

Preparation of Uniform Needle-Like Aragonite Particles by Homogeneous Precipitation

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Uniform needle-like aragonite particles were obtained by aging solutions of calcium salts in the presence of urea at 90°C. The effects of various experimental conditions, such as the concentration of reactants, temperature, aging time, agitation, mixing procedure, and the addition of divalent cations, surfactants, and polymers, on the precipitation of aragonite were investigated. It was found that the formation of different polymorphs of calcium carbonate was affected mostly by agitation and concentration of reactants, as well as by the mixing procedure. Thus, under otherwise the same experimental conditions, needles of aragonite were formed without stirring or at low-power ultrasound; rhombohedral calcite appeared when aging experiments were carried out under the influence of magnetic stirring, while irregular particles of mixed vaterite and calcite crystal structure were generated at higher CaCl₂ concentrations. Mixing the preheated reactant solutions resulted in unique “flower-type” vaterite particles. Finally, the presence of sulfonate or sulfate ions promoted precipitation of vaterite and calcite. © 1999 Academic Press

Key Words: aragonite needles; calcite colloidal; calcium carbonates monodispersed; vaterite colloidal.

INTRODUCTION

Aragonite is one of the less abundant crystalline polymorphs of calcium carbonate. It is formed under a much narrower range of physico-chemical conditions and is easily transformed into calcite by changes in the environment. The natural aragonite is mostly of biogenic origin, and many mineralizing organisms selectively produce calcium carbonate of this crystal structure (1). Recently, the interest in aragonite has increased substantially. Its needle-like crystals with high aspect ratios are used as fillers for the improvement of mechanical properties of paper and polymer materials (2). Aragonite is also a good biomedical material, because it is denser than calcite and could be integrated, resolved, and replaced by bone (3, 4).

Many studies have shown that the properties of aragonite, such as the particle size and shape, depend strongly on the preparation methods and conditions. Direct inorganic precipitation using soluble carbonate and calcium salts as initial materials produced irregular aragonite crystals (5, 6). This

method was modified by doping calcium salt solutions with small amounts of Sr²⁺, Ba²⁺, and Pb²⁺ (7–9). Another approach consisted of blowing CO₂ containing inert gas into a suspension of CaCl₂–MgCl₂–Mg(OH)₂ (10). Metastable formation of aragonite in gels has been achieved at elevated pressure over a temperature range of 100 to 270°C in the presence of Mg²⁺ (11). Furthermore, the seeding was used by introducing large amounts of aragonite and strontianite precursors into solutions containing Ca²⁺ and CO₃²⁻ (12, 13). Most of the synthesis methods summarized above are either involved or produce irregular particles in size and shape, which may limit their applicability.

Previous studies demonstrated that urea can play an essential role in the formation of uniform particles (14–17). Indeed, Kato and co-workers (18) have shown that calcium carbonates of different shape and composition can crystallize in solutions of calcium nitrate in the presence of urea. The purpose of the present investigation was to carry out a systematic study of direct precipitation of uniform needle-like aragonite particles using the hydrolysis of urea, including the effects of concentrations of reactants, temperature, aging time, agitation, mixing procedure, and addition of divalent cations, surfactants, and polymers.

EXPERIMENTAL

Materials

All inorganic chemicals and urea were reagent grade. Surfactant AVANEL S-150 (sodium alkylethersulfonate, PPG, 35 wt%), Tween 20 (Atlas Chemical Industries), dextran (Polyscience, MW 500,000), dextran sulfate (Polyscience, MW 500,000), polyvinylpyrrolidone (PVP, Aldrich, MW 40,000) were used as received. All solutions were freshly prepared and filtered through 0.22- μ m Millipore membranes before use.

Preparation of the Particles

The reactions were carried out in Pyrex bottles, by keeping from 2.5 to 72 h solutions containing CaCl₂ and urea in a forced convection oven at different temperatures (50, 70, and 90°C). The concentrations of CaCl₂ varied from 0.05 to 1.0 mol dm⁻³ and of urea from 0.25 to 2.25 mol dm⁻³. The aging

