

Morphosynthesis of CaCO_3 at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability

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Received 31 August 2006; received in revised form 27 February 2007; accepted 7 May 2007

Available online 13 May 2007

Abstract

Facile precipitation of CaCO_3 was performed using aqueous solutions of CaCl_2 with Na_2CO_3 over a wide range of mixing and aging temperatures. The precipitation process was then repeated in the presence of PDDA, CTAB, and EDTA at the mixing temperatures of 30 °C, 50 °C, 70 °C, and 90 °C. The presence of these additives was seen to greatly suppress the formation of aragonite. Among these additives, EDTA was the one that showed the most prominent effects on particle morphology of CaCO_3 . The sequence of pH adjustment appeared to be a critical factor for the additive functionality.

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Keywords: Calcite; Aragonite; Morphology

1. Introduction

CaCO_3 , a mineral abundantly found in nature and important from industrial and biomineralization view points, possesses three anhydrous polymorphs: calcite, aragonite, and vaterite. Among these forms, calcite is the most thermodynamically stable while vaterite is the least stable. Recently, there have been wide 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 out coming polymorph type. Different morphologies of CaCO_3 possess potential technical applications in fields like catalysis, ceramics, electronics, pigments, medicine, and cosmetics [1].

Wray and Daniels [2], in one of the pioneering studies, described the experimental conditions that lead to the formation of the three polymorphs of CaCO_3 by reacting calcium nitrate (calcium chloride) and sodium carbonate [2]. High fraction aragonite was isolated at temperature above ca. 50 °C and vaterite at about 30 °C at a digestion time of 0.1 h. As a general trend, it was reported that higher temperatures favor the formation of

aragonite, and that longer aging promotes calcite formation. Since then, many studies have been conducted to investigate the physico-chemical experimental conditions that promote the formation of each of the three polymorphs of CaCO_3 . These conditions include the reactant concentrations, mixing temperature, ionic strength, pH of the medium, aging time, in addition to the nature and concentration of a variety of inorganic/organic additives. The effects of supersaturation and ionic strength are reported to be less important in comparison to temperature, pH, and aging time [3]. Supersaturation is known to affect the nucleation and growth steps of CaCO_3 , with higher supersaturation conditions favoring calcite formation [4]. In line with this, the formation of aragonite at higher temperatures was attributed to a decrease in supersaturation conditions [5]. Higher temperatures were also reported to increase the aspect ratio of the precipitated crystals [4]. Relatively high supersaturation coupled with high pH values was cited to favor the precipitation of vaterite [6]. As far as the polymorphism of CaCO_3 is considered, pH is seen as the most important factor with the pH range 10–12 giving rise to aragonite [3,4]. At pH lower than 11 and low temperatures (~7 °C) nearly pure calcite was obtained, while almost pure aragonite resulted at 58 °C for a pH lower than 10 [3]. Aging time is also a critical factor in the morphosynthesis of CaCO_3 . Long aging is known to

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enhance the recrystallization of initially formed aragonite into calcite, leading as well to an increase in average particle size as a consequence of Ostwald ripening [4].

The effects of a variety of organic/inorganic additives and solvents on the morphosynthesis of CaCO_3 have been previously investigated. However, in general, less attention was paid to the polymorphic changes associated with the additive actions. It is reported that particle morphology is better controlled by either applying soluble additives that control the crystallization or by using macroscopic templates which can act as a mould [7]. Soluble additives broadly include sparingly soluble ionic compounds, some bio- and synthetic polymers [7]. Literature resources provide a wide variety of organic additives employed in the morphosynthesis of CaCO_3 . Among these additives are some organic solvents in the presence of CTAB [8], PVP [9], soluble proteins extracted from nacre [10], PEG, PVA, CTAB, and PAA [11], using of amino acids [12], applying ethanol as a solvent [13], and others.

In the first part of this work, calcium carbonate crystals were precipitated using aqueous mixtures of CaCl_2 and Na_2CO_3 in the absence of any type of additive at different mixing and aging temperatures, in addition to aging times. In literature, less attention was relatively paid to those factors compared to the others. The second part of this study contains an investigation of the effect of PDDA, CTAB and EDTA on the particle morphology and type of polymorph formed at the mixing temperatures of 30 °C, 50 °C, 70 °C, and 90 °C. The sequence of pH adjustment effect on the extent to which the given additives would affect the particle morphology and morphological identity of precipitated CaCO_3 is also studied. The samples were characterized using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), and FT-infrared spectroscopy (FTIR).

2. Experimental

2.1. Reactants and sample preparation

Aqueous solutions of 0.05 M Na_2CO_3 (Sigma, min. 99.0%, 106.0 g/mol) and of 0.05 M CaCl_2 (Horasan Kimya) were first prepared as stock solutions. 100 ml of 0.05 M CaCl_2 solution was poured into a 250-ml stirred Erlenmeyer flask containing 100 ml of 0.05 M Na_2CO_3 solution. The pH of the solution was adjusted to 9.0 using 0.5 M NaOH and HCl solutions. The mixture was stirred for a minute and allowed to stand at a certain aging temperature in a thermostatic water bath for various aging periods. The freshly precipitated CaCO_3 crystals were then

filtered, washed three times with deionized water and dried at room temperature. The experimental parameters included the preparation temperature (20–95 °C), aging temperature (–10–80 °C), and aging time (30 min–1 week).

