

Effect of monovalent salts on morphology of calcium carbonate crystallized in Couette-Taylor reactor

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Monovalent ionic additives, Na^+ , K^+ and NH_4^+ impact on the morphology and agglomeration of CaCO_3 crystals. As increasing the additive concentration, the regular shaped crystals such as rhombohedron and spindle are changed to irregular one due to the inclusion of Na^+ and K^+ into the crystal structure. The inclusion of Na^+ and K^+ is detected using ICP-AES. The partition of coefficients of Na^+ and K^+ are estimated as 9.74×10^{-4} , 9.73×10^{-4} , respectively and the amount of inclusion in the crystals is about 2×10^3 ppm. However, the inclusion of ions does not modify a crystal structure of calcite. Since NH_4^+ is large in radius, it is not included in crystal but shifts the spindle shape of crystal to the rhombohedral one. It is interesting to find that such modification of crystal morphology begins to appear at high additive concentration (0.05 M). In addition, the crystal agglomeration is promoted because the electric repulsive charge is reduced as increasing the additive concentration.

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1 Introduction

Since a liquid-liquid reaction system has advantages to crystallization in controlling reactant concentration, solution pH, temperature, mixing and flow rate (residence time) etc, which are most determining-factors on the crystallization processes, it is frequently adopted in study for the crystallization processes of CaCO_3 [1-5]. Dependency of the crystal structures of calcite, aragonite and vaterite on the pH, supersaturation and temperature is exhibited in the crystallization using liquid-liquid reaction [4, 6-9]. The kinetic studies of CaCO_3 , including crystal nucleation, growth and agglomeration, are also performed via liquid-liquid reaction systems [10, 11].

In addition, the ionic additives are used to modify the crystal morphology, structure and size in the crystallization. It is reported that polyvalent ions cause the habit change and inhibition of CaCO_3 crystal growth [12, 13]. Effects of monovalent ionic additives, NaCl and LiBr, on the crystal habit of CaCO_3 are investigated by Buehrer and Reitemeier [14] and Rajam and Mann [15], respectively. Also, the crystal growth is reduced and crystal morphology is changed as increasing the additive concentration of phosphonates [16-18].

As shown in above studies using the liquid-liquid reaction systems, although the ionic additives obviously influence on the crystallizations and critically modify the crystal size, shape and structure etc, the potential impact of ionic by-products of liquid-liquid reaction on the crystallization is little considered in care. As such, when cationic reagents (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$) and anionic reagents (Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$) are used for the reaction of CaCO_3 , NaCl, KCl and NH_4Cl etc are by-produced.

Yagi et al. [19] and Jones et al. [20] adopt the gas (CO_2)-liquid ($\text{Ca}(\text{OH})_2$) reaction for CaCO_3 crystallization, eliminating the potential influence of ionic by-products. In these studies, CO_2 gas flows gently over $\text{Ca}(\text{OH})_2$ solution to induce the crystallization at the gas-liquid interface. However, a homogeneous crystallization is not achieved. Although a gas sparger is used to increase the gas-liquid interface [21], such an

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operation in open tank reactor is still far from homogeneous crystallization. Couette-Taylor reactor is introduced to achieve the homogeneous mixing of gas-liquid reactants using strong radial turbulent vortex although a difficulty in controlling stoichiometric conditions of gas-liquid reaction is not overcome due to the gaseous feed [22, 23]. Unfortunately, in those above studies, the ionic additive is not attempted to analyze its effect on the crystallization.

In the present study, it is aimed to investigate the influence of monovalent ionic additives on the crystallization of CaCO_3 using $\text{Ca}(\text{OH})_2\text{-H}_2\text{CO}_3$ reaction containing advantages of liquid-liquid reaction system as well as unique merits of gas-liquid reaction systems to CaCO_3 crystallization. Since the by-products of the liquid-liquid reaction systems for CaCO_3 crystallization are in general monovalent ionic salts depending on the reactants, NaCl , KCl , NH_4Cl , NaNO_3 , KNO_3 and NH_4NO_3 are chosen as ionic additives for the present crystallization. Thereby, those additives are helpful to elucidate a potential influence of by-product on the crystallization by liquid-liquid reaction. Experiments are conducted in turbulent vortex region using a Couette-Taylor reactor, which would provide homogeneous mixing for the crystallization [22-24].