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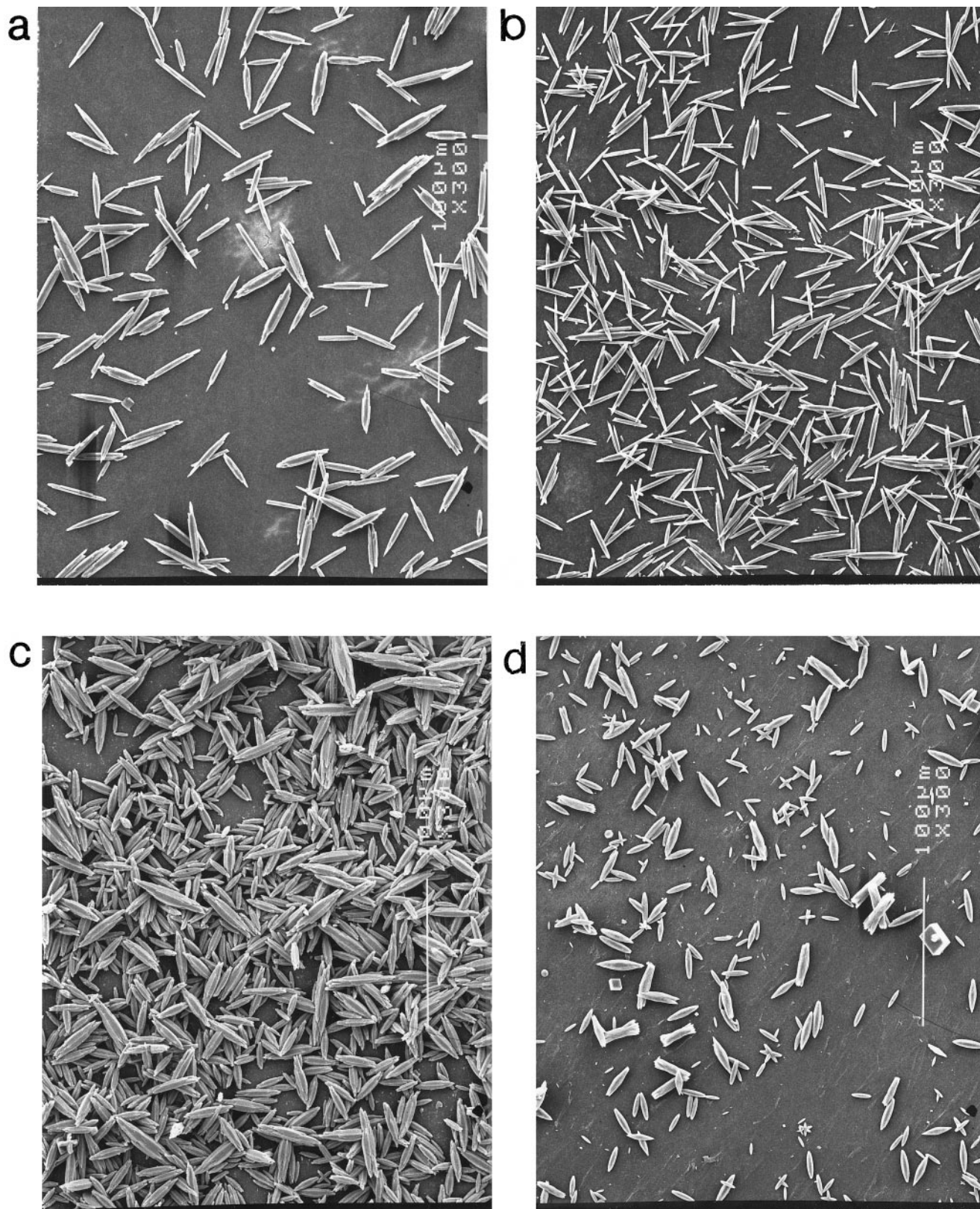


FIG. 1. Scanning electron micrographs (SEM) of aragonite particles obtained by aging (a) a solution containing $0.25 \text{ mol dm}^{-3} \text{ CaCl}_2$ and 0.75 mol dm^{-3} urea at 90°C for 3 h ("standard conditions," sample B), (b) a solution containing $0.25 \text{ mol dm}^{-3} \text{ CaCl}_2$ and 2.25 mol dm^{-3} urea at 90°C for 2.5 h (sample G), (c) a solution containing $0.25 \text{ mol dm}^{-3} \text{ CaCl}_2$ and 0.75 mol dm^{-3} urea, in an ultrasonication bath, at 90°C for 1 h, and (d) a solution containing $0.225 \text{ mol dm}^{-3} \text{ CaCl}_2$, $0.025 \text{ mol dm}^{-3} \text{ BaCl}_2$, and 0.75 mol dm^{-3} urea at 90°C for 3 h (sample R).

of a mixed solution containing 0.25 mol dm^{-3} CaCl_2 and 0.75 mol dm^{-3} urea at 90°C for 3 h has been designated as the "standard conditions." In some experiments, $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{CH}_3\text{COO})_2$ were used instead of CaCl_2 in order to ascertain the effect of different anions on the precipitation process. To evaluate the agitation effects on the particle forming process, the experiments were carried out under magnetic stirring and in a low-power (175 W) ultrasonic bath.

The changes in the particle properties affected by doping the system with alkaline earth salts were investigated by admixing MgCl_2 , SrCl_2 , and BaCl_2 , respectively, into CaCl_2 -urea solutions. The molar ratios of these additives to CaCl_2 were 1 and 10 mol% under otherwise standard conditions.

