Research Article

Effects of EDTA and Boric Acid on the Morphology of CaCO₃ Particles

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Calcium carbonate (CaCO₃) particles with different morphologies were prepared using calcium chloride (CaCl₂) and sodium carbonate (Na₂CO₃) aqueous solutions containing various amounts of ethylenediamine tetraacetic acid (EDTA) or boric acid. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The sphere-like CaCO₃ particle was inclined to be formed in EDTA or boric acid solution at room temperature. The surface of CaCO₃ is smooth in the presence of EDTA, and the crystal structure of CaCO₃ is majorly vaterite. However, the CaCO₃ has a rough surface in boric acid solution and pure calcite structure. The size of CaCO₃ particle decreases with the increase in the amount of EDTA or boric acid.

1. Introduction

Calcium carbonate (CaCO₃) is one of the most abundant materials on the planet and has been often used in ground form to produce polymer composites [1, 2]. Recently, there have been some interests in controlling the crystallization of CaCO₃ and the usage of various types of inorganic/organic additives in order to obtain unusual morphologies, crystal sizes, and control the outcome polymorph type [3, 4]. Research on the controlling mineralization of CaCO₃ has focused on the following two approaches: (i) organic additives controlling the morphology and crystal structure of CaCO₃. These water-soluble additives include hydrophilic synthetic polymers [5, 6] and low-molecular mass organic additives [7–9], such as carboxylic or amino acids. The second approach is (ii) inorganic ions controlling the morphology and crystal structure of CaCO₃. It has been reported that crystallization of CaCO₃ is also affected by inorganic ions, such as Ba²⁺ and Co²⁺ [10–12].

In this work, CaCO₃ crystals were precipitated using aqueous mixtures of CaCl₂ and Na₂CO₃ in the presence of EDTA or boric acid. The CaCO₃ particles were characterized with XRD and SEM.

2. Experimental

Calcium chloride (CaCl₂), sodium carbonate (Na₂CO₃), ethylenediamine tetraacetic acid (EDTA), and boric acid were purchased from Beijing Chemical Works. These agents were all analytical reagent degree.

Alkaline condition: an aqueous solution containing 50 mL Na₂CO₃ (0.5 M) was stirred continuously for about 15 min at room temperature (25°C), and then different amounts of EDTA or boric acid (0.5 g, 1.0 g, and 1.5 g) were added. The mixed solution was alkaline because of the small amount of EDTA or boric acid. 50 mL CaCl₂ (0.5 M) was gradually added into the above mixed solution and kept stirring for 60 min.

Acidic condition: the operation steps were same as above, the difference was only that 50 mL Na₂CO₃ (0.5 M) was added into the mixed solution of CaCl₂ and additives.

The precipitate was washed by deionized water and ethanol and then dried at 80°C for 24 h.

X-ray diffraction (XRD, 2500VB2+PC, Cu Ka radiation, Rigaku, Japan) was used to analyze the composition and crystal structure of the prepared micro-CaCO₃ products. The shapes of the products were characterized by scanning electron microscopy (SEM, S-4700, Hitachi, Japan).
Figure 1: SEM images and XRD patterns of CaCO$_3$ prepared in the presence of EDTA in alkaline condition. (A)–(C) SEM images of synthesized CaCO$_3$, (D) XRD patterns of product A (a), product B (b), and product C (c).

3. Results and Discussion

Figure 1 shows the SEM images and XRD patterns of the prepared CaCO$_3$ after adding different amounts of EDTA in alkaline condition. SEM image given in Figure 1(A) indicates that the particle, produced with addition of 0.5 g EDTA, is a majority of flower shapes with a size of 5 $\mu$m. The images in Figures 1(B) and 1(C) show that the products are composed of sphere-like particles in addition of 1.0 g or 1.5 g EDTA. The nanoparticle shown in Figure 1(C) (with a diameter of 0.5–2 $\mu$m) is smaller than those shown in Figure 1(B) (with a diameter of 1–3 $\mu$m). From the XRD patterns of the as-prepared CaCO$_3$ (Figure 1(D)), in comparison with their standard JCPDS files (calcite, 47-1743 and vaterite, 33-0268), the flower (Figure 1(D), (a)) and sphere-like (Figure 1(D), (b) and (c)) CaCO$_3$ particles are major vaterite structure.

Figure 2 shows the SEM images and XRD patterns of the synthesized CaCO$_3$ after adding different amounts of EDTA in acidic condition. Figure 2(A) indicates that the product is composed of a rodlike particle and a small part flower-like particle with a length of 3 $\mu$m with addition of 0.5 g EDTA. Figure 2(D) XRD patterns of the CaCO$_3$ demonstrate that pure calcite was produced (Figure 2(D), (a)). Figures 2(B) and 2(C) indicate that the products compose sphere-like CaCO$_3$ particle with a diameter of 1–2.5 $\mu$m in addition of 1.0 g or 1.5 g EDTA. The diffraction peaks (Figure 2(D), (b)) can be well indexed to the calcite and vaterite phase of CaCO$_3$. The diffraction peaks from (Figure 2(D), (c)) show that the hemispherical CaCO$_3$ is a pure vaterite structure.

