



Controlling the size and morphology of precipitated calcite particles by the selection of solvent composition



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ABSTRACT

Precipitated calcium carbonate is used as an additive in the manufacture of many products. Particles with specific characteristics can be obtained by the selection of precipitation conditions, including temperature and the composition of solvent. In this work, calcium carbonate particles were obtained in the reaction of calcium hydroxide with carbon dioxide at 65 °C. Initial Ca(OH)₂ suspensions were prepared in pure water and aqueous solutions of ethylene glycol or glycerol of the concentration range up to 20% (vol.). The course of reaction was monitored by conductivity measurements. Precipitated solids were analyzed by FTIR, XRD, SEM and the particles size distribution was determined by a laser diffraction method. The adsorption of ethylene glycol or glycerol on the surface of scalenohedral and rhombohedral calcite was tested by a normal-phase high-performance liquid chromatography. The addition of organic solvents changed the viscosity of reaction mixtures, the rate of carbon dioxide absorption and the solubility of inorganic components and therefore influence calcium carbonate precipitation conditions. All synthesized calcium carbonate products were in a calcite form. Scalenohedral calcite crystals were produced when water was a liquid phase, whereas addition of organic solvents resulted in the formation of rhombo-scalenohedral particles. The increase in organic compounds concentration resulted in the decrease of mean particles size from 2.4 μm to 1.7 μm in ethylene glycol solutions and to 1.4 μm in glycerol solutions. On the basis of adsorption tests, it was confirmed that calcite surface interact stronger with glycerol than ethylene glycol. The interaction between scalenohedral calcite and used organic additives was higher in comparison to the pure rhombohedral form applied as a stationary phase.

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1. Introduction

Precipitated calcium carbonate (PCC) is one of an extensive used additives in paper, rubber and plastics industry. The advantage of PCC compared to the powders of calcium carbonate produced from natural raw materials (ground calcium carbonate - GCC) is to obtain product of high purity with controlled properties, such as polymorphic composition, morphology, crystal size distribution, surface area, brightness, and so on [1]. The anhydrous calcium carbonate can exist in three polymorphic forms: vaterite, aragonite and calcite. The most thermodynamic stable polymorph is calcite, that can shape extremely variable crystals. Calcite can form scalenohedrons, rhombohedrons, hexagonal prisms, pinacoids, and combination of these, forming a multitude of crystal shapes [2].

The most common industrial method to produce calcium carbonate is a carbonation of calcium hydroxide slurry. The characteristics of PCC obtained via carbonation route can be controlled by the process variables such as temperature, supersaturation, gas mixture flow rate, stirring rate, calcium hydroxide concentration, pressure [2–5], organic and inorganic additives [6–8], and the composition of the solvent [1,9,10]. The increase in temperature (i) decreases the density and viscosity of the liquid phase, (ii) increases the solubility of calcium hydroxide and the achievement of species concentrations in solution resulting from the equilibria [11], (iii) decreases the solubility of carbon dioxide [12], and (iv) influence the polymorph formation and morphology [2,13,14]. Running the precipitation at higher supersaturation can lead to the higher rate of crystal growth, the formation of smaller primary particles as well as agglomerates and can affect the polymorph form of the product [2,15]. The increase of the mixing intensity results in the formation of smaller particles but then also increases the potential for agglomerate formation because of frequent collision of particles [16]. The additives present in the system may

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influence the precipitation process in various ways. Organic or inorganic additives can affect the rate and mechanisms of steps involved in crystallization process and thus may induce changes in the nuclei formation, crystal size distribution, and morphology [4,13]. The role of inorganic cations during precipitation of calcium carbonate is usually described as the promotion of specific polymorphic form [17]. However, intensive research on the effect of organic additives on the characteristics of PCC indicate that their presence in the solution favour the formation of calcium carbonate particles with complex shapes [18]. Organic additives can also control the polymorph composition, stabilize the metastable polymorph, or cause the formation of smaller particles [18].

In contrast to a large number of published research on the role of organic additives (especially surfactants) on the PCC characteristics, the test results on the influence of the type of solvent used for the precipitation is not extensive. When the synthesis of calcium carbonate carried out by the mixing the aqueous solutions containing reacting ions, the less stable polymorph is formed, and the addition of organic solvents (ethanol, isopropanol, ethylene glycol or diethylene glycol) inhibits transformation of the produced metastable form [19–23]. The production of less stable polymorphs, i.e. vaterite and aragonite, has been also observed when calcium carbonate was prepared by the reaction of calcium hydroxide with carbon dioxide in aqueous solutions of ethanol while its concentration has been above 50% [1]. However, the comparison of effect of alcohols with one –OH group and polyols on PCC characteristics indicates that better stabilization of metastable forms show polyols [24–26]. In contrast to the previously cited studies, the overall trend for investigated primary alcohols has been the preferential precipitation of thermodynamic stable calcite when calcium carbonate was prepared by the diffusion of gaseous CO₂ [27].