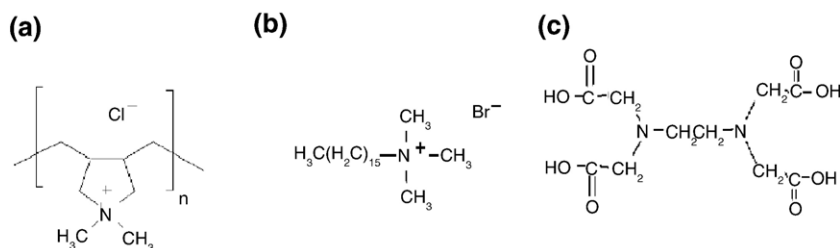
The second part of the study was performed to explore the effect of organic additives on the polymorph type, morphology, and aspect ratio of the precipitated CaCO_3 crystals. The organic additives used in this study were obtained from Aldrich chemicals and included poly(diallyldimethylammonium chloride), PDDA (409014-1L), cetyltrimethylammonium bromide, CTAB (85,582-0), ethylenediaminetetraacetic acid, EDTA, from Sigma-Aldrich (E9884-100G). The structural formulas of these chemicals are shown in Scheme 1. In the relevant experiments, 0.02 and 0.2 g of PDDA, CTAB, and EDTA were separately added into 250-ml Erlenmeyer flasks each containing 100 ml 0.05 M Na_2CO_3 solution. The samples were then mixed with 100 ml portions of 0.05 M CaCl_2 solution after being adjusted to the desired mixing temperature. Throughout the relevant experiments, CaCO_3 particles were prepared at pH 9.0 and aging time of 24 h. The temperature of mixing applied in these experiments were 30 °C, 50 °C, 70 °C, and 90 °C. The pH of the solutions was adjusted by two different procedures. In the first procedure, the pH of Na_2CO_3 solution containing the particular organic additive was adjusted after it reached the preparation temperature then the CaCl_2 solution was added. In the second procedure, the pH adjustment was performed after CaCl_2 solution was poured into the mixture. After mixing, the solutions containing precipitated CaCO_3 particles were kept in a thermostatic water bath at a specified aging temperature for a particular aging time. Finally, CaCO_3 crystals were filtered, washed three times with deionized water and dried at room temperature.

2.2. XRPD, SEM, and FTIR characterization

XRPD diagrams were recorded using a Philips X'Pert Pro diffractometer. The source consisted of Cu K α radiation ($\lambda = 1.54$ Å). Each sample was scanned within the 2θ range of 10–50. The step size was 0.020 with a time per step duration of 60 s.

SEM characterization was performed using a Philips XL-30S FEG type instrument. Prior to analysis, the solid samples were sprinkled onto adhesive aluminum tabs supported on metallic disks. Microimages were then recorded at different magnifications.

FTIR technique was used to record the spectra of the minerals in the middle IR region (400–4000 cm^{-1}) using a Nicole Magna 550 type instrument. The samples were introduced as pellets prepared after diluting with KBr powder. The resolution was



Scheme 1. The chemical formulas of: (a) PDDA, (b) CTAB, and (c) EDTA.

4 cm^{-1} and 32 scans were recorded for each spectrum. Omnic 1.3 software was used to process the results.

3. Results and discussion

3.1. Precipitation of CaCO_3 under different mixing and aging temperatures and aging times

The facile precipitation of CaCO_3 was achieved by mixing 100 ml aliquots of 0.05 M CaCl_2 and Na_2CO_3 to yield a supersaturated mixture. The fractions of aragonite in the precipitated CaCO_3 were calculated using a calibration curve (Fig. 1) that was prepared using different combinations of pure calcite and pure aragonite. The intensity ratio was calculated based on the peak areas of the 104 reflection of calcite and 111 reflection of aragonite. The data given in Fig. 1 were fitted to an equation that resembles a previously reported one [14], using MS Excel. The equation can be expressed as:

$$X_a = \frac{3.4(I_a/I_c)}{1 + 3.4(I_a/I_c)} \quad (1)$$

Here, X_a corresponds to the fraction of aragonite; I_a/I_c is the ratio of the integrated peak areas corresponding to aragonite (111) reflection ($2\theta=26.1$) and calcite (104) reflection ($2\theta=29.2$). The standard error fit of Eq. (1) was 1.6%. Artificial samples were prepared and checked, and the relative errors in aragonite fractions were roughly less than 8%.

The first set of experiments was performed at the temperatures (mixing and aging) of 20 °C, 30 °C, 40 °C 50 °C, 60 °C, 70 °C and 80 °C. In these experiments, the initial pH was brought to 9.0, and the aging time was 24 h. As expected, up to 50 °C, CaCO_3 crystals were entirely composed of calcite. SEM images given in Fig. 2a and b show that the particles possessed a rhombohedral shape, with the edge size showing a decrease accompanied with a tendency to form aggregates when moving from 20 °C (around 10 μm) to 50 °C (around 7 μm) mixing and aging temperatures. Beyond 50 °C, aragonite formation started and its fraction in the precipitated CaCO_3 prepared at 60 °C, 70 °C, and 80 °C temperatures were

