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# Morphology of calcium carbonate coating on amorphous silicate powder

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The amorphous silicate powders containing sodium, calcium, barium and magnesium were prepared by sol-gel and ion-exchange method, and calcium carbonate was coated on the powders for the purpose of industrial re-circulation of calcium carbonate. The calcium carbonate powder with micro pores was obtained by coating on amorphous CaO-$SiO_2$ powder, and the pore size distribution would be influenced by calcium on the surface of the powder. The coating on amorphous MgO-$SiO_2$ powder resulted in a hedgehog-like powder, which allowed needle-like crystal extended radially, and the coated powder was the mixed phase of aragonite and calcite. The use of amorphous BaO-$SiO_2$ and $Na_2O$-$SiO_2$ powders also led to the coating powder with the single phase of calcite. The morphology of calcium carbonate coating would be ascribed to cations on the surface of the amorphous silicate powders, because the amount of cations that would be dissolved in soaking solution was small and insufficient to affect the morphology. *© 2000 Kluwer Academic Publishers*

## 1. Introduction

Calcium carbonate has three polymorphs of calcite, aragonite and vaterite. Aragonite, a metastable phase of calcium carbonate, is known as a main crystal phase of pearls or corals. Calcium carbonate occurs abundantly in nature, and many chemists or mineralogists have studied on polymorphs of calcium carbonate in respect of bio-mineralization or bio-inspired chemistry [1–5]. They have clarified the formation mechanism of pearls and the effects of cations or anions on crystal growth of calcium carbonate.

The fixation and industrial recycle of calcium carbonate is also important for effective use of resources and environmental protect. Calcium carbonate powder with various crystal phases and various morphologies can be employed as a spacer for liquid crystal displays, adsorbents and packing for chromatography. If we easily fix calcium carbonate during the purification of water and obtain the powder with a desirable polymorph, calcium carbonate can be re-circulated inexpensively [6–8].

Previously we synthesized mono-dispersed amorphous powder composed of sodium and silica (NS powder) by sol-gel and simultaneous ion-exchange method [9–11]. The concentration of sodium in the amorphous powder was changed by various synthesis conditions. We also investigated the ion exchange between alkaline earth ion and sodium in NS powder, and amorphous silicate powders containing magnesium or calcium were obtained by using NS powder as a starting material and allowing ion exchange between magnesium or calcium and sodium in NS powder [12]. The amorphous silicate powders obtained by sol-gel and ion-exchange method include OH groups, and would have active surface to chemisorption or surface reactions. Calcium carbonate was coated on amorphous silicate powders with various cations, and the effects of cations in the amorphous powder on crystal phase and morphology of calcium carbonate were investigated in order to obtain calcium carbonate coating powder effectively.

## 2. Experimental

Four kinds of amorphous silicate powders were used as cores of $CaCO_3$ coating. The employed amorphous powders were composed of sodium, magnesium, calcium and barium, and abbreviated to NS powder, MS powder, CS powder and BS powder, respectively. NS powder was prepared as follows. The water adjusted to $pH = 3.0$ was mixed with the solution of tetraethylorthosilicate (TEOS), ethanol and hydroxypropyl cellulose [13]. The mixture was stirred at 40°C for 40 min and allowed hydrolysis and condensation of TEOS. Another solution containing NaOH, water and ethanol was poured into the mixture and allowed ion exchange between sodium and proton of OH group that was derived from TEOS. The amorphous powder that was obtained by sol-gel and ion-exchange method was filtered by a membrane filter with 0.1 $\mu$m pores, washed with ethanol several times and dried with a freeze-dryer. The composition of the obtained NS powder was investigated by energy dispersed X-ray spectroscopy (EDS). The molar ratio in NS powder was varied from $Na/Si = 0.2$ to 0.8 by using various synthesis conditions such as pH, sodium concentration and reaction time. The NS powder with Na/Si ratio of 0.5 was used for coating $CaCO_3$ on NS powder.

MS powder, CS powder and BS powder were prepared using NS powder and magnesium, calcium and barium ion exchange for sodium in NS powder was conducted under various conditions. The molar ratio of the employed NS powder was Na/Si = 0.7. The ratios of the obtained MS powder and CS were both (Mg or Ca)/Na/Si = 0.6/0.1/1.0. The ratio in BS powder was limited to Ba/Na/Si = 0.2/0.1/1.0, because most of inorganic barium salts are little soluble in water and we found no adequate conditions for barium ion exchange. The particle size of the amorphous silicate powder was estimated all at the range of 0.4–0.6 $\mu$m, and independent of cations and compositions in the powder. Fig. 1 shows the schematic scheme for preparing the amorphous silicate powders.

