the supersaturation degree of calcium carbonate to form spherical calcium carbonate. On the other hand, the amount of Ca^{2+} and CO_3^{2-} decreased as the reaction went on, and degree of supersaturation decreases, which makes spherical calcium carbonate tends to form more stable cube. Thus, the crystal manifests the topograph of calcite, and edges and corners become sharper. These two conditions affect each other. As a result, the calcium carbonate precipitate shows the rough spherical morphology. Meanwhile, it is assumed that calcium carbonate particles in the solution form cubic or spindle-shaped crystal nucleus. The crystal nuclei have high surface energy in the direction of edge and corner. With the steric effect of ammonia, partial Ca^{2+} and CO_3^{2-} at the edge and corner direction concentrate and grow quickly, and partial degree of supersaturation is very high. Many small crystal particles formed in the process of nucleation. Particles formed twin spherical calcium carbonate by combining themselves to achieve the minimization of surface area.

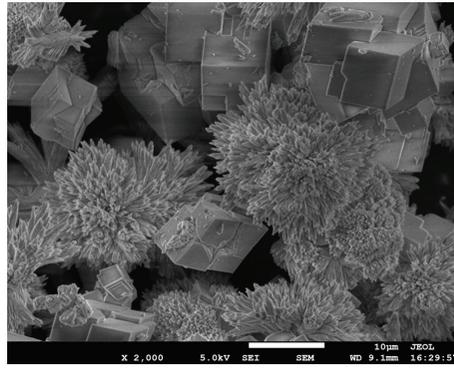
Figures 2(c) and 2(d) show another growth type of crystal. It is in the system of Ca^{2+} solution and CO_2 gas bubbles. Since CO_2 gas is continuously added to the solution, the degree of supersaturation in the reaction will not be decreased and can be maintained at a certain level. When the amount of ammonia is small and cannot maintain the degree of supersaturation at the level of producing vaterite, the calcium carbonate includes cube and needle-cluster shape. When the amount of ammonia is big, most of the calcium carbonate precipitate is spherical, which shows that ammonia has influence on the topograph of calcium carbonate. It means that ammonia can help the calcium carbonate to precipitate in the morphology of vaterite. In most cases, it is well known that the calcium carbonate tends to form the stable cube shape. Therefore, the needle-cluster calcium carbonate may be assumed to be the transition morphology between the cubic and spherical shape under the effect of ammonia.



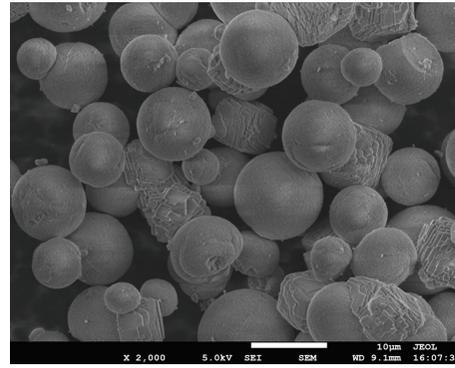
(a) Solutions: CaCl_2 , 0.18 mol/L; Na_2CO_3 , 0.18 mol/L



(b) Solutions: CaCl_2 , 0.18 mol/L; Na_2CO_3 , 0.18 mol/L; NH_3 , 3.39 mol/L



(c) Solutions: NH_3 , 0.36 mol/L; CaSO_4 , 0.15 mol/L. CO_2 gas: 60 mL/min \times 20 min



(d) Solutions: NH_3 , 1.47 mol/L; CaSO_4 , 0.15 mol/L. CO_2 gas: 60 mL/min \times 20 min

FIGURE 2: Morphology of calcium carbonate precipitate with and without ammonification.

