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Electronic Supplementary Information

Phase transformation of mesoporous calcium carbonate by mechanical stirring

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Materials

Calcium hydroxide (Nacalai Tesque Inc., Japan), ethylene glycol (Kanto Chemical, Japan), ethanol (Kanto Chemical, Japan), and calcite calcium carbonate (Nacalai Tesque, Japan) were guaranteed reagents and used as received.

Synthesis of porous calcium carbonate

A colloidal dispersion of calcium carbonate nanoparticles, which is the liquid precursor for meso-porous calcium carbonate particles, was prepared by carbonation of calcium hydroxide in an ethylene glycol and ethanol (3:7 by weight) organic solvent mixture [1, 2]. The synthetic procedure for the colloidal dispersion is described in detail elsewhere [3]. Briefly, calcium hydroxide (2.5 g) was mixed with an organic mixture (497.5 g) and reacted with 30 vol% CO_2 diluted with N_2. During the carbonation reaction, the solution was stirred at a rate of 400 rpm with a gas flow rate of 1.0 *l*/min. A water bath maintained the temperature at 293 K. After 90 min, the suspension was centrifuged at 3,500 rpm for 20 min (Model 5800, Kubota, Japan). From the collected supernatant, the transparent dispersion was used as the raw liquid material in the aging treatments. Dynamic light scattering analysis (DLS, Nanotrac UPA, Nikkiso, Japan) was conducted to determine the colloidal particle size distribution (Fig. S1). Prior to the DLS analysis, the transparent dispersion was immersed in an ultrasonic bath for 5 min to ensure homogeneity. The viscosity of the ethylene glycol and ethanol mixture (3:7 by weight), which was used as the parameter in the DLS analysis, was measured using a cone-plate rheometer (RheoStress600, HAAKE, Germany) at 293 and 303 K. The plates had a 50-mm diameter and a fixed gap distance of 52 μm. The viscosity of the mixture at 293 (303) K is 2.60 (2.10) mPa·s. To calculate the agitation Reynolds number (*Re*), the viscosity of the colloidal dispersion was also measured; it is 2.78 mPa·s at 293 K. The solid fraction of the dispersion was measured from the weight loss at 773 K using thermogravimetric-differential thermal analysis (TG-DTA, Exstar 6200N, Seiko Instruments, Japan). TG-DTA measurements were conducted with a nitrogen flow of 50 m*l*/min at a ramp of 10 K/min.

To investigate the effect of mechanical stirring on the morphology of mesoporous calcium carbonate, two-step aging treatments were carried out for the resulting transparent supernatant. The first step was pre-aging in which the transparent supernatant was stirred using a propeller-type impeller (0.05 m in diameter) or a reciprocal shaker (NEO–

SHAKER NS–LR, AS ONE). In the former case, the colloidal dispersion was stirred at 10 or 300 rpm for 0–24 hours (0 hours indicates no stirring), while in the latter case, the dispersion was shook at 100 rpm for 0–24 hours. After pre-aging, the colloidal dispersion was placed into an incubator for a predetermined time. Both treatments were conducted at 293 K. The cloudy suspension was washed twice with ethanol to eliminate the excess of ethylene glycol. The suspension was then centrifuged at 3,500 rpm for 15 min. The supernatant was discarded, and the residue was dried in vacuum for 24 hours.

Powder characterization

The resulting dry powder was used in the measurements. The specific surface area and pore size distribution of the powder were determined by nitrogen gas adsorption based on multi-point BET and the BJH method (Autosorb-1-c/MK2, Qantachrome, USA). In the BET and pore size distribution measurements, the powder was degassed for 2 hours at 473 K under a vacuum to remove adsorbed solvent molecules. To determine the polymorphs of calcium carbonate, X-ray diffraction (XRD, MultiFlex, Rigaku, Japan) powder patterns of the samples were obtained with Cu Kα radiation (40 kV, 40 mA). SEM studies were performed using a JEOL JSM-6380A.