2 Experiment

2.1 Couette-Taylor reactor

A Couette-Taylor reactor is composed of two annular cylinders of inner one made with stainless steel and outer one made with Lucite acrylic plastics. The detail design of the reactor is described in the previous report [22]. It is horizontally installed to minimize the effect of hydraulic static pressure on fluidic motion. Two aqueous feeds ($\text{Ca}(\text{OH})_2$ and H_2CO_3) are continuously injected into the reactor at two separate inlet ports located at one end of the annulus cylinder and the product suspension is flown out of the reactor at an outlet port located at the other end of the cylinder. To induce Taylor vortex, the internal cylinder of the reactor is rotated by DC motor controlling rotating speed. The gap at each end of the annulus is well sealed with O-ring, preventing the solution leaking out of the reactor. In the present study, the rotation speed of the inner cylinder is fixed at 800 rpm. At the present experimental condition, the Taylor number and axial Reynolds number are estimated as 35,500 and 20.0, respectively, indicating the strong radial and weak axial mixing substantially enough for homogeneous crystallization in the reactor.

2.2 Experimental procedure

CaCO_3 crystallization is commenced by feeding the aqueous reactants of $\text{Ca}(\text{OH})_2$ and H_2CO_3 . $\text{Ca}(\text{OH})_2$ solution is prepared by the reagent purchased from Shinyo Chem. Co. (Japan) and used without further purification. The reagent is dissolved into 20 L de-ionized water and the solid impurities are filtered out by 0.1 μm membrane filter (Whatman, 7181-004, U.K.). H_2CO_3 reactant solution is prepared by absorbing CO_2 gas (99%) into 20 L de-ionized water at 25 °C. To effectively dissolve CO_2 , a gas sparger having tiny pores is used. Using pH meter (Orion Research, Ross 8102BN, U.S.A.), the absorption of CO_2 into the water is monitored until reaching at equilibrium. The equilibrium concentration of H_2CO_3 at 25 °C is estimated as 0.025M.

Initially, the reactor is filled with deionized water and the internal cylinder is rotated at 800 rpm. Then, each reactant solution is fed into the reactor at 160 ml/min by pump (Cole-Parmer Instruments, Masterflex P-77921-20, U.S.A.). The mean residence time of the reactor is fixed at 10 min. Under various stoichiometric conditions for the reaction, the ionic additives of NaCl , KCl , NH_4Cl , NaNO_3 , KNO_3 and NH_4NO_3 (Oriental Chemical Industries, Korea) are applied to the crystallization. Additives are co-dissolved with $\text{Ca}(\text{OH})_2$ reagent in the aqueous feed solution. Additive and $\text{Ca}(\text{OH})_2$ reagent concentrations are varied up to 0.5 M and 0.05 M, respectively.

In the course of the crystallization, the pH and Ca^{2+} ionic concentration are monitored by pH ion and Ca^{2+} selective electrodes (Orion Research, Ion plus 9720BN, U.S.A.). Steady state is counted when pH and Ca^{2+} ionic concentrations at the outlet stream reach invariant relatively to time. Although the steady state is normally attained within 8 mean residence times, we allow always more than 10 mean residence times to guarantee the steady state in the reactor. Then, sample suspension is taken at the outlet stream and immediately diluted in deionized water to quench further crystallization in the sample. Crystals of sample suspension are separated with cellulose membrane filter (Advantec MFS Inc., A020A047A, 0.2 μm pore diameter) and are dried in a desiccator at room temperature.

2.3 Analysis

The size and morphology of individual crystals of dry sample crystals are analyzed with scanning electron microscopy (SEM; Leica, Stereoscan 440, Germany). The mean size of individual crystals is determined from the average Heywood diameter of 50 to 100 crystals of SEM images at least. X-ray diffractometer (XRD; MAC Science, M18XHF-SRA, Cu K_{α} line, Japan) is used to identify the crystal structure. Using 50 mg solid samples dissolved into 10 ml 0.1 M HCl, additive ions incorporated in crystals are detected with inductively coupled plasma-atomic absorption spectroscopy (ICP-AES; Shimadzu, ICPS-1000IV, Japan). Crystal agglomeration is observed with particle size analyzer (PSA; Malvern Instruments, Mastersizer 2000, U.K.) as well as SEM. To re-disperse the crystals weakly aggregated by physical interaction between crystals the sample suspension is treated with ultrasound. After 10 min treatment, there was no further change in agglomerated crystal size.

