

Morphologies of Aragonite Synthesized from Scallop Shells and Lime Stones by Successive Reaction

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Aragonite type of precipitated calcium carbonate was synthesized by the successive reaction with hybridization of waste scallop shells with limestone. In the first step, carbonation was performed by using calcined limestone with low brightness, followed by the additional carbonation using calcined-hydrous scallop shells with high brightness. The temperature and the amount ratio of calcined limestone to calcined-hydrous scallop shells were examined as parameters in the experimental conditions. The products were characterized by XRD, SEM, in addition to measurements of brightness index, the specific surface area, and bulk density. The amount ratio of limestone to scallop shell affected not only the brightness but also morphologies of products. The increase in relative amounts of limestone leads to decrease in brightness and bumpy surface of particles. High temperature reaction produces aragonite particles with longer sizes and higher bulk densities. This study has made an attempt to establish the synthesis of aragonite with high brightness and high strength by utilization of waste scallop shells.

Keywords: scallop shell, aragonite, morphologies, successive reaction.

Introduction

Scallop shells are representative fishery waste in Hokkaido, Japan, and more than 0.3 million tons of waste scallop shells are being discharged annually, leading to environmental and social problems such as lacking of land reclamation sites, legal controls for industrial wastes, and nasty smell. Some waste scallop shells have been already used to modify acidic soil, concrete aggregate, food additives, and so on. However, the advanced utilization of scallop shells has not yet been achieved and is highly needed on environmental grounds.

We have studied the synthesis of aragonite from calcined scallop shells by one step carbonation. Aragonite has a higher density and hardness than calcite and vaterite, making it a valuable inorganic material, used for armature of plastic, rubber, paper, glass fiber, print ink, paint pigment, and cosmetics (Yasue & Arai, 1995). Several investigators have reported on the synthesis of pure aragonite, however, synthesis has not been successful at ambient temperatures (Shinohara, et al. 1993; Kojima, et al.,

1994; Ohta, et al., 1996). The utility of functional aragonite is closely related to its morphology and degree of dispersion. It is important to examine the morphologies of aragonite which depends on several factors. In our previous work, it was found that aragonite can be formed even at ambient temperature under controlled the CO₂ flow rate, and that Mg²⁺ ions were not involved in crystals of aragonite but essential in synthesis. It was considered that aragonite acted as an inhibitor to calcite (Sasaki, et al., 1997; 1998a; 1998b; 1999).

In the present work, various morphological types of aragonite were synthesized by successive reaction using scallop shells and lime stones with different brightness. The proper conditions were elucidated to obtain high aspect ratio and high brightness of aragonite.

Experimental

Preparation and chemical composition of calcined-hydrous scallop shells and calcined lime stones

Scallop shells obtained from Tokoro (Hokkaido, Japan) were ground by crusher, calcined for 120 min at 1000-1200 °C and hydrolyzed for 30-60 min at 100-200 °C. The product consists of mainly calcium hydroxide as confirmed by XRD analysis (JCPDS 4-0733). The detailed methodology of chemical composition of the calcined-hydrous scallop shells was determined as follows: 250 mg of calcined-hydrous scallop shells was decomposed with a microwave in 3.0 cm³ of 60% HNO₃, 2.0 cm³ of 35% HCl, and 1.0 cm³ of HBF₄ heated at 220 °C for 50 min. After cooling, 17 elements were determined by SEIKO 7800 ICP-AES. The results are shown in Table 1. It indicates that calcium hydroxide (over 92.43 %) is the main component with trace amounts of heavy metal oxide. The brightness was found to be 97.78%. Lime stones, obtained from Shiriya, Aomori in Japan, were calcined 100-1200 °C for 120 min. The product was also confirmed to be mainly calcium oxide by XRD (JCPDS 4-0777). The chemical composition indicated 95.15% purity as calcium oxide (Table 1), however, the brightness was lower than calcined-hydrous scallop shells (83.03%). It is considered that the impurities consist of white-colored compositions such as SiO₂, MgO and so on in calcined lime stones.