In some experiments, the procedure was modified, by first preheating the reactant solutions (CaCl_2 and urea) to 90°C for 3 h, and then the two solutions were rapidly mixed at the same temperature.

To assess the influence of surfactants and polymers on the morphology and the crystal structure of the resulting particles, AVANEL S-150 (0.01 – 0.50 g dm^{-3}), Tween 20 (0.25 , 1.0 g dm^{-3}), PVP (10 g dm^{-3}), dextran (10 g dm^{-3}), and dextran sulfate (1 g dm^{-3}) were added into CaCl_2 -urea system under the standard conditions.

The obtained solids were separated by filtration using $0.22\text{-}\mu\text{m}$ Millipore membranes and rinsed with distilled water. The precipitates were finally dried in a vacuum oven overnight at 90°C and then stored in a desiccator.

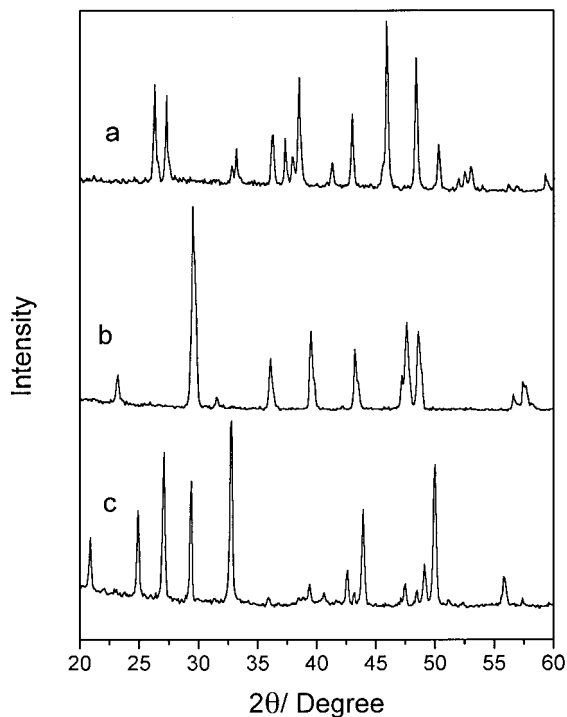


FIG. 2. X-ray diffraction (XRD) pattern of (a) needle-like aragonite particles illustrated in Fig. 1a, (b) rhombohedral particles of calcite shown in Fig. 5, and (c) spherical particles shown in Fig. 7a.

TABLE 1
Crystallographic Parameters of Aragonite

	Crystallographic parameters (Å)			Fig.
	a_0	b_0	c_0	
Aragonite 1	4.947	7.958	5.739	1a
Aragonite 2	4.952	7.948	5.740	1c
JCDPES card 5-0453	4.959	7.968	5.741	

Characterization of the Particles

The morphology and the size of the particles were examined by scanning electron microscopy (SEM), and their structure as well as the lattice parameters were evaluated by X-ray diffraction (XRD). Crystalline phases of calcium carbonate were identified according to the ICDD Powder Diffraction File (19). The positions of the aragonite reflections were corrected using quartz as an internal standard, and the size of the crystallites was estimated from the full width of the half-maximum of the X-ray diffraction peak by means of the Scherrer equation (20). The thermal behavior of the powders was studied by thermogravimetric (TGA) and differential thermal (DTA) analyses with a heating rate of $10^\circ\text{C min}^{-1}$ in the flow of nitrogen. Infrared spectra were recorded with the Perkin-Elmer 280 Fourier transform infrared (FTIR) spectrometer on pellets containing 2 mg of a sample in 100 mg of KBr.

RESULTS

Preparation of Particles

Using the standard conditions, uniform needle-like aragonite particles were generated as illustrated in Fig. 1a. The pH of the solution changed from 5.8 at the beginning to 7.6 at the end of the precipitation process. These particles have a mean length of $45 \mu\text{m}$ with an aspect ratio of ~ 10 . Similar results were obtained when CaCl_2 was replaced by $\text{Ca}(\text{NO}_3)_2$ or $\text{Ca}(\text{CH}_3\text{COO})_2$.

The XRD pattern of the obtained precipitates (Fig. 2a) can be assigned to that of aragonite crystals with the lattice parameters listed in Table 1 (aragonite 1). According to the Scherrer equation, aragonite particles are composed of a large number of subunits with an estimated size of 45 nm. The infrared spectrum (Fig. 3a) of this precipitate, recorded over the region from 500 to 1000 cm^{-1} , provides further evidence for the pure aragonite composition (21). The TGA analysis gives a 44% weight loss for the solid between 400 and 850°C , which is attributed to the decomposition of CaCO_3 to CaO (Fig. 4). The small endothermic peak at 430°C in the DTA curve (Fig. 4) arises from the phase transformation of aragonite to calcite.

