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Synthesis of large silicalite-1 single crystals from two different silica sources

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Abstract

Large silicalite-1 crystals were hydrothermally synthesized at 150–200 °C by using reaction mixtures of the system SiO_2–TPABr (tetropylammonium bromide)–NH_4F–H_2O. Fumed silica or a quartz glass plate was used as the silica source. Large crystals up to 1800 μm were obtained in reaction mixtures containing a quartz glass plate at 180 °C for 5 weeks; on the other hand, for fumed silica, the crystal sizes were lower than 690 μm. It was found that the use of a quartz glass plate was effective for obtaining large crystals than fumed silica, presumably due to the slow dissolution rate of the quartz glass plate in the presence of fluoride ion. In addition, the crystal sizes were largely dependent on the reaction mixture composition used as well as the reaction temperature employed.

Keywords: Crystal growth; Hydrothermal synthesis; Zeolite; Large crystals

1. Introduction

Microporous crystalline solids of zeolites with well-defined structures are now widely used for heterogeneous catalysis, gas separations, ion-exchange applications, and so on. They are often used in the form of minute crystals and it is normally difficult to synthesize large crystals. In addition to the above conventional utilizations, a new type of applications have recently been proposed; for example, light-emitting [1,2] and second harmonic generation (SHG) devices [3,4], in which zeolite crystals act as host matrices for dye molecules. Such applications, however, require crystals as large as possible and it is thus desired to develop a novel method for synthesizing large zeolite crystals.

The first attempt for synthesizing large crystals of zeolites was made by Charnell [5] in 1972, who reported that large crystals of NaA (LTA-type; $(Na_{12}[Al_{12}Si_{12}O_{48}] \cdot 27H_2O)_8$) and NaX (FAU-type; $Na_nAl_nSi_{192-n}O_{384} \cdot xH_2O$ ($n = 77$–96)) zeolites could be obtained by a hydrothermal synthesis method. As for MFI-type zeolite ($Na_n[Al_nSi_{96-n}O_{192}] \cdot xH_2O$ ($n < 27$)), synthesis conditions for obtaining large crystals have extensively been studied. MFI-type zeolite, ZSM-5 or silicalite (all-silica ZSM-5), is normally synthesized hydrothermally from a reaction mixture of the system SiO_2 (and Al_2O_3)–tetrapropylammonium bromide (TAPBr, or tetrapropylammonium hydroxide (TAPOH))–NaOH–H_2O. NaOH and TAPBr act as mineralizing and structure-directing agents, respectively. Sand and coworkers [6–9] investigated the effects of synthesis parameters on the crystal growth of ZSM-5. They reported that when a colloidal silica sol was used, large crystals were formed [8], and found that the substitution of sodium

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salts for NaOH as the mineralizing agent is effective for obtaining large crystals [9]. Hayhurst and coworkers [10,11] also reported the effects of TPABr (or TPAOH) and NaOH contents in a reaction mixture on the crystal growth of silicalite-1. On the other hand, Fegan and Lowe [12] investigated the effect of alkalinity on the crystallization of silicalite-1, and found that the size of crystals and their aspect ratio (the ratio of crystal length to width) decrease with increasing NaOH content. From these findings, it has become clear that low alkalinity reduces the rate of the dissolution of a silica (or alumina) source as well as of crystal nucleation; consequently, nuclei can grow into large crystals. Furthermore, a different approach for synthesizing large crystals has been introduced and developed by Guth and coworkers [13–16], who used fluoride ion as a mineralizing agent in place of hydroxide ion in order to reduce the solubility of the silica source in a reaction mixture. This method has many advantages in that crystals obtained in a reaction mixture containing F^- are larger than those usually obtained, and show fewer twinned crystals and intergrowths, which are often observed when an alkaline reaction mixture is used [17–21].

