



Synthesis and characterization of calcite and aragonite in polyol liquids: Control over structure and morphology

Srečo D. Škapin^a, Ivan Sondi^{b,*}

^aAdvanced Materials Department, Jožef Stefan Institute, Ljubljana, Slovenia

^bCenter for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia

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ABSTRACT

An innovative precipitation process, achieved through the thermal decomposition of urea in polyols containing hydrated calcium salts, was used to prepare calcite and aragonite at elevated temperatures (120–180 °C). The effect of various experimental conditions, such as the media of different polyols (ethylene glycol, EG; diethylene glycol, DEG; and tetraethylene glycol, TEG), the temperature, the reaction time, and the addition of magnesium salts, on the structure, size, and morphology of the obtained solids is described. It was found that the formation of calcium carbonate polymorphs, i.e., calcite or aragonite, their morphology and their size was predominantly influenced by the type of polyols used, and by the diverse growing mechanisms occurring in the different polyol systems. Structurally and morphologically different calcite precipitates were formed in the DEG and TEG solvents *via* classical crystallization processes, while colloidal and nanostructured aragonite particles were assembled in the EG through a recently reaffirmed mechanism based on the role of nanoscale aggregation processes in the formation of carbonate solids. This study highlights the importance of the presence and concentration of magnesium ions in the inhibition of the crystal growth of nanosized aragonite, and in the stabilization of amorphous calcium carbonate (ACC) precipitates in polyol solutions.

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1. Introduction

Anhydrous calcium carbonate polymorphs, i.e., vaterite, aragonite, and calcite, are widespread minerals found throughout nature, commonly occurring in rocks, sediments and in the bio-inorganic structures of the skeletons of mineralizing organisms. Processes leading to the formation of calcium carbonate polymorphs of different sizes, morphologies, and surface properties, have been intensively investigated due to their importance in geo- and biosciences, and in numerous industrial applications [1–3].

These solids have important uses in industrial applications as versatile additives in a wide range of plastics production, in elastomeric and paper manufacture, and in numerous medical and dietary applications and supplements. In the past decade, a number of different methods have been developed and used for the preparation of calcium carbonate solids with diverse structural, morphological and surface properties. Most of the previously reported work deals with the precipitation of carbonates in aqueous media [2,4–6]. Recently, Matijević and Sapieszko [7] have demonstrated that monodispersed metal (basic) carbonates of different sizes and shapes can be obtained by homogeneous precipitation in a solution of metal salts through the thermal decomposition of urea. Following this concept,

a new approach effectuated by the thermal and enzymatic decomposition of urea in aqueous solutions of alkali-earth metals has been employed in the preparation of anhydrous calcium carbonate polymorphs, strontium, and barium carbonates, and their mixed compounds [8–12]. It was shown that the variation of the experimental conditions, such as the temperature, the concentration of the reactants, and the agitation and mixing procedure, exerts a significant influence on the development of carbonate polymorphs with different structural and morphological properties [2].

Presently, there is a need for new approaches to the preparation of precipitated calcium carbonate solids (PCC) with desirable physical and chemical properties using environmentally friendly materials and methods. So far, only modest attention was devoted to the precipitation of carbonate solids in aqueous media with the addition of non-aqueous solvents or in pure, non-aqueous media [13–18]. Recently, several studies have reported on how simple alcohols [13,14,18] and polyols [14–17], affect the precipitation rate, morphology and size of the resulting solids. These solvents, mostly in different ratios with water, have been used as additives, rather than as the main reacting media. Following this concept, significant progress in the development of new methods that lead to a fresh approach to the synthesis of novel PCC solids can be accomplished. At present, neither standardized preparation processes, nor the mechanisms determining the size and shape of the calcium carbonate particles in the non-aqueous media are known.

* Corresponding author.

E-mail addresses: sreco.skapin@ijs.si (S.D. Škapin), sondi@irb.hr (I. Sondi).

Table 1

The effects of polyols on the properties of calcium carbonate precipitates obtained after 10 min of reaction time.

Sample	[CaCl ₂] (mol dm ⁻³)	[Urea] (mol dm ⁻³)	Polyols	T (°C)	Obtained precipitates
1	0.25	0.75	EG	120	Aragonite
2	0.25	0.75	EG	160	Aragonite
3	0.25	0.75	EG	180	Aragonite
4	0.25	0.75	DEG	120	Calcite
5	0.25	0.75	DEG	160	Calcite
6	0.25	0.75	TEG	120	Calcite
7	0.25	0.75	TEG	160	Calcite

The present study deals with the precipitation of anhydrous calcium carbonate solids in solutions containing polyols, ethylene glycol (EG), diethylene glycol (DEG), tetraethylene glycol (TEG), and hydrated calcium and magnesium salts and urea at elevated temperatures. The aim of this study was to determine the effect of different polyols on the structural and morphological characteristics of the resulting solids, with the emphasis on their surface physico-chemical properties. The results of this study may lead to new strategies for the synthesis of calcium carbonate solids with the desired structural and morphological properties in non-aqueous solvents at elevated temperatures.