The addition of organic solvent to the reaction medium may also affect the size of the PCC particles. Typically, the size of PCC decreases with the increase of organic additive in the solution [1,9,10,26], although in some cases the addition of an organic solvent favour in the formation of highly aggregated crystals [6,19]. The changes in the morphology of vaterite crystals precipitated in the presence of organic solvent have been reported, as well [19,23,24].

Our previous works have concerned the influence of mixtures organic solvent – water composition on the PCC characteristics precipitated at ambient temperature [9,10]. The obtained particles have been rhombohedral calcite agglomerates, and the organic additives have influenced mainly the size of final agglomerates. The aim of this work is to compare the effect of the composition of solvent on the characteristics of PCC particles produced in the reaction of calcium hydroxide and carbon dioxide at temperature 65 °C. The selection of temperature was based on the analysis of previously published studies in which precipitated calcite particles were scalenohedral habits [2,11,28]. There are only few works reporting the precipitation of calcium carbonate at elevated temperature in mixed solvents by solution mixing method or solvothermal method [20,21,24,26], and we have not found the information about influence of organic solvent additives on the PCC formation at elevated temperature via carbonation route.

2. Experimental

2.1. Reagents

Calcium hydroxide (Reachim), glycerol (POCH), ethylene glycol (CHEMPURE), ethanol (POCH) were of analytical reagent grade and were used in this study without further purification. Deionised water was used to prepared solutions. Carbon dioxide was

purchased from Oxygen s.c. Selected properties of organic solvent – water mixtures at 65 °C are summarized in Table 1.

2.2. Preparation

Calcium carbonate was precipitated in a tank-type reactor. Specific dimensions of the reactor are the same as in [9,10]. The reactor was isolated with polystyrene foam (thickness 20 mm) to better stabilize a temperature. The precipitation was conducted in a semi-batch manner at 65 °C. The reading of the volumetric gas flow rate was corrected to the atmospheric conditions at the top of the reactor by pressure and temperature measured under the gas distributor. Calcium hydroxide concentration was 10 g/dm³ and a carbon dioxide flow rate was 250 cm³/min in all experiments. The reaction was investigated in the presence of glycerol or ethylene glycol at different concentration in the range from 0 to 20% (vol.). The reaction progress was determined by conductivity measurements. The minimum of the conductivity obtained during the registration of a curve conductivity vs. time corresponds to the end point of the reaction and allowed to determine the end time precipitation. The samples of precipitated CaCO₃ were filtered, washed with ethanol and dried at 100 °C for 12 h.

2.3. Characterization of CaCO₃ particles

The size of calcium carbonate particles was determined by a laser diffraction method (SALD 2300, SHIMADZU). Precipitated particles were observed by a microscope (DELTA OPTICAL ME1000 equipped with a digital camera and a computer; effective magnification used 3200×). To determine crystalline structure of samples and to characterize polymorph composition of calcium carbonate the conventional XRD technique (Philips X'Pert diffractometer system) with Co K_α radiation was used. The XRD spectra were collected at a scan rate 0.2° and 2 theta range 20–60° at room temperature. Taking into account precision of measuring system, the sensibility of proposed method was about 2%. The types of chemical bonds in the structural units present in the samples were identified using Fourier transform infrared spectroscopy (FT-IR). Measurements were carried on a Nicolet 8700 Spectrometer (Thermo Scientific) at room temperature. FTIR method is highly sensitive and allows the detection in a test sample of even small quantities of the substance of less than 0.1%. Attenuated total reflectance (ATR) technique was used. The ATR-FT-IR spectra were obtained between 4000 cm⁻¹ and 400 cm⁻¹ using average of 64 scannings at 2 cm⁻¹ resolution. Both, the XRD and FT-IR measurements, were repeated for several samples obtained under the same conditions. For the particle characterization scanning electron microscope FEI Quanta FEG 250 with an Everhart-Thornley (ET) secondary electron detector was used.

2.4. Adsorption tests

The normal-phase high-performance liquid chromatography (NP-HPLC) was used to compare the interaction between organic compounds and calcium carbonate. Columns of dimensions 100 × 4 mm were loaded with CaCO₃ particles. Two types of calcite were used as a sorbent: scalenohedral calcite prepared in this study (without additives) and pure rhombohedral calcite obtained in a previous experiment with triethylamine [34]. The tested column was connected to a chromatograph (Merck-Hitachi gradient chromatograph equipped with a L-7100 pump, a Rheodyne injector with a 20 µl sample loop, a L-7455 UV diode array detector, a model ERC-7511 refractive index detector, and HSM software). Tetrahydrofuran (THF) flowing at a rate of 0.7 ml/min was used as an eluent. Solutions of 20 mg/ml organic substance in THF were samples injected to the tested column.

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