Table 1 Elemental compositions of calcined-hydrous scallop shells and calcined lime stones/ mg g⁻¹

Element	calcined-hydrous scallop shells	calcined lime stones
Ca	500.00	680.00
Fe	0.0250	0.344
Zn	0.0026	0.0078
K	0.0928	0.360
Si	2.74	2.81
Al	0.0292	0.580
Pb	n.d.	n.d.
Mg	0.700	3.14
Sb	0.0034	0.0066
Na	6.84	0.468
Co	0.0006	0.0006
Mn	0.0092	0.0602
P	0.4458	0.149
S	3.68	0.243
Sr	1.18	0.562
Ba	0.0032	0.0162
Ni	0.0024	0.0028
others	484.2458	311.2498

n.d.: not detected

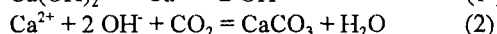
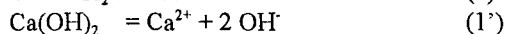
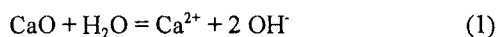
Table 2 Details of synthesis for precipitated calcium carbonate from calcined-hydrous scallop shells and calcined limestones by successive reaction, and the properties of the products

Details of synthesis					Properties of products			
Exp.	[Ca _s]/([Ca _l]+[Ca _s])* ¹	Temp./°C		CO ₂ flow rate /cm ³ min ⁻¹	Crystal form	Brightness /%	S _{BET} * ² /m ² g ⁻¹	Bulk* ³ /cm ³ g ⁻¹
		1st step	2nd step					
1	0.25	35	35	12.5	Arg* ⁴	87.6	3.12	n.d.* ⁵
2	0.33	35	35	12.5	Arg	90.0	5.74	n.d.
3	0.50	35	35	12.5	Arg	91.5	4.87	n.d.
4	0.50	60	35	12.5	Arg	88.6	4.79	n.d.
5	0.50	35	60	12.5	Arg	90.6	3.45	n.d.
6	0.50	60	60	12.5	Arg	89.6	2.57	2.92
7	0.83	35	35	12.5	Arg	94.4	5.56	2.32
8	0.83	20	60	12.5	Arg	95.8	7.85	3.11
9	0.83	35	60	12.5	Arg	94.8	11.68* ⁶	n.d.
10	0.83	60	35	12.5	Arg	94.1	4.72	n.d.
11	0.83	60	60	12.5	Arg	95.2	4.31	1.79
12	0.90	35	35	12.5	Arg	95.4	5.17	2.36
13	0.90	20	60	12.5	Arg	96.3	5.60	3.08
14	0.90	35	60	12.5	Arg	96.4	5.78	n.d.
15	0.90	60	60	12.5	Arg	95.2	4.68	2.11

*1: [Ca_s], concentrations of calcium from calcined-hydrous scallop shells; [Ca_l], concentrations of calcium from calcined limestones *2: specific surface area by BET method *3: JIS K5101-1991 *4: Arg: aragonite (JCPDS 5-0453) *5: not determined *6: average of two measurements.

Synthesis and characterization of aragonite

Carbonation was carried out by the successive reaction in combination of the 1st step by calcined lime stones with the 2nd step by calcined-hydrous scallop shells. The appropriate amounts of calcined lime stones were suspended in 400 cm³ of 0.335-1.341 mol dm⁻³ MgCl₂ solutions (to be 0.0891 mol dm⁻³ as total Ca²⁺ ion concentrations), and stirred by an impeller at 200 rpm at 35-60 °C under the constant, 12.5 cm³ min⁻¹. The reaction temperature and combination ratios of calcium sources, $\frac{[Ca_S^{2+}]}{([Ca_L^{2+}] + [Ca_S^{2+}])}$ ($[Ca_L^{2+}]$: concentration of calcium ions from calcined lime stones; $[Ca_S^{2+}]$: concentration of calcium ions from calcined-hydrous scallop shells) were changed in the successive reaction as shown in Table 2. The end point of reaction was decided by monitoring pH in the solutions. In the first step, the reaction of calcined lime stones with CO₂ proceeds according to eqs. (1) and (2), producing OH⁻ ions with eq. (1) and consuming OH⁻ ions with eq. (2):



During the reaction of calcined lime stones with CO₂, the pH is initially increased for a short time dominating eq. (1), and then gradually decreased to an almost constant value. After the completion of the 1st step reaction, the appropriate amounts of calcined-hydrous

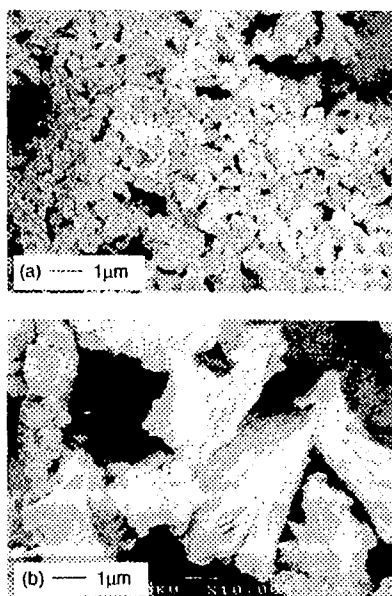


Fig. 1 SEM images of (a) calcined hydrous scallop shell and (b) calcined lime stone.

