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Formation of Vaterite by the Reaction of Calcium Methoxide with Aqueous Sodium Carbonate Solution

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Synopsis. A mixture of vaterite and calcite was formed by the reaction of calcium methoxide with aqueous sodium carbonate solutions. The reaction temperature was found to be a dominant factor for the formation of vaterite. The kinetics of the transformation of vaterite into calcite was studied.

Calcium carbonate exists in three polymorphic modifications: calcite(hexagonal), aragonite(orthorhombic) and vaterite(hexagonal). Calcite is stable at ordinary temperature and pressure. Both aragonite and vaterite are transformed into calcite on heating. Although the formation of calcite and aragonite has been studied by many investigators, only a few papers$^{1-4)}$ have appeared on the formation of vaterite. It was found that the mixture of vaterite and calcite is formed by the reaction of calcium methoxide with aqueous sodium carbonate solution. The present study deals with the conditions on the formation of vaterite and the kinetics of the transformation of vaterite into calcite.

Experimental

The starting material calcium methoxide was prepared by heating calcium metal in an excess dehydrated methanol:

$$Ca + 2CH_3OH \xrightarrow[64\,^{\circ}C,\ 5\,h]{CH_3OH} Ca(OCH_3)_2 + H_2 \qquad (1)$$

Calcium metal of purity 99 % was used. 20 cm^3 of a methanolic solution containing 1 g calcium methoxide was added rapidly to the stirred 100 cm^3 aqueous sodium carbonate solution, and the resulting colloid was stirred for 5 min. The product was separated immediately from the suspension by filtration, washed repeatedly with hot water, and dried at 40 °C under reduced pressure. The product was examined by means of X-ray diffraction using nickel filtered copper *Ka* radiation and differential thermal analysis.

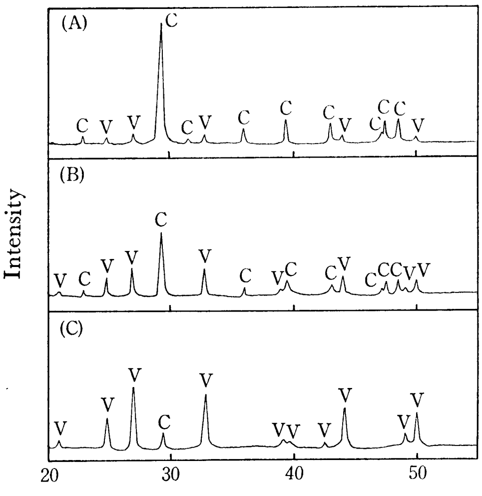

Fig. 1. X-Ray diffraction patterns of $CaCO_3$ prepared from solutions of various temperatures and concentrations. (A): 0.25 N 30 °C, (B): 0.5 N 50 °C, (C): 1 N 90 °C. For Na_2CO_3 solutions, 1 N=0.5 mol/dm^3. V: Vaterite, C: calcite.

TABLE 1. FRACTION OF THE TWO MODIFICATIONS FOR $CaCO_3$ PREPARED BY THE REACTION OF $Ca(OCH_3)_2$ WITH AQUEOUS Na_2CO_3 SOLUTION

Run	Concentration of aq Na_2CO_3 soln/N$^{a)}$	Temp/°C	Fraction/%	
			Vaterite	Calcite
1	0.25	30	14	86
2	0.25	50	41	59
3	0.25	70	72	28
4	0.25	90	86	14
5	0.5	30	25	75
6	0.5	50	52	48
7	0.5	70	74	26
8	0.5	90	86	14
9	1	30	40	60
10	1	50	66	34
11	1	70	74	26
12	1	90	87	13

a) 1 N=0.5 mol/dm^3 (for Na_2CO_3 solutions).

