

Effects of malonic acid on calcium carbonate crystalline phases and morphology

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Abstract—Industrial applications of calcium carbonate (CaCO₃) is dictated by its crystal properties. To a large extent, CaCO₃ scaling which is prevalent in industrial equipment is also governed by such properties. Detailed understanding of alteration of CaCO₃ properties is therefore of prime importance. This paper reports CaCO₃ precipitation conducted by drop-wise addition of Na₂CO₃ solution into solution of CaCl₂ with stirring. The precipitation was done with and without malonic acid. Precipitates were filtered, centrifuged, and oven dried overnight at 60°C. The samples were characterized using SEM, XRD, and FTIR. In all cases amorphous calcium carbonate precipitated first and with time it transformed into calcite via vaterite and aragonite. It was found that malonic acid was able induce vaterite growth in solution. Higher amounts of malonic acid (ppm amounts) resulted in more vaterite phase alongside calcite. Both calcite and vaterite morphology changed with malonic acid in the solution as compared with pure precipitation with the acid.

Keywords—CaCO₃; crystal phases; malonic acid; scale control

I. INTRODUCTION

Calcium carbonate (CaCO₃) crystals have wide industrial applications, and each application requires certain crystalline phase and morphology. CaCO₃ is also one of the main components of scale which can develop in industrial equipment, particularly in the piping system and heat exchangers. The properties of the scale is often dictated by the phases and morphological nature of the crystals [1]. Under ambient conditions and in a pure precipitation system the crystalline carbonate mineral comprises three anhydrous crystalline polymorphs: vaterite, aragonite, and calcite, and two hydrous crystalline forms: CaCO₃·H₂O, and CaCO₃·6H₂O [2, 3]. Additionally, there is one non-crystalline, i.e amorphous calcium carbonate (ACC) which is hydrous and normally precipitates first in the system [4]. A number of studies have been conducted on the phenomenon of phase change from vaterite and aragonite which transformed into calcite [5, 6].

Morphologies of CaCO₃ vary widely and extensive research have been carried out to mimic such variations either by the assistance of templates, additives, or manipulation of precipitation conditions [7-11].

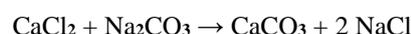
Organic compounds are known to effectively modify crystal structure, morphology and properties of CaCO₃ crystals. The growth kinetics of CaCO₃ under the influence of organic compounds is therefore an area of intensive research [10, 12, 13]. When properly applied, an organic anti-scalant has the advantage of effectively inhibiting scale formation at very low dosages, typically below 30 ppm. A number of organic additives, especially of carboxylic species, were shown to substantially suppress carbonate mineral precipitation and its practical application in scale control has been confirmed [3, 5, 14-22].

This paper discusses the modification of the three well-known crystalline phases of CaCO₃, namely vaterite, aragonite, and calcite which was precipitated under the influence of malonic acid. Malonic acid was selected as additive since it is a di-carboxylic acid and is frequently found as trace component in the wastewater of fruit canning industries.

II. EXPERIMENTAL

A. Preparation

The precipitation was carried out batch-wise using 0.5 M CaCl₂ and 0.5 M Na₂CO₃ solutions, following the reaction as follows:



Malonic acid [CH₂(COOH)₂], in the form of a weak solution, was added into the precipitating carbonate solution in varied ppm quantities. The crystals obtained from the precipitation were characterized using SEM-EDX, XRD and FTIR.

In a typical synthesis, eight precipitation runs were carried out as follows. The solutions of CaCl₂ (50 mM, 50 mL) and Na₂CO₃ (50 mM, 50 mL) were quickly mixed in a 200-mL beaker with rigorous stirring which continued for two minutes. Then the beakers were sealed and allowed to stand undisturbed at room temperature. As arranged for the experimental design, the beakers were separately decanted after a pre-determined time period: 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 6h, 48 h.

Similar experiments were conducted with the addition of malonic acid solution. The precipitates were washed thoroughly with distilled water, and then dried in a vacuum oven at 60°C overnight. The dried precipitates were stored in vials for subsequent analysis.

B. Characterization

The morphology of the crystals obtained was characterized by scanning electron microscopy (SEM) with an accelerating voltage of 30 kV (FEI – Inspect-S-50). The SEM was coupled with an energy dispersive spectroscopy (EDS) system. For these observations the samples were embedded in epoxy on glass slides. The prepared samples were then sputtered with Au for SEM analysis.

