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A novel route to prepare the metastable vaterite phase of $CaCO_3$ from $CaCl_2$ ethanol solution and Na_2CO_3 aqueous solution

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ABSTRACT

Vaterite, the least stable phase among three anhydrous polymorphs of calcium carbonate ($CaCO_3$), was prepared *via* the reaction between the ethanol solution of calcium chloride ($CaCl_2$) and the aqueous solution of sodium carbonate (Na_2CO_3), which is named ethanol-calcium method. The effects of aging times and reaction temperatures on the formation of vaterite were investigated. The polymorphs and morphologies were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively, and Fourier transform infrared spectroscopy (FT-IR) was used to verify the existence of vaterite. XRD results indicate that the amount of vaterite decreases from 90.4% to 81.4% as increasing in aging times from 0 min to 42 h and decreases from 85.8% to 70.2% as increasing in reaction temperatures from 0 °C to 60 °C. SEM results show that vaterite and calcite as-prepared are their typical morphologies of spherical and rhombohedral, respectively. This research extends the route to prepare the metastable vaterite and provides new insights into its controllable synthesis.

1. Introduction

Vaterite, a polymorph of calcium carbonate ($CaCO_3$), is the least stable phase at ambient conditions among the three anhydrous crystalline phases (calcite, aragonite and vaterite) of $CaCO_3$ [1]. Vaterite is expected to have potential applications for personal care (abrasives, anticaking agents, colorants and emulsion stabilizers) [2] and biomedical areas (preservative containers for growth factors and encapsulating carriers for drugs) [3,4] because of its high solubility, high specific surface area, high dispersion and lower specific gravity.

The preparation methods of $CaCO_3$ include carbonation method [5,6], double decomposition method [7,8], microemulsion method [9], solvothermal method [10], self-assembled monomolecular membrane method [11,12], biomimetic synthesis method [13,14] and the thermal decomposition of calcium bicarbonate [15,16]. However, the formation of vaterite are influenced not only by preparation method (solution composition [17] and type of the reactants [18]), but also by reaction parameters, such as supersaturation [19], temperature [20], reaction time [21], additives [8] and so on. Except for pure aqueous system, organic solvent-aqueous is the common reaction system. Liu et al. [14] reported a method, CO_2 gas decomposed from ammonium bicarbonate (NH_4HCO_3) diffusing into calcium chloride ($CaCl_2$) solution containing ethanol-water mixed solvents, to prepare vaterite at the assistance of poly (sodium 4-styrenesulfonate) (PSS), in which pure vaterite is obtained only at high ethanol/water ratio of 7/3 and low temperature of about 10 °C, while calcite/vaterite and calcite/aragonite mixed phases are prepared at decreased ethanol/water ratio and elevated temperature (40 °C), respectively. In another reaction system, mixing of the solution of $CaCl_2$ and sodium carbonate (Na_2CO_3) dissolved in the ethanol-water binary solvent (EWBS, 1:1), the content of vaterite dramatically decreases when the molar ratios of Ca^{2+} to CO_3^{2-} increase from 1:1.1 to 1.1:1, and the possible mechanism is that Ca^{2+} and CO_3^{2-} have different solvation behaviors in EWBS [17]. When $CaCl_2$ aqueous solution is added into Na_2CO_3 ethanol-water solution, the ratio of vaterite decreases from 21% to 0% (aging times from one hour to one week) under gentle shaking speed and from 75% to 0% (aging times from one hour to one day) under vigorous shaking speed in EWBS with the volume ratio of ethanol to water of 1:9, while vaterite cannot be obtained

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under gentle shaking speed and the ratio of vaterite decreases from 48% to 0% (aging times from one hour to one month) under vigorous shaking speed in EWBS with the volume ratio of ethanol to water of 1:1 [22]. In addition, utilizing the reaction between calcium acetate and hydrolysis product of urea in EWBS at 90 °C, the phase compositions of $CaCO_3$ transform from a two-phase mixture of aragonite (dominant) and calcite to another two-phase mixture of vaterite (dominant) and aragonite when the volume ratio of ethanol to water increases from 0 to 3, while increasing temperature to 120 °C when the volume ratio of ethanol to water is 3, a two-phase mixture composed of more aragonite and less vaterite is obtained [23]. However, there are very few research on the synthesis of vaterite in ethanol-water reaction system by ethanol-calcium method.

