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Original Research Paper

Template-free synthesis and particle size control of mesoporous calcium carbonate

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A B S T R A C T

Controlling particle size is important in powder technology. Here we report a scalable production process of mesoporous calcium carbonate with a controllable particle size. We focus on the effect of the aggregation rate on the obtained particles. In this study, we change the particle concentration (1.2–12 mass%) to control the aggregation rate and then obtained particles with relatively narrow range of particle size (310 ± 30–560 ± 100 nm) and nearly identical specific surface areas and particle structures by template-free method. We proposed the aggregation model to describe the formation of meso-porous calcium carbonate.

1. Introduction

The process of controlling particle properties (particle size, particle shape, etc.) is important in powder technology. Generally, powders have a particle size distribution with different shapes. Compared to coarser powders, handling of fine powders creates issues as the particle properties drastically change. For example, some problems such as increased frictional resistance, increased stickiness or adhesion, and scattering can arise. Shape variations affect the preparation time, quantitative capability, and product qualities. Hence, homogenization of particle size and the shape of raw material are necessary to improve product quality and handling properties.

Calcium carbonate is a common biomineral. The development of functional materials that mimic peculiar structures such as pearls and shells has attracted attention. Because biomineralization is a self-organization process in nature and can be effectively used for many materials, extensive research has occurred in the last few decade [1–3]. To design functional materials, it is necessary to understand the formation mechanism of calcium carbonate. The crystallization process is important in the synthesis and purification of calcium carbonate as well as in applications of solid materials. Research has been conducted to precisely control the crystal structure (calcite, aragonite, vaterite), particle size, particle shape, and pore structure by syntheses using interactions with macromolecules [4,5] or additives [6–8]. Calcium carbonate that controls these particle characteristics is expected to be applied in various fields [9–11].

The most used industrial process of obtaining calcium carbonate involves the following steps [12]: (a) Calcination of limestone to produce quicklime and carbon dioxide; (b) A slaking process, where the quicklime is transformed into a slaked lime slurry (a $Ca(OH)_2$ suspension), which is controlled by the addition of water; (c) A carbonation reaction, where CO_2 is bubbled through an aqueous slurry of slaked lime. The carbonation reaction is the crucial step determining the particle characteristics of the obtained products. Especially, when calcium carbonate is applied as a filler, its particle size is important and has been controlled by adding additives [13–15]. Templates and additives are often used to control the particle characteristics (especially particle size and pore structure) of calcium carbonate and there is a problem that they must be removed.

In our research, we have improved the carbonation process, which is used in industry, and have advanced mass-production of mesoporous calcium carbonate by a template-free method in an organic solvent. Performing the carbonation reaction in an organic solvent yielded a calcium carbonate colloidal dispersion. Aging the obtained dispersion under various conditions gave the following results [16]: (1) When a colloidal solution with dispersed nano-sized calcium carbonate is aged statically, the solution becomes cloudy after gelation. (2) The aging temperature greatly affects particle formation. For example, when the aging temperature is 20 °C, egg-like shaped calcite particles (specific surface area: ~200 m^2