Crystal sizes are also dependent on silica sources. Recently, Shimizu and Hamada [22,23] have synthesized large silicalite-1 crystals using a quartz tube as the silica source. On the other hand, Gao et al. [24] reported that a bulk material of a monocrystalline silicon slice could also be used to obtain large silicalite-1 crystals. The above reports indicate that it is possible to reduce the rate of dissolution of silica source and of crystal nucleation by using a bulk silica source. In the above methods, HF was used as the mineralizing agent. In this study, we synthesized large silicalite-1 crystals from two different silica sources, i.e., fumed silica and a quartz glass plate, and using NH_4F as the mineralizing agent. The use of NH_4F is more favorable than HF due to its ease of handling. We also investigated the effect of the composition of a reaction mixture and reaction temperature on the crystallization of silicalite-1. The purpose of this study is to develop a reliable method for synthesizing large zeolite single crystals.

2. Experimental

2.1. Synthesis from fumed silica

Large crystals of silicalite-1 ($Si_{96}O_{192}$), the aluminum free form of ZSM-5 [25], were synthesized hydrothermally from the system SiO_2–TAPBr–NH_4F–H_2O. Molar compositions of the reaction mixtures used in this study are shown in Table 1. For the syntheses using fumed silica, reaction mixtures A–D were used. NH_4F and TAPBr were dissolved in deionized water and the mixed solution thus prepared was filtered through a membrane filter (0.2 μm in pore-diameter) to remove impurities from the solution. The designated amount of fumed silica (Aerosil 200) was placed in a Teflon-lined stainless autoclave (capacity 50 ml), which was then filled with an aqueous solution containing NH_4F and TPABr. After aging at 25 °C for 1 day, the autoclave was kept in a convection oven controlled at 150 °C for 1–5 weeks. After the hydrothermal reaction, the crystals thus obtained were washed with distilled water and dried at 100 °C.

Table 1
Molar composition of reaction mixtures

Reaction mixture	SiO_2	TPABr	NH_4F	H_2O
A	1.00	0.125	0.250	66.0
B	2.00	0.250	0.500	66.0
C	3.00	0.375	0.750	66.0
D	1.00	0.125	0.125	66.0
E	1.38	0.660	1.080	66.0

2.2. Synthesis from quartz glass plate

Large crystals were synthesized by using a quartz glass plate (30 mm × 30 mm × 3 mm) as the silica source. Reaction mixtures A and E shown in Table 1 were used and the syntheses were carried out at various temperatures, i.e., 150, 180 and 200 °C, for 2 or 5 weeks in order to examine the effects of reaction temperature and reaction mixture composition on the crystal growth. Other procedures are the same as those described in the previous section.

2.3. Analysis of products

The morphology and size of the crystals thus synthesized were studied with an optical microscope (NIKON 72956) equipped with a digital camera (Olympus DP-10) for image acquisition. The crystals obtained were identified on a X-ray diffractometer (Rigaku, RINT-1400) using Cu Kα radiation. For the XRD analysis, the crystals were ground into fine particles, with Si added as an internal standard.

3. Results and discussion

3.1. Large silicalite-1 crystals synthesized from fumed silica

Fig. 1 shows photographs of large silicalite-1 crystals synthesized from various reaction mixtures containing fumed silica; most of the crystals are relatively large compared with those obtained in alkaline reaction mixtures [6–12] and the crystal shape is well defined with few multiple twins and overgrowths. Fig. 2 shows XRD patterns of silicalite-1 synthesized from the reaction mixture A at 150 °C. Diffraction peaks corresponding to silicalite-1 began to appear in the XRD patterns after hydrothermal treatment for 2 weeks and crystallization was almost complete after 3 weeks. A long induction period, as observed in this study, is often reported and is indispensable in the synthesis of large zeolite crystals. It is suggested that the formation of large crystals become more probable if the rate of nucleation