Effects of the Concentration of Reactants

The concentration of the reactants affects the uniformity and the structure of the resulting particles, as shown in Table 2. At

the CaCl_2 concentration of 0.25 mol dm^{-3} , uniform aragonite needles were obtained when the urea concentration ranged between 0.25 and 2.25 mol dm^{-3} , although their length decreased somewhat with the increasing urea content. The influence of CaCl_2 concentration is more significant; aragonite was generated at the lower concentration, while vaterite and calcite precipitated at higher CaCl_2 concentration (samples E and F).

Effects of Aging Temperature and Time

The reaction temperature obviously affected the particle generation rate; no particles could be detected on aging at 50°C for 7 days. Aragonite particles appeared at 70°C after 1 day and at 90°C for after 2.5 h. Shorter aging time produced smaller uniform particles at 90°C (Fig. 1b, sample G). At the lower temperature (70°C) and longer aging times (>8 h), the resulting particles were longer, but their size distribution was wider. Thus, polydispersed aragonite particles of $\sim 100 \mu\text{m}$ were formed on aging at 70°C for one day (sample L).

Effects of Agitation

The crystal structure, particle size, and morphology of calcium carbonate were sensitive to the agitation during the aging process. Figure 1c illustrates the spindle-like aragonite formed on aging the same solution as sample B under ultrasonication for 1 h. A comparison with particles produced at standard

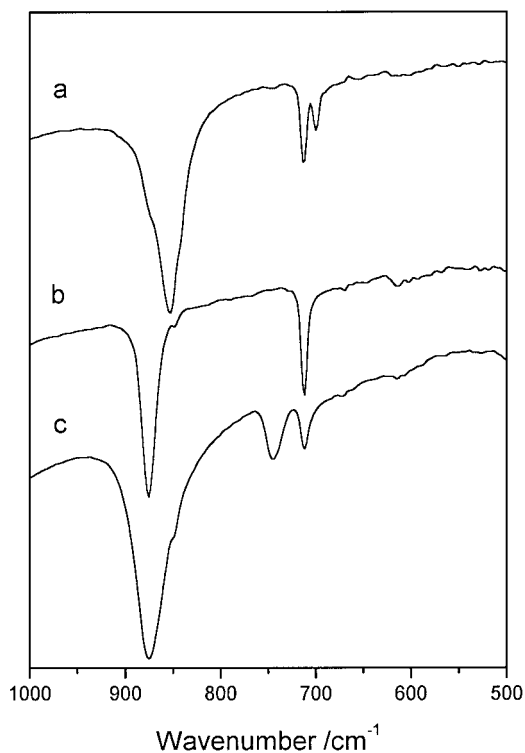


FIG. 3. FTIR spectra of (a) aragonite shown in Fig. 1a (sample B), (b) calcite shown in Fig. 5, (c) calcite and vaterite shown in Fig. 7a.

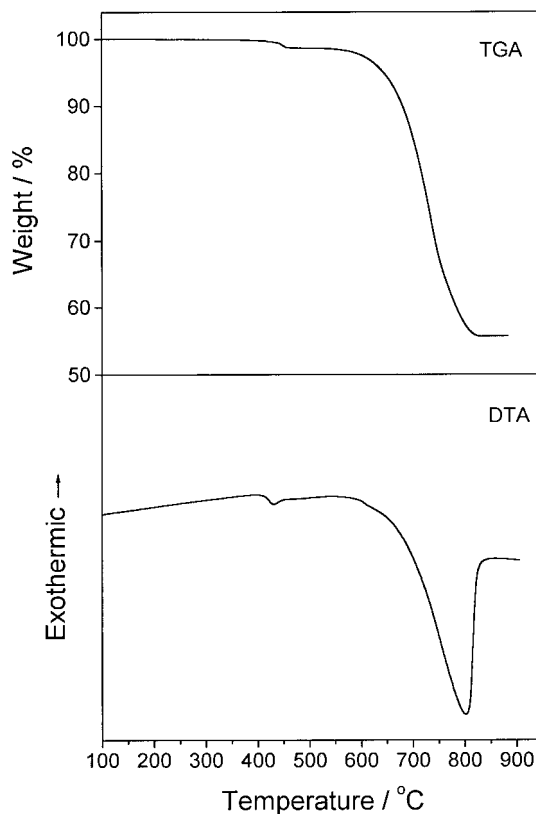


FIG. 4. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves obtained for the particles shown in Fig. 1a.

conditions without agitation shows them to be shorter ($\sim 26 \mu\text{m}$) and of a lower aspect ratio (~ 5). The lattice parameters of those solids are listed in Table 1 (aragonite 2). A more significant difference was found when magnetic stirring was applied during the aging process. Figure 5 shows the rhombohedra obtained at the standard conditions under magnetic stirring, the XRD pattern of which (Fig. 2b) indicated these particles to have the calcite structure.