The samples were also subjected to X-ray diffraction (XRD) analysis. They were ground with a mortar and pestle. These specimens were then manually front-loaded into a plastic well mounted by lightly pressing with a glass slide. Next, data collection for crystal phase identification were performed to determine the identity of the crystalline phase. The peak positions and peak heights were checked against the data of the standard spectrum for CaCO₃ (JCPDS - #47-1743).

To identify that the functional groups of the malonic acid involved in the precipitation process, an FTIR analysis was conducted (Shimadzu – IR-Prestige-21).

III. RESULTS AND DISCUSSION

A. SEM-EDX Analysis

SEM analysis indicates the morphological changes as affected by the experimental conditions: precipitation times and amount of malonic acid added.

Under pure system, when no additive were added, and ambient conditions, the presence of all three phases: vaterite, aragonite, and calcite was evident (Fig 1). On the other hand, when ppm amounts of malonic acid were added the formation of vaterite and aragonite was less dominant compared to that of calcite (Fig 2). It was postulated that the malonic acid functional groups may have suppressed the nucleation or retarded the growth of vaterite and aragonite. Such suppression and retardation can be due to the complexation of Ca²⁺ with functional groups of malonic acid, hence reducing the amount of Ca²⁺ required for nucleation and growth.

Comparison of longer precipitation times both in the absence (Fig 3) and in the presence (Fig 4) of malonic acid reveals that malonic acid may have interfered with nucleation and growth as stated previously. Complexation of carboxylic functional groups with Ca ions [23] reduces the saturation levels for the formation of CaCO₃. This may explain the prolongation of the life time of the unstable phases: either vaterite or aragonite, as can be seen in Fig 4 to achieve the final and stable phase of calcite. On the other hand, a much shorter precipitation time with no additive has resulted in the attainment of the stable phase: calcite (Fig 3). That the complexation of Ca-malonic acid took place can also be confirmed by the FTIR data. As can be seen (Fig 10), the FTIR

show peaks of malonic acid components that may have attached or reacted on the surface of CaCO₃.