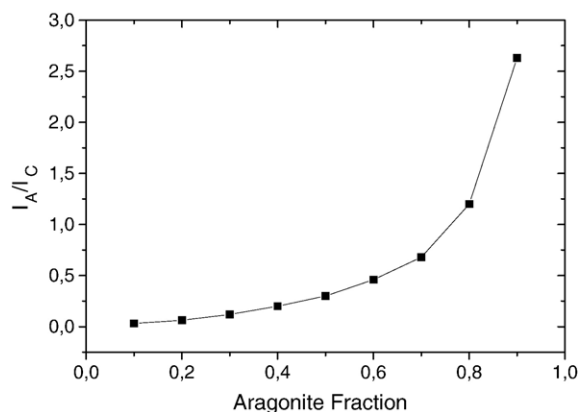


Fig. 1. Variation of the ratio of peak areas of aragonite (111)/calcite (104) with the fraction of aragonite in the calcite-aragonite mixtures. The data are based XRD measurements.

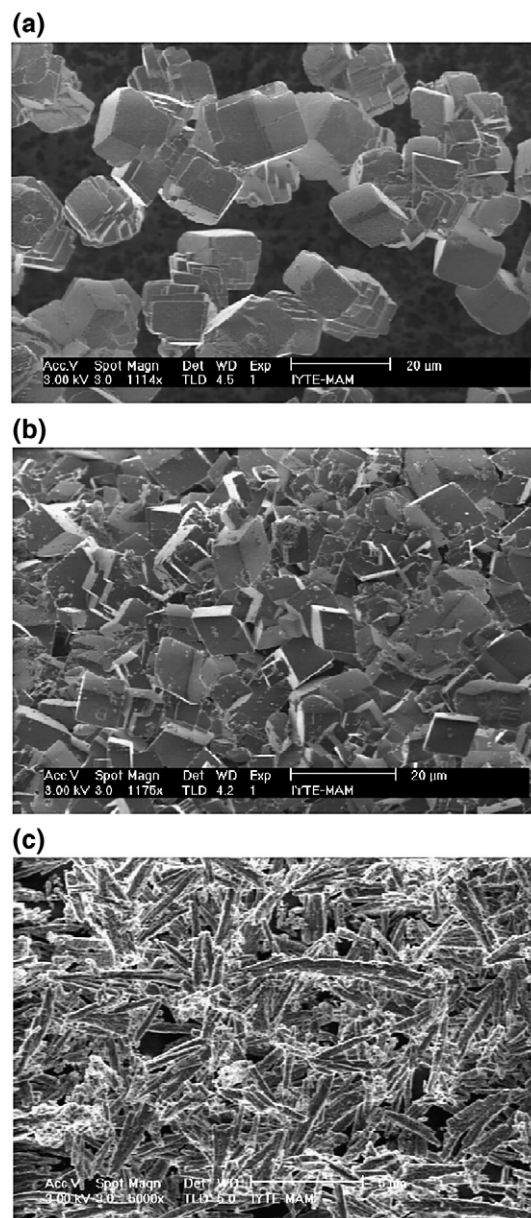


Fig. 2. SEM micrographs of CaCO_3 crystals prepared at mixing temperatures of: (a) 20 °C, (b) 50 °C, and (c) 80 °C.

calculated using Eq. (1) as 0.33, 0.48 and 0.59, respectively. Aragonite crystals appeared to possess branch-like morphology with the particle size being around 5–6 μm . Typical SEM images are shown in Fig. 2c.

The partial formation of aragonite in the precipitated CaCO_3 resulted in the activation of the symmetric stretching mode ($\nu_1=1088 \text{ cm}^{-1}$) in the FTIR spectra of CaCO_3 . It is known that the D_{3h} symmetry of free carbonate ion is lowered to D_3 in the case of calcite and C_s in the case of aragonite the thing that leaves the carbonate vibrational modes unchanged for calcite but activates the ν_1 mode in aragonite [15]. Fig. 3 gives the FTIR spectra of a CaCO_3 sample entirely composed of calcite (a), and that of the CaCO_3 sample that is composed of 59% aragonite (b). In addition, slight peak position shifts and/or peak broadening were recorded for the other vibrational modes in the latter sample.

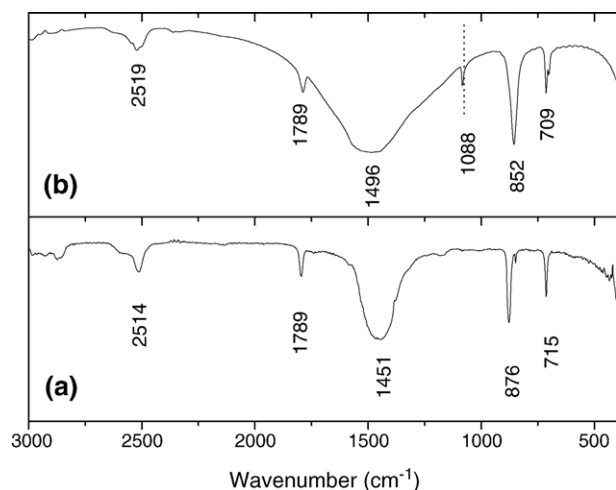


Fig. 3. FTIR spectra of CaCO_3 prepared at mixing temperatures of: (a) 30 °C; entirely composed of calcite, and (b) 90 °C; dominated by aragonite.