Initial phase of calcium carbonate

FTIR spectra were measured by an FT/IR-460PlusK (JASCO) spectrometer with the KBr pellet technique ranging from 600 to 2000 cm^{-1}. The KBr pellets contained 1–2 mass% of the colloidal dispersion, the resultant precipitates (calcite and vaterite), and reagent calcite powder. Figure S2 shows the IR spectra of the colloidal dispersion, resultant precipitates (calcite and vaterite), and regent calcite powder. Amorphous calcium carbonate (ACC) contains water in its structure.[4] The absorption peak at 1640 cm^{-1} (HOH bending) except reagent calcite, are due to ACC. Except for the colloidal dispersion, the internal modes of the carbonate ion in calcite (710 cm^{-1}) or vaterite (740 cm^{-1}) are detected. These data suggest that ACCs are dispersed in the organic solvent mixture and are contained in the mesoporous calcium carbonate particles. The splitting bands that originate from ethylene glycol in the FTIR spectra at 864, 882 cm^{-1} (CC stretching, CH_2 rocking), 1040, 1085 cm^{-1} (CO stretching), and 1410, 1462 cm^{-1} (COC bending, CH_2 bending) reveal that ethylene glycol remains on the surface of mesoporous calcium carbonate.[5]

To identify the initial colloid phase in the dispersion, we conducted an XRD study of the separated solid sample from the dispersion. Because the sample obtained by above process (see ***Synthesis of porous calcium carbonate***) is small in amount, we raised the solid concentration of calcium carbonate in the dispersion. Calcium hydroxide (25 g) was mixed with an organic mixture (475 g) [3]. The conditions of the carbonation reaction, and the collection method of the colloidal dispersion were the same as that described in ***Synthesis of porous calcium carbonate***. Then, the colloidal dispersion was directly dried in vacuum overnight, washed twice with ethanol, and then centrifuged at 3,500 rpm for 15 min. The supernatant was discarded, and the residue was dried in vacuum overnight. The XRD profile of this separated solid lacks peaks (Fig. S3), indicating the initial phase is ACC.

References

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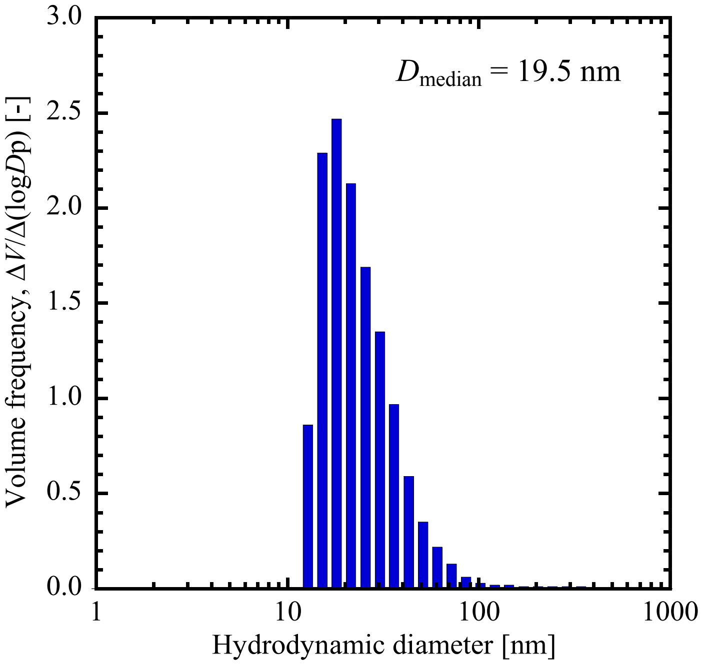

Figure S1. Particle size distribution of the colloidal calcium carbonate particles dispersed in the supernatant.

