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COMMUNICATION

Phase transformation of mesoporous calcium carbonate by mechanical stirring

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We report a simple strategy to synthesize vaterite/calcite mesoporous calcium carbonate through collisions and organization of colloid particles accelerated by mechanical stirring. Mechanically stirring the precursor colloidal dispersion can control the calcium carbonate polymorphs.

Due to the diverse applications of calcium carbonate (e.g., controllable release and encapsulation of drugs1–3 catalyst support4, gas adsorbent5, and abiotic and biogenic mineral formation6–9), polymeric selectivity or pore formation of calcium carbonate is of considerable interest. However, controlling the polymorphs during large-scale productions of porous calcium carbonate remains challenging. Crystalline calcium carbonate polymorphs of calcite, aragonite, and vaterite are thought to crystallize via unstable amorphous calcium carbonate (ACC).6, 7, 9, 10

Classical nucleation theory, which is based on the works of Gibbs11, Volmer and Weber12, 13 Becker and Doring14, and Frenkel15 stipulates that the birth of a crystal in solution is governed by the free energy barrier, which corresponds to the energy required to generate a critical nucleus. Visible and stable crystals undergo a pre-nucleation stage16 due to cluster fluctuations, critical nuclei generation, and subsequent growth of nuclei. Clusters, which are widely thought to be the origin of nucleation or crystal birth16, have been observed experimentally.13, 17–19

These pre-nucleation clusters are often observed during precipitation of crystalline calcium carbonate. Initially formed ACC is a transient phase, which is subsequently transformed into more stable crystalline polymorphs according to Ostwald's rule.16 Because the transformation of ACC into crystalline calcium carbonate depends on the thermodynamic equilibrium, the thermal history20, 21 and the water content22 have been investigated to determine the kinetics and mechanism of the ACC transformation. Rodriguez-Blanco et al. have proposed a two-stage crystallization process in an aqueous solution23; in the first stage, rapid dehydration of ACC forms the vaterite phase, whereas dissolution of vaterite and subsequent reprecipitation forms calcite. That is, by tuning the ACC stability, crystallization of calcium carbonate can be controlled10, 24, 25 For example, to obtain stable vaterite, several additives (e.g., ethanol, dopamine, dendrimers, poly acrylic acid, and mesoporous silica21) have been studied to prevent the phase transformation into calcite. In addition to polymeric considerations, the formation of pores in calcium carbonate crystals has advanced. Porous calcium carbonate is produced mainly via heterogeneous nucleation on templates.32–35 Here we report a scalable production strategy for mesoporous calcium carbonate that controls the polymorphs. Mechanical stirring accelerates the incorporation of pores via collisions of colloid particles. Applications of mechanical stirring to the colloidal dispersion confirm that an energy-induced phase transformation can convert ACC to vaterite or calcite.

We prepared a transparent colloidal dispersion, which is a precursor for porous calcium carbonate (see ESI†). Slight mechanical stirring during the pre-aging process affects the aggregation route of the colloid particles. Without agitation, the transparent supernatant requires one-month to become a cloudy sol, but mixing reduces the transformation time. For example, the cloudy sol is obtained two days after stirring the dispersion for 24 hours. These observations suggest that agitation accelerates nanoparticle collisions, resulting in organization of porous calcium carbonate particles in a shorter amount of time. We initially characterized the transparent colloidal dispersion. Dynamic light scattering (DLS) analysis was conducted to determine the size distribution of the colloidal particles. The DLS

Figure 1. Typical XRD patterns of the prepared particles after an aging treatment. (a) Sample obtained without stirring. Crystallite size of 13 nm for (104) calcite roughly coincides with the primary particle size from the DLS median size of 19.5 nm. Samples obtained after stirring for (b) 12 hours and (c) at 24 hours.
Next we investigated the particle properties of porous calcium carbonate. The peak positions of the XRD profiles correspond to those of the calcite (ICDD#05-0586) and/or vaterite (ICDD#33-0268) phase for all samples (Fig. 1). Diffraction indicates that the calcite phase is formed without stirring the colloidal dispersion (Fig. 1a). When pre-aggregating is carried out, the amount of the vaterite increases with stirring time (Fig. 1b). Only the vaterite phase is detected after stirring for 24 hours, indicating that the calcite phase completely disappears (Fig. 1c).