In the next set of experiments, the aim was to reveal the effect of mixing the reactants at a particular temperature and aging them at a different temperature. For this purpose CaCO_3 particles were first synthesized at 30 °C, 50 °C, 80 °C, and 90 °C mixing temperatures, while the aging temperature was kept at 10 °C. Throughout these experiments, the initial pH was brought to 9.0, and the aging time was 24 h. The results showed that again at the

mixing temperature of 30 °C and 50 °C, rhombohedral calcite particles were formed. However, at 50 °C mixing temperature, calcite particles showed a tendency of agglomeration with their surfaces and edges possessing serious defects, and a few number of aragonite particles were also occasionally observed. Increasing the mixing temperature to 80 °C and 90 °C promoted the formation of branch-like aragonite further. In these experiments, the fraction of aragonite was calculated using Eq. (1) to be 0.72 and 0.86 at the mixing temperatures of 80 °C and 90 °C, respectively. From this set of experiments it seemed that mixing at a temperature above 50 °C while aging at a lower temperature (in this case 10 °C) will, to a certain extent, promote further formation of aragonite. Along with this, another set of experiments was carried out in which the reactants were mixed at 90 °C, and then aged for 24 h at the temperatures of 70 °C, 50 °C, 30 °C, 10 °C, 0 °C, and –10 °C. In all cases, the fraction of aragonite was around 0.9 ± 0.05 , thus indicating that the difference between the temperature of mixing and that of aging had minimal effects on the obtained aragonite fraction. SEM images showed that aragonite crystals were dominated by branch-like morphologies but the aspect ratio values (defined as ratio of length to diameter of the crystal) seemed to slightly increase as the aging temperature was decreased ranging from 8 to 12. Typical SEM images are provided in Fig. 4.

The experiments aiming at revealing the effect of aging time were first performed at a set of conditions that leads to calcite formation; i.e., 30 °C mixing and aging temperatures, 0.05 M initial concentration of Na_2CO_3 and CaCl_2 , and pH of 9.0. The aging time ranged from 6 h up to 1 week. According to the results, the morphology of the calcite particles retained the characteristic rhombohedral shape over the range of aging time together with an increase in the edge size of the crystals with the increase in aging time (8 μm at 6 h to 12 μm at 1 week), which can probably be attributed to Ostwald ripening.

Another set of experiments was conducted to study the effect of aging time on the extent of aragonite formation. For this purpose, facile precipitation of CaCO_3 was carried out at mixing temperatures of 70 °C, 80 °C and 90 °C and various aging times

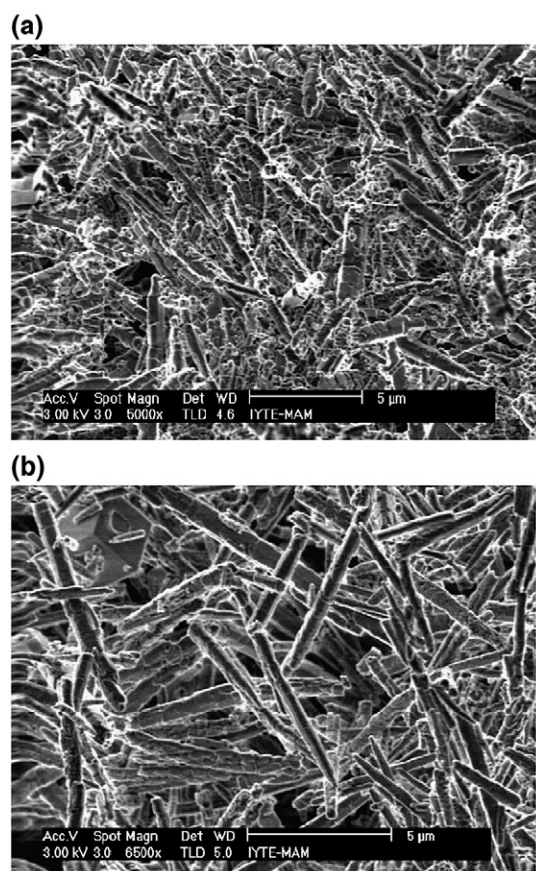


Fig. 4. Typical SEM images for aragonite crystals prepared at a mixing temperature of 90 °C, and aging temperature of: (a) 70 °C, (b) 0 °C.

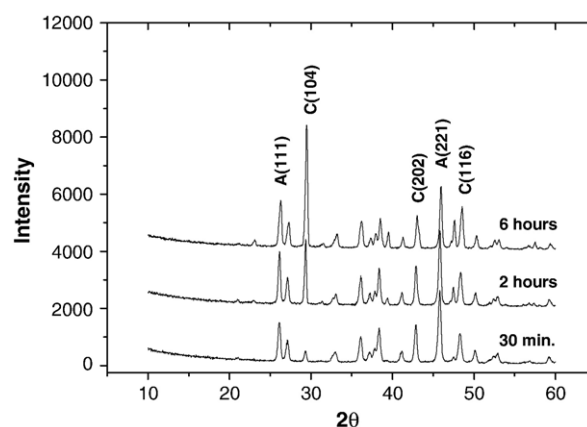


Fig. 5. XRD diagrams of the samples prepared at various aging times. ($[\text{C}_0] = 0.05 \text{ M}$, $\text{pH} = 9.0$, mixing temperature = 70 °C and aging temperature around 25 °C). A: aragonite, C: calcite.

