CRYSTAL GROWTH OF HIGH SILICA ZSM-5 AT LOW TEMPERATURE SYNTHESIS CONDITIONS

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Abstract—At the temperature of 90°C and under atmospheric pressure, growth kinetics of high silica ZSM-5 was investigated through a long induction, nucleation and crystal growth periods. It was found the entire crystallization mechanism of ZSM-5 seems to be the combined process of the nucleation via solid-solid transformation, intergrowth among seed crystals and the normal growth in the reaction mixture. Nuclei were initially formed on the Si-rich surface of the amorphous intermediates, indicating that the reaction of TPA with Si species was prior to that with Al species. As the reaction time proceeded, various types of intergrowth among the seed crystals were observed along with the crystals growing independently. The intergrowth seems to play a role for forming typical ZSM-5 crystal shapes. And then ZSM-5 crystals further grew in the reaction mixture, so that the bulk Si/Al_2 ratio of crystals approached that of the initial reaction mixture.

INTRODUCTION

The nucleation and crystal growth mechanisms of various zeolites have been investigated extensively last over 20 years. Ciric [1968] and McNicol et al. [1966] have proposed a solid-solid transformation from the surface of amorphous silica gel into crystalline zeolites. In contrast, Kerr [1966], Cournoyer et al. [1975], Ueda et al. [1980] and Padovan et al. [1984] have suggested that zeolite crystals in the synthesis of various types of zeolites are formed from the solution. Furthermore, Deruane et al. [1981] have reported that two different mechanisms are observed depending on the working materials and their contents, i.e. silica sources, Si/Na, Al/Na and (Si+Al)/TPA ratios etc., in ZSM-5 synthesis. Here TPA represents the tetrapropyl ammonium ion, which is frequently used as a templating agent. Therefore, the proposed growth mechanism of zeolites has been controversial and has remained a long-term problem.

In general, studies on the crystallization of ZSM-5 have been performed in the hydrothermal autoclave reactor under the autogeneous pressure and at the high temperature of 150-300°C [Narita et al., 1985; Minotova et al., 1993; Lermar et al., 1985; Konatowski, 1988]. In this environment, a precise observation of the growth kinetics of zeolites may be prevented due to the rapid crystallization. Therefore, a detailed investigation on the nucleation during crystallization of ZSM-5, which might provide insight for the growth mechanisms of zeolites, has been very few to date.

Recently, we have manufactured ZSM-5 zeolites at atmospheric pressure and the temperature of 100°C and have examined mainly the effect of crystallization time on the physico-chemical properties of zeolites [Suzuki et al., 1987, 1988]. In the present study,

as an extension of the previous works, we have synthesized ZSM-5 under atmospheric pressure with the temperature as low as 90°C. The reaction conditions adapted in this experiment are expected to provide a long induction period of crystallization and, thus, enable us to investigate the entire crystallization processes precisely. In this article, the growth kinetics of ZSM-5 crystals will be discussed to analyze mainly the initial stage of the crystallization.

EXPERIMENTAL

The synthesis method of the ZSM-5 used in this study was similar to that given by our previous articles [Suzuki et al., 1987, 1988]. As sources of silica, aluminum and alkali, silica sol (Cataloid SI-30, Catalysis and Chemicals Co., 30 wt% of SiO_2 with water), $Al(NO_3)_3 \cdot 9H_2O$ and NaOH were used, respectively. Tetrapropyl ammonium bromide (TPABr, Wako Pure Chemicals Co.) was selected as a templating agent.

Mole ratios of the reaction mixture were chosen as $Si/Al_2=350$, $OH/Si=0.1$, $TPA/Si=0.1$ and $H_2O/Si=41$. The reaction mixture was agitated for an hour at room temperature. And then the uniformly mixed solution was then transferred to a 1000 ml round flask made of Teflon, in which a long glass capillary tube was attached for reflux. Here the glass capillary was open to air. The flask containing the reaction mixture was placed in a constant temperature bath, with continuous stirring by a magnetic bar. The bath was maintained at the temperature of 90°C through the experimental run of 400 hours (about 17 days). Samples were taken as a function of the reaction time and were characterized by the following procedure.