Figure 3 shows the SEM images and XRD patterns of the synthesized CaCO$_3$ in the presence of EDTA in alkaline condition. Figure 3(A) indicates that the product is a sphere-like particle with a length of 2.5 $\mu$m and a rough surface in the presence of 0.5 g boric acid. Figures 3(B) and 3(C) indicate that the product is a cubic particle (size length of 500 nm or 300 nm) in the presence of 1.0 g or 1.5 g boric acid. The XRD patterns of the CaCO$_3$ can be indexed that the three kinds of products are composed of pure calcite structure (Figure 3(D)).

Figure 4 shows the SEM images and XRD patterns of the synthesized CaCO$_3$ in the presence of boric acid in acidic condition. Figures 4(A), 4(B), and 4(C) indicate that the products are sphere-like particle with a diameter of 2.5 $\mu$m, 1 $\mu$m, and 500 nm by adding 0.5 g, 1.0 g, and 1.5 g boric acid, respectively. The particle surface is rough. The XRD patterns of the CaCO$_3$ can be indexed that the three kinds of products are composed of pure calcite structure (Figure 3(D)).

Mann et al. [13] investigated the crystallization of CaCO$_3$ from supersaturated solutions. The formation of a Stern layer of Ca counterions favors the oriented nucleation of crystal faces consisting of only Ca atoms and the (0001) face of vaterite fits this criterion. Charge accumulation, however, cannot account for the structural selectivity of vaterite, as the (0001) face of calcite is also uni-charged. The trigonal planar carbonate anions are oriented parallel to the (0001) face of calcite, whereas in vaterite they are aligned perpendicularly, and the latter arrangement is equivalent to the orientation of the carboxylate headgroups with respect to the Ca-bound
Figure 2: SEM images and XRD patterns of CaCO₃ prepared in the presence of EDTA in acidic condition. (A)–(C) SEM images of synthesized CaCO₃, (D) XRD patterns of product A (a), product B (b), and product C (c).

Figure 3: SEM images and XRD patterns of CaCO₃ prepared in the presence of boric acid in alkaline condition. (A)–(C) SEM images of synthesized CaCO₃, (D) XRD patterns of product A (a), product B (b), and product C (c).
Figure 4: SEM images and XRD patterns of CaCO₃ prepared in the presence of boric acid in acidic condition. (A)–(C) SEM images of synthesized CaCO₃, (D) XRD patterns of product A (a), product B (b), and product C (c).

Figure 5: The chelation of EDTA and Ca²⁺.

Figure 6: Formation mechanism of CaCO₃ with various shapes.
Stern layer. Thus, the stereochemical arrangement of the carboxylates in conjunction with Ca binding generates a two-layer subunit cell motif of the vaterite structure, rather than calcite. Subsequent addition of carbonate from solution will be similarly stereochemically directed extending the vaterite motif towards a stable nucleus. In our investigation, the electrostatic and stereochemical interactions of EDTA at the inorganic-organic interface are similar to the above mechanism. The chelation of EDTA with Ca$^{2+}$ can be seen in Figure 5. The product was a major spherical CaCO$_3$ particle, which was induced by the addition of EDTA. The size of CaCO$_3$ decreased with increasing in the content of EDTA.

The size of CaCO$_3$ particle decreases with increase the amount of EDTA or boric acid, which can form nucleation point, and the larger size of CaCO$_3$ particle was obtained in the acidic conditions. The sphere-like CaCO$_3$ particle is obtained in the additives containing multicarboxyl or multihydroxyl. However, the carboxyl has a stronger induction than hydroxyl, so the surface of CaCO$_3$ was smooth formed in multicarboxyl compound. According the previous research [11], the formation mechanism of CaCO$_3$ with various shapes was shown in Figure 6.

4. Conclusion

The sphere-like CaCO$_3$ particles were obtained when the amount of EDTA was more than 1.0 g. The surface of CaCO$_3$ is smooth in the presence of EDTA, and the crystal structure of CaCO$_3$ is major vaterite. However, the sphere-like CaCO$_3$ particle was obtained when the amount of boric acid was less than 1.0 g. The CaCO$_3$ has a rough surface in boric acid solution and a pure calcite structure. The size of CaCO$_3$ particle decreases with increase in the amount of EDTA or boric acid, especially in alkaline condition.

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References

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