A clear water solution composed of $CaCl_2$ and $NaHCO_3$ at the same molar ratio was prepared for coating $CaCO_3$. After an amorphous silicate powder (0.10 g) was put into the solution (200 ml), the solution was stirred at 100 rpm for 5 days. The temperature of the solution was kept at 24°C. The obtained $CaCO_3$ powder was separated from the solution by filtration with a membrane filter with 1 $\mu$m pores, washed with deionized water several times, and dried with a freeze-dryer (Fig. 2).

Crystal phase was investigated by powder X-ray diffraction (XRD), and particle size and morphology of the powder were examined by scanning electron microscopy (SEM). The effects of cations in the amorphous silicate powders and the coating solution on polymorphs of $CaCO_3$ coating were investigated to prepare $CaCO_3$ coating powder with various crystal phases and morphologies.

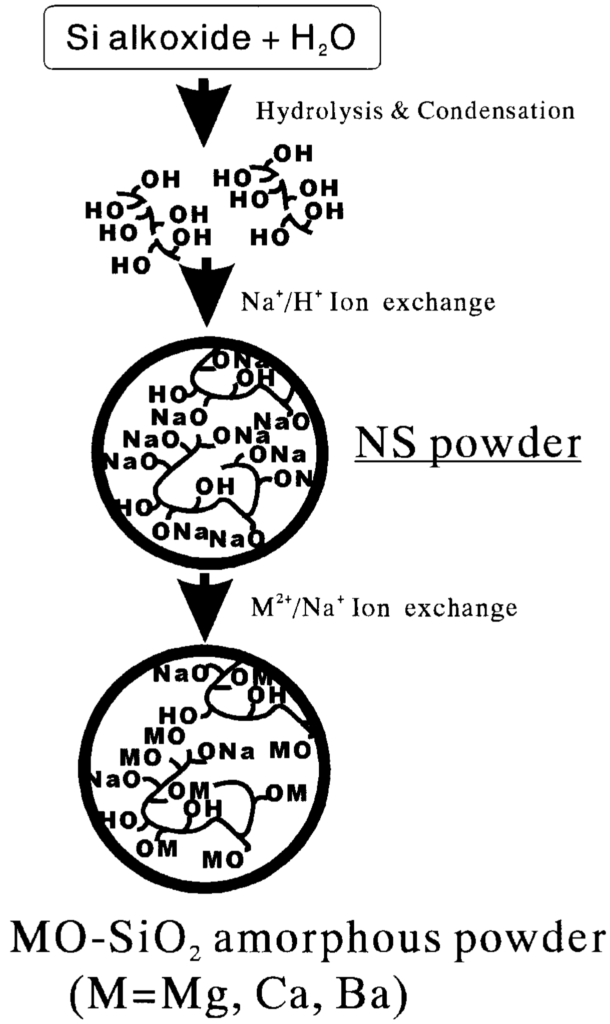

*Figure 1* Schematic scheme for preparing NS, CS, BS, and MS powders.