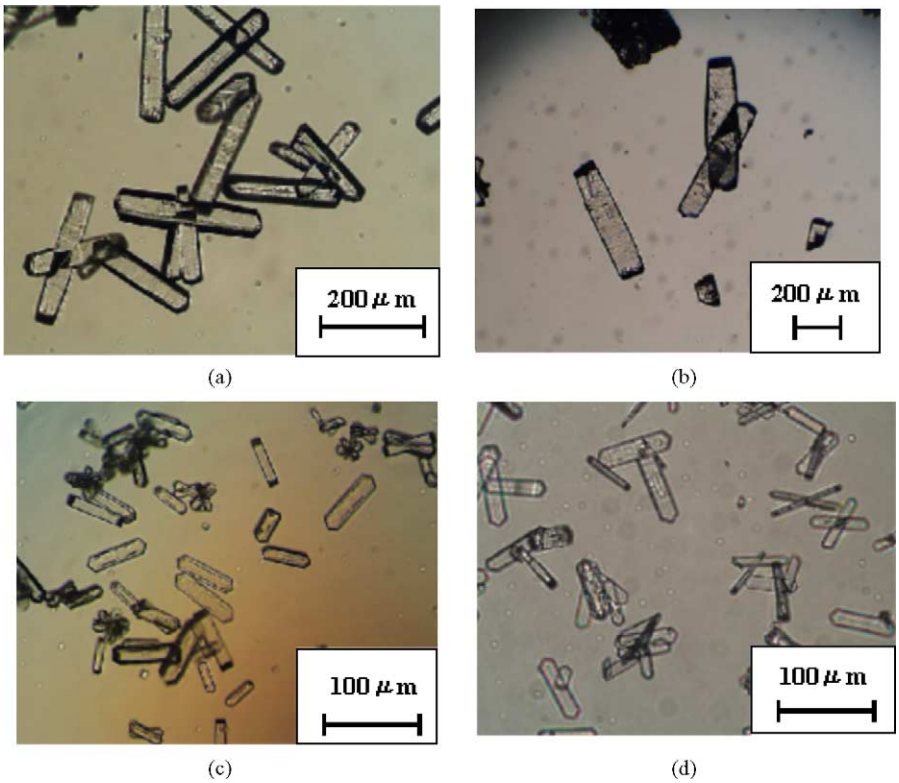

Fig. 1. Photographs of silicalite-1 large crystals synthesized from various reaction mixtures containing fumed silica: (a) reaction mixture A, (b) reaction mixture B, (c) reaction mixture C, (d) reaction mixture D. Each composition of the reaction mixtures is noted in Table 1.

is very low. The powder XRD analysis indicated that the crystals synthesized were single-phase silicalite-1 without any crystalline impurity phases.

Table 2 shows the effect of reaction mixture composition on the crystal size. When the reaction mixture B was used, the maximum crystal size was 690 μm in length. However, the crystal size depended largely on the composition of the reaction mixtures used. In particular, when the concentrated reaction mixture C was used, the maximum crystal size decreased significantly, as compared to those observed for the