scallop shells were added to them. The solution pH increases again by the progress of eq.(1'), followed by eq.(2). A similar pH trend is observed in the 2nd step. The product was filtered with a glass filter G4, thoroughly washed with 400 cm³ of distilled water at once to remove the simply adsorbed Mg²⁺ ions on the surface of the product, and then dried at 40 °C overnight. The products were analyzed by XRD, and observed by FE-SEM. The specific surface area, the brightness and the bulk density were also determined.

Results and Discussion

Effect of $\frac{[Ca_S^{2+}]}{([Ca_L^{2+}] + [Ca_S^{2+}])}$ in successive reaction on morphologies of aragonite

Figure 2 shows SEM images of the products dependent on combination ratios, $\frac{[Ca_S^{2+}]}{([Ca_L^{2+}] + [Ca_S^{2+}])}$, as shown in Nos. 1, 2, 3, 7, and 12 in Table 2. The reaction temperature was kept constant at 35 °C in these experiments. As an example, pH-changes in No. 7 are shown in Fig. 3. The end point of the 1st stage can be seen clearly by an arrow. At this point, addition of calcined-hydrous scallop shells was performed, with no addition of Mg²⁺ ions. As previously reported, Mg²⁺ ions are not involved in aragonite, but essential to form aragonite (Sasaki, et al., 1999). Therefore, the solutions contain enough Mg²⁺ ions at the start of the 2nd stage to form the aragonite

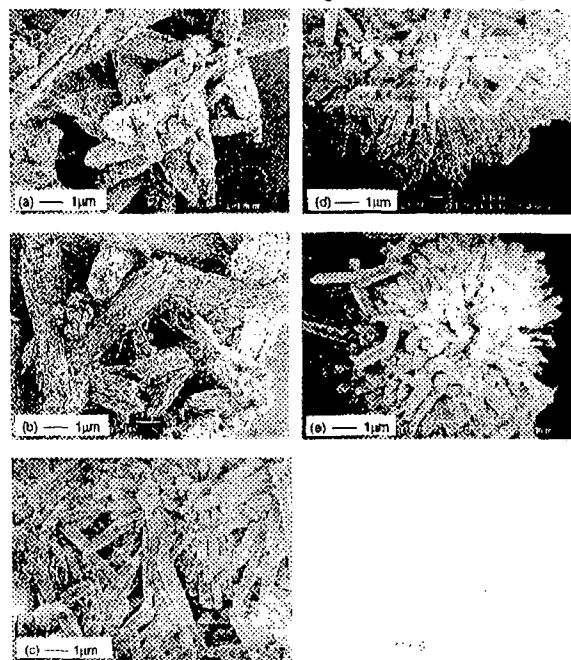


Fig. 2 SEM images of the products dependent on $\frac{[Ca_S^{2+}]}{([Ca_L^{2+}] + [Ca_S^{2+}])}$. (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 7, (e) No. 12 in Table 2.

and it is not necessary to add the Mg^{2+} ions again. Expectedly, the products were confirmed to be aragonite by XRD, though their morphologies were different. In case of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}]) \leq 0.33$ (Fig. 2(a), (b)), it was observed that the sizes of core crystals were relatively large, and that many small crystals were embedded on the surfaces of large crystals as cores. In case of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}]) \geq 0.50$ (Fig. 2(c), (d), (e)), there were many uniformed rod type of crystals with smooth surfaces.

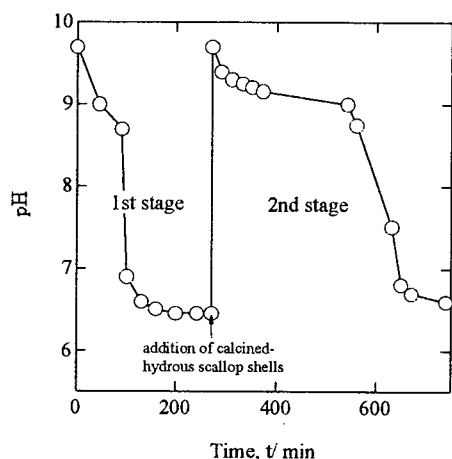


Fig. 3 pH-changes in successive reaction of calcined lime stones and calcined-hydrous scallop shells with CO_2 (No. 7 of Table 2).