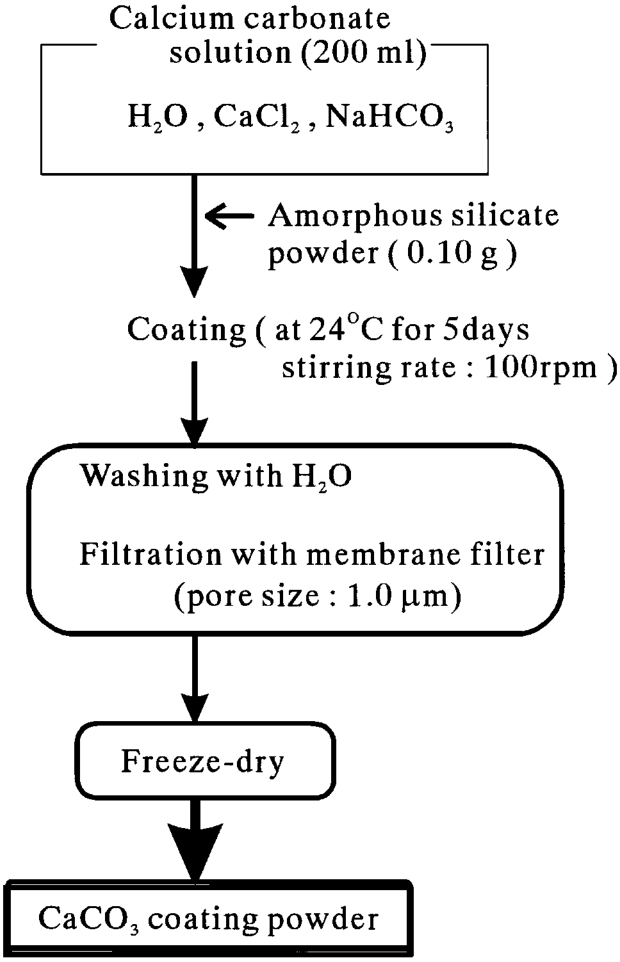

*Figure 2* Preparation of $CaCO_3$ coating powder.

## 3. Results

### 3.1. Calcium carbonate coating on Na-$SiO_2$ amorphous powder

Fig. 3 shows SEM photographs of NS powder and $CaCO_3$ powders coated on NS powder. The $CaCO_3$ powders were prepared by soaking the solutions with the $CaCO_3$ concentrations of 4.0 mM and 6.0 mM. The particle size of the $CaCO_3$ powder was 5–6 $\mu$m, while that of NS powder was 0.4–0.6 $\mu$m. The use of the dilute solution such as 4.0 mM resulted in thick coating on NS powder. Spherical $CaCO_3$ powder which had a smooth surface was obtained by coating on NS powder.

Crystal phase of the powder coated on NS powder was investigated by XRD (Fig. 4). NS powder was amorphous and no precipitate such as sodium carbonate and nitrate was observed in NS powder. The crystal phase of the $CaCO_3$ powder coated on NS powder was calcite, stable phase of calcium carbonate, and that little depended on $CaCO_3$ concentration in the coating solution.

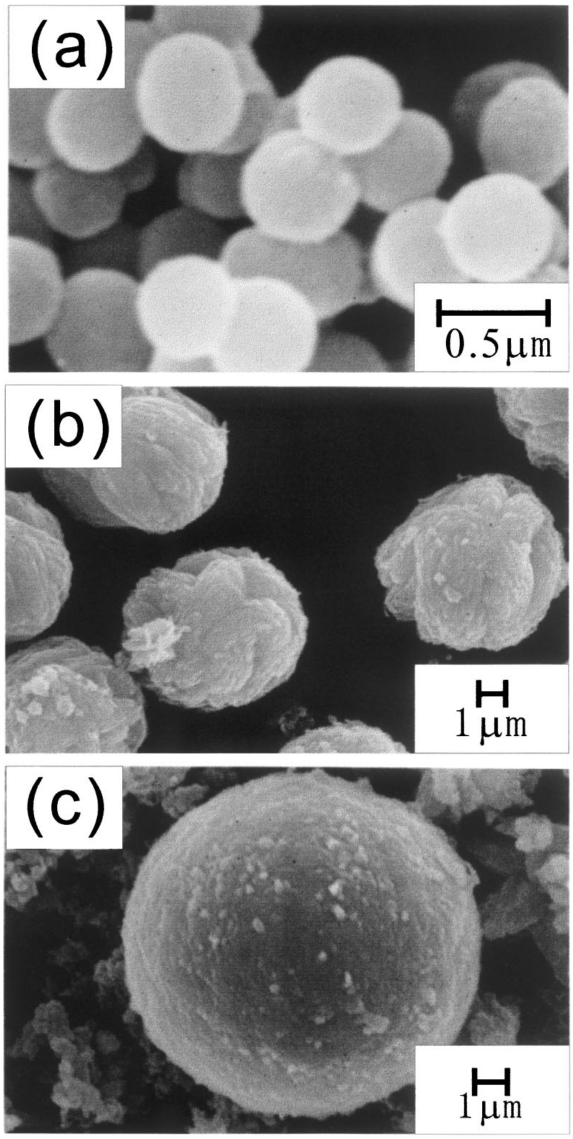

*Figure 3* SEM photographs of NS powder (a) and $CaCO_3$ powder coated on NS powder. The $CaCO_3$ powders were prepared with $CaCO_3$ solutions of 4 mM (b) and 6 mM (c).