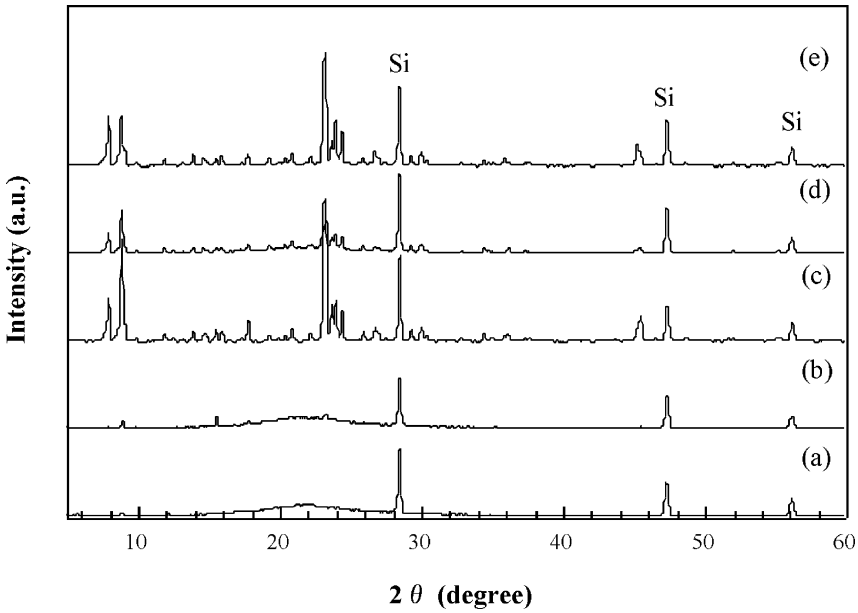

Fig. 2. XRD patterns of silicalite-1 crystals synthesized from reaction mixture A for several weeks: (a) 1 week, (b) 2 weeks, (c) 3 weeks, (d) 4 weeks, (e) 5 weeks.

Table 2
Crystal size of silicalite-1 synthesized from reaction mixtures containing fumed silica

Run No.	Reaction mixture composition	Reaction temperature (°C)	Reaction period (day)	Maximum crystal size (μm in length)
1	A	150	35	380
2	B	150	35	690
3	C	150	35	85
4	D	150	35	80

Each reaction mixture composition is noted in Table 1.

reaction mixtures A and B. It is considered that, in a concentrated reaction mixture, the rate of nucleation is high, preventing nuclei from growing into large crystals. On the other hand, when the NH_4F content was decreased as in the reaction mixture D, the maximum crystal size also decreased. It is known that the crystallization of zeolite occurs via supersaturation of a reaction mixture, crystal nucleation, and crystal growth [26]. Thus the formation of smaller crystals in the reaction mixture D is probably due to an insufficient degree of supersaturation for both nucleation and crystal growth to proceed. This is because when the F^- content is low, nutrients, presumably silicate species resulting from the dissolution of fumed silica, are present in low concentration. The above results confirm that an optimum composition for the reaction mixture exists for synthesis of large zeolite crystals.

Table 3
Crystal size of silicalite-1 synthesized from reaction mixtures containing a quartz glass plate

Run No.	Reaction mixture composition	Reaction temperature (°C)	Reaction period (day)	Maximum crystal size (μm in length)
1	A	150	35	170
2	A	180	35	410
3	A	200	35	330
4	E	180	14	650
5	E	180	35	1800
6	E	200	14	760
7	E	200	35	780

Each reaction mixture composition is noted in Table 1.

3.2. Large silicalite-1 crystals synthesized from quartz glass plate

In order to obtain larger crystals, we used a quartz glass plate in place of fumed silica as the silica source. Fig. 3 shows photographs of crystals synthesized from reaction mixture A containing a quartz glass plate at 150, 180, and 200 °C. Almost all crystals were formed on the surface of the quartz glass plate. The yields and morphology of the crystals depended on reaction temperature; at 150 °C, small crystals were obtained and the yield was very low, as compared to those obtained and attained for fumed silica. On the other hand, when synthesized at 180 °C or 200 °C,