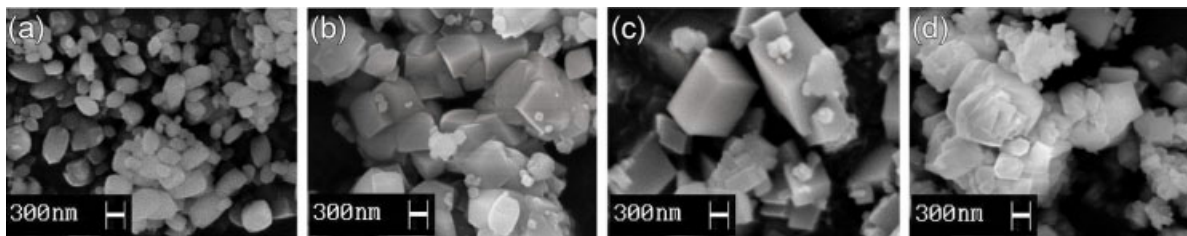


Fig. 1 Morphological change depending on additive (Na^+ and K^+) concentration in CaCO_3 crystallization. (a) no additive under excess Ca^{2+} condition of reaction (0.05 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3), (b) 0.25 M KNO_3 additive under excess Ca^{2+} condition of reaction, (c) no additive under stoichiometric ratio of reaction (0.025 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3), and (d) 0.25 M NaNO_3 additive under stoichiometric ratio of reaction.

3 Results and discussion

3.1 Morphology and size of crystals

In the present study, it is observed that the crystal morphology depends on the stoichiometric condition of reactants for the crystallization (Fig. 1 (a) and (c)). For example, the large rhombohedral crystals are produced at the stoichiometric ratio of reactants. When $\text{Ca}(\text{OH})_2$ is in excess, the crystal size is reduced and the crystal morphology is shifted to spindle and needle eventually. However, the rhombohedral morphology remains at H_2CO_3 in excess. Such morphological shifts are frequently reported in crystallizations using divalent salts of additives [12, 13]. In addition, when we add the various monovalent salts into the crystallization, they cause the morphological changes of crystals, as shown in Fig. 1. Here, $\text{Ca}(\text{OH})_2$ concentration is spanned from 0.015 M to 0.05 M although H_2CO_3 concentration is fixed at 0.025 M. The crystal of CaCO_3 loses its characteristic configuration in shape as increasing the additive concentration. As such, the crystal shape of spindle, which is typical in excess $\text{Ca}(\text{OH})_2$ reactant, becomes irregular at 0.25 M of KNO_3 (Fig. 1 (a) and (b)). The rhombohedral crystals produced at stoichiometric ratio of reactants are also turned to irregular ones by adding 0.25 M of NaNO_3 (Fig. 1(c) and (d)).

The impacts of monovalent salts on the crystals appear different from those of divalent salts reported in previous studies. First, the monovalent salts change the rhombohedral (or spindle-like) shape of crystals to the irregular one without structural modification whereas the divalent salts shift the crystal structure as well as crystal shape. Secondly, such modification of crystals occurs at much higher additive concentration of monovalent salts ($C_{\text{ad}}/C_{\text{A}0} = 2.0 - 10.0$) than that of divalent salts ($C_{\text{ad}}/C_{\text{A}0} = 10^{-5} - 10^{-2}$), where C_{ad} and $C_{\text{A}0}$ are salt and limiting reactant concentrations, respectively. This second observation may give a tip on why the irregular crystal shape have not occurred without an additive in the crystallization using conventional liquid-liquid reaction system inevitably producing by-products of salts.

