Powder Technology 270 (2015) 387–392

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

From nano-cubic particle to micro-spindle aggregation: The control of long chain fatty acid on the morphology of calcium carbonate

Jiuxin Jiang [a,b,*], Dongdong Xu [a], Ying Zhang [a], Shipeng Zhu [a], Xinpeng Gan [a], Jianing Liu [c,**]

[a] School of Material Science and Engineering, Hubei University of Technology, Wuhan 430068, China
[b] Hubei Provincial Key Laboratory of Green Materials for Light Industry, Hubei University of Technology, Wuhan 430068, China
[c] School of Physics and Optoelectronic Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

ARTICLE INFO

Article history:
Received 18 July 2014
Received in revised form 20 October 2014
Accepted 29 October 2014
Available online 1 November 2014

Keywords:
$CaCO_3$
Fatty acid
Carbonation
Surfactant
Template

ABSTRACT

The morphological control of calcium carbonate ($CaCO_3$) colloidal particles, which allows us to obtain specific material properties, is one of the key challenges in various applications. To this end, we have studied the formation of $CaCO_3$ particles by adding different long chain fatty acids—lauric acid, palmitic acid and stearic acid—into calcium hydroxide ($Ca(OH)_2$) slurry, and then, by dispersing carbon dioxide (CO_2) gas into the slurry via a micropore plate. Their polymorph, morphology and surface feature were characterized by XRD, TEM and FTIR, respectively. It is shown that the crystalline phase of $CaCO_3$ particles leaves unchanged with respect to the used species and amounts of fatty acids, what is changed is the shape of $CaCO_3$ particles from nano-cubic to micro-spindle. Thus we underlined the tuning mechanism of precipitation.

1. Introduction

In addition to the wide application in areas of plastics, rubber, papermaking, paints, pigment, oil point, toothpaste, textiles and food, precipitated calcium carbonate ($CaCO_3$) is one of the most widely existing biominerals produced by organisms. The application of $CaCO_3$ powder is determined by a great number of defined parameters, such as chemical purity, particle size, dispersity, particle morphology, structure, powder brightness and so on [1], in which particle morphology and polymorph are considered to be the most important factors. $CaCO_3$ crystals include three polymorphs—rhombic calcite, needle-like aragonite and spherical vaterite. Although calcite is the most stable phase and vaterite is the least from the point of thermodynamic view, the superstructures of vaterite can be obtained from various routes, e.g., without [2–4] or with the assistance of surfactants [5–7], especially by adding block copolymer [8–10], under the control of reaction temperature [3,5], in ethanol/water solution or their interface [2,6], after mineralization for a long time [2, 7–10], etc., while a control on the superstructure of pure calcite without crystalline phase transition has rarely been reported, which might be due to the difficulty on assembly of a thermodynamically stable phase through a well-organized dispersibility, for instance, self-stacked calcite "pancakes" can be only obtained after 2 weeks of mineralization [11].

In recent decades, it has been proven that fatty acids can effectively tune the morphology of $CaCO_3$ particles. Ukrainczyk et al. [12] and García-Carmona et al. [13] have investigated the different impacts of sodium stearate on the morphology of $CaCO_3$ particles at different concentrations of dissolved Ca^{2+}. Such as, spindle $CaCO_3$ aggregation are obtained when both $Ca(OH)_2$ slurry with the concentration of Ca^{2+} of 17.0 mmol/L and 1.12 wt.% sodium stearate are slowly added [12]. This is because hydrophobic alkyl chains can be chemically absorbed onto the mineral surface [14,15], thus resulting in improved surface feature and dispersibility of particles [12,16]. Particularly, according to Shi et al. [15], the homogeneous spherical micelles that are composed of amphiphilic molecules, when $CaCO_3$ particles are present in the system, will deform into ellipsoid micelles in hydrophilic polar solvents. Trana et al. [16] have successfully modified nano-$CaCO_3$ particles by adding sodium stearate at the end of carbonation stage, by which well-dispersed nano-$CaCO_3$ particles and rod-like or spindle aggregates of primary particles are obtained. In addition, Wang et al. [17] have synthesized $CaCO_3$ powder which consists of most rod-like particles with a diameter of 200–400 nm and a length of 2–4 μm and few elliptic particles with a diameter of about 100 nm when lauric acid is used as organic substrate.

Although the different fatty acids are usually applied to precipitate $CaCO_3$ [12,13,15–17], a comparative investigation on the fatty acids with different carbon chain lengths—lauric acid, palmitic acid and

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[*] Correspondence to: J. Jiang, School of Material Science and Engineering, Hubei University of Technology, Wuhan 430068, China. Tel.: +86 27 5975 0457; fax: +86 27 5975 0454.

[**] Correspondence to: J Liu, School of Physics and Optoelectronic Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China. Tel.: +86 25 58731031; fax: +86 25 58731031.

E-mail addresses: jiuxinjiang@hotmail.com (J. Jiang), jl2009@hotmail.de (J. Liu).

http://dx.doi.org/10.1016/j.powtec.2014.10.047
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stearic acids in modification of the morphologies of $CaCO_3$ particles—has not been reported. And this will be presented in our work.

2. Experimental section

2.1. Materials and reaction equipments

$Ca(OH)_2$ and absolute ethyl alcohol, purchased from Sinopharm Chemical Reagent Co., China, are analytical grade. Lauric acid, palmitic acid and stearic acid, purchased from the same corporation, are analytical grade. Water is distilled water and the purity of CO_2 exceeds 99.5%. The schematic of reaction equipment refers to our previous research [18].