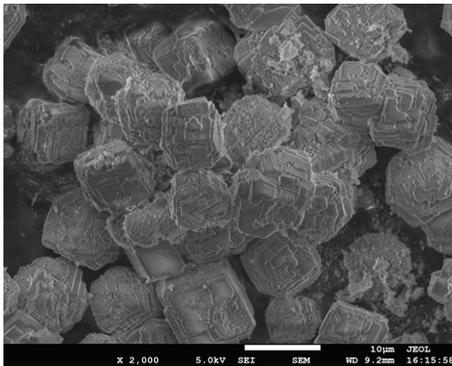
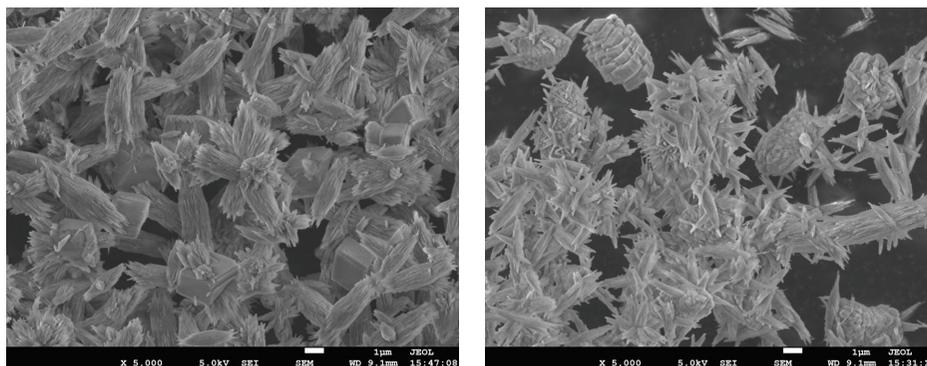


FIGURE 3: Morphology of calcium carbonate precipitate. Solutions: CaSO_4 , 0.15 mol/L. CO_2 gas: 55 mL/min \times 20 min. Final pH = 10.

Figure 3 shows the precipitate of calcium carbonate in another reaction system. Constantly adding CO_2 in the saturated solution of calcium sulfate until pH decreases from 7 to 4.6 and adding ammonia liquid and controlling the pH of the solution at 10, the precipitate of the calcium carbonate is shown in Figure 3. Before adding ammonia liquid, the Ca^{2+} , SO_4^{2-} , and H_2CO_3 will not react. After adding ammonia, calcium carbonate precipitate and ammonia sulfate are formed instantly. The reason inferred is

that the degree of supersaturation became high suddenly. Therefore, the crystal morphology is the spherical vaterite. However, without new supplementing CO_2 , the amount of Ca^{2+} and H_2CO_3 decreased as the reaction went on, and the degree of supersaturation is decreased as well. The shape of vaterite gradually transforms into calcite. Figure 3 shows the intermediate state of spherical crystal morphology transforming into cubic crystal morphology, and the comparison with Figure 2(a) explains that the effect of ammonia in the calcium carbonate crystal growing process is to accelerate the precipitate into spherical morphology.

The ultrasound usually has an influence on the precipitation of calcium carbonate [21]. Ultrasound can make the suspended particles dispersed and has a role in preventing the formation of large particles precipitated. Therefore, under the effect of ultrasound, the precipitate formed will be relatively small. With the interference of ultrasound, we can see clearer the effect of ammonia on shaping particle morphology of precipitate. Without ammonia, calcium carbonate precipitate with ultrasound shows the cubic and spindle-shaped morphology, like in Figure 4(a). Figure 4(b) indicates that when increasing the amount of ammonia, ammonia accelerates the transformation of cubic calcium carbonate particles into rough spherical morph and egg-shaped morphology, as shown in Figure 4(a). Apparently, the surface is a bit sharp, which means the formation still



(a) Solutions: NH_3 , 1.47 mol/L; CaSO_4 , 0.15 mol/L. CO_2 gas: 1560 mL/min \times 20 min. CO_2 (v%) = 3.88%

(b) Solutions: NH_3 , 3.39 mol/L; CaSO_4 , 0.15 mol/L. CO_2 gas: 1560 mL/min \times 20 min. CO_2 (v%) = 3.88%

FIGURE 4: Morphology of calcium carbonate precipitate under ultrasound.

obeys the rule of forming calcite, while the look is more like a sphere. Ammonia can influence the morphology of calcium carbonate precipitate developing into sphere. Apart from increasing the degree of supersaturation, steric effect may be used to accelerate the spherical formation of calcium carbonate.