Table 1
pH values measured during the experiments conducted to reveal the effect of the given additives on the morphology and polymorph types of CaCO_3 (1: pH of the Na_2CO_3 solution, 2: pH values after the addition of 1.0 g/l additive, 3: pH values immediately after the adjustment to 9.0, 4: pH values after the addition of CaCl_2)

Mixing temperature	Additive type	pH values			
		1	2	3	4
30 °C	PDDA	10.70	10.66	9.00	7.05
	CTAB		10.61	9.02	7.00
	EDTA		9.64	9.04	7.60
90 °C	PDDA	9.53	9.79	9.00	6.03
	CTAB		9.98	9.08	6.25
	EDTA		9.17	9.02	6.75

(30 min, 2 h, 6 h and 24 h). The solutions were aged at room temperature. The results showed that the amount of aragonite decreased with the increase in aging time, with the most prominent effect observed for the samples mixed at 90 °C. As demonstrated by the XRD diagrams in Fig. 5, the decrease in the extent of aragonite was significant during the initial 6 h and did not change much in the following period. The resulting aragonite crystals exhibited a mixture of needle-like and branch-like morphologies with an average size of 3–4 μm , and shorter aging times resulted in higher aspect ratio at each mixing temperature. The samples were analyzed again 1 month after their preparation (stored under ambient conditions) to check the morphological stability over time. The XRD and

SEM characterization indicated no serious change in the fraction of aragonite as well as in the particle morphology.

3.2. Effect of PDDA, CTAB, and EDTA on the morphosynthesis of CaCO_3 at different temperatures

The study of the effect of organic additives on the crystal type and on the corresponding morphologies of CaCO_3 polymorphs is important from the industrial viewpoint due to the role of such additives in the production of new morphologies in addition to affecting the transformations of the polymorphs of CaCO_3 . In general, additives may affect the nucleation steps and the crystal growth of CaCO_3 by virtue of their molecular structure framework and functional groups. Moreover, such additives are expected to show direct effects on the ionic availability of Ca^{2+} and CO_3^{2-} ions in the solution medium, and the way these ions interact and build a particular structure, however, not much information are available about the mechanistic details of the process.

In this work, the effects of PDDA, CTAB and EDTA on the morphology and the polymorph transformation of CaCO_3 were studied at the mixing temperatures 30, 50, 70, and 90 °C. The experiments were conducted by first introducing Na_2CO_3 solution followed by the additive, then adjusting the pH to 9.0, and finally adding the CaCl_2 solution. The measured pH values after each of the above steps at the mixing temperatures of 30 °C and 90 °C are given in Table 1. Throughout these experiments, the aging time was 24 h.

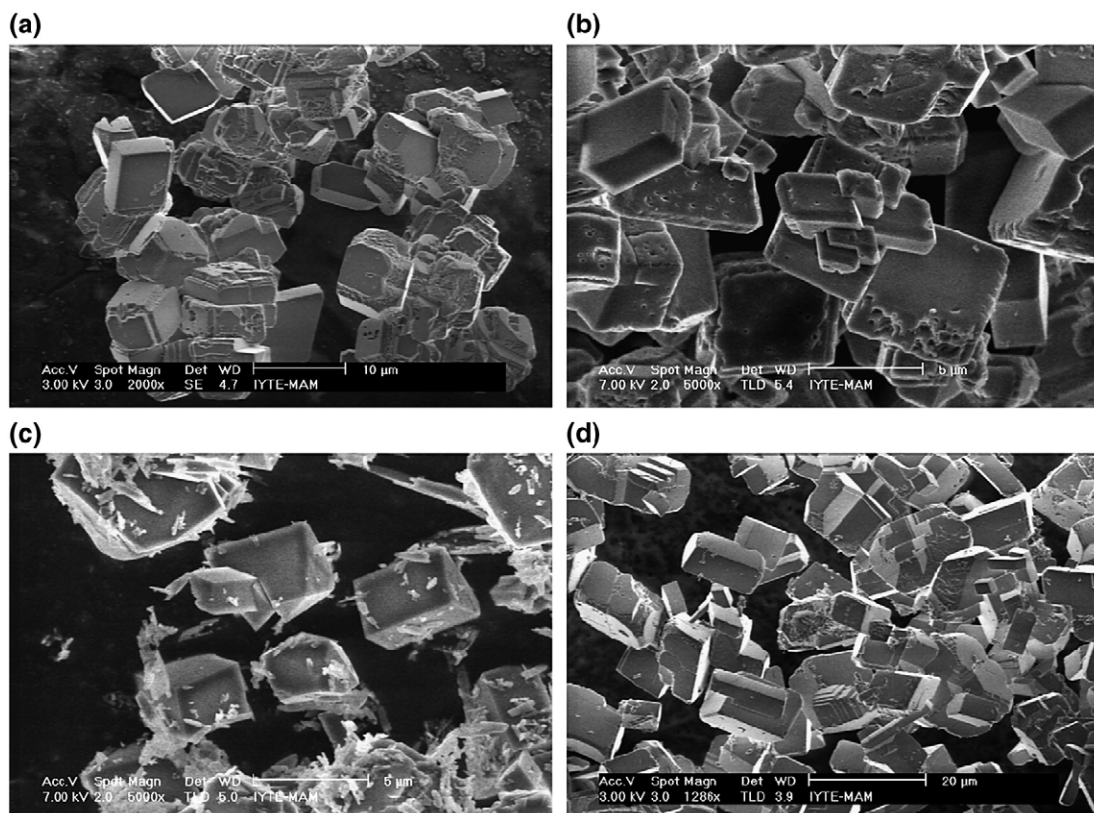


Fig. 6. SEM images of CaCO_3 precipitated in the presence of PDDA at different mixing temperatures: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

