Original Research Paper

On the kinetics of phase transformations of dried porous vaterite particles immersed in deionized and tap water

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ABSTRACT

Calcium carbonate exists in three allotropic forms: vaterite, aragonite and calcite. Metastable vaterite can be easily transformed into calcite and/or aragonite via different routes. We report how dry vaterite particles transform into aragonite and calcite when they are immersed into deionized (DI) or tap water without additives at different temperature (22, 40 and 60 °C) with and without stirring. We show that the transformation rate of vaterite into more stable crystallographic forms is influenced not only by temperature but also by stirring and water purity. Low temperature, absence of stirring and absence of ions in water significantly slows down the kinetics of transformation of vaterite. Additionally, water purity influences the nature of the allotropic phase obtained after transformation. High temperatures and deionized (DI) water favor the transformation of vaterite into single crystalline nanowires of aragonite, while tap water yields the transformation of vaterite into calcite. The absence of aragonite in tap water at high temperature can be explained by the presence of sulfate ions, which inhibit the formation of this phase. On the contrary, Mg^{2+} ions tend to stabilize vaterite.

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1. Introduction

Calcium carbonate is one of the most employed materials in the world. It is used in many industrial applications, e.g. either as a filler in paper industry [1,2], as a host matrix in pharmaceutical industry [3,4] or in cement. Vaterite exhibits a porous spheroidal morphology that can be used in protein encapsulation or in drug delivery [5–7]. Yet it is unstable in aqueous solution which is a major drawback for its exploitation. Indeed, it is well established that vaterite undergoes a phase transformation into its more stable allotropic forms that are calcite and/or aragonite when kept for a prolonged amount of time in water. The phase transformation is the consequence of a dissolution recrystallization process where the vaterite particle progressively dissolves at the benefit of the simultaneous recrystallization of rhombohedral calcite [8–11] or needle-like aragonite [12,13]. The rate of dissolution of vaterite in water is thus a key parameter to monitor when one wants to functionalize vaterite and/or to control the release of an encapsulated agent. It is of great interest to evidence whether some external parameters could delay this transformation or even better could stabilize the vaterite allotropic form.

The transformation of vaterite is driven by the minimization of its Gibbs energy. Despite their high free energy, vaterite dry particles are stable in normal conditions and their transformation needs to be activated. The activation energy can be supplied either by a thermal treatment or by immersion into aqueous media. In water, the dissolution recrystallization process proceeds with an activation energy between 24 and 55 kJ/mol [9,14], while the internal rearrangement of atoms during the solid-state transition occurs with an activation energy between 250 and 580 kJ/mol [15–18].

The influence of external parameters during the phase transformation has been already reported in the literature. Among the parameters are the saturation of the solution [9,10], the pH (if >10) [10,19] and the temperature (if >45 °C) [9,20]. Another important parameter that influences the transformation rate and the final polymorph is the use of external salts [8,21,22]. Their addition can prevent the precipitation of calcite as is the case with phosphate, magnesium [8,22] and sulfate ions [23,24]. Additionally, the literature reports that increasing the stirring rate favors the stability of vaterite [25,26]. The aforementioned papers describe the phase transformation occurring in a 'one-pot' process. Namely,

the strategy consists in rapidly mixing initial precursors of $CaCO_3$ such as, for example, sodium carbonate and calcium chloride yielding the formation of a precipitate. These studies were focused on the analysis of the precipitate kept in mother solution for a given period of time to induce the transformation and then dried [8,11,13,19–22,25,26]. In the 'one-pot' synthesis, the transformation of vaterite into calcite in solutions with a high degree of saturation can be delayed at room temperature in a pH lower than 10, at high stirring rate and eventually by adding sulfate and magnesium ions which inhibit the recrystallization of the calcite phase.

In the present work, we have adopted another strategy that consisted in immersing dry vaterite particles, having similar shape and size, either in tap or deionized (DI) water without polymer additives. Usually when dry vaterite is added in aqueous solution it transforms into calcite except if inhibitors of the calcite structure are present [12] which in this case can favor the formation of aragonite. Studies of dry vaterite immersed in water are rather scarce. They were undertaken to investigate the role of ions and/or salts to control pH and ionic strength or to inhibit the calcite reprecipitation [9,10,12]. They show that additives like KCl or $SrCl_2$ increase the transformation rate of vaterite into calcite, while the presence of $MgCl_2$, K_2SO_4 or metallic Li^+ decreases it [9,10,12]. Here we focus on the transformation rate in DI water without additives in comparison with tap water, which was never addressed before. Studying the stability of vaterite in tap water is of major interest for industrial applications since tap water is mainly used, e.g. in paper or cement productions.

