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Factors affecting the phase and morphology of $CaCO_3$ prepared by a bubbling method

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Abstract

Precipitated calcium carbonate (PCC) was prepared by bubbling a CO_2/N_2 mixed gas into a $CaCl_2$ solution. The influence of preparation conditions on the phase and morphology of PCC was discussed with the help of XRD and SEM measurements. The results showed that the initial $CaCl_2$ concentration, flow rate and temperature play an important role on the morphology of PCC. At low initial $CaCl_2$ concentration or high flow rate, spherical vaterite was preferably formed. Otherwise, the rhombic calcite was ready to form. Temperature is a determining factor on the formation of aragonite. Needle-like aragonite was precipitated at 60 °C. The results also indicated that both the bubbling time and stirring rate have a minor effect on the phase and morphology of PCC.

Keywords: Grain growth; X-ray methods; Chemical properties; Biomedical

1. Introduction

The demand for precipitated calcium carbonate (PCC) has been rapidly growing in recent years in the fields of paper making, rubber, plastics, paints, food and horticulture.[1,2] The application of PCC particles is mainly determined by a great number of strictly defined parameters, such as particles morphology, structure, size, surface area, brightness, and so on.[3] One of the most important parameters is the particles morphology. Calcium carbonate has three kinds of crystal polymorphs, which is generally classified as rhombic calcite, needle-like aragonite and spherical vaterite. The physicochemical properties of these polymorphs, such as solubility, density and morphology, are different, which results in different properties in application. For example, the properties of printing characteristic, brilliancy and color are greatly influenced by their polymorphs, when calcium carbonate particles are used as an additive to paper. Therefore, polymorphic control of the precipitate is very important.

A considerable amount of attention and effort have been devoted to investigate the preparation of PCC, to elucidate the relationship between the preparation condition and the particle morphology.[4–6] Tai and Chen[4] attributed the morphological change of calcium carbonate to the supersaturation level and the pH of solution. Charkraborty and Bhatia[5] observed that the crystalline form and particles size distribution are dependent on the supersaturation level and ionic ratio of $[Ca^{2+}]/[CO_3{}^{2-}]$ in solution. While Jung et al.[6] have demonstrated that the change in particles morphology was mainly caused by the excess species of the reactants in the solution rather than by supersaturation. Although there are many investigations in the precipitation of calcium carbonate, the relationship between precipitation conditions and product morphology is still cloudy and disputed.

The main purpose of this paper is to investigate the influence of preparation parameters on the morphology of PCC. The relationship between preparation conditions and morphology are briefly discussed and the major factors affecting the morphology of PCC are pointed out.

2. Experiments

Calcium chloride (Wako Pure Chemicals, Japan) and ammonia (Wako Pure Chemicals, Japan) were mixed and

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diluted to form a solution. The freshly prepared solution reacted with a gas mixture ($CO_2 + N_2$) that was introduced to the bottom of the reactor vessel via a micropore-sized gas distributor. The reaction temperature was kept constant by a water bath. During the carbonation, the solution was continuously stirred at a constant rate by means of Teflon-coated magnetic stirring bar. The total volume of the working solution was 500 mL and the pH of the solution was measured by a pH meter (Cyberscan, made in Singapore). The precipitation was assumed to be finished with the indication of no further change in pH value. The prepared solids were collected by filtering through membrane filters (0.2 μm) and dried at 120 °C for at least 24 h, and used for measurements. SEM (JEOL JSM-6100) was used to observe the morphologies of the samples. XRD (RINT, Rigaku, Japan) measurements were conducted using Cu Kα radiation (40 keV, 30 mA) to identify the composition of the samples. The scanning step is 0.02° and 2θ ranges from 20° to 60°.