The pH of each sample was measured at room temperature when a pH meter (M620, Fisher Co.) indicated a steady state

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and viscosity was also measured with a viscometer (Haake Co.). And then the solid and liquid phases were separated by using a centrifuge followed by the filtering papers. Si and Al compositions in the liquid phases were determined by atomic absorption (Hitachi Co.). The solid phases were washed with the distilled water and dried for 16 hours under the reduced pressure at 25℃.

Degree of the relative crystallinity of the solid phases was determined using a X-ray Diffractometry (PW1710, Philips Co.) with a monochromatic CuKα radiation, comparing with a selected reference sample. In addition, a Fourier Transform Infrared Spectrometer (FTIR: MB-102, Bomen Co.) was used to determine the crystallinity of samples by the KBr pellet Technique [Lee, 1992]. The morphological changes and crystal sizes of the solid samples which were coated with gold, were observed and measured by using a Scanning Electron Microscopy (SEM : S-800, Hitachi Co.).

To determine the amounts of TPA ion, Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out with a heating rate of 10℃/min in air flow. The air flow rate was controlled by a Mettler TA3000 system. Bulk and surface contents of Si and Al in the solid phases were determined by a X-ray Fluorescence Spectroscopy (XRF : Rigaku Co.) and an Energy Dispersive X-ray Analyzer (EDX : Kevex Delta Co.), respectively.

RESULTS AND DISCUSSION

1. Crystallinity, pH and Viscosity

Under the present conditions for the ZSM-5 synthesis, S-shaped curves of crystallinity have been obtained by XRD and IR analyses, as shown in Fig. 1. Both curves (T=90℃) clearly show the very long induction and nucleation periods followed by the crystal growth period. Based on XRD-crystallinity in Fig. 1, the induction period is estimated to be about 1 day and the nucleation period (about 20 % crystallinity) is elongated for the following reaction time of 2 days (total about 70 hrs). And then crystallinity increases and reaches the maximum value after about 7 days (total about 240 hrs). Therefore, as the reaction proceeded (as the degree of crystallinity increased), the reaction mixture, initially in turbid state, was observed to change to a clear solution, and gradually to a milk-like suspension state. Note that the entire crystallization process in the conventional hydrothermal conditions of 160℃ is terminated within 5 hours, with the same reaction mixture used in the present experiments, as can be seen from Fig. 1.

It is interesting that the variations of pH and viscosity of the reaction mixture with the reaction time are consistent with those of the crystallinity curves as shown in Fig. 2. The magnitude of the pH change of the reaction mixture was measured to be approximately 0.5 through the crystallization process. The pH of the reaction mixture was measured to drop from 11.55 to 11.35 at the induction period and the value of 11.35 remained during the nucleation period. Finally, as degree of crystallinity increases, the pH increases monotonically with a similar slope of crystallinity curves and reaches the maximum value of about 11.8. Lowe [1983] has discussed the behavior in pH when high silica zeolites are synthesized under the hydrothermal conditions. Our measurements of the pH change support the possibility of the pH change as an indicator for the progress of the zeolite crystallization, as the proposed by Lowe. Viscosity of the solution also shows qualitatively similar trend with pH change as can be seen from Fig. 2.
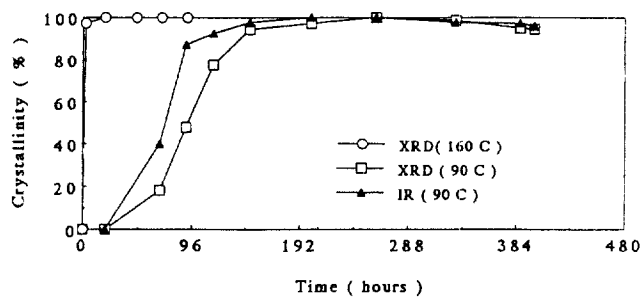

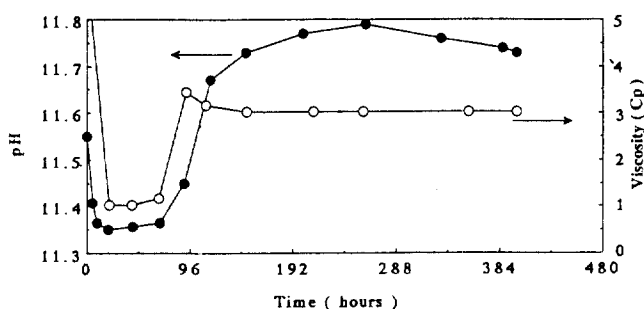Fig. 1. Degree of crystallinity with the reaction time.