## 3.2. Calcium carbonate coating on Ca/Na-$SiO_2$ amorphous powder

Calcium carbonate was then coated on the amorphous silicate powder containing calcium, CS powder. Fig. 5 shows SEM photograph of the $CaCO_3$ powder coated on CS powder. The solution with $CaCO_3$ concentration of 6.0 mM was prepared for coating and stirred at 24°C for 5 days. The particle size of the $CaCO_3$ powder was approximately estimated at 7.0 $\mu$m and the coating rate on CS powder was larger than that on NS powder. The particle was apart from a sphere, and has micro pores, which were not observed in the $CaCO_3$ powder coated on NS powder. XRD patterns of the $CaCO_3$ powder prepared with various $CaCO_3$ solutions were shown in Fig. 6. Some weak peaks assigned to aragonite were observed in the XRD patterns for the $CaCO_3$ coated powder prepared with the $CaCO_3$ solution of 7.0 mM, but the use of more dilute solution than 7.0 mM resulted in a single phase of calcite.

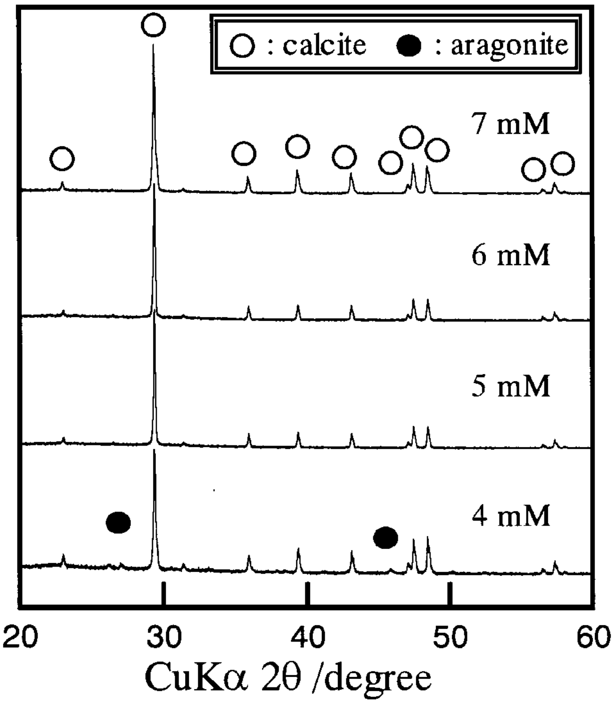

*Figure 4* XRD patterns of $CaCO_3$ powder coated on NS powder using the coating solutions with various $CaCO_3$ concentrations.

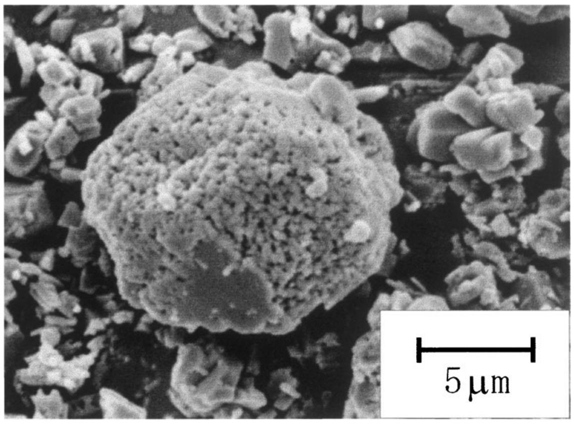

*Figure 5* SEM photograph of $CaCO_3$ powder coated on CS powder.

## 3.3. Calcium carbonate coating on Ba/Na-$SiO_2$ amorphous powder

Calcium carbonate was coated on the amorphous silicate powder containing small amount of barium, BS powder. Fig. 7 shows SEM photograph of the $CaCO_3$ powder prepared with the $CaCO_3$ solution of 5.0 mM. The $CaCO_3$ powder with particle size of 5 $\mu$m was formed through aggregation of primary particles that were 0.2 $\mu$m in particle size. The crystal phase of the $CaCO_3$ powder coated on BS powder was calcite.