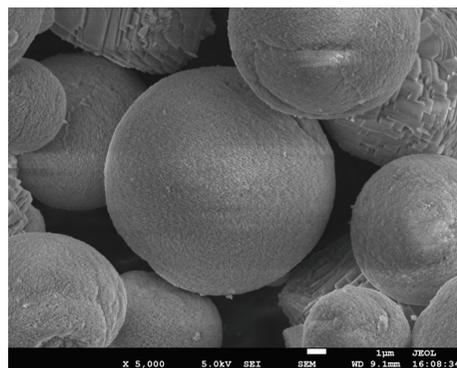
3.3. Controlling the Morphology of Calcium Carbonate by Electrolyte and Surfactant. With different types of electrolyte, ammonia can have different effects on calcium carbonate particles, as shown in Figures 5(a) and 5(b). When adding inorganic salt to increase the ion strength, morphology of calcium carbonate particles has two conspicuous changes. First, the diameter decreases from 5~12 μm to 5 μm . Second, clustering of particles and twin spherical polymorph appear. Figures 5(c) and 5(d) show that, by adding alcohol and organic acid and salt, the diameter of calcium carbonate particles decreases to about 3 μm and the clustering effect becomes more conspicuous. In Figure 5(e), the anionic surfactant can decrease the diameter of calcium carbonate particles to 500 nm~1 μm .

In most of the conditions, calcium carbonate in calcite crystal type shows the spindle-shaped and cubic polymorph, while the vaterite type resembles the spherical shape. In the formation process of calcium carbonate, calcite is the stable crystal polymorph. Thus, the crystal grows into the prism shaped calcite without additives. Sphere is shaped since the ions have different effects in the electrolyte or the additives have large steric effect to deter the growth of calcium carbonate crystal. According to the dynamics of crystal growing, the nucleation rate of calcium carbonate is positive to the degree of supersaturation. Adding dissolvable salt can cause the salt effect to increase supersaturation degree of calcium carbonate. The critical dimension of particle nucleus and energy required in the nucleation process are decreased, while the nucleation rate increases. The rates of nucleation and growth are of competing relation, which means when the nucleation rate is high, the growth rate is low. On a macrolevel, the particle diameter decreases and, meanwhile, the gradient of concentration increases when the degree of supersaturation is high. Clustering or other polymorphs will

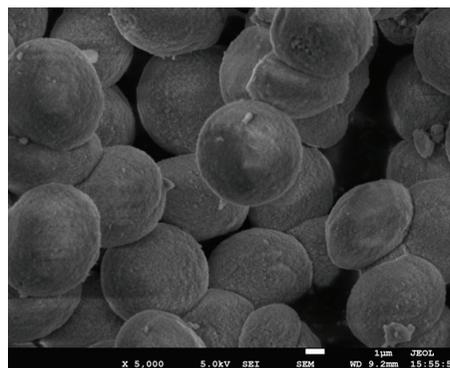
be shaped since corners and edges of the crystal have larger areas than the center of the surface to take the accumulation of mass points. That is why in Figure 5 adding inorganic salt, alcohol, and organic acid salt, the particle diameter and polymorph of calcium carbonate will change significantly. In addition, the surfactant can change the surface state of the solution system and make the indissoluble particles disperse. In terms of Figure 5(e), the interaction of surfactant and Ca^{2+} helps the nucleation of vaterite in supersaturation solution and stops the growth and clustering of calcium carbonate particles. Thus, the diameter is shrunk.