Effect of the Mixing Procedure

The shape and crystallinity of the precipitated calcium carbonate also depended on the mixing methods. "Flower-type" particles were generated if CaCl_2 and urea solutions were first preheated separately at 90°C for 3 h, followed by rapid mixing at the same temperature, under otherwise standard conditions (Fig. 6). The XRD pattern showed these solids to be crystalline of vaterite structure.²

² Many years ago, the senior author (E.M.) received from the late Professor Eiji Suito (Kyoto, Japan) an electron micrograph of similar "flower-like" particles of BaCO_3 , without details of the experimental conditions. Apparently, his photo was never published. Obviously, the reason for the formation of particles of such unique shapes (which seems to be characteristic of alkaline earth carbonates) defies any explanation.

TABLE 2
Effects of Reactant Concentrations and Aging Conditions on the Properties of Needle-Like Aragonite Particles

Sample code	[CaCl ₂] (mol dm ⁻³)	[Urea] (mol dm ⁻³)	Aging temp. (°C)	Aging time (h)	Particle length (μm)	Aspect ratio	Uniformity ^d	Fig.
A	0.25	0.25	90	3	45	10	Y	
B ^a	0.25	0.75	90	3	45	10	Y	1a
C	0.25	2.25	90	3	40	10	Y	
D	0.05	0.75	90	3	60	15	Y	
E	0.50	0.75	90	3	~ 2 ^b		N	
F	1.00	0.75	90	3	~ 3 ^c		N	
G	0.25	2.25	90	2.5	30	10	Y	1b
H	0.25	0.75	90	2.5	40	10	Y	
I	0.25	0.75	90	8	~50	~10	N	
J	0.25	0.75	90	24	~50	~12	N	
K	0.25	0.75	90	72	~60	~12	N	
L	0.25	0.75	70	24	~100	~11	N	

^a Standard conditions.

^b Mixture of aragonite, vaterite, and calcite, irregular shapes.

^c Mixture of vaterite and calcite, irregular shapes.

^d Y, uniform; N, not uniform.

Effects of Doping

It was found that in most of the investigated cases the incorporation of divalent cations such as Mg²⁺, Sr²⁺, or Ba²⁺ in aragonite had a small effect on the properties of the resulting solids (Table 3); only 10 mol% of SrCl₂ produced somewhat shorter particles. The addition of BaCl₂ also yielded shorter needles (sample P) and altered the structure partly to calcite

(sample R). The morphology of the obtained particles was also affected, as illustrated in Fig. 1d.

Effects of Surfactants and Polymers

The effects of surfactants and polymers on particle properties are listed in Table 4. Nearly spherical particles (Fig. 7a), being a mixture of vaterite and calcite (Fig. 2c), were obtained

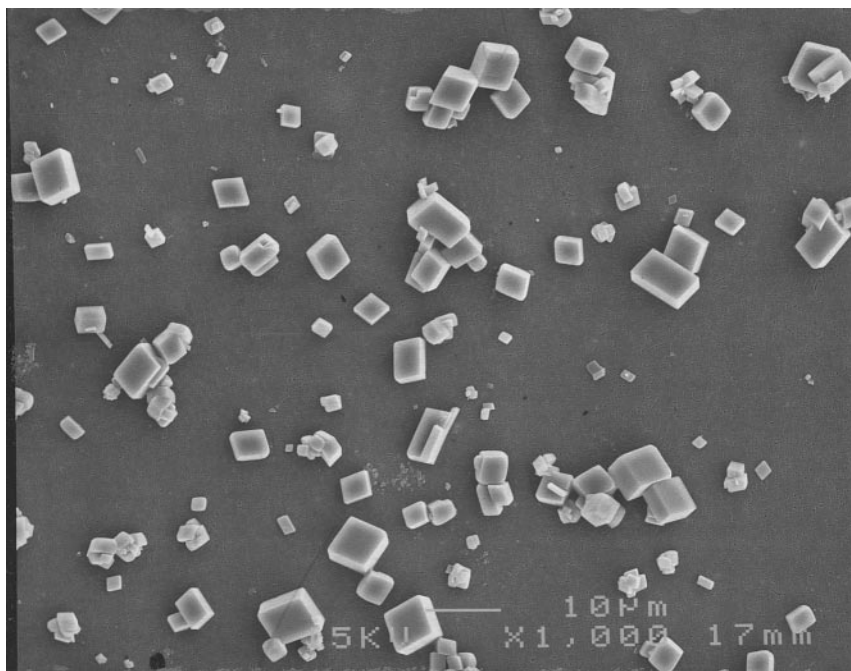


FIG. 5. SEM of the particles obtained by aging a solution containing 0.25 mol dm⁻³ CaCl₂ and 0.75 mol dm⁻³ urea, under magnetic stirring, at 90°C for 3 h.