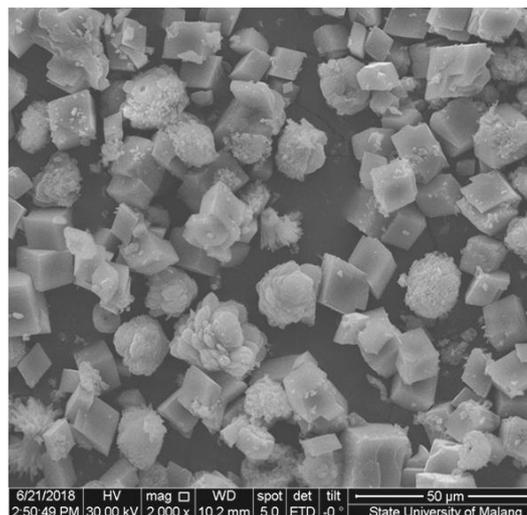


Fig. 1. SEM graph of CaCO₃ crystals in a pure system after 4 min

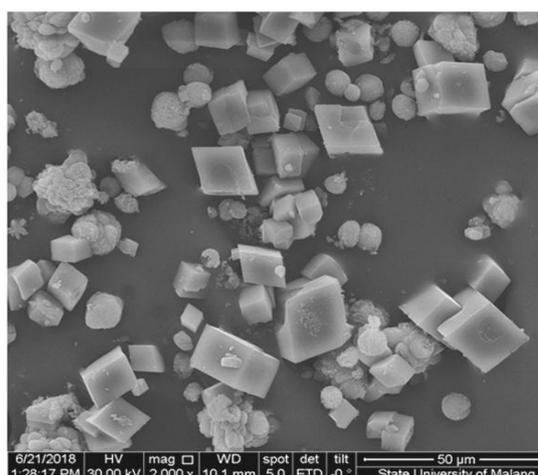


Fig. 2. SEM graph of CaCO₃ with 20 ppm malonic acid after 4 min

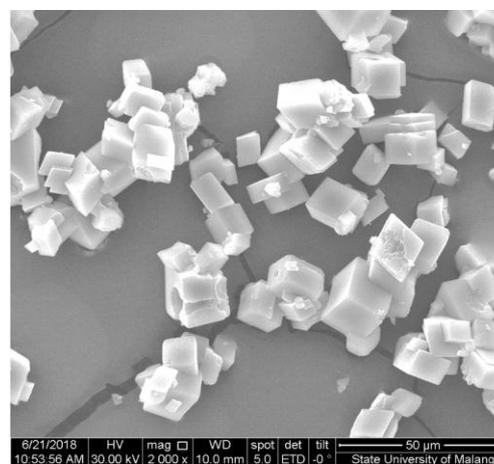


Fig. 3. SEM graph of CaCO₃ crystals in a pure system after six hours

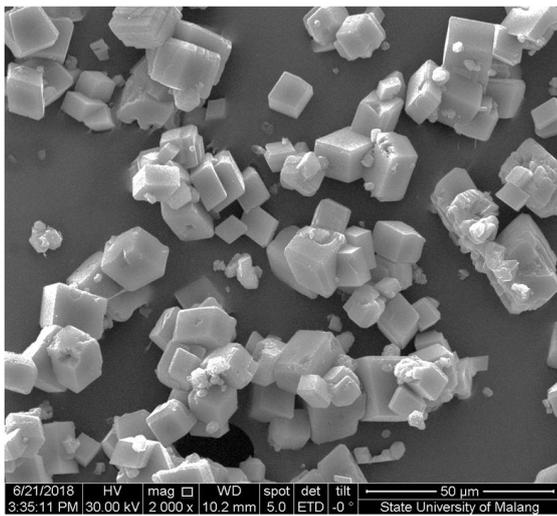


Fig. 4. SEM graph of CaCO_3 with 20 ppm malonic acid after 48 hours

B. X-Ray Diffraction

The XRD spectra show the difference in the amount of the crystalline phases (Figs 5 and 6). In the pure system the percentage of the three polymorphs is: V = 14.59%, A = 1.72%, and C = 83.69%, respectively (Fig 5). In contrast, under the influence of 30.00 ppm malonic acid the corresponding values are: 49.10%, 0.00%, and 50.90%, respectively (Fig 6). These data indicate the retarding effect of malonic acid on the transformation toward the stable phase, i.e calcite. The ppm amounts of malonic acid under the current experimental conditions have been able to retard the progress toward the stable phase by as much as 32.79%. The transformation is also visually shown in Figs 7 and 8.

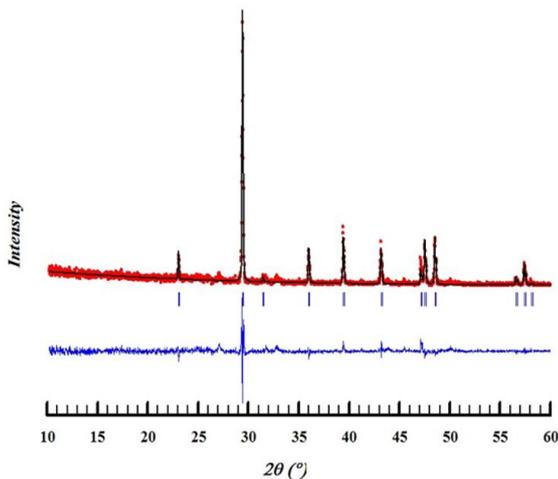


Fig. 5. XRD of CaCO_3 precipitated after 5 min without malonic acid

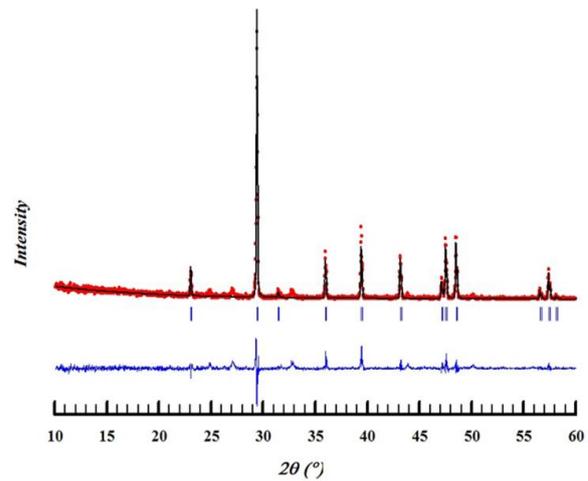


Fig. 6. XRD of CaCO_3 precipitated after 5 min with 20.00 ppm malonic acid.

