

The Effect of Ionic Liquids on the CaCO₃ Crystal Growth

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Abstract: In this paper, the effect of ionic liquids on the CaCO₃ crystal growth has been studied for the first time. The obtained CaCO₃ crystals were characterized by the X-ray diffraction and scanning electron micrographs. The results showed that the control ability of ionic liquids for CaCO₃ crystals growth was dependent on the counter anion very much.

Keywords: Ionic liquids, CaCO₃ crystal growth, 1-butyl-3-methylimidazolium salt.

Ionic liquids are known to have a number of unusual characteristics including negligible volatility, non-flammability, high thermal stability, low melt point, broad liquid range, and controlled miscibility with organic compounds¹⁻³. So in recent years they have been attracted enormous attention as green solvent for synthesis and successfully used to realize many important reactions, especially organic reactions^{4,5}. Our interest is to synthesize inorganic materials by using the ionic liquids as media.

The control of the chemical composition, polymorphism, morphology and texture of the crystals has been studied at molecular level following the crystallization of CaCO₃ under compressed Langmuir monolayers⁶, in the presence of synthesized polymer⁷, or proteins extracted from shells⁸, or double-hydrophilic compounds⁹. However, to the best of our knowledge, there is no report about the influence of ionic liquids on the crystal growth of inorganic materials. In this paper, the growth of calcium carbonate crystals in the ionic liquids solution has been studied and the lamellar CaCO₃ has been prepared for the first time.

The ionic liquids used in this work are 1-butyl-3-methylimidazolium (BMIM⁺) salts (BMIM·X, X=Br⁻, BF₄⁻, NO₃⁻, SCN⁻). This ionic liquid was synthesized as described in the literature¹⁰. The growth of CaCO₃ crystals were conducted by the following process: Na₂CO₃ aqueous solution (5×10⁻², wt%) containing ionic liquid (0.1~10, wt%) was added to CaCl₂ aqueous solution (5×10⁻², wt%) containing the same ionic liquid (0.1~10, wt%), and the deposition was aged for 24 hours at room temperature. The depositions obtained were washed with CH₂Cl₂ and distilled water for three times successively to remove the ionic liquid and other ions absorbed in CaCO₃.

The CaCO₃ crystals growth was studied in aqueous [BMIM]⁺Br⁻ solution first. It is shown that rhombohedral calcite crystals were deposited in the absence of ionic liquid. In

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contrast, the addition of ionic liquid $[\text{BMIM}]^+\text{Br}^-$ to the solution of CaCl_2 and of Na_2CO_3 induced the deposition of lamellar CaCO_3 , as shown in **Figure 1**. The average thickness of these lamellar CaCO_3 is about $0.25\ \mu\text{m}$. The concentration of $[\text{BMIM}]^+\text{Br}^-$ influenced the growth of CaCO_3 crystals greatly. When the concentration of $[\text{BMIM}]^+\text{Br}^-$ is lower than 1% (wt%), the crystals are amorphous. When the concentration of $[\text{BMIM}]^+\text{Br}^-$ increased, the content of lamellar CaCO_3 increase and the crystals are more regular.

Figure 1 Scanning electron micrographs of lamellar CaCO_3 grown in the presence of $[\text{BMIM}]^+\text{Br}^-$ (10, wt%)