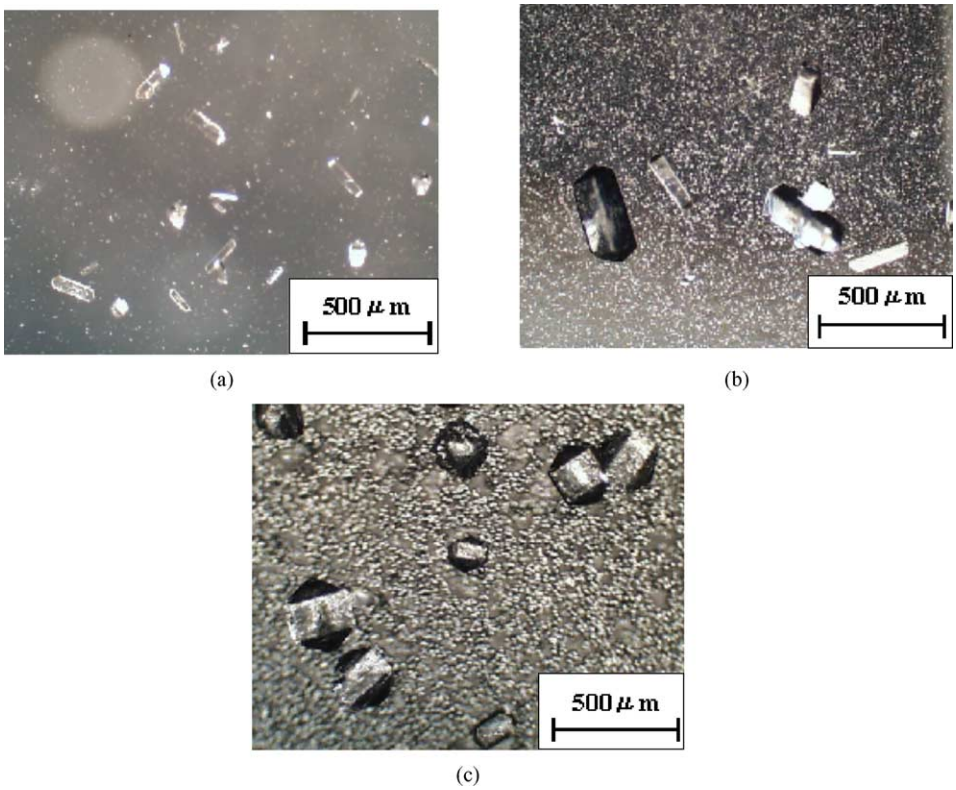

Fig. 3. Photographs of silicalite-1 large crystals synthesized from the reaction mixture A containing a quartz glass plate for 5 weeks at different temperatures: (a) 150 °C, (b) 180 °C, (c) 200 °C.