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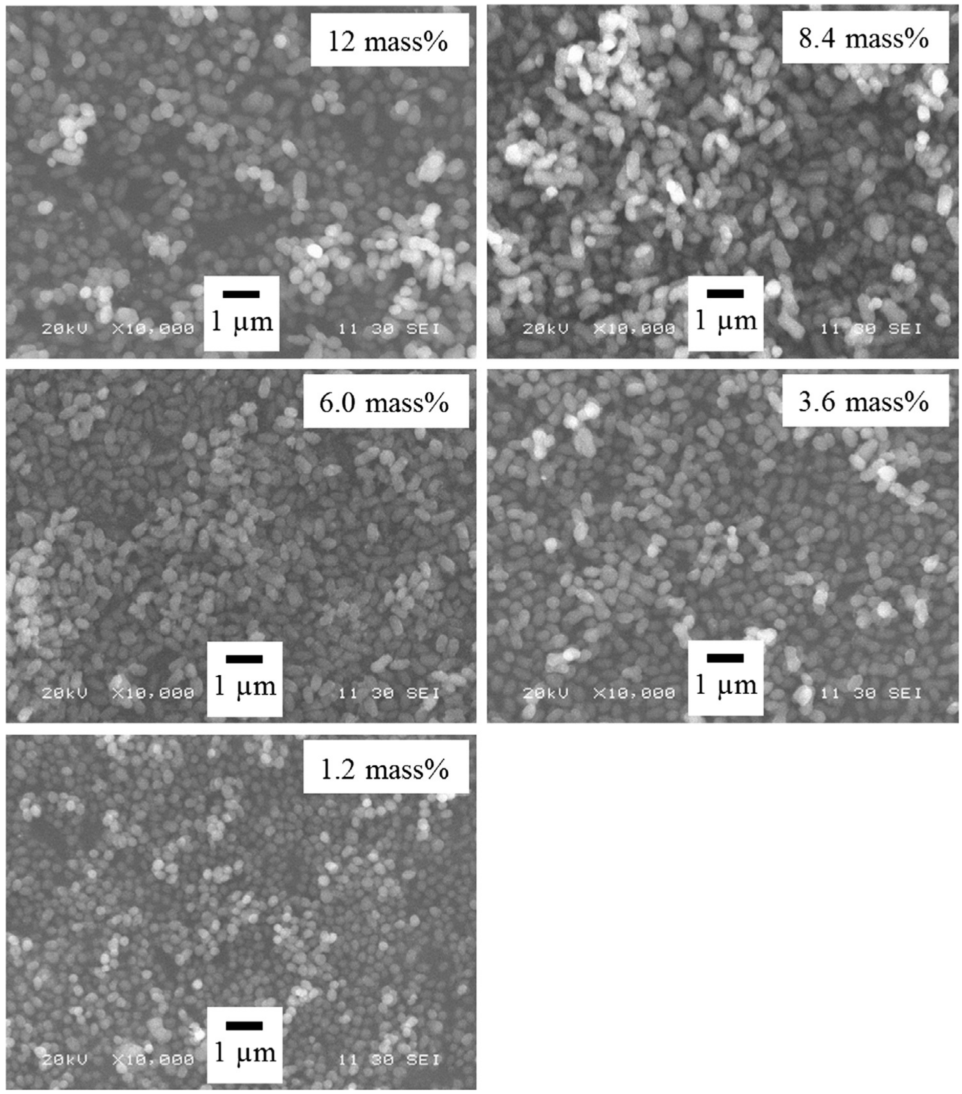

Fig. 1. SEM images of the particles obtained at each particle concentration.

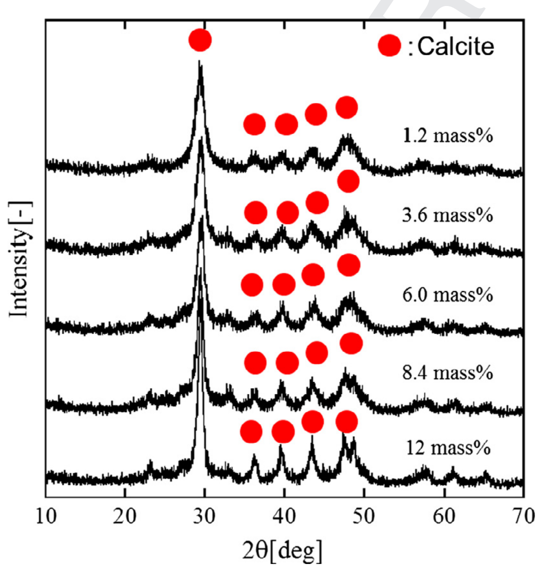

Fig. 2. XRD patterns of the particles obtained at each particle concentration.

g^{-1}) with particle sizes of ~500 nm are obtained. When the aging temperature is 200 °C, rod-like shaped vaterite particles (specific surface area: ~65 $m^2\,g^{-1}$) with a major diameter of 1.2–1.5 µm are obtained. (3) In the aging process, the phase transition of the crystal and the aggregation of the colloid occur simultaneously. Consequently, the resulting particles have various shapes and crystal structures.

In this research, we focus on particle aggregation and attempt to synthesize mesoporous calcium carbonate with particle size controlled by template-free method. Concretely, we examine the influence of particle concentration, which is an aggregation rate–determining factor, based on the aggregation rate formula of the particle in solution [17]. As aggregation rate determining–factors, there are three parameters of temperature, viscosity, particle concentration. Controlling the temperature or the viscosity is difficult. It is especially challenging to realize a uniform system temperature during high-temperature aging. A mixture of crystal polymorphs and variations in shape are observed [16]. So, we conducted experiments focusing on particle concentrations, which are relatively easy to control among these determinants. Then we assess the particle properties of mesoporous calcium carbonate obtained from the calcium carbonate dispersion as a function of particle concentration.

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