Such impacts by the monovalent salts are considered due to the inclusion of additive salts into the crystal structure in the course of the crystallization. Using ICP-AES the monovalent salt ions (Na^+ and K^+) included into the crystal structure is examined and the degree of inclusion is evaluated via partition coefficient (k_p), as suggested by Doerner and Hoskins [25] as,

$$k_p = \frac{x_{ad}/x_{Ca}}{C_{ad}/C_{A0}} \quad (1)$$

where x_{ad} and x_{Ca} are the fraction of monovalent cation and Ca^{2+} in crystals, respectively. The x_{ad} and x_{Ca} measured by ICP-AES result in k_p of Na^+ and K^+ as 9.74×10^{-4} , 9.73×10^{-4} respectively. These values are consistent with the Curti's results for inclusions of Na^+ and K^+ in $CaCO_3$, respectively [27]. At low concentration of monovalent salts (below 0.05 M), the inclusion of salts is not considerably detected and no shape change of crystals was observed.

Similarly, inclusions of monovalent ions of Li^+ and K^+ into the crystal structures are observed by Rajam and Mann [15] and Haley et al. [27] in $CaCO_3$ and $BaSO_4$ crystallizations, respectively. In their studies, the inclusion of monovalent ions occurs at high salt concentration, bringing about an irregular shape of the crystals, like in the present study. Also, it is thought that small radius of monovalent ion (Li^+ and K^+) is suitable to the interstitial inclusion of crystals ($CaCO_3$ and $BaSO_4$). Based on our preliminary studies [28], it should be noted that the supersaturation does hardly change the rhombohedral crystal shape.

Although the amount of monovalent ions included into the crystals is estimated as about 2×10^3 ppm based on the above partition coefficient, it does not cause a structural modification of calcite, as shown in Fig. 2. This inclusion of monovalent ions in the crystals is consistent with the Busenberg and Plummer's study (Na^+ , 4×10^3 ppm) [29], where a slight shift of the characteristic XRD peaks occurs by the inclusion of ions, yet the crystal structure of calcite remains, as like solid solution.

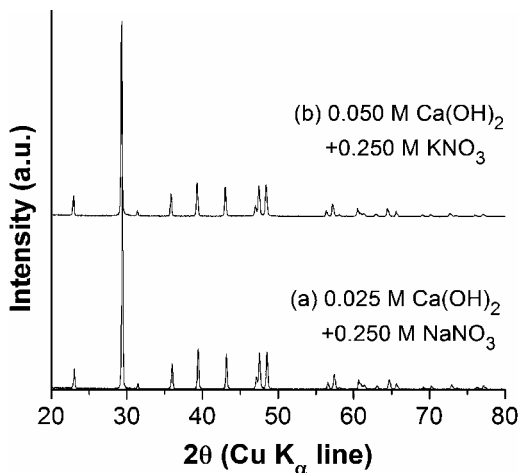


Fig. 2 Powder XRD pattern of $CaCO_3$ interstitially including cations (Na^+ and K^+) of additives. (a) 0.025 M $NaNO_3$ under reaction condition of 0.025 M $Ca(OH)_2$ and 0.025 M H_2CO_3 . (b) 0.025 M KNO_3 under reaction condition of 0.05 M $Ca(OH)_2$ and 0.025 M H_2CO_3 .

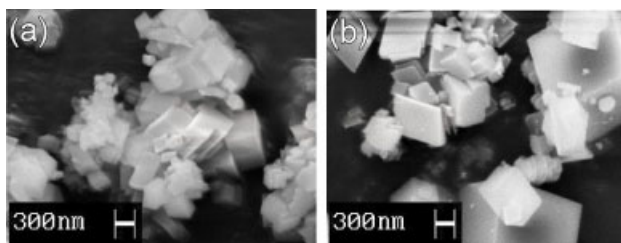


Fig. 3 Influence of ionic additive (NH_4^+) on $CaCO_3$ morphology crystallized under excess Ca^{2+} condition of reaction (0.05 M $Ca(OH)_2$ and 0.025 M H_2CO_3) (a) 0.250 M NH_4NO_3 , (b) 0.050 M NH_4Cl .