2. Experimental section

2.1. Materials

Reagent-grade calcium chloride dihydrate (CaCl₂ × 2H₂O), magnesium chloride hexahydrate (MgCl₂ × 6H₂O), urea and polyols – ethylene glycol (EG), diethylene glycol (DEG) and tetraethylene glycol (TEG) – were obtained from the Aldrich Chemical Co. and used without further purification.

2.2. Preparation and characterization of the precipitates

The precipitation was carried out in 250-mL Pyrex flat-bottom flasks, where 50 mL of the reacting solutions contained different polyols, calcium and magnesium chloride and urea. A series of reacting solutions was prepared and kept separately for 10 min, 1 and 3 h in a silicon-oil bath at temperatures of 120, 160 and 180 °C. The experiments were carried out under the conditions given in Table 1. The concentration of the calcium chloride was 0.25 mol dm⁻³, that of the urea was 0.75 mol dm⁻³, while the concentrations of the magnesium chloride varied from 0 to 0.1 mol dm⁻³. The onset of precipitation was determined by the appearance of milky clouds (whiting) in the reacting solutions. Matijević and co-workers [2,8] have shown that the initial formation of carbonate particles during the thermal or enzymatic decomposition of urea in a reacting solution containing calcium salts occurs in a remarkably short period of time, overlapped by a rapid and massive precipitation of solids. Thus, the visual observation of turbidity can be used to approximately determine the onset of the precipitation process. The obtained precipitates were sequentially filtered through polycarbonate filter membranes after 10 min, 1 and 3 h of the reaction time in order to remove the excess of the reacting components. This procedure stops the formation of the new solid phase. The wet precipitates were freeze-dried and kept until further analyses were performed.

2.3. Characterization of particles

The crystalline phases of the carbonate precipitates were analyzed by X-ray powder diffraction (XRD) using a D4 Endeavor, Bruker AXS instrument, and identified according to the JCPDS pow-

Table 2

The effects of magnesium ions on the properties of calcium carbonate precipitates obtained at 160 °C after 10 min of the reaction time.

Sample	[CaCl ₂] (mol dm ⁻³)	[Urea] (mol dm ⁻³)	[MgCl ₂] (mol dm ⁻³)	Polyols	Obtained precipitates
1A	0.25	0.75	0.05	EG	Aragonite
2A	0.25	0.75	0.1	EG	Aragonite
3A	0.25	0.75	0.05	DEG	ACC + calcite
4A	0.25	0.75	0.1	DEG	ACC + calcite
5A	0.25	0.75	0.05	TEG	ACC + calcite
6A	0.25	0.75	0.1	TEG	ACC + calcite

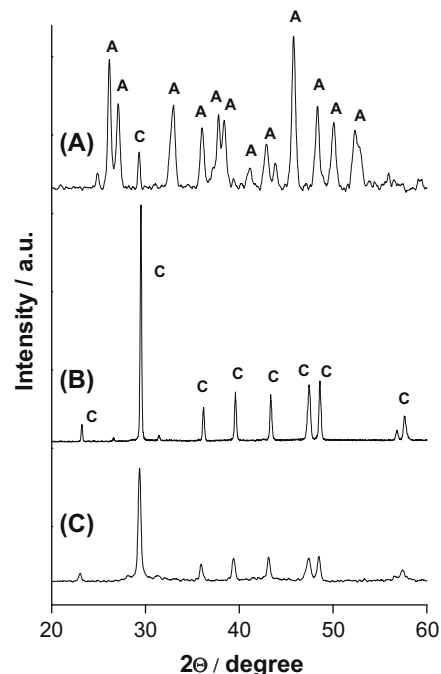


Fig. 1. XRD patterns of calcium carbonate precipitates obtained by aging EG (A), DEG (B), and TEG (C) solutions containing 0.75 mol dm⁻³ urea, 0.25 mol dm⁻³ CaCl₂, at 160 °C for 10 min. (the corresponding SEM micrographs are shown in Fig. 2A–C).

der-diffraction files. The diffraction peaks on the XRD patterns were coded as follows: A – aragonite, C – calcite, V – vaterite. The particle size of the crystallites was determined using the XRD Debye–Scherrer equation. The size and the morphology of the prepared solids were examined by scanning field-emission electron microscopy (FEG-SEM, Zeiss Supra 35 VP). Specific surface area (SSA) measurements of the freeze-dried powder of the carbonate solids were made using the single-point nitrogen-adsorption technique, using a Micromeritics FlowSorb II 2300 instrument. Electrokinetic measurements of the carbonate particles, as a function of pH, were made in a 10⁻³ mol dm⁻³ aqueous KCl solution by using a Malvern Nanosizer instrument. The FTIR spectrum was recorded at room temperature on a pellet containing 2 mg of a sample in 100 mg of KBr in the region 4000–600 cm⁻¹ with a Perkin–Elmer 280 spectrometer.

3. Results

The formation of the calcium carbonate polymorphs by a spontaneous and homogeneous precipitation process was investigated in the EG, DEG, and TEG solutions containing urea and calcium and magnesium salts at temperatures of 120, 160, and 180 °C (Tables 1 and 2).

In all cases the precipitates were rapidly formed, with the onset of the precipitation happening in approximately 10 min. According

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