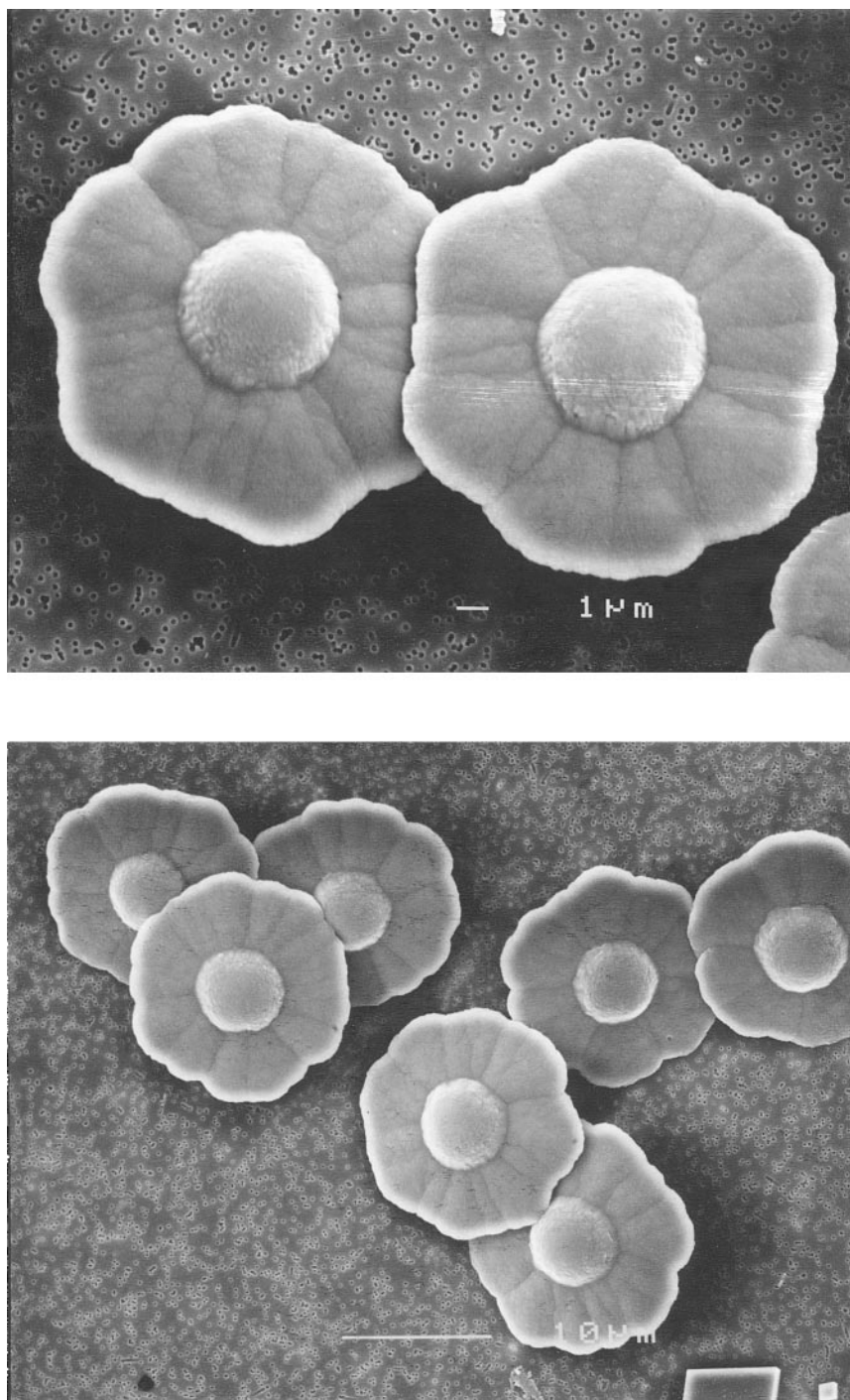


FIG. 6. SEM of particles prepared by separately preheating a 0.25 mol dm^{-3} CaCl_2 solution and a 0.75 mol dm^{-3} urea solution at 90°C for 3 h, then rapidly mixing the two solutions at the same temperature.

if AVANEL S-150 was added under otherwise standard conditions into the reactant solutions before aging. On extended aging time (>1 day), the crystal structure changed into pure calcite. The same results were obtained when dextran sulfate

(1 g dm^{-3}) instead of AVANEL S-150 was introduced into the system (sample W). Tween 20 yielded irregular aragonite particles (sample T), while PVP and dextran had no effect on the resulting needles (sample U and V).