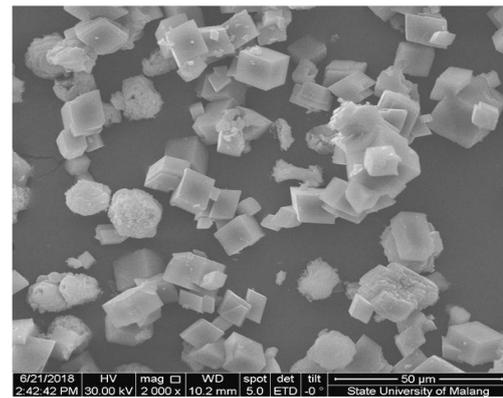


Fig. 7. SEM of CaCO_3 precipitated after 5 min without malonic acid

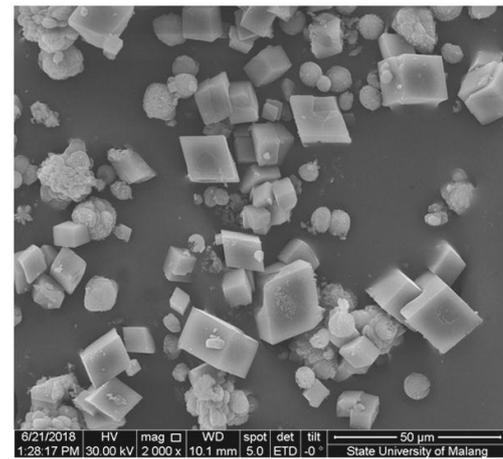


Fig. 8. SEM of CaCO_3 precipitated after 5 min with 20.00 ppm malonic acid showing less calcite.

C. FTIR

The FTIR spectra comparing the pure system and that under malonic acid are shown below (Figs 9 and 10).

The FT-IR spectra of the samples show a sharp peak at 873.68 cm^{-1} which corresponds to the out-of-plane bending

vibration (ν_2) of carbonate, while another sharp peak observed at 711.73 cm^{-1} corresponds to the in-plane bending vibration of carbonate [24]. These two peaks are characteristics of calcite. Further, two peaks appearing at 1083.99 and 1166.93 can be assigned to aragonite. Further, the sharp peak appears at 416.62 cm^{-1} can be assigned to Ca-O bond [25].

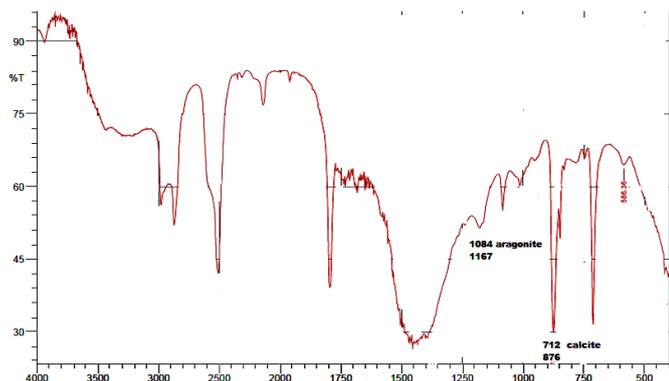


Fig. 9. FTIR of the sample without malonic acid

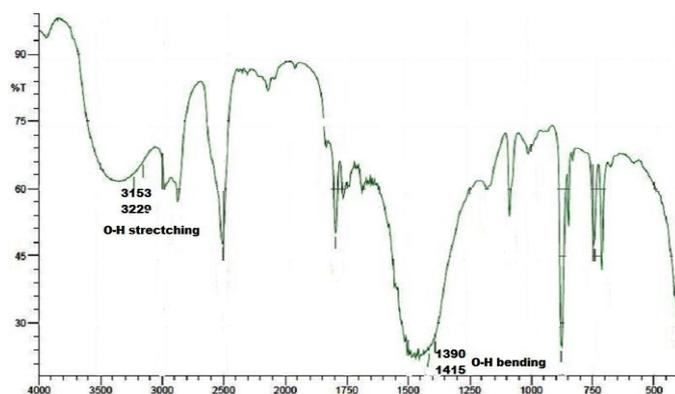


Fig. 10. FTIR spectra of the samples with malonic acid (see peaks for O-H stretching and bending, respectively)

IV. CONCLUSION

The present study shows that malonic acid in trace amounts was able to influence the precipitation of calcium carbonate, in terms of crystalline phases and morphology. The di-carboxylic acid used was able to suppress the nucleation and growth of CaCO_3 , since the functional groups of the acid formed complexation with Ca ions and thus reducing the saturation levels of the precipitating solution. Low saturation results in less nucleation and growth.

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