Results and Discussion

All the products obtained under various conditions were identified as calcium carbonate, which is a mixture of vaterite and calcite. No aragonite was formed. The yield was about 96%. Figure 1 shows the X-ray diffraction patterns of calcium carbonate. No line broadening was observed. The fraction of the two modifications for each calcium carbonate powder is given in Table 1. The fraction was determined from Eqs. 2$^{4,5)}$ and 3 by measuring the intensity of the (104) reflection of calcite and the intensities of the (110), (112), and (114) reflections of vaterite:

$$f_c = \frac{I_{104(c)}}{I_{110(v)}+I_{112(v)}+I_{104(c)}+I_{114(v)}} \qquad (2)$$

$$f_c + f_v = 1 \qquad (3)$$

where f_c and f_v are the fraction of calcite and vaterite, respectively. For all the concentrations of aqueous sodium carbonate solutions, the fraction of vaterite increased with rise in reaction temperature up to 90 °C, no product consisting of only vaterite being formed. Formation of vaterite at low temperature was promoted with increase in the concentration of aqueous sodium

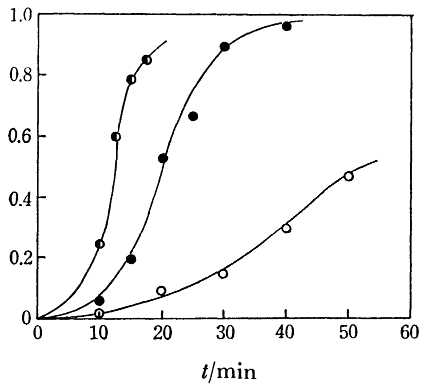

Fig. 2. Phase transformation from vaterite to calcite as a function of time at different temperatures.
○: 360 °C, ●: 380 °C, ◐: 400 °C.

carbonate solution, but not at high temperature. The reaction temperature is a dominant factor in the formation of vaterite. It is important to consider two stages for the formation of calcium carbonate: (a) aggregation velocity of ions; (b) crystallization velocity at which the ions in colloidal state form crystals. The aggregation velocity is considered to be very high. On the other hand, a period of a few seconds to a few minutes is required for crystallization. Increase in the reaction temperature reduces the time of transformation from colloid into crystal. The formation of vaterite seems to be determined by the crystallization velocity which changes with the reaction temperature. Differential thermal analysis was carried out in the air from room temperature to 600 °C. An exothermic reaction was observed in the temperature range 390—430 °C. From the results of X-ray diffraction, the reaction was found to be the transformation of vaterite to calcite. Figure 2 shows the fraction of the transformation of vaterite to calcite (Table 1, run 12) as a function of time at different temperatures. The average particle size of the specimen was 0.14 μm. Transformation isotherms were characterized by sigmoidal shape, the kinetics being best described by the Avrami equation[6] (Fig. 3),

$$\ln(1-\alpha) = -kt^n \qquad n = (2.8-3.1) = 3 \tag{4}$$

where α, t, k, and n are the fraction of transformation, time, rate constant, and proportionality constant, respectively. The activation energy calculated by the Arrhenius plot is *ca.* 130 kJ/mol, representing that of the nucleation growth of calcite. Rao[5] reported that vaterite prepared by the same method as that given by McConnel[1] is transformed into calcite in the temperature range 540—580 °C, the kinetic data being represented by the Avrami equation with $n=4/3$. Higher activation energy 356 kJ/mol was required for the progress of transformation. Our results do not agree with those of Rao.[5] The discrepancy might be attributed to difference in type of impurity and the average particle size of vaterite, which affects the temperature and kinetics of transformation.

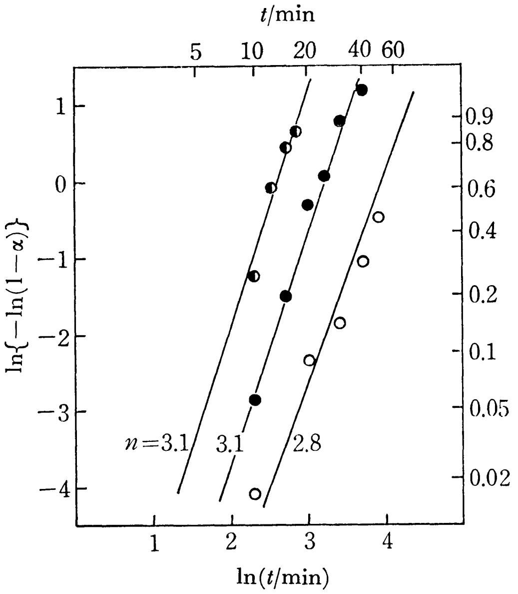

Fig. 3. Plot of ln(1−α) *vs.* time *t*.
○: 360 °C, ●: 380 °C, ◐: 400 °C.

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