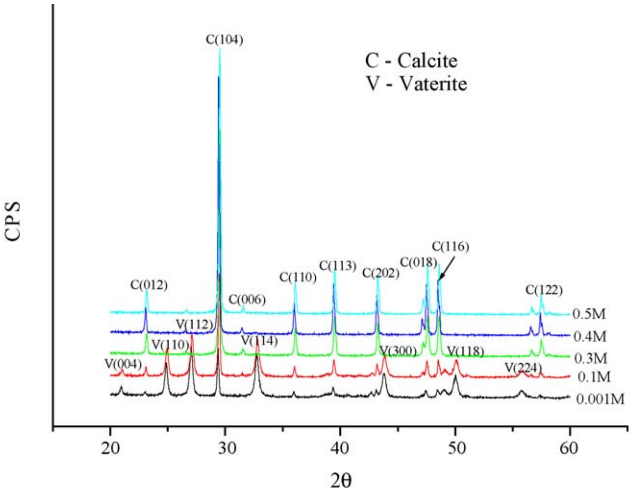
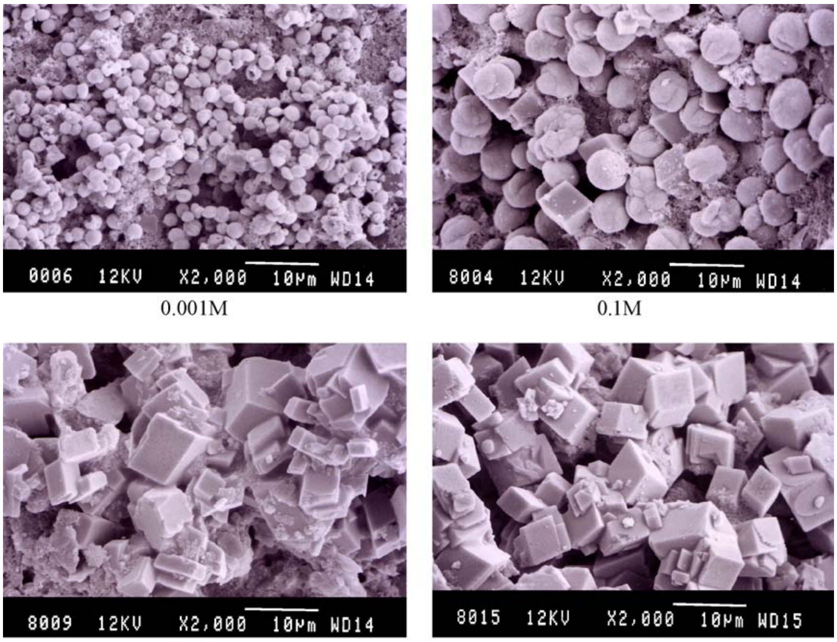


Fig. 2. XRD patterns of PCC prepared at different initial $CaCl_2$ concentration.

3. Results and discussion

3.1. Initial $CaCl_2$ concentration

Fig. 1 shows the influence of the initial $CaCl_2$ concentration on the morphology of $CaCO_3$ particles, where the flow rate, temperature and stirring rate were kept at 0.9 L/min, 25 °C, 400 rpm, respectively. The morphology of $CaCO_3$ particles was quite sensitive to the variations of the initial $CaCl_2$ concentration. Spherical particles with a diameter of 1–2 μm were formed at 0.001 M. With the increase of initial $CaCl_2$ concentration, more and more rhombic particles were formed with a mixture of spherical particles. When the initial $CaCl_2$ concentration increased to 0.3 M, the spherical particles disappeared and only rhombic particles were observed. Fig. 2 shows the XRD patterns of the prepared samples. When the initial $CaCl_2$ concentration was below 0.1 M, the samples contain two crystal phases, namely vaterite and calcite. When the initial $CaCl_2$ concentration was increased to 0.3 M, only calcite was found in the samples. The change of PCC morphology with the initial $CaCl_2$ concentration may be attributed to the change of $[Ca^{2+}]/[CO_3{}^{2-}]$. Our results indicated that the formation of calcite is favored by the increase



0.001M 0.1M

0.3M 0.5M

Fig. 1. SEM image of PCC prepared at different initial $CaCl_2$ concentration.

of the $[Ca^{2+}]/[CO_3{}^{2-}]$ ratio in the mother solution, which is consistent with the result of Morales et al.,[7] which has been ascribed to the formation of $CaCO_3{}^0$ growth unites at the $CaCO_3$-solution interface. The formation of this neutral pair was enhanced by increasing the ratio of $[Ca^{2+}]/[CO_3{}^{2-}]$ in the mother solution because of their different largmurian adsorption coefficients on the rhombohedral calcite surface, i.e. $KCO_3{}^{2-} > KCa^{2+}$.[8] In our experiments, the flow rate was kept constant so that the concentration of $CO_3{}^{2-}$ ion was the same in each experiment. When the initial $CaCl_2$ concentration increased, the $[Ca^{2+}]/[CO_3{}^{2-}]$ ratio would increased, which is in favor for equal adsorption of Ca^{2+} and $CO_3{}^{2-}$ on the surface of calcite, thus improving the growth of calcite. Usually, the supersaturation is the main factor affecting the crystal structure of PCC. However, when one of the reactants is extraordinary excess, only the factor of supersaturation is not enough to explain the experimental results. At that time, we have to consider the influence of the $[Ca^{2+}]/[CO_3{}^{2-}]$ ratio.