Fig. 2. pH and viscosity change of the reaction mixture with the reaction time.

2. Growth Mechanisms

Fig. 3 illustrates series of microphotographs of solid phases taken by SEM as a function of the reaction time: 0, 5, 20, 48, 68, 91, 115, 260, 330 and 400 hours. Fig. 3A is an image of the initial reaction mixture. Round particles observed here are seemed to be the undissolved silica sol with the size of 150-200 μm. For the convenience, let us divide the entire crystallization process into three periods : the induction, nucleation and crystal growth periods.

2-1. The Induction Period

As the reaction time elapses (about 5 hours), one can easily observe that the tiny particles are twinkling in the reaction mixture under the electric light. These particles are shaped like lamellae with the size of about 800-1000 μm, as shown in Fig. 3B. The formation of lamellae might be explained as the following manner. As soon as the flask with the reaction mixture is placed in the constant temperature bath, the temperature of the solution will rise slowly to the pre-setted temperature of 90℃. Then the surface of agglomerates of undissolved silica will start to melt and collide each other by the mechanical force generated by the magnetic bar. In this circumstance, silica particles seem to stick together and deform to lamella-like shape under the existence of sodium and TPA ions which can easily be incorporated with the silica surface.

Further the reaction time passes (20 hrs), it is observed that the size of lamellae is reduced to the order of microns with the decreasing pH of solution, indicating the incorporation of Na ions into silica network. The change in morphology also is noticeable as shown in Fig. 3C. At this period, Si content in the liquid phases was found to decrease rapidly and the solid intermediates were found to be highly siliceous. In the EDX analysis given in Table 1, Si/Al_2 ratio of the surface of the lamella structure is shown to be about 1000. This value is 3 times higher than that of the initial reaction mixture. Therefore, it is considered that the solid
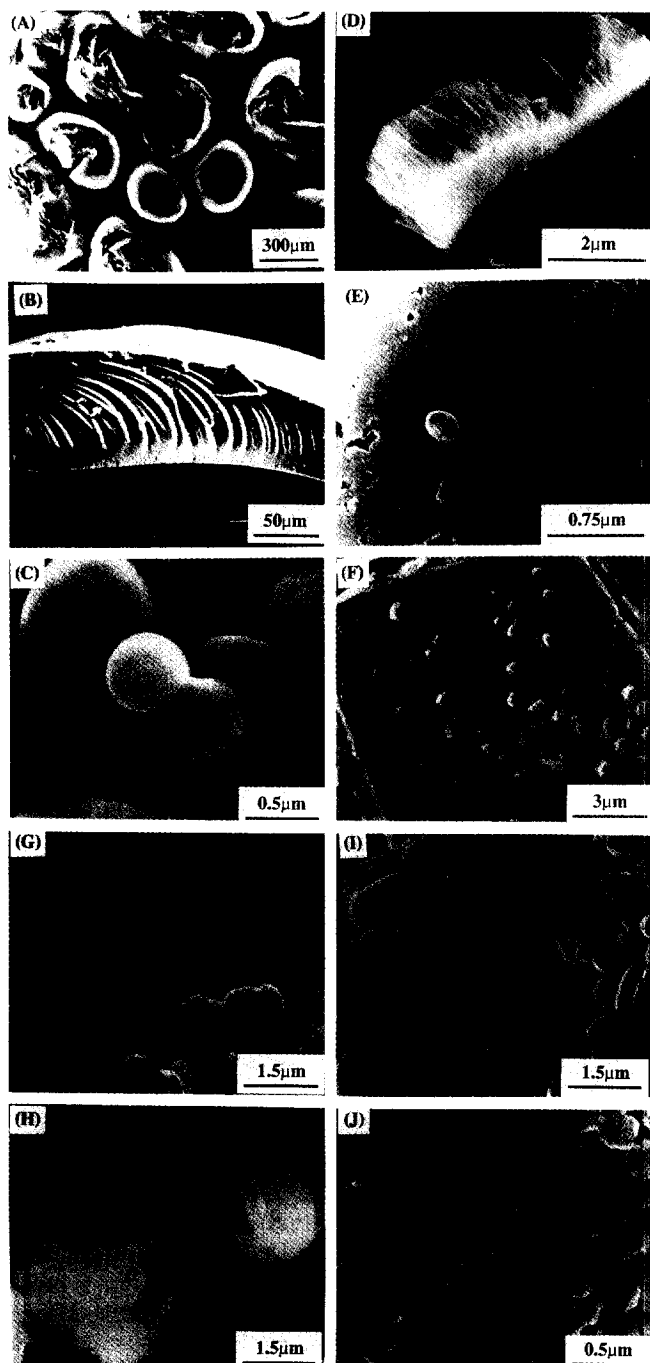
Fig. 3. Morphological change of the solid phases with the reaction time.