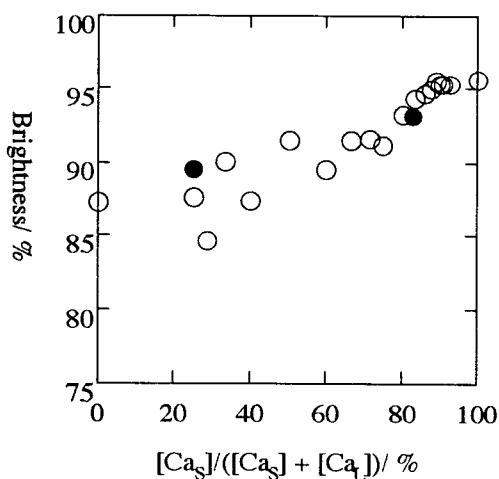


Fig. 4 Effect of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}])$ on the brightness of products. ○, successive reaction; ●, one step reaction.

As a matter of fact, the brightness of the products increased with increase in scallop shells. A merit of successive reaction was expected to enhance the brightness in products, compared with in one step reaction. However, it was difficult to find the difference in brightness of the products in both reactions (Fig. 4).

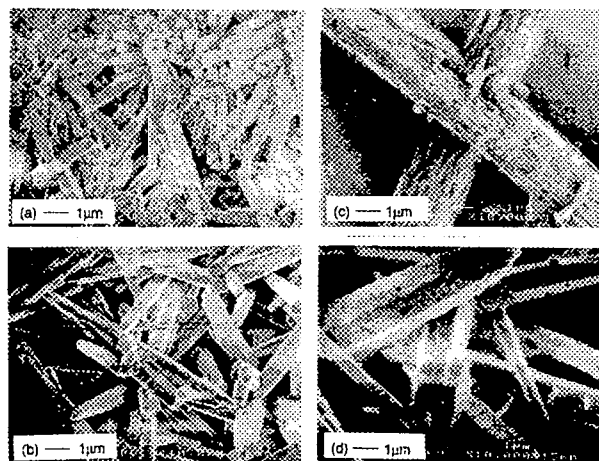


Fig. 5 SEM images of the products dependent on reaction temperature. $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}]) = 0.50$. (a) No. 3, (b) No. 4, (c) No. 5, (d) No. 6 in Table 2.

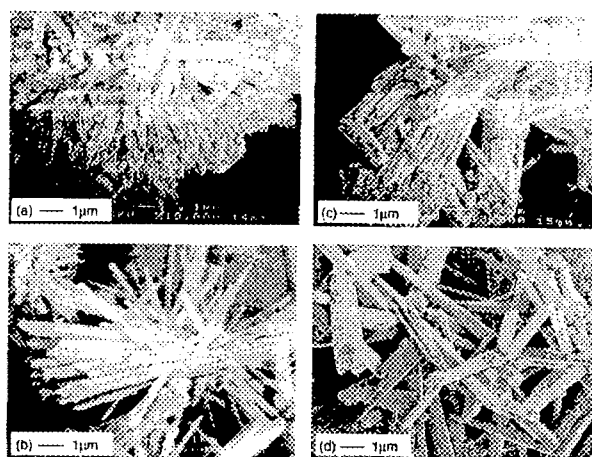


Fig. 6 SEM images of the products dependent on reaction temperature. $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}]) = 0.83$. (a) No. 7, (b) No. 9, (c) No. 10, (d) No. 11 in Table 2.

It has been previously reported (Sasaki, et al., 1998b) that temperature affect dramatically to the morphologies and sizes of aragonite. One of the advantages in successive reaction is to able to control the reaction temperature in each step. Figure 5 shows SEM images of the products dependent on reaction temperatures: (a) No. 3; (b) No. 4; (c) No. 5; and (d) No. 6 in Table 2. In these conditions, the ratio of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}])$ was constant to be 0.50. They were identical to aragonite by XRD, though their morphologies and sizes were different from each other. Naturally, the largest aragonite was obtained under the high temperature in all processes of successive reaction, as shown in Fig. 5(d). In case of ambient temperature through all the processes (Fig. 5(a)), the products have the same shape (short rod-type) and size as produced in one step reaction (Sasaki, et al., 1999). Increase in temperature in the 2nd step (Fig. 5(b)) leads to high dispersion of particles, compared with Fig. 5(a), however, other differences were not observed. As can be seen in Fig. 5(c), large particles which were formed under the high temperature in the 1st step, act as a seed in the 2nd step of successive reaction. High temperature in the 2nd step leads to high dispersion of particles as shown in Fig. 5(b) and (d).