3.2.1. Effect of PDDA

PDDA is one of the polycationic electrolytes that is capable of interacting with solid surface and ions in solution by virtue of its positive centers. According to our literature search, the effect of PDDA on the morphology/polymorphs of CaCO_3 has not been studied before.

Based on the XRD results of the experiments, when PDDA concentration is 1.0 g/l, only calcite polymorph is obtained at all temperatures. This means that aragonite formation observed beyond 50 °C in the absence of any additive has been totally suppressed at the given conditions. SEM images, provided in Fig. 6, showed that at 30 °C and 50 °C, PDDA caused step defects and a tendency to form agglomerations of the calcite rhombohedral particles. When the mixing temperature was raised to 70 °C, prismatic calcite particles appeared. At 90 °C, calcite dominated by rectangular-prism morphology was present. The average particle size of the obtained particles was approximately 10 μm .

The suppression of aragonite formation at high temperatures was dependent of the additive concentration. When PDDA concentration is lowered to 0.1 g/l, only a partial suppression of aragonite formation was observed. Experiments performed at 90 °C showed that at the given additive concentration, the percentage of aragonite was 25% of the overall precipitated CaCO_3 (compared to about 85% in the absence of PDDA). Aragonite particles exhibited a rod-like morphology with their aspect ratio being around 25.

3.2.2. Effect of CTAB

CTAB is a cationic surfactant the effect of which on CaCO_3 synthesis was previously investigated in different reaction media [8,16,17]. In these studies, it is reported that the functionality of CTAB is affected by the type of solvent used, and that CTAB addition does not significantly affect the morphosynthesis of CaCO_3 in aqueous media at lower temperatures.

In the presence of CTAB at 1.0 g/l concentration, XRD diagrams showed that the precipitated CaCO_3 was completely in the form of calcite at 30 °C and 50 °C. At the mixing temperatures of 70 °C, CaCO_3 particles consisted of 6% aragonite and 94% calcite. When the temperature was raised to 90 °C, the amount of aragonite was around 10% of the precipitated CaCO_3 . This shows that CTAB also has greatly reduced the formation of this polymorph. SEM images showing the morphology of the precipitated particles at different temperatures are given in Fig. 7. At 30 °C, agglomerations of rhombohedral and plate-like crystals are observed. The agglomerations decreased at 50 °C and crystals possessing various surface and step defects dominated by plate-like and rhombohedral shapes were observed. At 70 °C, calcite particles showed well-defined rhombohedral shapes while the aragonite particles possessed a branch-like morphology. The same shapes seemed to persist at 90 °C, but with aragonite crystals more frequently observed. The edge size of calcite crystals was around 2–3 μm , while the length of aragonite particles was about 10–15 μm .

