Research Article

Effects of EDTA and Boric Acid on the Morphology of CaCO_3 Particles

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Calcium carbonate (CaCO_3) particles with different morphologies were prepared using calcium chloride (CaCl_2) and sodium carbonate (Na_2CO_3) 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 CaCO_3 particle was inclined to be formed in EDTA or boric acid solution at room temperature. The surface of CaCO_3 is smooth in the presence of EDTA, and the crystal structure of CaCO_3 is majorly vaterite. However, the CaCO_3 has a rough surface in boric acid solution and pure calcite structure. The size of CaCO_3 particle decreases with the increase in the amount of EDTA or boric acid.

1. Introduction

Calcium carbonate (CaCO_3) 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 CaCO_3 and the usage of various types of inorganic/organic additives in order to obtain unusual morphologies, crystal sizes, and control the outcoming polymorph type [3, 4]. Research on the controlling mineralization of CaCO_3 has focused on the following two approaches: (i) organic additives controlling the morphology and crystal structure of CaCO_3 . 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 CaCO_3 . It has been reported that crystallization of CaCO_3 is also affected by inorganic ions, such as Ba^{2+} and Co^{2+} [10–12].

In this work, CaCO_3 crystals were precipitated using aqueous mixtures of CaCl_2 and Na_2CO_3 in the presence of EDTA or boric acid. The CaCO_3 particles were characterized with XRD and SEM.

2. Experimental

Calcium chloride (CaCl_2), sodium carbonate (Na_2CO_3), 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 Na_2CO_3 (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 CaCl_2 (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 Na_2CO_3 (0.5 M) was added into the mixed solution of CaCl_2 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 K α radiation, Rigaku, Japan) was used to analyze the composition and crystal structure of the prepared micro- CaCO_3 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 μm . 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 μm) is smaller than those shown in Figure 1(B) (with a diameter of 1–3 μm). 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 μm 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 μm 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 boric acid in alkaline condition. Figure 3(A) indicates that the product is a sphere-like particle with a length of 2.5 μm 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 μm , 1 μm , 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 CaCO_3 prepared in the presence of EDTA in acidic condition. (A)–(C) SEM images of synthesized CaCO_3 , (D) XRD patterns of product A (a), product B (b), and product C (c).

FIGURE 3: SEM images and XRD patterns of CaCO_3 prepared in the presence of boric acid 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).

FIGURE 4: SEM images and XRD patterns of CaCO_3 prepared in the presence of boric acid in acidic condition. (A)–(C) SEM images of synthesized CaCO_3 , (D) XRD patterns of product A (a), product B (b), and product C (c).

FIGURE 5: The chelation of EDTA and Ca^{2+} .

FIGURE 6: Formation mechanism of CaCO_3 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

- [1] A. L. N. Da Silva, M. C. G. Rocha, M. A. R. Moraes, C. A. R. Valente, and F. M. B. Coutinho, "Mechanical and rheological properties of composites based on polyolefin and mineral additives," *Polymer Testing*, vol. 21, no. 1, pp. 57–60, 2002.
- [2] M. C. G. Rocha, A. H. M. F. T. Silva, F. M. B. Coutinho, and A. L. N. Silva, "Study of composites based on polypropylene and calcium carbonate by experimental design," *Polymer Testing*, vol. 24, no. 8, pp. 1049–1053, 2005.
- [3] R. R. Fay, "The goldfish ear codes the axis of acoustic particle motion in three dimensions," *Science*, vol. 225, no. 4665, pp. 951–954, 1984.
- [4] H. Yang, W. Yao, L. Yang et al., "The self-assembly of CaCO_3 crystals in the presence of protein," *Journal of Crystal Growth*, vol. 311, no. 9, pp. 2682–2688, 2009.
- [5] E. Altay, T. Shahwan, and M. Tanoğlu, "Morphosynthesis of CaCO_3 at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability," *Powder Technology*, vol. 178, no. 3, pp. 194–202, 2007.
- [6] J. Rudloff and H. Cölfen, "Superstructures of temporarily stabilized nanocrystalline CaCO_3 particles: morphological control via water surface tension variation," *Langmuir*, vol. 20, no. 3, pp. 991–996, 2004.
- [7] L. A. Gower and D. A. Tirrell, "Calcium carbonate films and helices grown in solutions of poly(aspartate)," *Journal of Crystal Growth*, vol. 191, no. 1-2, pp. 153–160, 1998.
- [8] C. A. Orme, A. Noy, A. Wierzbicki et al., "Formation of chiral morphologies through selective binding of amino acids to calcite surface steps," *Nature*, vol. 411, no. 6839, pp. 775–779, 2001.
- [9] M. Maas, H. Rehage, H. Nebel, and M. Epple, "A detailed study of closed calcium carbonate films at the liquid-liquid interface," *Langmuir*, vol. 25, no. 4, pp. 2258–2263, 2009.
- [10] A. J. Xie, Y. H. Shen, X. Y. Li et al., "The role of Mg^{2+} and Mg^{2+} /amino acid in controlling polymorph and morphology of calcium carbonate crystal," *Materials Chemistry and Physics*, vol. 101, no. 1, pp. 87–92, 2007.
- [11] G. Gao, P. Huang, K. Wang, R. He, and D. Cui, "Gram-scale synthesis and shape evolution of micro- CaCO_3 ," *Powder Technology*, vol. 205, pp. 270–275, 2011.
- [12] K. B. Lee, S. B. Park, Y. N. Jang, and S. W. Lee, "Morphological control of CaCO_3 films with large area: effect of additives and self-organization under atmospheric conditions," *Journal of Colloid and Interface Science*, vol. 355, no. 1, pp. 54–60, 2011.
- [13] S. Mann, B. R. Heywood, S. Rajam, and J. D. Birchall, "Controlled crystallization of CaCO_3 under stearic acid monolayers," *Nature*, vol. 334, no. 6184, pp. 692–695, 1988.