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Effect of Oleic Acid Addition on Crystallinity of Mesoporous Calcium Carbonate[†]

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Abstract

We report a scalable and template-free production method of mesoporous calcium carbonate particles, of which specific surface areas were 16-207 m²/g, and polymorphs were calcite and/or vaterite. We obtain the transparent colloidal dispersion of calcium carbonate (10 nm less in size) by means of a modified industrial carbonation reaction. Here the effect of oleic acid addition on particle shape, polymorphs, specific surface area, and pore structure of mesoporous calcium carbonate is investigated. The particle properties depend on the additive amount of oleic acid. When the oleic acid was added in small amount to the colloidal dispersion, crystal phase of mesoporous calcium carbonate was calcite. While, the addition in large amount was favorable to form vaterite phase.

KEY WORDS: (Mesoporous calcium carbonate), (Calcite), (Vaterite), (Template-free), (Colloidal dispersion), (Oleic acid)

1. Introduction

Calcium carbonate is one of the most abundant minerals. The organization of its primary building units into hollow and porous superstructures is of considerable interest due to their promising applications in controllable release of drugs ¹⁾, and catalyst support ²⁾, as well as biomimetics ³⁾. Heterogeneous nucleation or surface crystallization on soft/hard templates has been thought to be the main process capable of ordering superstructures of calcium carbonate ⁴⁻⁷⁾. However, this method requires an additional process to remove the template from the system, and also is a relatively unproductive process because the concentration of calcium carbonate should be low during nucleation event in order to avoid unwanted homogenous nucleation. Hence, large-scale production of porous calcium carbonate without template remains challenging. With this protocol in mind, we have reported a scalable and template-free production method for mesoporous calcium carbonate particles ⁸⁾. Their specific surface area and mean pore size were ca. 60-200 m²/g and 3-20 nm, respectively. Additionally, we have confirmed its potential use as a formaldehyde vapor adsorbent. The vaterite was an appropriate polymorph of calcium carbonate in formaldehyde vapor adsorption compared to the calcite ⁸⁾.

We produced the mesoporous calcium carbonate by

means of a modified industrial carbonation process. In a usual industrial production system, calcium carbonate is produced on a large scale by carbonation of calcium hydroxide in water. While, we only switch the solvent from water to the organic solvent mixture. After carbonation reaction, the colloidal calcium carbonate particles (10 nm or less in size ⁸⁾) can be obtained. They assemble into porous 3-D structures via temperature induced aggregation. The particle properties of mesoporous calcium carbonate depend on aging temperature because thermal energy leads to Brownian aggregation of the colloid particles. The repulsive force would be extremely vulnerable to the van der Waals attractive force because electrostatic interactions are negligible in such a relatively low dielectric constant medium ⁹⁾. Simultaneously, the colloids undergo polymorphic transformation from amorphous to calcite and/or vaterite phase. When the colloid aged at 293 K, the mainly calcite calcium carbonate with high specific surface area (~200 m²/g) was obtained. While, the vaterite-rich one with the low area (~60 m²/g) was formed at the aging temperature of 473 K ⁸⁾.

Polymorphs of crystalline calcium carbonate; i.e. calcite, aragonite, and vaterite are commonly thought to crystallize via unstable amorphous calcium carbonate (ACC) ³⁾. ACC transforms into calcite via dissolution and

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subsequent reprecipitation mechanism, depending on the thermodynamic equilibrium. Therefore, the water content plays a crucial role in the polymorphic transformation^{10,11}). Here, we report the effect of oleic acid on the polymorphs, particle shape, and pore structure of mesoporous calcium carbonate.

2. Experimental

Calcium hydroxide (Nacalai Tesque Inc., Japan), ethylene glycol (Kanto Chemical Co., Inc., Japan), ethanol (Kanto Chemical Co., Inc., Japan), and oleic acid (Tokyo Chemical Industry Co., Ltd., Japan) were guaranteed reagents. All commercial reagents were used without further purification.

Figure 1 provides a process flow chart for production of mesoporous calcium carbonate. Colloidal calcium carbonate was prepared by carbonation of calcium hydroxide in ethylene glycol-ethanol mixture (3:7 by weight)⁸). Firstly, 25.0 g of calcium hydroxide was mixed with 475.0 g of the mixture in the reactor. Calcium hydroxide reacted with CO₂, which was blended with N₂ at the concentration of 30 vol%, and the flow rate of mixed gas was 1.0 l/min. After the carbonation, the suspension was centrifuged at 3,500 rpm for 20 min (Model 5800, Kubota, Japan) in order to remove an unreacted calcium hydroxide, and the transparent supernatant was obtained. The solid concentration of the dispersion was measured from the weight loss at 773 K using TG-DTA (Exstar 6200N, Seiko Instruments, Japan). Consequently, the solid concentration of calcium carbonate was ca. 6.0 mass%.