TABLE 3
The Effects of Doping with Alkaline Earth Cations on the Properties of Calcium Carbonates Precipitated in the Presence of Urea

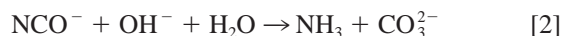
Sample code	[CaCl ₂] (mol dm ⁻³)	[MgCl ₂] (mol dm ⁻³)	[SrCl ₂] (mol dm ⁻³)	[BaCl ₂] (mol dm ⁻³)	[Urea] (mol dm ⁻³)	Particle length (μm)	Aspect ratio	Particle composition
M	0.25	0.0025	0	0	0.75	45	10	Aragonite
N	0.225	0.025	0	0	0.75	45	10	Aragonite
O	0.25	0	0.0025	0	0.75	45	10	Aragonite
P	0.225	0	0.025	0	0.75	35	8	Aragonite
Q	0.25	0	0	0.0025	0.75	40	10	Aragonite
R	0.225	0	0	0.025	0.75	20	4	Calcite aragonite

Note. In all experiments, the aging temperature was 90°C and the aging time was 3 h.

DISCUSSION

It was shown that the precipitation of aragonite, a thermodynamically less stable phase of calcium carbonate, can be achieved by aging solutions of calcium salts in the presence of urea at moderately elevated temperatures.

It has been amply documented that the aging of metal salt solutions in the presence of urea may yield uniform particles of colloidal (basic) carbonates (22). The hydrolysis of urea in aqueous solutions at elevated temperatures and under various conditions is well understood (23, 24). First, reaction [1] results in the formation of ammonium cyanate, and then in neutral and basic solutions, the cyanate ion rapidly hydrolyzes according to reaction [2].



Accordingly, at elevated temperatures, carbonate ions (CO₃²⁻, HCO₃⁻) are released under simultaneous increase in the pH. The rate of these processes can be carefully controlled, which made it possible to establish conditions that would result in the formation of uniform aragonite particles by homogeneous precipitation in calcium salts solutions (18). In other

studies irregular aragonite particles were obtained, if carbonate ions were introduced by CO₂ or soluble carbonate salts (13, 6).

The present work indicates that the agitation during the particle formation process might destabilize the aragonite crystal structure. For example, aging the solution under magnetic stirring produced well-defined rhombohedral calcite particles. The transformation might proceed through a dissolution and recrystallization mechanism, controlled by surface reactions (6). According to Kato and co-workers (18), agitating reacting solutions with a magnetic stirrer yielded first aragonite, which then transformed into calcite. The energy generated by the collision of the magnetic stirrer with the glass-wall was suggested to promote the dissolution of aragonite due to a mechanochemical effect. In the present experiments, without agitation aragonite remained stable in aqueous solutions for 3 days at 90°C. In addition, under otherwise standard conditions, shorter aragonite particles were formed when low-power ultrasound was applied during the precipitation process.

The incorporation of divalent cations, Mg²⁺ and Sr²⁺, in interstitial positions of the host crystal of aragonite did not affect the shape, size, or lattice of the particles. However, the much larger Ba²⁺ ion significantly changed the unit-cell parameters and the morphology of aragonite particles when 1 mol% of Ca²⁺ was substituted. At still higher concentrations of incorporated Ba²⁺ (>1 mol%), the crystal structure of aragonite is destabilized, resulting in the formation of rhombohedral calcite crystals.

The properties of the particles could be modified by the concentration of the reactants. At 0.5 mol dm⁻³ of CaCl₂, dispersions of solids having mixed aragonite, vaterite, and calcite structures were obtained (sample E), while at 1.0 mol dm⁻³ of CaCl₂ no aragonite was detected in the resulting precipitates (sample F). On the other hand, at a higher CO₃²⁻ concentration achieved by preheating the urea solution at 90°C for 3 h before mixing, "flower-type" vaterite particles (Fig. 6) were produced. This effect may be explained by the influence of Ca²⁺ and CO₃²⁻ concentrations on the nucleation and crystal growth of CaCO₃ (25).

This investigation has also shown that the formation of

TABLE 4
Effect of Surfactants and Polymers on Particle Properties

Sample code	Additive	Conc. of additive (g dm ⁻³)	Particle composition	Particle morphology
S	AVANEL S-150	0.5	Vaterite/calcite	Spherical
T	Tween 20	1.0	Aragonite	Irregular
U	PVP	10	Aragonite	Needle-like
V	Dextran	10	Aragonite	Needle-like
W	Dextran sulfate	1.0	Vaterite/calcite	Spherical

Note. In all cases, the experiments were carried out under otherwise standard conditions (sample B, Table 2).

