

Regulation of Low-Molecular-Weight Organic Acids on CaCO₃ Crystallization

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ABSTRACT

Biomimetic synthesis and shape-control of CaCO₃ has been studied in great detail due to its abundance in nature and also its important industrial application in the paint, plastics, rubber and paper industries. Besides, CaCO₃ is rich polymorphism, and it has been widely used as a model mineral in biomimetic experiments, leading to increased understanding of the mechanisms of biogenic control over mineral polymorph, orientation, and morphology. Currently known CaCO₃ crystal types include three anhydrous polymorphs (trigonal calcite, orthorhombic aragonite, and hexagonal vaterite) and two hydrated polymorphs (monoclinic hexahydrate ikaite and calcium carbonate monohydrate), in which calcite is the most thermodynamic stable phase. The implementation of natural or specifically designed molecular additives to control the morphology and crystal type of CaCO₃ have long been a source of fascination. However, the application of this approach for achieving controlled crystallization of CaCO₃ poses significant challenges due to inherent simplicity of its constituent components and the straightforward nature of surface packing patterns, which hinder the application of synthesis of CaCO₃ with complex superstructure.

Keywords: CaCO₃; Organic acid; Calcite; Carboxyl group; Hydroxy group

DESCRIPTION

In contrast to polymeric additives, monomeric organic acids possess relatively low molecular weights of less than a few hundred with few carboxyl groups and exhibit only a limited number of potential binding sites [1]. Low-Molecular-Weight Organic Acids (LMWOAs) are a favorable option for CaCO₃ due to the structural resemblance between the carboxyl groups present in the additive and carbonate groups found in the mineral [2]. Furthermore, LMWOAs exhibit high selectivity towards crystal faces [3], thereby enhancing our comprehension of the specific interaction between functional groups and crystal face. The carboxyl and hydroxyl anions of organic acids can interact with the CaCO₃ surface through geometrical matching, hydrogen bond, electrostatic interaction, or even incorporation into the crystal lattice. It is widely acknowledged that the interfacial interaction between organic acid and CaCO₃ can be influenced by variations in organic acid concentration, functional group composition and stereochemical structure.

Citric acid, with three carboxyl groups, predominantly exists as a metal-ligand complex in solution, which exhibits a strong affinity

towards the partially positively charged surface of CaCO₃. It has been demonstrated that citrate can effectively regulate the crystallization process of CaCO₃ by inhibiting growth rates at relatively low concentration regime, resulting in the formation of both vaterite and calcite. However, at higher concentrations, citrate promotes nucleation leading solely to elongated calcite formation [4]. Besides, the concentration of citrate can significantly impact the morphology of CaCO₃ crystals, causing them to transform from dumbbell-like shapes to rod-like or flower-like structures [3].

The dicarboxylic acid of malic acid and succinic acid have been observed to exert an inhibitory effect on the calcite growth. The adsorption of malic acid and succinic acid on calcite predominantly occurs through the coordination of their deprotonated carboxyl groups to the same surface Ca²⁺ site, resulting in the formation of a seven-membered chelate ring for succinic acid. In contrast, for malic acid, its hydroxyl group and one of its two carboxylic groups bind to the CO₃²⁻ and Ca²⁺ sites, respectively. Malic acid exerts a notable influence on CaCO₃ morphology by adsorbing onto specific crystal faces during calcite dissolution/crystallization processes. The sorption

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of malic acid onto the (011) faces of calcite leads to the elongated morphology along the c-axis [3]. Succinic acid is known for its ability to hinder calcite dissolution by competitive adsorbing succinate ions and carbonate ions on the surface of calcite. It shows a mild impact on calcite dissolution due to its adsorption on rate-controlling surface sites [5].

The regulatory effects of functional groups of LMWOAs on CaCO_3 crystallization are also influenced by molecular chain length and stereochemical isomerism. The adsorption experiments reveal that the dicarboxylic acids demonstrate significantly affinity for the aragonite surface with oxalic acid exhibiting the highest affinity followed by malonic acid and glutaric acid [6]. Chiral organic acids are enantiomeric forms of a chiral molecule, differing solely in the spatial orientation of their functional groups within the overall molecular structure. The calcite exhibits right-handed spirals when deposited in the presence of L-malic acid, while displaying an achiral microstructure in a racemic mixture of d- and l-malic acid [7].

CONCLUSION

Organic acids may exert regulatory effects on the crystallization of CaCO_3 through similar mechanisms, yet their stereochemical variances can result in disparities in binding energy between identical functional groups and the surface of CaCO_3 . Although, the affinity of carboxylic acids towards CaCO_3 surfaces exhibits a stronger manifestation compared to alcohols. The adsorption behaviors are contingent upon the side groups present in organic molecules. The intriguing role of LMWOAs in controlling CaCO_3 crystallization serves as an inspiring lesson derived from nature, which can be further developed into an advanced strategy for precise material fabrication control.

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