3.2. Flow rate

A gas mixture ($CO_2 + N_2$) containing 33.3 vol% of CO_2 was used to investigate the influence of flow rate on the morphology of PCC, where the initial $CaCl_2$ concentration, temperature and stirring rate were kept 0.1 mo/L, 25 °C and 400 rpm, respectively. Fig. 3 showed the morphology change of PCC prepared at different flow rates. When the flow rate was 0.03 L/min, only rhombic particles were observed. With the increase of flow rate, spherical particles appeared. The results of XRD measurement revealed that only rhombic calcite were found at 0.03 L/min while the peaks of vaterite appeared and increased obviously with flow rate. Because there is no signal for amorphous phase in XRD pattern, the equation as proposed by Subba Rao[9] can be used to express the relative fraction (fc) of vaterite in the crystalline phases.

$$\text{fv} = \frac{I_{110V} + I_{112V} + I_{114V}}{I_{110V} + I_{112V} + I_{114V} + I_{104C}}$$

The subscripts V and C here indicate vaterite and calcite, respectively. The fraction of calcite is (1 − fv). The calculation results of fv at different flow rate were shown in Fig. 4. It is easy to conclude that the fraction of vaterite increase with flow rate.

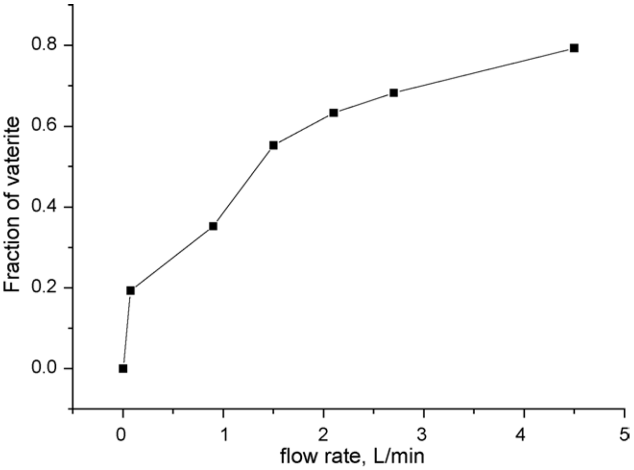
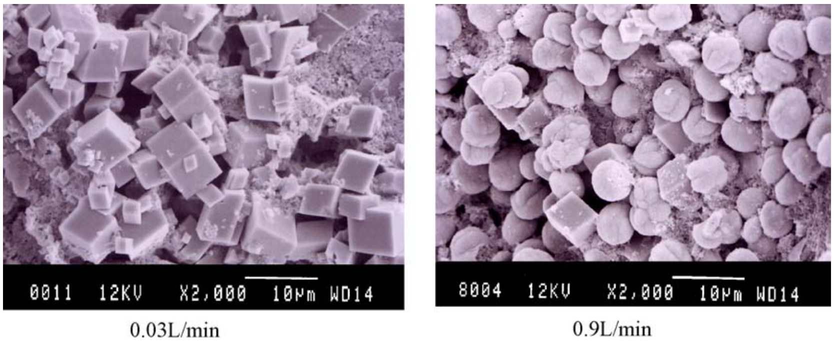


Fig. 4. Relative fraction of vaterite in the samples prepared at different flow rate.

The change of PCC morphology and phase with flow rate may be attributed to the dissolution rate of CO_2 at different conditions. The increase of flow rate would enhance the dissolving of CO_2 and the accumulation of H^+, $HCO_3{}^-$, $CO_3{}^{2-}$ ions, thus increasing the supersaturation of solution. The high supersaturation leads to the quick nucleation and precipitation, which limits the transformation of vaterite to calcite. So the spherical vaterite were preserved and became the major phase at the high flow rate.[10,11] On the other hand, a low flow rate leads to low supersaturation because of insufficient supply of CO_2, which is in favor of dissolution of vaterite, thus accelerating the transformation from vaterite to calcite.[11] So only calcite was observed at a low flow rate.

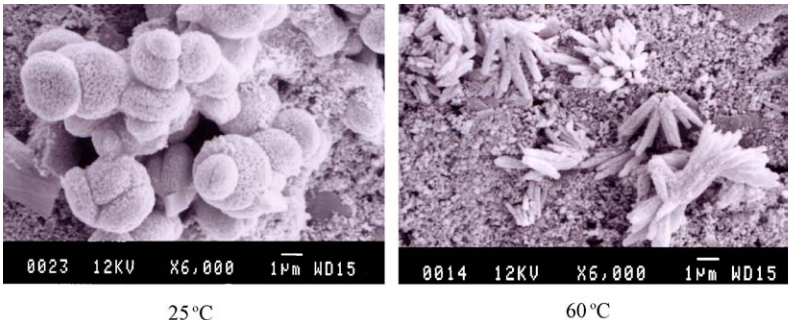
When the flow rate was fixed at 0.9 L/min and the CO_2 content changed from 33.3 vol% to 66.6 vol%, the increase of vaterite fraction was also observed, which clearly supported the above explanation that the CO_2 concentration in the solution influenced the polymorphs formation of calcium carbonate.