Then, in order to evaluate the effect of the oleic acid addition on crystallinity of mesoporous calcium carbonate, predetermined amount of oleic acid was added to the transparent colloidal dispersion, and the mixture was aged at 293 K. Added amount of oleic acid was from 0 to 20 mass% of the total mass of the calcium carbonate particles. After aging treatment, the cloudy suspension was obtained. The suspension was then centrifuged at 3,500 rpm for 15 min. The supernatant was discarded, and washed twice with ethanol to eliminate the excess of ethylene glycol. The residue was dried in vacuum for 24 hours.

The specific surface area and pore size distribution of the resulting samples was determined by nitrogen gas adsorption based on the multi-point BET method and BJH method (Autosorb-1-c/MK2, Qantachrome, USA). To determine the crystal structure, X-ray diffraction (MultiFlex, Rigaku, Japan) of the samples were obtained. The ratio of vaterite to calcite crystal (f_v) as functions of added amount of oleic acid was calculated using Rao's equation¹²).

$$f_v = \frac{I_{100V} + I_{112V} + I_{114V}}{I_{100V} + I_{112V} + I_{114V} + I_{104C}}$$

where the subscripts V and C indicate the intensity for each vaterite and calcite crystal face, respectively. The particle shape was determined using SEM (JSM-6380A, JEOL, Japan).

Table 1 Particle properties of mesoporous calcium carbonate at several amount of oleic acid

Added amount of oleic acid	SSA ^{a)}	Mean pore size	Pore vol.
[mass%]	[m ² /g]	[nm]	[cm ³ /g]
0 ^{b)}	207.3	8.8	0.454
1	205.9	11.5	0.520
10	48.6	12.4	0.152
20	16.2	30.3	0.123

a) Specific surface area of sample

b) The data without additive are from ref. 8

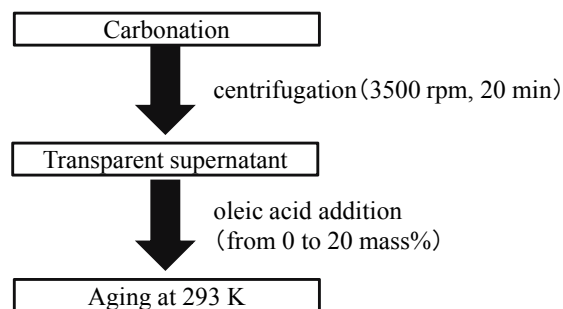


Fig. 1 Process flow of mesoporous calcium carbonate with oleic acid.

3. Results and Discussion

We firstly investigate the effect of oleic acid addition on the pore structure of mesoporous calcium carbonate. The particle properties (specific surface area, mean pore size, and pore volume) are summarized in **Table 1**. The specific surface area and pore structure highly differed according to the additional amount of oleic acid. The specific surface area and mean pore size without oleic acid were 207.3 m²/g and 8.8 nm, respectively⁸). The specific surface area was decreased, and the mean pore size was increased with adding the acid. When 20 mass% of the acid was added, the specific surface area and mean pore size were 16.2 m²/g and 30.3 nm, respectively, indicating the oleic acid had dramatic impact on assembling to porous 3-D structure via aggregation. In our previous research¹³), we have reported the saturated fatty acids (butanoic acid, octanoic acid, and decanoic acid) addition did not affect the specific surface area, mean pore size, or pore volume. The used acid was short chain length (C4, C8, and C10), and saturated fatty acid¹³). In present case, unsaturated and relatively long chain (C18) fatty acid was used. Further investigation regarding the adsorbed state of fatty acid and its role in the self-assemble route of the dispersed nanoparticles will be done in the future.