## 3.4. Calcium carbonate coating on Mg/Na-$SiO_2$ amorphous powder

Calcium carbonate coating was underwent using the powder containing magnesium, MS powder. Fig. 8

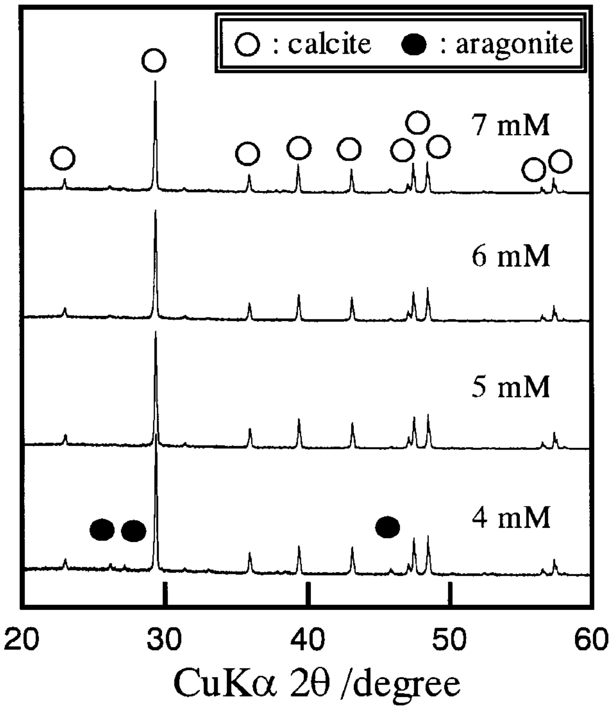

*Figure 6* XRD patterns of $CaCO_3$ powder coated on CS powder using the coating solutions with various $CaCO_3$ concentrations.

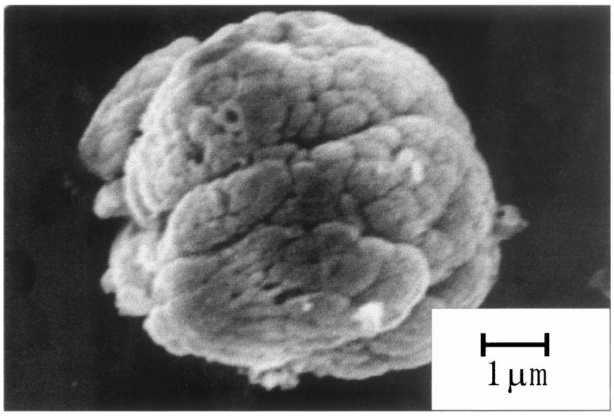

*Figure 7* SEM photograph of $CaCO_3$ powder coated on BS powder.

shows SEM photographs of the $CaCO_3$ powders coated with 4.0 mM and 6.0 mM solutions. The morphology of the $CaCO_3$ powder coated on MS powder was much different from that on NS powder, CS powder and BS powder. The shape of the $CaCO_3$ powder was like a hedgehog and needle-like crystals were extended radially. This hedgehog-like powder was obtained by using the $CaCO_3$ solution at the concentration range of 4.0–8.0 mM. The particle size of the $CaCO_3$ powder was approximately 8 $\mu$m, and independent of $CaCO_3$ concentration. Fig. 9 shows XRD patterns of the hedgehog-like powder. The $CaCO_3$ powder coated on MS powder contained aragonite much more than that coated on other silicate powder. The ratio of aragonite to calcite in the hedgehog-like powder depended on $CaCO_3$ concentration in the coating solution and the use of the $CaCO_3$ solution with the concentration of 5.0 mM led to the $CaCO_3$ powder that had aragonite at the highest ratio.