0.03L/min

0.9L/min

Fig. 3. SEM images of PCC prepared at different flow rate.



25 °C 60 °C

Fig. 5. SEM image of PCC prepared at different temperature.

3.3. Temperature

The morphology of $CaCO_3$ particles prepared at 25 °C and 60 °C were shown in Fig. 5. Spherical particles were formed at 25 °C whereas needle-like particles were formed at 60 °C. These results in combination of XRD data reveal that the samples prepared at 25 °C composed of vaterite and calcite while only aragonite was observed in powder prepared at 60 °C. This result indicates that the temperature plays an important role on the crystallization behaviors of polymorphs, which agrees well with other researches on the influence of temperature.[12,13]

The change of polymorphs with temperature may be ascribed to the thermal vibrations. Aragonite was coordinated to nine oxygen atoms to the calcium atoms, probably accounting for an increase in effective radii of the calcium atoms at high temperature.

Gabrielli has investigated the growth of aragonite and two growth models have been proposed.[14] In the first case, primary aragonite appeared as isolated thin needles with their growth along their c-axis. In the second case, aragonite crystals presented the aspect of irregular spindle subdivided in small cubic blocks. Our results on the growth of aragonite seem to fulfill second model.

3.4. Bubbling time

Fig. 6 showed the influence of bubbling time on the morphology of PCC, where the bubbling time is referred to the time for bubbling before the reaction finish. All the samples were prepared at the conditions of 0.1 mol/L initial $CaCl_2$ concentration, 25 °C, 0.9 L/min flow rate and 400 rpm stirring rate. Fig. 6a showed the sample prepared after 2 min bubbling while Fig. 6b showed the samples after 15 min bubbling. It can be concluded that the morphology of samples prepared at different bubbling time are not too much different except that the particles prepared at short bubbling time contain some small particles, as shown in Fig. 6a. There are two possible reactions during the process of bubbling. One is the formation of new precipitation. Another is the transformation of vaterite to calcite because calcite is the thermodynamic stable phase of calcium carbonate. From SEM results, we can conclude that the transformation mainly happens at the beginning of bubbling. With prolonging of bubbling time, the new precipitates are formed and particles grow.

3.5. Stirring rate

The experiments have been carried out at different stirring rate. The results revealed that the spherical particles were formed by the aggregation of fine particles with a diameter of 50–100 nm. At low stirring rate, the fine particles were aggregated and formed dense particles, while the particles prepared at high stirring rate looked loosely. This result can be ascribed to the influence of hydrodynamics on the particles formation. In the carbonation of $CaCl_2$ solution, the initial precipitate is amorphous calcium carbonate,[15] which is the unstable form and is often described in spherical shapes. The initial formed

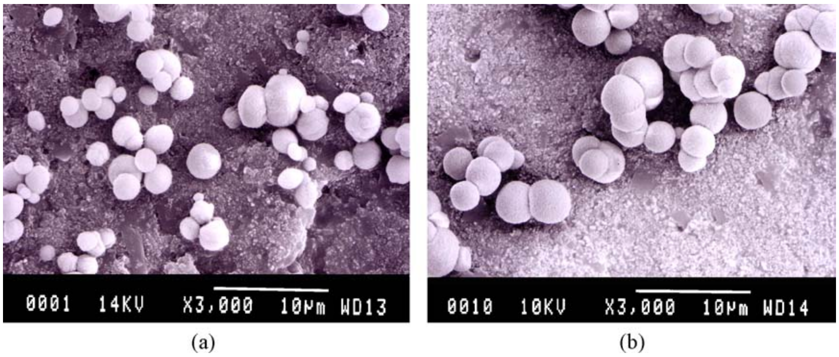


Fig. 6. SEM image of PCC prepared at different bubbling time.

$CaCO_3$ is quickly transformed to two crystalline phases, namely calcite and vaterite. The freshly prepared fine particles are not stable because of its high surface free energy, the crystalline fine particles tend to aggregate to achieve a minimum total surface free energy. At the high stirring rate, the aggregation was influenced by the stirring rate and formed the loose particles.

4. Conclusions

Precipitated calcium carbonate was prepared by bubbling a CO_2/N_2 gas into a $CaCl_2$ solution. The influence of preparation conditions on the phase and morphology of PCC were discussed. The results showed that the initial $CaCl_2$ concentration, flow rate and temperature played an important role on phase and morphology of PCC while the bubbling time and stirring rate did not show obvious effect. Both a low initial $CaCl_2$ concentration (from 0.001 M to 0.1 M) and a low flow rate (from 0.9 L/min to 3 L/min) are in favor of the formation of spherical vaterite. Temperature is a determining factor for the formation of aragonite. The needle-like aragonite was prepared at 60 °C in this paper.

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