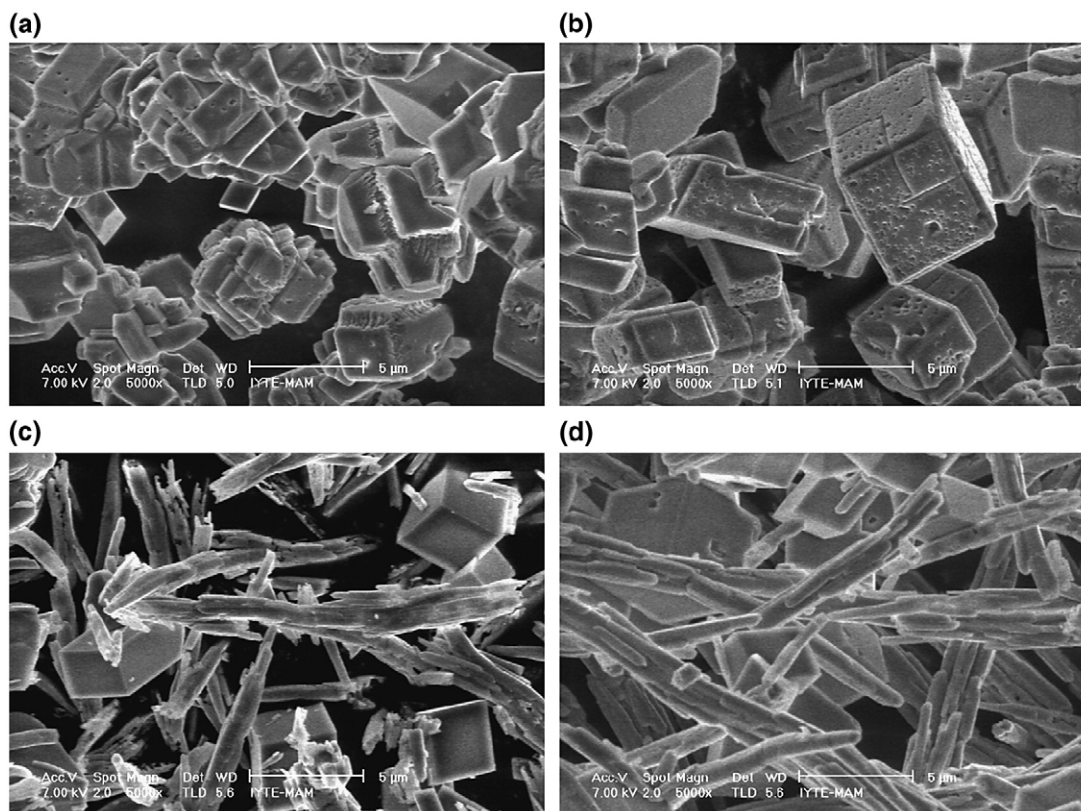


Fig. 7. SEM images of CaCO_3 precipitated in the presence of CTAB at different mixing temperatures: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

When CTAB concentration is reduced to 0.1 g/l, less suppression of aragonite formation was observed. According to the XRD results, at a mixing temperature of 90 °C, the percentage of aragonite in the precipitated CaCO_3 was 19%, with the rest being calcite. The calcite particles demonstrated deformed rhombohedral and plate-like morphologies, while aragonite crystals possessed branch-like shapes.

3.2.3. Effect of EDTA

Unlike PDDA and CTAB which contain positive cationic centers, EDTA contains four carboxylic and two amine groups. EDTA is well known as a complexing agent of Ca^{2+} , and its presence in solution would consequently lower the amount of free ions thus decreasing the driving force towards nucleation [18]. EDTA is furthermore reported to retard the crystal growth of calcite

and aragonite with this effect being concentration-dependent and more pronounced in the case of the latter mineral [19].

Among the additives studied in this work, EDTA was the one that showed the highest impact on the morphology of CaCO_3 . In the experiments performed at 30 °C, at EDTA concentration of 1.0 g/l, calcite particles with apple core-type morphology were observed, as shown in Fig. 8a. The crystals showed a large variation in length which amounted from 5 to more than 20 μm . Similar morphology of calcite particles but with smaller aspect ratio was reported earlier by the utilization of the sodium salts of poly(L-isocyanoalanyl-D-alanine) to achieve shape persistent polymeric crystallization template for CaCO_3 [20]. In line with the findings of that study, and as revealed in Fig. 8b, the calcite crystals appeared to elongate along the crystallographic *c*-axis with three (104) end faces on each side of the formed crystals. The