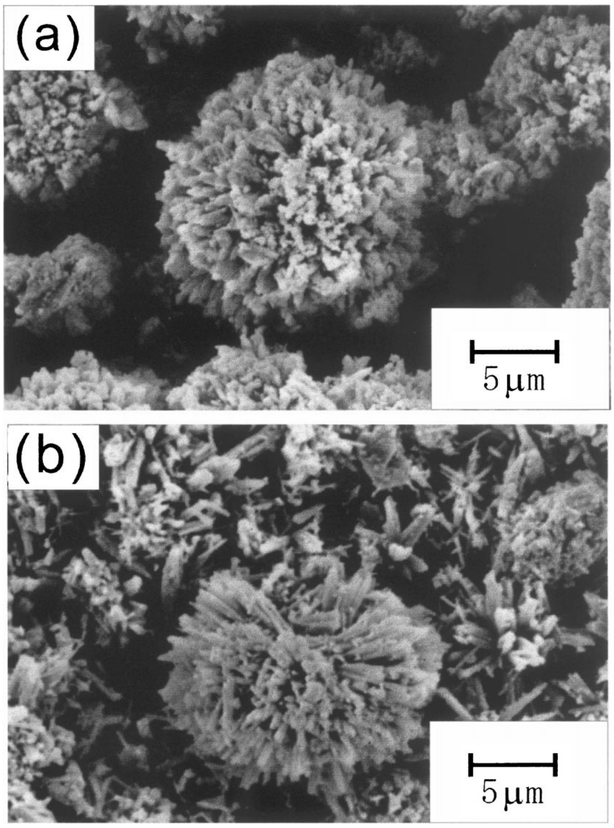

*Figure 8* SEM photographs of $CaCO_3$ powder coated on MS powder. The $CaCO_3$ powders were prepared with the $CaCO_3$ solutions of 4 mM (a) and 6 mM (b).

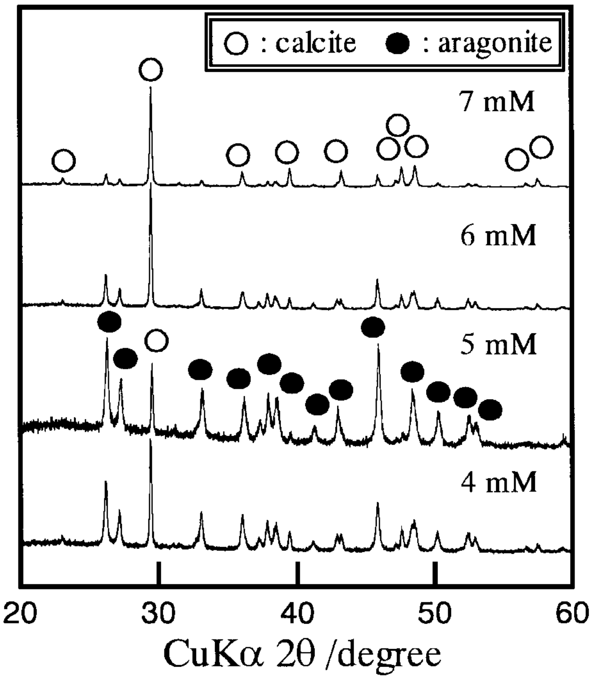

*Figure 9* XRD patterns of $CaCO_3$ powder coated on MS powder for 5 days using the soaking solutions with various $CaCO_3$ concentrations.

## 4. Discussion

### 4.1. Effects of cations in the amorphous silicate powders on polymorphs of calcium carbonate coating

The cations in the amorphous silicate powders would be dissolved into the coating solution during $CaCO_3$

coating. The amounts of the cations in the powder were investigated by TG-DTA, and the amounts of the cations that might be dissolved into the solution were estimated under some assumptions. The amorphous silicate powders, cores of the coating, were composed of solvents and OH or $OC_2H_5$ residue, because the powder was untreated with firing. The amounts of the cations and silica in the amorphous silicate powders were thus estimated by weight loss at 900°C. Firing NS powder at 900°C reduced 31.2 mass%. Therefore, 0.1 g of NS powder comprised $6.65 \times 10^{-4}$ mol of $0.7Na_2O$-$SiO_2$ amorphous silicate. When MS powder or CS powder was previously synthesized by using NS powder as a starting powder of the ion exchange, sodium in NS powder was dissolved in reaction mixture at the Na/Si ratio of 0.1 except the ion exchange. The amounts of cations dissolved in the coating solution are different with cations, because dissolution ratio in water is extremely different with cations. The cation concentrations in coating solution would be very dilute, and we then assumed that the amounts of cations dissolved in coating solution was almost independent of cations in order to simplify the estimation. The concentrations of cations that would be dissolved in the coating solution with $CaCO_3$ concentration of 5.0 mM were estimated under this assumption. The molar ratio of sodium derived from NS powder to calcium in the coating solution, Na/Ca(s), was estimated at $6.65 \times 10^{-2}$. The ratios of barium and magnesium that might be dissolved from BS powder and MS powder to calcium in the coating solution, Ba/Ca(s) and Mg/Ca(s), respectively, were also estimated at $6.8 \times 10^{-2}$ and $7.2 \times 10^{-2}$, respectively.