Regardless of the phase, all the profile peaks are relatively weak and broad, suggesting a small crystallite size. The crystallite size of porous calcium carbonate was calculated from the full width at half maximum (FWHM) of the corrected diffraction profile. A Pseudo-Voigt fitting was conducted to obtain the FWHM for the (104) calcite diffraction. If the precursor dispersion is not agitated during the pre-aging treatment, the crystallite size is 13 nm for (104) calcite, which is close to the colloidal particle size of the DLS median (19.5 nm), indicating that pores may form between the aggregated primary particles.

Figure 2 shows the specific surface area, average pore size, and ratio of vaterite to calcite crystal (fV) as functions of stirring time. fV was calculated using Rao's equation

\[
f_V = \frac{I_{104V} + I_{122V} + I_{444V}}{I_{104C} + I_{122C} + I_{444C}}
\]

where the subscripts V and C indicate the intensity for each vaterite and calcite crystal face, respectively. The specific surface area of porous calcium carbonate is 148±22 m²/g (Fig. 2a), regardless of stirring time. The average pore size and fV depend on the stirring time (Figs. 2b, c). For short stirring times (less than 12 hours), calcite is the main crystal phase. As the stirring time increases up to 12 hours, fV drastically increases and the average pore size decreases from ~10 nm to ~4 nm.

We have previously reported a self-assembly route for porous calcium carbonate, which is associated with the phase transformation from ACC to calcite and/or vaterite, and demonstrated the effect of aging temperature on the morphology of porous calcium carbonate (i.e., thermal energy leads to Brownian aggregation of the colloidal particles). Consequently, the colloidal aggregates form more preferred structures due to the reduced surface free energy.

The solubility of calcium carbonate is crucial for the transformation. The FTIR spectra (see ESI†, Fig. S2) and XRD (see ESI†, Fig. S3) suggest that ACCs are dispersed in an organic solvent mixture as well as contained in mesoporous calcium carbonate particles. Although the carbonation process in this study contains little water, stoichiometrically produces equimolar amounts of water and calcium carbonate. To obtain the calcite phase of mesoporous calcium carbonate, a long aging process (one month) is required. During the aging treatment, dissolution of the vaterite and subsequent reprecipitation forms calcite. The FTIR studies reveal that ethylene glycol remains on the surface (see ESI†, Fig. S2), which may prevent vaterite dissolution and calcite transformation. Thus, the water content in the transparent supernatant (colloidal dispersion) should play an important role in the polymorphs.

We also added water (1.0–10.0 mass%) to the colloidal dispersion (9:1–100:1 by the molar ratio of water and calcium carbonate). After 24 hours of agitation and a subsequent aging treatment, the ratio of vaterite phase was determined. As shown in Fig. 3, adding over 3.0 mass% water decreases the ratio of vaterite, indicating that the vaterite crystal dissolves in water to form the calcite phase.

Previous studies have investigated the effect of the stirring rate on controlling the crystal morphology of calcium carbonate; they have demonstrated that adjusting the stirring rate tunes the vaterite and/or calcite phase. To investigate the true role of stirring in the system, we examined the influences of stirring rate and stirring method on the polymorphs using two different stirring rates (10 and 300 rpm) and a reciprocal shaker (100 rpm), respectively. Figure 2c plots the results. Although the appearance time of vaterite phase (fV>0) for 10-rpm stirring is delayed...
Figure 3. Effect of water addition on the ratio of the vaterite phase. Water (1.0–10.0 mass%) is added to the colloidal dispersion (corresponding to 9:1–100:1 by molar ratio of water and calcium carbonate) before agitation for 24-hours and a subsequent aging treatment.

Compared to 300-rpm stirring, only the vaterite phase ($f_v=1.0$) is obtained after stirring for 24 hours. The agitation Reynolds number ($Re$) for 10 (300) rpm stirring rate is 140 (4000) ($Re = \rho n d^2/\mu$, where $\rho=900$ kg/m$^3$ is the density of dispersion, $n=1.7\times10^{-3}$ (5.0) s$^{-1}$ for a stirring rate of 10 (300) rpm, $d=5.0\times10^{-2}$ m is the impeller diameter, and $\mu=2.78\times10^{-3}$ Pa·s is the viscosity of the colloidal dispersion). Although the pre-aging treatment was conducted in the laminar and turbulent flow, this range of stirring has a negligible effect on the kinetics of vaterite formation. The required time to obtain the vaterite phase is the same, indicating that the transformation of ACC to the vaterite phase is accomplished by adding an imperceptible but continuous energy fluctuation from the agitation impeller to the precursor colloids.