(A) 0 hr, (B) 5 hrs, (C) 20 hrs, (D) 48 hrs, (E) 68 hrs, (F) 91 hrs, (G) 115 hrs, (H) 260 hrs, (I) 330 hrs, (J) 400 hrs

Fig. 4. XRD and IR spectra with the reaction time.
(A) XRD, (B) IR

phases mainly compose of Si-rich phases.

As shown in Fig. 4, the lattice vibration bands of ZSM-5 crystals are observed at 550 cm⁻¹ and 1220 cm⁻¹ when FTIR spectroscopy is used to determine the degree of crystallinity. 550 cm⁻¹ band is assigned to distorted D_5R unit in the crystal framework and 1220 cm⁻¹ to the external vibration modes of chainlets of tetrahedra. Therefore, the lack of the 550 cm⁻¹ band at the induction period (Fig. 4B) indicates that the structure of the lamellae observed during this stage is in the amorphous state. The crystallinity
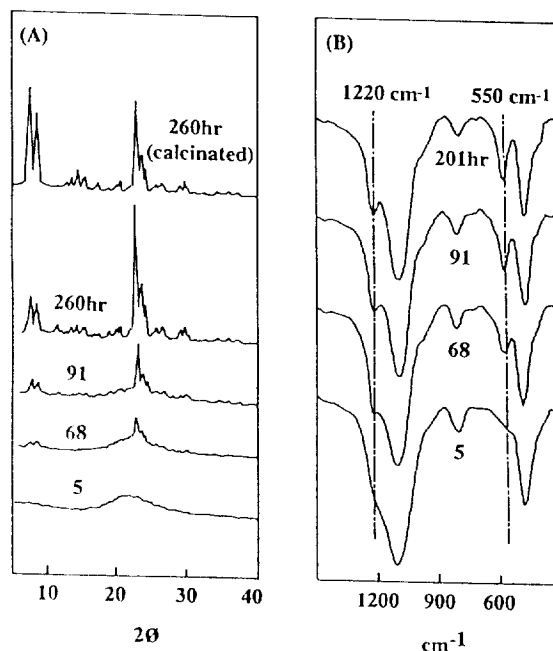
obtained by XRD and IR through the induction period (about 20 hrs), as shown in Fig. 1, clearly supports that any crystal structure does not exist.

2-2. The Nucleation Period

In the reaction mixture of 2-days, the family of dense flat intermediates were observed to be formed as shown in Fig. 3D. The degree of crystallinity measured by XRD and IR (Fig. 1) are shown to be 10 and 20%, respectively. The morphology of these flat intermediates is different from that of the lamellae observed during the induction period (Fig. 3B and 3C). Therefore, it is unlikely that the small round particles shown in Fig. 3C have been transformed directly to the flat intermediates of Fig. 3D.