Barium and magnesium affect the polymorphs of calcium carbonate [14–16]. Wada *et al.* reported that the effects of cations on polymorphs of calcium carbonate [17, 18]. The addition of barium in calcium carbonate solution leads to form vaterite and the ratio of vaterite in calcium carbonate polymorph increases with increasing amount of barium. Calcium carbonate that has vaterite at the ratio of 35% are formed by using the $CaCO_3$ solution with barium at the ratio of $Ba/Ca(s) = 3.1 \times 10^{-2}$. As for the addition of magnesium, the $CaCO_3$ that is composed of 60% aragonite and 40% calcite is obtained by using the $CaCO_3$ solution containing magnesium at the ratio of $Mg/Ca(s) = 1.3 \times 10^{-1}$, and the $CaCO_3$ that is composed of 98% aragonite and 2% calcite is, by using the $CaCO_3$ solution at the ratio of $5.0 \times 10^{-1}$.

We consider two mechanisms that cations of the core powders affect the polymorphs of $CaCO_3$ coating; one is that cations dissolved into the coating solutions affects the polymorphs, and the other is that cations on the core powders directly affects the polymorphs. The former mechanism can be proved by investigating the relations between the cation concentration in the coating solution and polymorphs of the $CaCO_3$ powder, while the latter is, by investigating the relations between the M/Si (M: cation) ratio in the core powders and the polymorphs. As our results of $CaCO_3$ coating on BS powder, crystal phase of the $CaCO_3$ powder was a single phase of calcite and independent of cation concentration of the coating solution. The amount of barium that actually dissolved in the solution would be much different from that estimated under the assumption. Otherwise, the amount of barium in BS powder was small because of insufficient solubility in water. Insufficient amount of barium in BS powder then would result in single-phase calcite.

Calcium carbonate that had the crystal phase mixed with aragonite and calcite was obtained by adapting adequate $CaCO_3$ concentration. If the former is a dominant mechanism of the $CaCO_3$ coating on the silicate powders, the estimated amount of the magnesium dissolved in the coating solution was much smaller than that would be. Therefore, the latter mechanism would be suitable for $CaCO_3$ coating on MS powder. Aragonite would be formed through growing $CaCO_3$ around magnesium on MS powder with introducing magnesium. The concentration of magnesium on the surface of MS powder was much higher than that of the bulk of the coating solution, and thus the coating of $CaCO_3$ was influenced by cations of the core powders. Crystal phase of $CaCO_3$ can be controlled by changing kinds and concentrations of cations adequately.

### 4.2. Effects of calcium in the amorphous silicate powder on morphology of $CaCO_3$ coating

The $CaCO_3$ powder with micro pores was obtained by coating on CS powder and the coating on CS powder was faster than that on NS powder. The calcium concentration around CS powder was much higher than that of the bulk of the $CaCO_3$ solution. The surface of CS powder had high supersatuation and was promoted to coat $CaCO_3$ on CS powder. The coating of $CaCO_3$ was selectively promoted at calcium sites on CS powder, and calcium-free sites would result in micro pores. The high supersatuation of calcium on the surface of CS powder would also induce induction time for forming calcite and result to fasten the coating. Calcium distribution on CS powder would much affect pore size distribution of the $CaCO_3$ powder. Therefore, $CaCO_3$ coating powder with micro pores that are suitable for adsorbents or packing for chromatography can be prepared by close control of calcium distribution on CS powder.

## 5. Conclusion

Calcium carbonate coating was prepared using amorphous silicate powders as core powders. The $CaCO_3$ powder with micro pores, which was single-phase calcite, was obtained by coating on CS powder, and pore size distribution of the $CaCO_3$ coating powder would be influenced by the distribution of calcium on CS powder. The use of NS powder and BS powder led to both single-phase calcite. Hedgehog-like coating powder, which had needle-like crystals extended radially, was obtained by coating on MS powder. The hedgehog-like powder had mixed phase of aragonite and calcite, and the ratio of aragonite to calcite was dependent on $CaCO_3$ concentration in the coating solution. The effects of cations on the silicate powders on morphology of $CaCO_3$ coating was observed by using dilute solution with the cations, and the effects would be attributed to cations on the surface of the amorphous silicate powders.

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