Table 1 Ionic radius of additives and reactant species [32, 33].

ion	radius (nm)	ion	radius (nm)
Li^+	0.078	Ca^{2+}	0.106
Na^+	0.098	CO_3^{2-}	0.178
K^+	0.133	OH^-	0.133
NH_4^+	0.148	NO_3^-	0.179
Rb^+	0.149	Cl^-	0.181

The monovalent ion of NH_4^+ produces the rhombohedral shape of crystals under excess condition of Ca^{2+} reactant species, as shown in Fig. 3. According to Okumura and Kitano [30], the inclusion of monovalent ions into calcium carbonate crystals tends to increase inversely with ionic radius as in the sequence of Li^+ , Na^+ and K^+ (Table 1). Also, it is observed that Rb^+ is not included in the calcium carbonate structure due to the large

ionic radius [31]. Thereby, it may be guessed that NH_4^+ having a similar ionic size with Rb^+ is hardly fitted into the crystal structure, exerting different influence on the crystal from the alkali ions of Na^+ and K^+ . The spindle shape of crystals produced under the Ca^{2+} excess condition is shifted to rhombohedral one by adding NH_4^+ . This result implies that the preferential adsorption of the excess Ca^{2+} on the crystal surface is disturbed by NH_4^+ additive. When comparing the crystal morphologies formed in additives of NH_4Cl , NaCl , NaNO_3 , NH_4NO_3 and KNO_3 , it is interesting to find that the shape change of crystals depends little on the anions due to large ionic radii of monovalent anions.

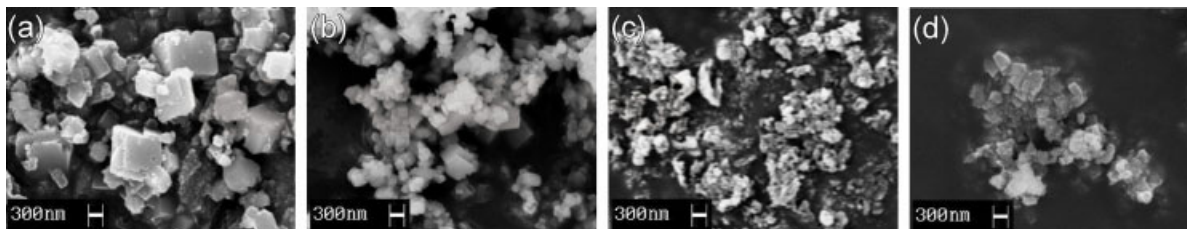


Fig. 4 Influence of additives on crystal morphology and size of CaCO_3 crystallized under excess CO_3^{2-} condition of reaction (0.015 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3). (a) no additive, (b) 0.250 M NaNO_3 , (c) 0.250 M NH_4Cl and (d) 0.050 M NH_4NO_3 .

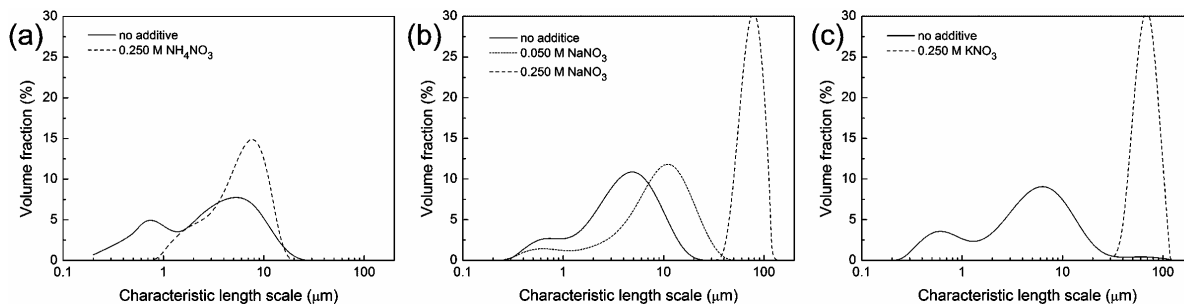


Fig. 5 Influence of ionic additives on agglomerate size distributions in CaCO_3 crystallization. (a) NH_4NO_3 additive under CO_3^{2-} excess condition of reaction (0.015 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3), (b) NaNO_3 additive at stoichiometric ratio of reaction (0.025 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3) and (c) KNO_3 additive under Ca^{2+} excess condition of reaction (0.05 M $\text{Ca}(\text{OH})_2$ and 0.025 M H_2CO_3).