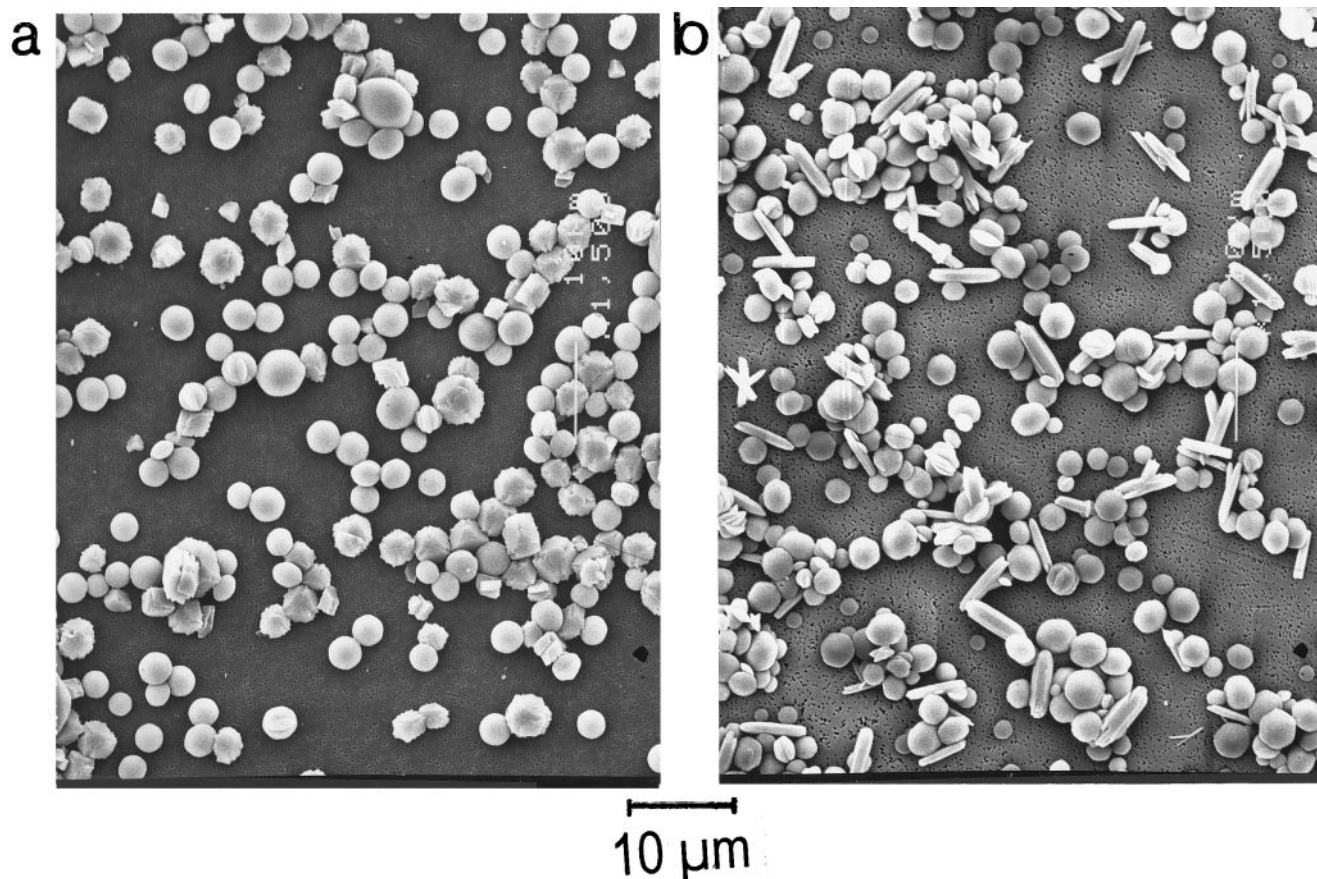


FIG. 7. SEM of the particles obtained by aging a solution containing $0.25 \text{ mol dm}^{-3} \text{ CaCl}_2$ and 0.75 mol dm^{-3} of urea at 90°C for 3 h in the presence of (a) 0.5 g dm^{-3} AVANEL S-150 and (b) $7 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$.

different types of calcium carbonate polymorphs in the presence of urea can be affected by surfactants and polymers containing sulfate or sulfonate groups. Anions, and especially sulfate ion, are known to play a significant role in the formation of colloidal particles (26–28). For example, it was shown that anions, such as SO_4^{2-} and PO_4^{3-} , can alter the shape and internal structure of precipitated monodispersed Fe_2O_3 particles (29–31). This investigation indicates that the sulfate anion promotes precipitation of calcite and vaterite. The reaction rate was obviously slow, and no aragonite formed if a small amount of AVANEL S-150 (0.05 g dm^{-3}) was added into the reacting solution before aging. To confirm the role of the sulfate ion, $7 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ was included in the CaCl_2 and urea solutions, yielding spherical vaterite and calcite (Fig. 7b). It appears that a complex formed between sulfate and calcium ions retarded the formation of the calcium carbonate and changed the crystal structure of the resulting particles. Finally, this finding is in agreement with the investigation of Cölfen and Antonietti (32), who showed that it was possible to grow two of the three different crystal modifications of calcium carbonate (vaterite and calcite) under similar conditions by using different types of polymers.

In conclusion, uniform aragonite particles can be prepared directly in the presence of urea at elevated temperature, under restricted experimental conditions.

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