Figure 2 depicts typical SEM images of mesoporous calcium carbonate particles by adding several amount of oleic acid. The particles form small ellipsoidal structure (500 nm in size) at 0, and 1 mass% addition, size up to 1 μm at 10 mass%, and doughnut-like structure at 20 mass%. Additionally, two types of mesoporous particles with difference in polymorphs were obtained as shown in **Fig. 3**. When the acid was added in low concentration (0

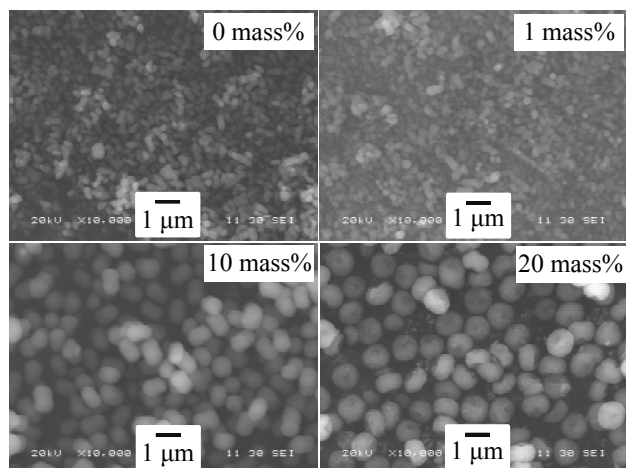


Fig. 2 Typical SEM images of particles by adding several amount of oleic acid.

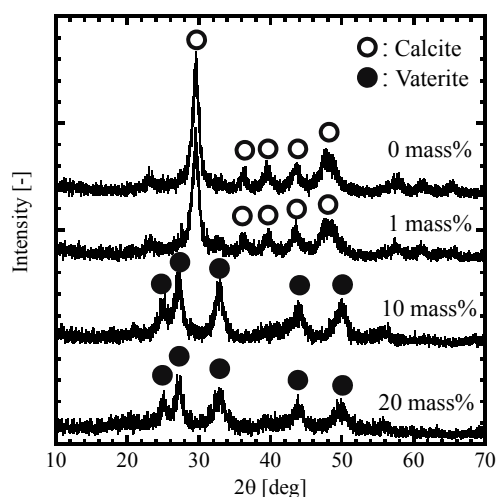


Fig. 3 XRD patterns of mesoporous calcium carbonate particles. Additional amount of oleic acid was 0, 1, 10, and 20 mass%, respectively from the top.

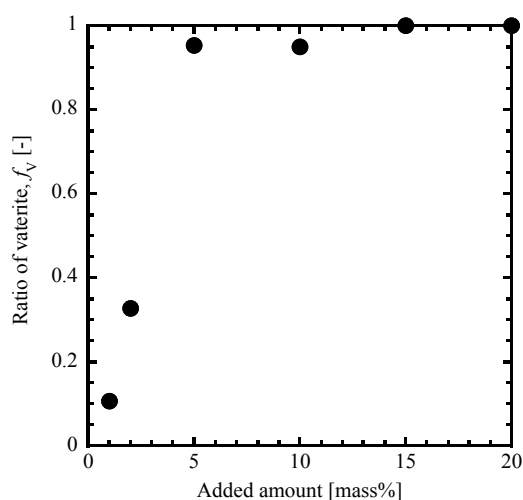
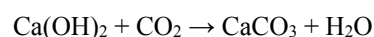


Fig. 4 Relationship between the additive amount and ratio of vaterite (f_v).

and 1 mass%), the calcite diffraction peaks were detected. While vaterite phase of calcium carbonate was obtained at high concentration of the acid (10, and 20 mass%). These shape and polymorphic variations show the same tendency as our previous results⁸⁾. **Figure 4** demonstrates how the acid affects the ratio of vaterite phase. Over 5 mass% addition, the main crystal phase converted to vaterite, indicating adsorption area of the acid on the colloidal calcium carbonate is associated with interaction between the colloid and water because the solubility of calcium carbonate is essential for the transformation^{10,11)}. Calcium hydroxide reacts with CO_2 to form calcium carbonate and water as follow.



As the organic solvent is used in this study, little water is contained in the system. However, a tiny amount of water is produced. The water dissolves vaterite calcium carbonate, that leads to transform into calcite. Therefore, oleic acid adsorbed on the colloid may have prevented phase transformation into calcite. We successfully produced vaterite type mesoporous calcium carbonate. This fact suggests that the resulting mesoporous calcium carbonate may be a promising adsorbent material because the vaterite is favorable structure for formaldehyde adsorption⁸⁾.

4. Conclusion

We have demonstrated the effect of oleic acid addition on the particle properties of mesoporous calcium carbonate. The mesoporous calcium carbonate with high specific surface area of 16-207 m^2/g was successfully synthesized by adding oleic acid. Oleic acid also controlled the polymorphs of calcium carbonate.

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