Subsequently, when the ratio of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}])$ was up to 0.83, the morphologies of products were shown in Fig. 6. These were also confirmed to be aragonite by XRD. More addition of calcined-hydrous scallop shells in the 2nd step affects on the morphologies of aragonite. In case of No. 9, the aspect ratio of aragonite particles is dramatically increased, resulting in 50-100 of aspect ratio with 0.2-0.5 μm in diameter by 10-15 μm in length, as shown in Fig. 6(b). The product has large specific surface area, 11.68 $\text{m}^2 \text{g}^{-1}$, and high brightness (94.8%), as shown in Table 2. The high reproducibility was exemplified in No. 8 of Table 2. Moreover, when the ratio of $[Ca_S^{2+}]/([Ca_L^{2+}]+[Ca_S^{2+}])$ was increased to 0.90, the same trend was observed in Nos. 12-15 of Table 2.

The mechanism is proposed as follows: a lot of relatively small particles of aragonite are formed in the 1st step under the ambient temperature, following that long size aragonite particles grow using the products in the 1st step as seeds in the 2nd step under the high temperature. The successive reaction was very effective to produce aragonite of high aspect ratio.

Conclusions

Aragonite type of precipitated calcium carbonate was synthesized by the successive reaction with hybridization of waste scallop shells with limestone. In the first step, carbonation was performed by using calcined limestone with low brightness, following by the carbonation using calcined-hydrous scallop shells with high brightness. The temperature and the amount ratio of calcined limestone to calcined-hydrous scallop shells were examined as parameters in the experimental conditions. The products were characterized by XRD, SEM, in addition to measurements of brightness index, the specific surface area, and bulk density. The amount ratio of limestone to scallop shell affected not only whiteness but also morphologies of the products. The increase in relative amounts of limestone leads to decrease in brightness and bumpy surface of particles. Higher temperature reaction produced aragonite particles with longer sizes and higher bulk densities. This study has made an attempt to establish the synthesis of aragonite with high brightness and high strength by utilization of waste scallop shells.

ACKNOWLEDGMENTS

This work was partly supported by the Hosokawa Powder Technology Foundation and Showa Shell Oil Foundation of Environmental Research.

References

- Kojima, Y., Kawanobe, A., Yasue, T. & Arai, Y. (1994): "Controls of polymorphism and morphology of calcium carbonate compounds formed by crystallizing amorphous calcium carbonate hydrate." *J. Ceram. Soc. Jpn.*, 102, 1128-1136.
- Sasaki, K., Konno, H. & Inagaki, M. (1994): "Structural strain in pyrite evaluated by X-ray powder diffraction." *J. Mat. Sci.*, 29, 1666-1670.
- Sasaki, K. Hongo, M. & Tsunekawa, M. (1997): "Synthesis of aragonite-type of calcium carbonate from calcined scallop shell (1st. Report) -with amorphous calcium carbonate as intermediate -", *Shigen-to-Sozai*, 113, 1055-1058.
- Sasaki, K. Hongo, M. & Tsunekawa, M. (1998a): "Synthesis of aragonite-type of calcium carbonate from calcined scallop shell (2nd. Report) - with carbonates of aragonite-structure as seeds -", *Shigen-to-Sozai*, 114, 709-713.
- Sasaki, K. Hongo, M. & Tsunekawa, M. (1998b): "Synthesis of aragonite-type of calcium carbonate from calcined scallop shell (3rd. Report) - in aqueous system at ambient temperatures -", *Shigen-to-Sozai*, 114, 715-719.

- Sasaki, K., Hirajima, T. & Tsunekawa, M. (1999): "Morphological control of aragonite formed from waste scallop shells." *Proc. 5th Intl. Symp. East Asian Recycling Technology*. 147-150.
- Sasaki, K., Kobayashi, H. & Tsunekawa, M. (in press): "Synthesis of aragonite from scallop shells and lime stones ~Morphological control by successive reaction~" Shigen-to-Sozai.
- Shinohara, A. H., Sugiyama, K., Kasai, E., Saito, F. & Waseda, Y. (1993): "Effects of moisture on grinding of natural calcite by a tumbling ball mill." *Adv. Powder Technol.*, 4(4), 311-319.
- Ohta, Y., Inui, S., Iwashita, T., Kasuga, T. & Abe, Y. (1996): "Synthesis of aragonite whisker by CO₂." *J. Ceram. Soc. Jpn.*, 104, 196-200.
- Yasue, T. & Arai, Y. (1995): "Particle design for new development of calcium compound", *Shigen-to-Sozai*, 111, 439-448.