Under excess reactant species, CO_3^{2-} , the monovalent salts result in a serious size reduction as well as shape change of crystals, as shown in Fig. 4. Due to the adsorption and inclusion of salts ions, the crystal size much decreases and the crystal shape becomes irregular. Especially, when adding NH_4Cl , the crystal size is less than 100 nm and appears too small to define its shape.

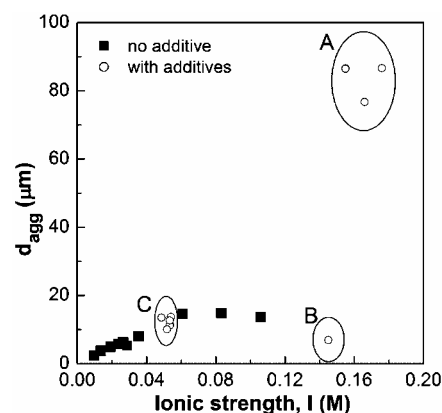
3.2 Agglomeration

During crystallization, the crystals in the suspension are collided and adhered to form agglomerates, as shown in the above microscopic images. When the crystal agglomerate size is measured using particle size analyzer (PSA), typical particle size distributions of the suspensions produced with and without monovalent salts are displayed in Fig. 5. As increasing the salt concentration, the particle size distribution is shifted to a larger scale and becomes narrower because of promotion of crystal agglomeration. For example, the mean agglomerate size (d_{agg}) increases from 5.232 μm up to 86.610 μm , as NaNO_3 concentration increases from 0 to 0.250 M under a stoichiometric ratio of reaction (Fig. 5(b)). In excess reactant species of Ca^{2+} and CO_3^{2-} , the impact of KNO_3 and NH_4NO_3 on the mean agglomerate size and distribution are similarly observed.

The promotion of crystal agglomeration by salts appears due to reduction of electric repulsion of crystals depending on ionic strength of solution [34]. As increasing the ionic strength of the solution by salts, the electric charge around crystals is neutralized by the salts ions. Then, the electrical double layer length of crystals decreases to enhance the collision efficiency of crystals. Therefore, the mean size of agglomerates is found to proportionally increase with the ionic strength, as displayed in Fig. 6. Here, the ionic strength of the

CaCO_3 solution is estimated on the basis of Ogino et al.'s method [31]. In the case of no salts, the ionic strength of the solution is mainly originated from the excess reactant species and solubility product of CaCO_3 .

Fig. 6 Correlation of mean agglomerate size with ionic strength of solution (A) 0.250 M additives at 0.025–0.05 M Ca(OH)_2 (B) 0.250 M additives at 0.015 M Ca(OH)_2 . (C) 0.050 M additives at 0.025 M Ca(OH)_2 .



4 Conclusion

Monovalent salts of NaCl , KCl , NH_4Cl , NaNO_3 , KNO_3 and NH_4NO_3 give significant influence on crystal morphology and agglomeration in the crystallization of CaCO_3 at both stoichiometric and nonstoichiometric ratio of reactants. When the small radius ions of Na^+ and K^+ are added, the crystal shape is changed from regular rhombohedron and spindle to irregular ones as increasing the ion concentration. The monovalent ions of Na^+ and K^+ are included into crystal structure in the course of the crystallization, resulting in the irregular shape of crystals. However, the inclusion of monovalent ions does not cause a structural modification of calcite. Since NH_4^+ is too large in radius to be interstitially included in the crystal, it does not bring about the irregular shape of crystal but shifts the spindle shape of crystal into the rhombohedral one under excess Ca^{2+} reactant condition. In addition, the crystals are seriously agglomerated because the salts neutralize the electrical repulsive charge and improve the collision efficiency.

According to the present study, the by-products in the conventional liquid-liquid reaction systems for CaCO_3 crystallization such as NaCl , KCl , NH_4Cl , NaNO_3 , KNO_3 and NH_4NO_3 are obviously potential to modify the crystal morphology. Such salts begin to work at high concentration as above twice as the reactant concentration. Thereby, it may little appear in crystallization using the conventional liquid-liquid reactions that the irregular shape and structural modification of crystal is induced without an additive.

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