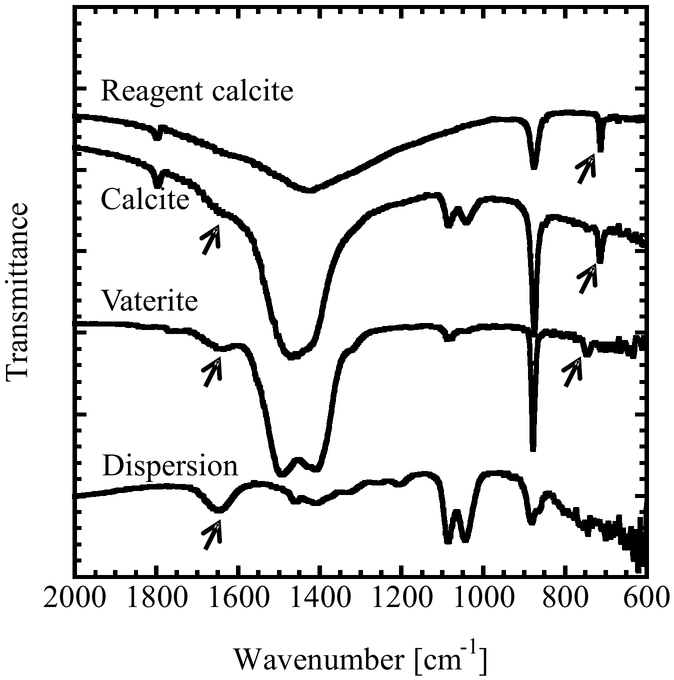

Figure S2. FTIR spectra of the colloidal dispersion, mesoporous vaterite (24 hours agitation at 300 rpm), mesoporous calcite (without agitation), and reagent calcite powder.

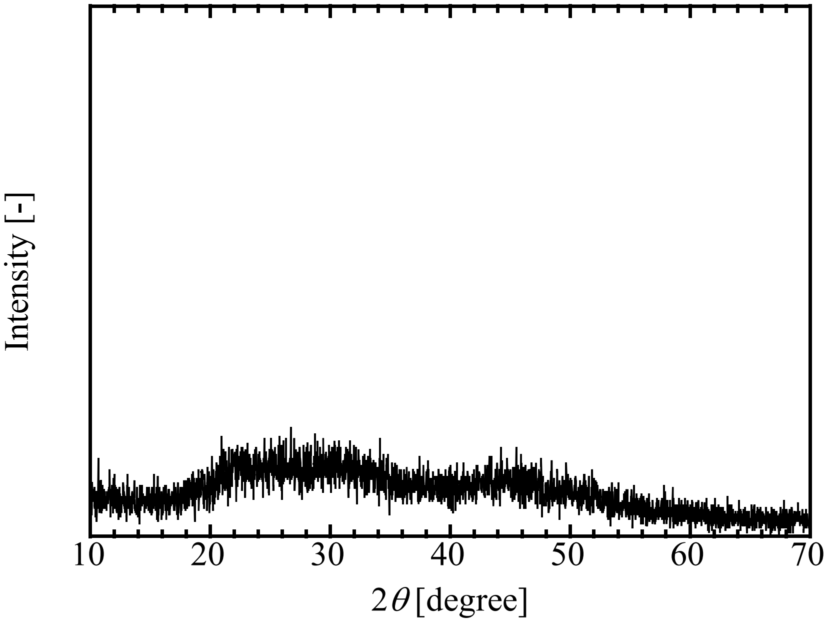

Figure S3. XRD pattern of the solid sample separated from the dispersion.

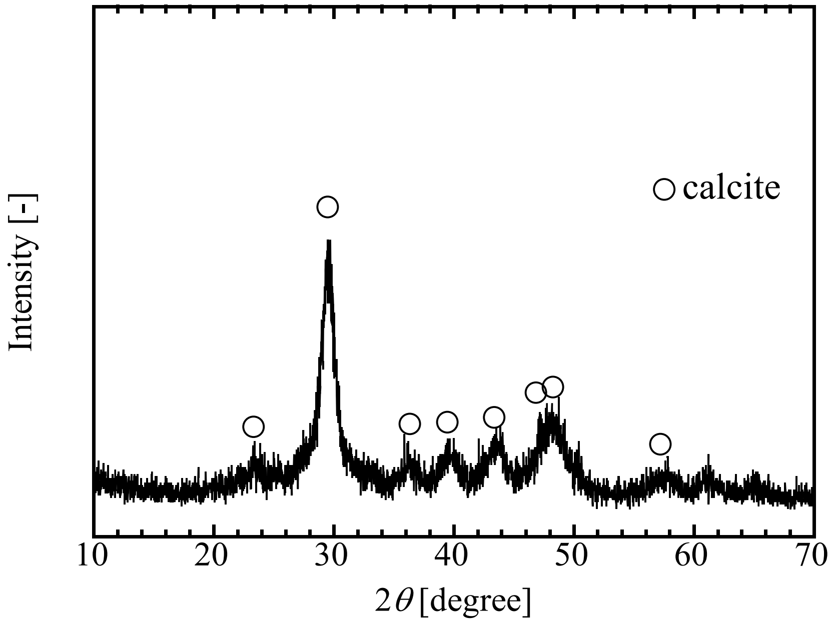

Figure S4. XRD pattern of the prepared particles after shaking the colloidal dispersion for 24 hours using a reciprocal shaker at 100 rpm and subsequent aging treatment.