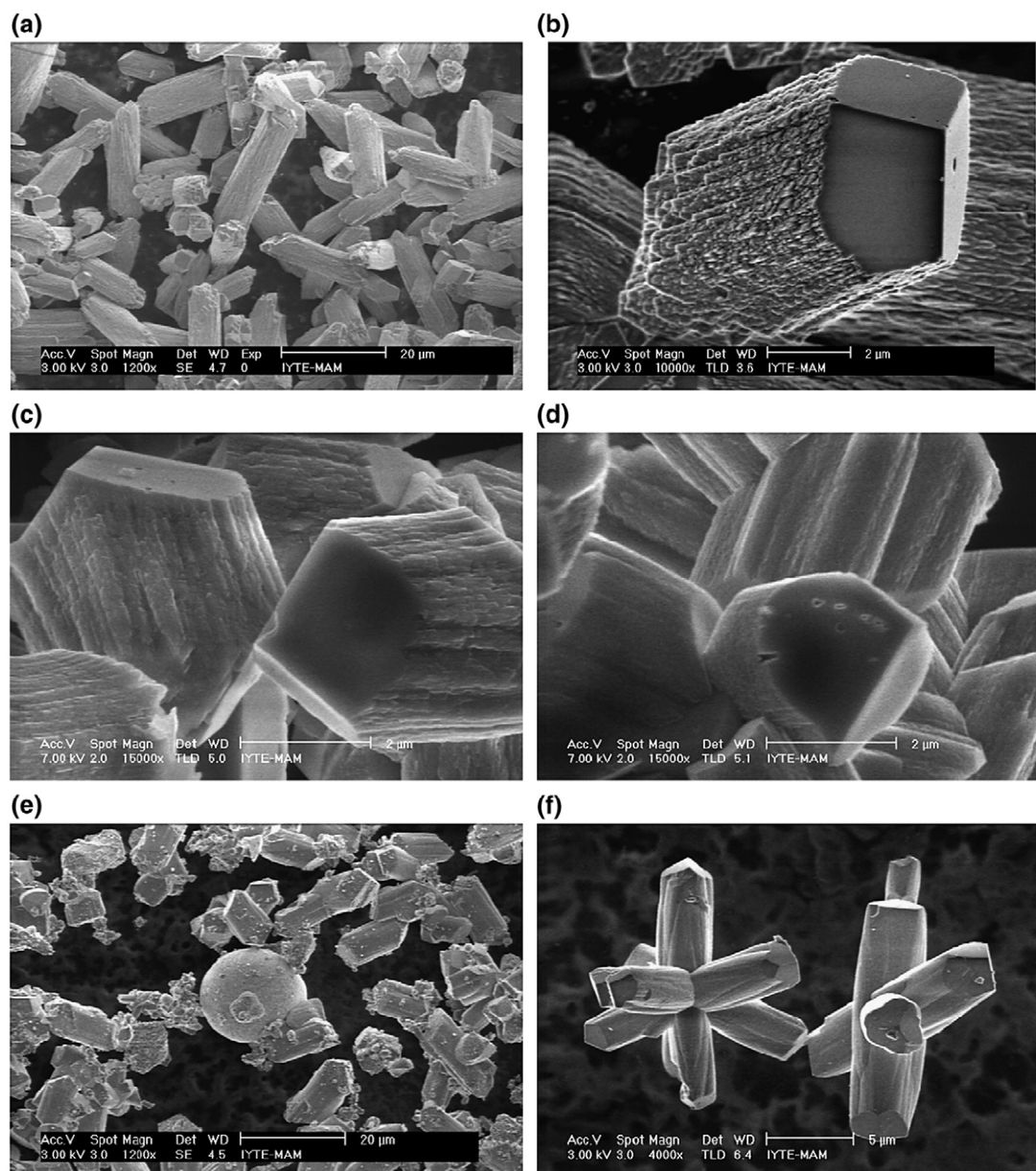


Fig. 8. SEM images of CaCO_3 precipitated in the presence of EDTA at different mixing temperatures: (a, b) 30 °C, (c) 50 °C, (d) 70 °C, (e) 90 °C, 1.0 g/l EDTA, and (f) 90 °C, 2.0 g/l EDTA.

similarity of the results obtained in this study by applying EDTA with the ones reported in the presence of poly(L-isocyanoalanyl-D-alanine) might be originating from the presence of carboxylic groups in the molecular structure of the two substances. Increasing the mixing temperature to 50 °C leads to the formation of calcite structure with same apple core morphology but with less particle size variation. In this case, the length of the crystals was 2–3 µm as presented in Fig. 8c. The same morphology seemed to persist also at 70 °C as can be seen in Fig. 8d. At the mixing temperature of 90 °C, prismatic rods of calcite were observed (Fig. 8e).

XRD diagrams showed that at the mixing temperatures of 30 °C, 50 °C and 70 °C, the precipitated CaCO₃ was entirely composed of calcite. At 90 °C, a small amount of aragonite (less than 5%) was present, with the remaining being calcite. As in the case of the other additives, the suppression of the aragonite formation was dependent on the additive quantity. When EDTA concentrations was lowered to 0.1 g/l, the fraction of aragonite at 90 °C increased to about 27%. However, when the concentration of EDTA was raised to 2.0 g/l, the formation of aragonite was completely suppressed. As shown in Fig. 8f, the resulting calcite particles possessed an interesting morphology, with each crystal appearing to be composed of a number of prismatic columns extending from a common center. It might be assumed that at high EDTA concentration, during the stage of nucleation, the functional groups of EDTA molecules attach to the crystal surface in different favored alignments, thus simultaneously orienting the crystal growth in different directions.

3.2.4. Further considerations

The experiments aiming to investigate the effects of PDDA, CTAB, and EDTA were also paralleled by experiments in which the pH adjustment was carried out after the addition of CaCl₂ solution to the mixture of Na₂CO₃ and the particular additive. The results indicated that under such condition the additives lost, to a large extent, their effects on the particle morphology and polymorph transformation of CaCO₃. For the experiments carried out at 30 °C, the precipitated CaCO₃ appeared to be entirely composed of aggregates of rhombohedral calcite particles that suffer from surface and edge defects. In the experiments done at 90 °C, aragonite particles were dominating and the morphology was primarily branch-like. This could be suggesting that the functionality of the additives is primarily operative over a short time scale at the start of the crystallization process, and that this functionality is very sensitive to pH alterations.

The amount of free Ca²⁺ available in solution at the end of the precipitation experiments carried out at 90 °C was measured using atomic absorption spectroscopy (AAS). The results indicated that at the end of 24 h of aging time, about 230 mg/l of Ca²⁺ ions (out of the initial amount of 2000 mg/l) was present when no additive was used. This amount increased to 252, 264, and 410 mg/l when 2.0 g of PDDA, CTAB, and EDTA were, respectively, added. From these data it is clear that EDTA have a higher impact on the availability of Ca²⁺ ions compared to other two additives.

4. Conclusions

In the absence of additives, calcite possessed a rhombohedral morphology while aragonite crystals appeared to be branch-like.

The amount of aragonite increased with the increase in medium temperature beyond 50 °C. The difference in the temperature of mixing and the temperature of aging had minimal effects on the extent of aragonite formation, but some increase in the aspect ratio of the crystals was observed to parallel the decrease in the aging temperature. Shorter aging times were observed to favor aragonite formation, and the impact of aging time increased with the increase in the mixing temperature.

The additives applied in this work appeared to suppress the formation of aragonite. The extent of this suppression was concentration-dependent. Among these additives, EDTA was the one that caused the most prominent effects on the particle morphology of CaCO₃. Investigating the additive effects at different pH values in addition to further manipulation of the additive amounts is required to provide more understanding of the topic.

Acknowledgements

The authors acknowledge TUBITAK for its financial support (Project No. 104T089). The authors would like to thank the Center of Material Research/Izmir Institute of Technology for the assistance in the SEM and XRPD measurements.

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