Although more than 12 hours of stirring is necessary to produce the vaterite phase, the crystalline phase transformation requires less time (minutes or hours).\cite{23,31} Shaking the colloidal dispersion using a reciprocal shaker at 100 rpm yields only the calcite phase after 24 hours (see Fig. 2(c) and ESI†, Fig. S4).

In the future, we should examine the density of water molecules around the colloids because the water addition tests suggest that dissolution and reprecipitation may occur during the pre-aging treatment. The effects of the flow condition and water content on the polymorphic transformation need to be further investigated.

As mentioned above, the FTIR spectra demonstrate mesoporous calcium carbonate particles include ACCs (see ESI†, Fig. S2). ACC typically has a high specific surface area with 140–160 m$^2$/g and 100–300 m$^2$/g.\cite{42} Thus, the high specific surface area (148±22 m$^2$/g) of the mesoporous calcium carbonate is due to the ACC in its structure. Although the actual particle size from the SEM images in Fig. 4 differs from its crystallite size (13 nm for calcite (104) and 10 nm for vaterite (112)), the calculated equivalent diameter is 14–24 nm, which is consistent with the crystallite size. The equivalent spherical diameter is equal to $6(\rho_p \times \text{SSA})$, where $\rho_p=2000–2500$ kg/m$^3$ is the density of ACC\cite{44} and SSA=148±22 m$^2$/g is the specific surface area from the BET measurement. The pores in mesoporous calcium carbonate are formed by void spaces between the primary particles.

Figure 4. Typical SEM images of the porous calcium carbonate particles obtained with stirring for (a) 0 hours, (b) 4 hours, (c) 8 hours, (d) 12 hours, (e) 18 hours, and (f) 24 hours. Scale bar is 2 µm. The stirring rate was 300 rpm.

Figure 4 depicts typical SEM images of the porous calcium carbonate particles for different stirring times (0, 4, 8, 12, 18, and 24 hours) at a stirring rate of 300 rpm. The porous particles assume one of two shapes: tiny (~300 nm) almost-spherical particles or relatively large ellipsoidal one. The major and minor axis sizes for the ellipsoidal shape of vaterite calcium carbonate are 2 and 1 µm, respectively. Spherical particles form without or with a mechanical stirring for a short time (Figs. 4a, b), but once a certain moment is reached, an ellipsoidal structure is obtained (Figs. 4e, f). This transition occurs around 8 and 12 hours of stirring, and both shapes are observed (Figs. 4c, d). Stirring for 12 hours coincides with the anticipate variations in the pore and crystallographic structure from Fig. 2.

To investigate the effect of mechanical stirring on the transition period, we conducted an experiment where the sample was stirred at 10 rpm or shaken at 100 rpm. The time required for the only vaterite phase to appear is at about the same (24 hours stirring) regardless of the stirring rate (10 or 300 rpm). However, shaking did not produce the vaterite phase, indicating that the flow condition is crucial in the transformation of metastable vaterite to stable calcite. These findings suggest that porous calcium carbonate may be a promising adsorbent material because the vaterite structure can easily adsorb formaldehyde.\cite{38}

Conclusions

This study demonstrates the production method for mesoporous calcium carbonate for two individual polymorphs: vaterite and calcite. The influence of mechanical stirring on the polymorphic...
transformation was investigated. Applying continuous agitation into the colloidal intermediate dispersion forms pores in the crystal via organization of the colloid particles. The mechanical stirring time influences not only the polymorphs, but also the rate of organization. The water content in the colloidal dispersion plays a crucial role in the transformation from vaterite to calcite.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details. Size distributions of colloidal calcium carbonate determined by DLS analysis (Fig. S1). FTIR spectra for colloidal dispersion and mesoporous powder (Fig. S2). XRD pattern for the solid sample separated from the dispersion (Fig. S3), and mesoporous calcium carbonate obtained using a reciprocal shaker (Fig. S4)]. See DOI: 10.1039/b000000x

Graphical and Textual abstract

Mechanically stirring the precursor colloidal dispersion can control the polymorphs of mesoporous calcium carbonate.