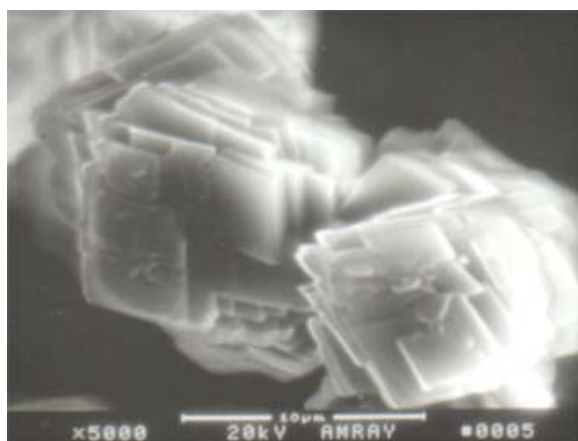
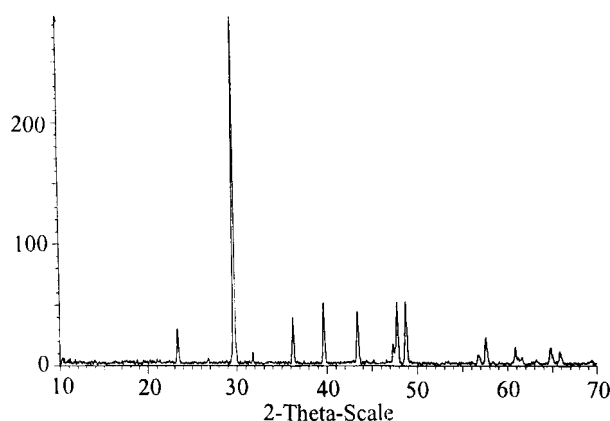


Figure 2 The X-ray diffraction pattern of lamellar CaCO_3 grown in the presence of $[\text{BMIM}]^+\text{Br}^-$ (10, wt%)



Unambiguous evidence for the formation of calcite polymorph in the presence of $[\text{BMIM}]^+\text{Br}^-$ is obtained from our FT-IR and powder XRD measurements. Calcite has a strong reflection in the x-ray diffraction patterns at $2\theta = 29.36^\circ$, $d = 3.035\ \text{\AA}$ (**Figure 2**), and shows characteristic bands in the infrared spectrum at 1799 , 876 and 713cm^{-1} . Their IR spectra show only characteristic peaks of calcite at 3443 , 2513 , 1799 , 1418 , 876 and

713cm⁻¹, and the C-H stretching vibration of the ionic liquid around 2900cm⁻¹ disappeared after washing and vacuum drying. This indicated that all ionic liquid molecules were removed through washing. Therefore, it is appropriate to state that ionic liquids only control the crystals growth of CaCO₃, but do not form organic/inorganic composite materials with CaCO₃ unlike polymers and proteins^{7,8}.

We have also studied the effect of other ionic liquids on the crystals of CaCO₃ (**Table 1**). It is found that in the presence of [BMIM]⁺BF₄⁻, [BMIM]⁺NO₃⁻ or [BMIM]⁺SCN⁻, the CaCO₃ crystals are calcite, which also has a strong reflection in the XRD patterns at 2θ = 29.36°, d = 3.035Å, but its morphology is a mixture of rhombohedral and lamellar. Compared with [BMIM]⁺Br⁻, these three ionic liquids are weak in controlling the growth of CaCO₃ crystals. The results demonstrated that ionic liquids have no effect on the crystal structure of CaCO₃, but can control the morphology of the CaCO₃ crystals, and their control ability for the crystals growth depended on the nature of anion of ionic liquids.

Table 1 The effect of ionic liquid on the growth of CaCO₃ crystal

Entry	Ionic liquid	CaCO ₃ crystal	
		Shape	Structure
1	[BMIM] ⁺ Br ⁻	Lamellar	Calcite
2	[BMIM] ⁺ BF ₄ ⁻	Lamellar & rhombohedral	Calcite
3	[BMIM] ⁺ NO ₃ ⁻	Lamellar & rhombohedral	Calcite
4	[BMIM] ⁺ SCN ⁻	Lamellar & rhombohedral	Calcite

In summary, ionic liquids has been applied successfully to control the growth of CaCO₃ crystals. The lamellar calcite has been prepared for the first time. The results demonstrate that ionic liquids only affect the morphology of CaCO₃ crystals, but no influence on its crystal structure. The control ability for the crystals growth is dependent on the counter anion of ionic liquids very much.

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