In this paper, we aim to find a new controllable method (ethanol-calcium method) to prepare vaterite, at least the dominant crystalline phase, at room temperature without any additives. The significantly difference from previous study is that the $CaCl_2$ ethanol solution is prepared firstly, which is named ethanol-calcium. The effect of aging times and reaction temperatures on the amount of vaterite are focused on in the present work and the possible reaction process is tentatively proposed. It is of great significance to understand the formation mechanism of vaterite in this system.

2. Experimental details

2.1. Chemicals

Anhydrous calcium chloride ($CaCl_2$), anhydrous sodium carbonate (Na_2CO_3) and anhydrous ethanol, obtained from Sinopharm Chemical Reagent Limited Liability Company (Shanghai, China), are of analytical purity and water is deionized water.

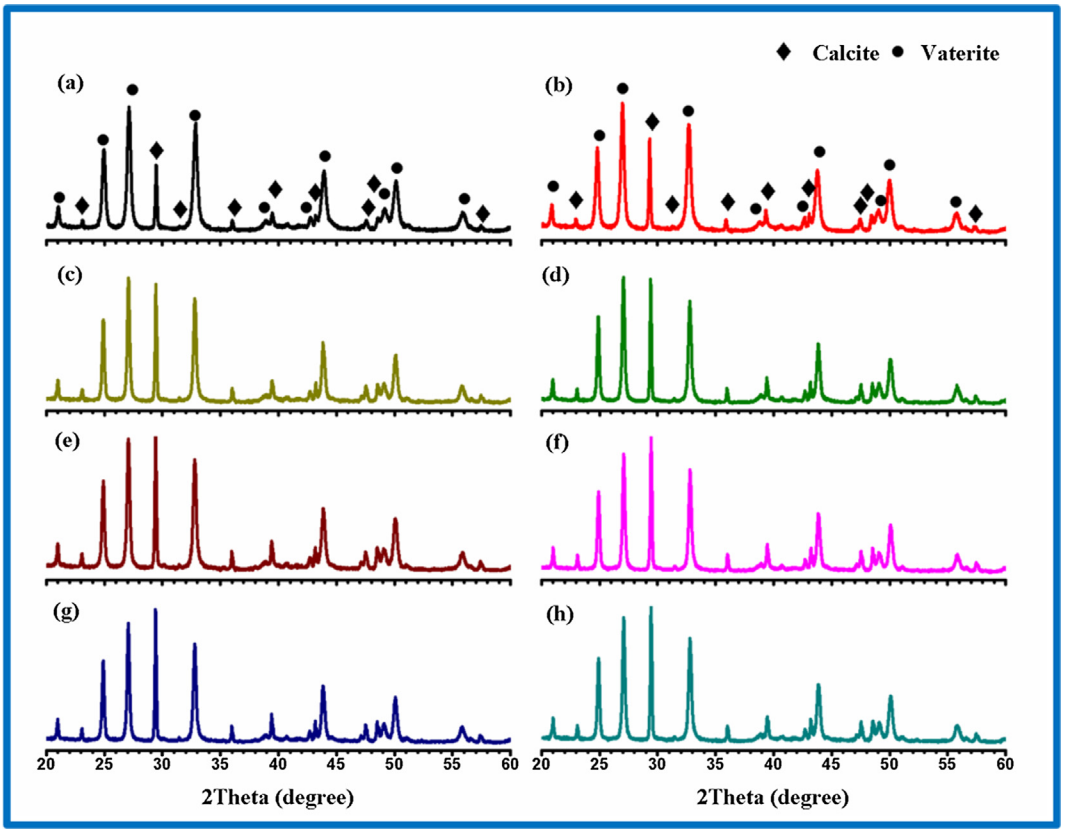

Fig. 1. XRD patterns of $CaCO_3$ particles obtained in the presence of different aging times (a) 0 min; (b) 10 min; (c) 20 min; (d) 60 min; (e) 90 min; (f) 2 h; (g) 22 h; (h) 42 h, the reaction temperature is 20 °C.

Table 1
Phase compositions of $CaCO_3$ prepared at different aging times.

Number	Reaction temperature (°C)	Aging time	Phase compositions	
			Vaterite (%)	Calcite (%)
a	20	0 min	90.4	9.6
b	20	10 min	87.5	12.5
c	20	20 min	84.4	15.6
d	20	60 min	84.1	15.9
e	20	90 min	83.5	15.9
f	20	2 h	82.7	17.3
g	20	22 h	82.5	17.5
h	20	42 h	81.4	18.6

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