4. Conclusion

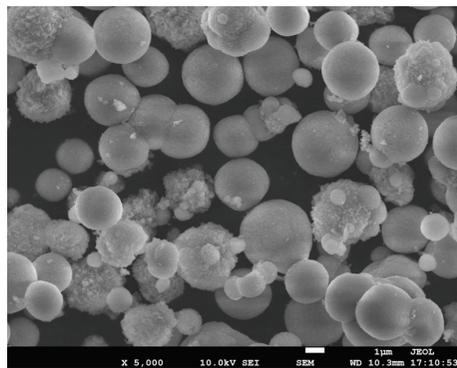
In the solution of low degree of concentration with about 0.015 mol/L Ca^{2+} and under the condition of low degree of supersaturation, ammonification and carbonization methods are applied to make ultrafine particles of calcium carbonate. With low degree of supersaturation, the reaction rates of Ca^{2+} and CO_3^{2-} are not that quick, so that it is expected to be easy to control the crystal polymorph. When the reaction system does not include ammonia, the precipitate of calcium carbonate is mainly of the crystal morphology of calcite and a little crystal morphology of vaterite. The proportion of calcite will be over 98%. Adding ammonia to the solution helps to form the vaterite, and the precipitate of calcium carbonate is the mixture of calcite and vaterite. At the same time, a little aragonite is also formed. The influence of ammonia on crystal morphology of calcium carbonate precipitate is achieved by creating great partial degree of supersaturation. Ultrasound can also be applied to infer that ammonia can form calcium carbonate into spherical shape with steric effect. In addition, with forming the cubic or spindle-shaped crystal nucleus of calcium carbonate in the solution, ammonia can also function to concentrate partial Ca^{2+} and CO_3^{2-} at the edge and corner direction and form the twin spherical calcium carbonate. Without other additives, the calcium carbonate formed is with a diameter of about 5~12 μm . Inorganic salt, alcohol, or organic acid and salt can have significant effect on controlling the particle diameter of calcium carbonate and will trigger salt effect, which increases the degree of supersaturation of



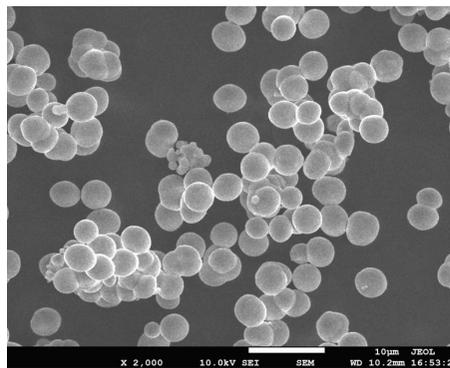
(a) Solutions: NH_3 , 1.47 mol/L; CaSO_4 , 0.15 mol/L. CO_2 gas: 55 mL/min \times 20 min



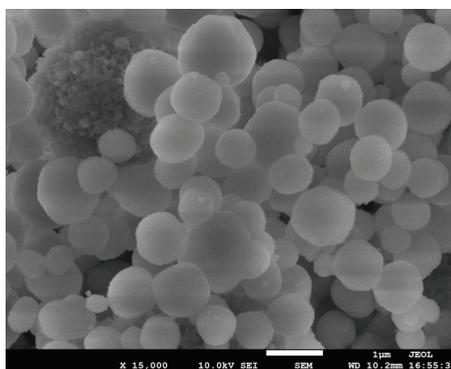
(b) Solutions: NH_3 , 1.47 mol/L; CaSO_4 , 0.15 mol/L; NaCl , 1.65 mol/L. CO_2 gas: 55 mL/min \times 20 min



(c) Solutions: NH_3 , 0.29 mol/L; CaSO_4 , 0.15 mol/L; $\text{CH}_3\text{CH}_2\text{OH}$, 1.72 mol/L. CO_2 gas: 40 mL/min \times 20 min



(d) Solutions: NH_3 , 0.29 mol/L; CaSO_4 , 0.15 mol/L; CH_3COONa , 1.21 mol/L. CO_2 gas: 40 mL/min \times 20 min



(e) Solutions: NH_3 , 0.29 mol/L; CaSO_4 , 0.15 mol/L; anionic surfactant, 2 mL/L. CO_2 gas: 40 mL/min \times 20 min

FIGURE 5: Morphology of calcium carbonate precipitate with different additives.

calcium carbonate and shrinks its size to about $3\ \mu\text{m}$. What is more, clustering occurs and the anionic surfactant can deter the clustering of calcium carbonate particles and shrink its size to $500\ \text{nm}\sim 1\ \mu\text{m}$.

Conflict of Interests

The authors declare that they have no financial and personal relationships with other people or organizations that can inappropriately influence their works; there is no professional

or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, the paper.

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