2.2. Experimental procedure

Five grams of pre-ground $Ca(OH)_2$ was added in distilled water to prepare 100 ml $Ca(OH)_2$ slurry. Lauric acid, palmitic acid and stearic acid were separately dissolved in absolute ethyl alcohol to form a solution with a concentration of 0.1 mol/L. And each solution with weight ratios of acid to prepared $CaCO_3$ of 1.5% or 3.5%, was added into $Ca(OH)_2$ slurry, of which were marked as CL-1.5 and CL-3.5, CP-1.5 and CP-3.5, and CS-1.5 and CS-3.5 for lauric acid, palmitic acid and stearic acid, respectively. The sample without addition of any fatty acid is marked as C-0. After stirring vigorously for 30 min, the mixture was transferred into micropore dispersion reactor. The gas of CO_2 was introduced into the mixture and reaction was not stopped until pH value dropped to 7. The final suspension was centrifuged at 8000 rpm for 10 min and the supernatant solution was discharged, and then the solid was redispersed in distilled water. This process was repeated in absolute ethyl alcohol for the second time and in distilled water for the third time in order to rinse the particles. After the last centrifugation, the sedimented particles were dried in the oven at 80 °C for 3 h then slightly grinded for studies.

2.3. Characterization of the products

The crystal type of $CaCO_3$ particles was detected by X-ray diffraction (D/MAX-RB, RIGAKU, Corporation, Japan). The morphologies were characterized by transmission electron microscope (TEM, TECNAI G20). For TEM, the powder was dispersed in absolute alcohol, dropped onto carbon-covered copper grids placed on filter paper and dried at room temperature. In order to study the surface characteristic, Fourier transform infrared spectroscopy (FTIR) was recorded on an NEXUS with the KBr pellet method.

3. Results and discussion

3.1. Polymorphs of $CaCO_3$ particles with different fatty acids

Different crystalline phases highly rely on different preparation methods. For instance, calcite phase can be obtained through the carbonation of $Ca(OH)_2$ aqueous slurry [12,13,17–19], vaterite phase emerges in system of Ca^{2+}–CO_3^{2-} [20,21], Ca^{2+}–CO_2 [22,23] or by mineralization for long period [2,7–10], and aragonite phase can be generated at high reaction temperature [3,24–26]. Furthermore, the additive in different routes of preparation methods has different effects [18,27,28], Such as in the system of Ca^{2+}–CO_3^{2-}, the addition of oleic acid can alter the crystal type of $CaCO_3$ [20,21], but in carbonation of $Ca(OH)_2$ aqueous slurry, it does not affect the polymorph of $CaCO_3$ [18,19]. In line with that, XRD patterns (Fig. 1) of the prepared $CaCO_3$ powder show that calcite is the only crystalline phase in all samples, unchanged with the difference of the fatty acids.

3.2. Morphologies of $CaCO_3$ particles with different additions of fatty acid

TEM photographs of $CaCO_3$ particles in the presence of fatty acid with the amount of 1.5 wt.% and 3.5 wt.% are illustrated in Figs. 2 and 3, respectively. From Fig. 2a, although some particles with size less than 100 nm exist in the sample without addition of any fatty acid, lots of large particles and serious aggregation can be found. In the sample with the addition of 1.5 wt.% lauric acid, as shown in Fig. 2b and c, the average particle size is about 30–40 nm, the aggregation is markedly improved and it is irregular. Although similar sizes of particles and improved aggregation are found in the sample with the addition of 1.5 wt.% palmitic acid, the aggregation tends to be chain-like, as illustrated in Fig. 2d and e. However, much difference in the morphology of $CaCO_3$ particles is observed in the sample with the addition of 1.5 wt.% stearic acid, in which small $CaCO_3$ particles gather into irregular rods, as shown in Fig. 2f.

Although there is little difference in particle morphology when the amount of lauric acid is increased to 3.5 wt.%, much difference is

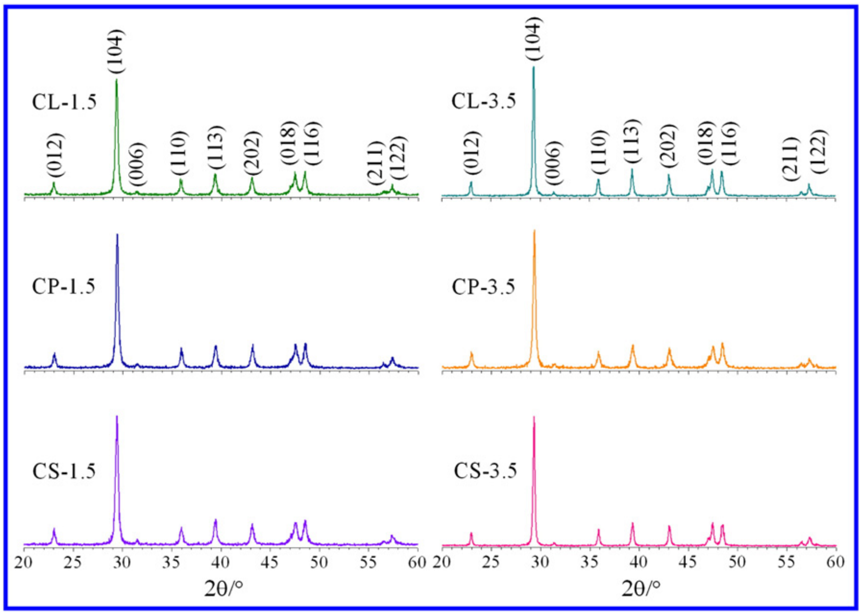

Fig. 1. XRD patterns of $CaCO_3$ with the addition of different fatty acids.