This work evidences that by tuning the stirring rate, the temperature and the purity of water one can influence not only the transformation rate but also the allotropic forms, favoring either rhombohedral calcite or nanowires of aragonite. Note that previous studies have shown that nanowires of aragonite were obtained when using additives [27–29]. Appearance of aragonite nanowires was also reported in DI water at 110 °C following Constantz et al. [30] patent, where they studied the stability of vaterite in DI water versus sea water. The nanowires of aragonite have a great interest because they can reinforce composite materials like paper [29] and/or plastics. For instance, aragonite brings a higher toughness to sea shells [31].

The vaterite phase transformation was monitored by quantitative X-ray powder diffraction. Pristine and immersed-in-tap-water particles were also studied by Coherent X-ray Diffraction Imaging (CXDI). CXDI provides a 3D image of particles that reveals how their morphology evolves when vaterite transforms into calcite.

2. Experimental section

2.1. Precipitation and transformation of vaterite particles

The precipitation of vaterite particles was performed by rapidly mixing equal volumes (100 ml) of calcium chloride (0.5 M, $CaCl_2H_2O$) and sodium carbonate (0.5 M, $Na_2CO_3 H_2O$) in DI water at room temperature under stirring for 300 s. The solution was then filtered and the residual powder was washed with ethanol. The filtrate was then dried in an oven at 50 °C for 3 h.

2.1.1. Vaterite transformation in aqueous solution

To study the vaterite transformation, 0.2 g of dried powder was added to the 20 ml of tap or DI water with (730 rpm) or without magnetic stirring at 22 °C, 40 °C and 60 °C. After a certain time, the immersed particles were filtered, washed with ethanol and dried again in an oven at 50 °C. The reproducibility of all the preparation steps was carefully monitored, resulting in a variability in the phase content within 10%, as measured by X-ray diffraction.

Experiments at room temperature were performed in a closed vial. In the experiments at 40 and 60 °C vials were opened for the on-line temperature checking.

2.1.2. Ions influence study

To monitor the influence of ions, 400 mg/l of sodium sulfate (Na_2SO_4), potassium nitrate (KNO_3) and magnesium chloride ($MgCl_2 6H_2O$) were added sequentially in DI water. After dissolution of the added salt, the solution was heated to 60 °C. Vaterite particles were then added and kept in the water solution for 2 h. The particles were filtered afterwards, washed in ethanol and dried in an oven at 50 °C. Complementary experiments were carried out to monitor the specific influence of Mg^{2+} ions at 22 °C.

2.2. Diffraction analysis

The polymorphism of calcium carbonate particles was analyzed by X-ray powder diffraction using a Panalytical Empyrean diffractometer equipped with a copper anode (λ = 1.54 Å) working at 40 kV and 30 mA and a Pixel 3D detector. X-ray diffraction patterns were recorded between 20° and 38° in scattering angle 2θ. The diffraction patterns were then refined using the MAUD software [32]. In the refinement procedure, we started with the ".cif" input files reported in the literature [33–35]. In a first step, we refined the background level, the overall scale factor and the 2θ zero shift. In order to prevent any bias, the content of calcite was guessed by adjusting the intensity ratio between the (1 0 4) Bragg peak of calcite located at 2θ = 29.3° and the one of the (1 1 2) Bragg peak of vaterite located at 2θ = 27.0°. Finally, when a correct ratio was found, we refined the phase fraction of calcite, the lattice parameters with the original atomic positions for calcite and vaterite, the size of the coherently diffracting grains and the strain. Note that given the limited range of measured intensities, the Debye Waller factors were kept fixed to positive values as found in the ".cif" files. To ascertain the reliability of this type of refinement, a calibration chart was prepared by using a mixture of calcite with vaterite dry powders with ratios 0/100, 5/95, 10/90, 20/80, 50/50, 70/30 and 100/0% (Note that we were able to produce in some cases samples containing a very low amount of calcite less than 1%; these samples were used for calibration). The intensity ratio between the (1 0 4) peak of calcite and the (1 1 2) peak of vaterite plotted as a function of the content of calcite was used to calculate the calibration curve. The obtained results via calibration were similar (±4%) to the refined ones via the Rietveld method. In the end, the calculation via the Maud software gave us a maximum uncertainty of 1% on the content of calcite. The same fitting procedure used for the calcite/vaterite mixture was also utilized in the case of vaterite/aragonite/calcite mixture. When a ternary mixture was found, we did not use the calibration method but only the refinement.

2.3. Scanning electron microscopy (SEM)

The morphology of different allotropic phases was studied by a JEOL JSM 6510 LV microscope at 5 kV acceleration using 10 mm working distance and the secondary electron mode of detection. To prevent charging, the samples were metalized with gold.

The particles analyzed by CXDI technique were imaged by the JEOL 6310F microscope at 3 kV, 10 mm working distance, using the secondary electron mode of detection. The samples were metalized after the CXDI measurements.

2.4. Transmission electron microscopy (TEM)

The aragonite particles were analyzed by JEOL, JEM2100 HR transmission microscope at an acceleration voltage of 200 kV and with selected area electron diffraction (SAED). The samples were