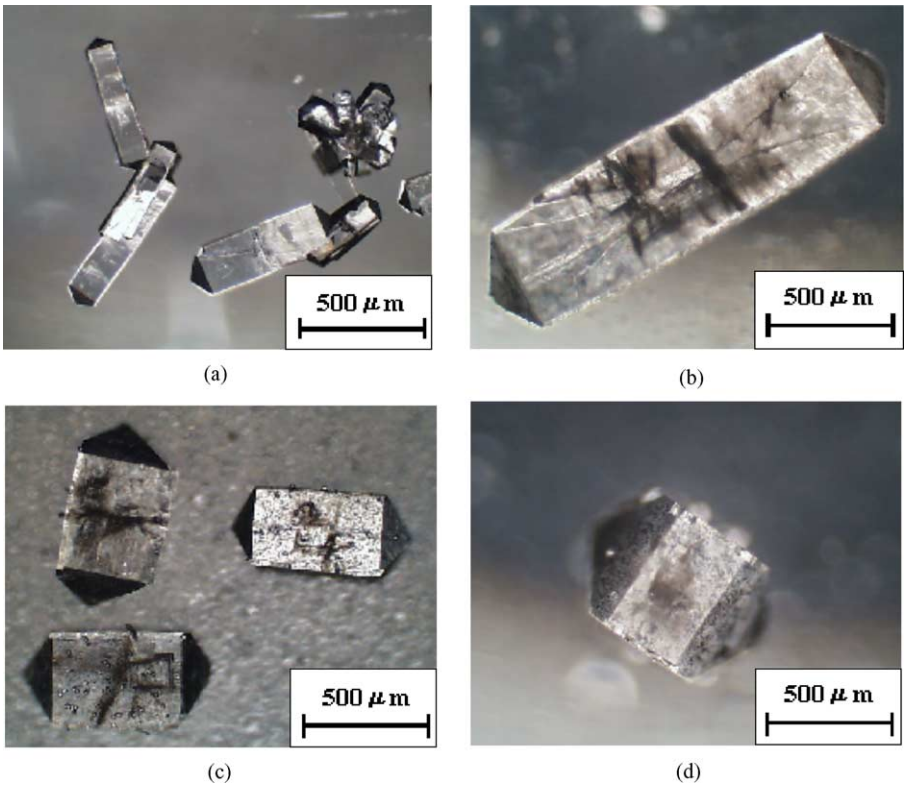

Fig. 4. Photographs of silicalite-1 large crystals synthesized from reaction mixture E containing a quartz glass plate for 2 or 5 weeks at different temperatures: (a) 180 °C, 2 weeks, (b) 180 °C, 5 weeks, (c) 200 °C, 2 weeks, (d) 200 °C, 5 weeks.

crystals grew larger and the yields were much improved. From the facts that large silicalite-1 crystals were synthesized at 200 °C by using a quartz tube or silicon slice in the literature [22–24], it can be assumed that reaction temperatures higher than 180 °C are necessary to effectively dissolve a bulk silica source into a reaction mixture and to attain supersaturation. Furthermore, in order to examine the effect of reaction mixture composition on the crystal growth, the reaction mixture E, which is more concentrated in nutrients than the reaction mixture A, was used. The reaction mixture E was prepared on the basis of the report made by Shimizu and Hamada [22]. Fig. 4 shows the morphology of crystals obtained in the reaction mixture E. The size of crystals became longer and the yield was improved. Moreover, relatively large crystals were obtained at both 180 °C and 200 °C within 2 weeks. Gao et al. [24] reported that the crystal sizes increased with increasing the F^- content in a reaction mixture containing silicon slices. Thus, in addition to higher reaction temperature, sufficient amounts of F^- are required to obtain large crystals when a bulk material is used. However the crystals synthesized at 180 °C have larger sizes and aspect ratio than those synthesized at 200 °C. It has been reported that higher crystal growth rates result in higher numbers of defect sites in growing crystals [20,27], which may adversely prevent the further crystal growth. Therefore the rates of nucleation as well as of crystal growth should be controlled to obtain large crystals by lowering the reaction temperature from 200 to 180 °C. Table 3 summarizes the crystal sizes of silicalite-1 synthesized by this method. The largest crystals of 1800 μm were obtained when synthesized at 180 °C for 5 weeks.

As noted above, the use of a quartz glass plate allows the crystallization of large silicalite-1 crystals. However, the products yields were much less than those attained for fumed silica; for example, 0.012 g of silicalite-1 crystals was obtained per 1.0 g of a quartz glass plate for the synthesis at 180 °C for 5 weeks using the reaction mixture E (Fig. 4). Such a low yield must be mainly due to the extremely small surface area of the quartz glass plate and low rates of nucleation and crystal growth. Furthermore, the reproducibility of the synthesis was relatively low; the surface conditions of a quartz glass plate seem to affect on the crystallization of silicalite-1. Further study is still needed to synthesize large crystals with good reproducibility and improved yields.

4. Conclusions

The following conclusions were drawn from the present study:

1. Large silicalite-1 crystals up to 690 μm were synthesized hydrothermally at 150 °C for 5 weeks from the system, SiO_2–TPABr–NH_4F–H_2O, by using fumed silica as the silica source.

2. Large silicalite-1 crystals up to 1800 μm were synthesized at 180 °C for 5 weeks from an aqueous reaction mixture containing a quartz glass plate, NH_4F, and TPABr. It was found that NH_4F could work as a mineralizing agent for dissolving the quartz glass plate and attaining supersaturation.
3. Reaction mixture composition as well as the nature of silica sources significantly affect on the crystallization of silicalite-1. It is confirmed that the use of a bulk silica source is quite effective for synthesizing large silicalite-1 crystals, presumably owing to its slow dissolution rate in the presence of F^-.

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