At the reaction time of about 68 hours (Fig. 3E), numerous bead-aggregates with the size of about 0.05 μm begin to appear on the Si-rich surface of the flat intermediates and the degrees of the XRD and IR crystallinity were about 20 and 40%, respectively. It is noteworthy that the degree of crystallinity from IR measurements is shown to be always higher than that measured by XRD at this stage. The ability of IR spectra in the detection of crystalline structure is known to be very sensitive even to small amount of short-distance ordered structure in the solid phases, which is not easily detected by an X-ray diffraction. Therefore, higher values of crystallinity by IR imply that large amount of solid phases is in short-distance ordered structure rather than long-distance ordered structure observed in the complete crystalline phases. Consequently, the crystallinity detected by IR indicates that tiny nuclei of seed crystals of zeolites considered to be already formed at the reaction time of about 30-50 hours, which may be less than submicrons in size or have short-distance ordered structures in amorphous intermediates. A discrepancy of the crystallinity of zeolites in XRD and IR has been reported in elsewhere [Jacobs et al., 1981]. At this stage, nucleation in solution phase seems to be difficult to form, because ²⁹Si NMR spectra of solution exhibit Q_0 and Q_1 species which do not form
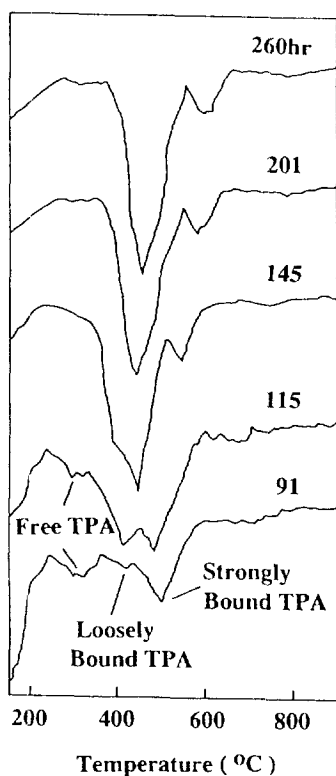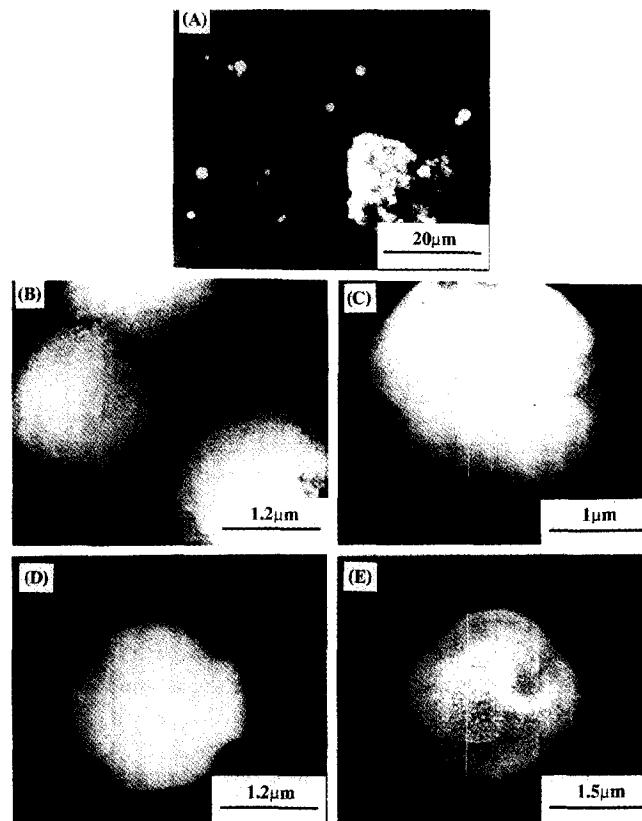
Fig. 5. DTA spectra with the reaction time.

Fig. 6. Various types of intergrowth of ZSM-5 seed crystals.

Table 1. Elemental analysis data with the reaction time

Reaction time (hours)	SiO₂/Al₂O₃ at surface (EDX)		SiO₂/Al₂O₃ of bulk (XRF)	Particle size (μm)
	Intermediate	Crystal		
0	350*	-	-	-
20	968-1033	-	-	-
68	985-1027	-	-	0.01-0.09
91	50-120	589-∞	481	0.05-0.35
115	52-129	308-671	427	0.90-1.10
260	-	57-150	377	0.30-2.75
400	-	55-119	370	0.02-0.70

*Initial SiO₂/Al₂O₃ Ratio of The Reaction Mixture

secondary building units for nucleation [Jacobs, et al., 1981; Lee, 1992].

Fig. 5 illustrates the results of DTA analyses of the solid samples with the reaction time under atmosphere. There are various forms in TPA ions incorporated on the solid gel at the early stage of crystallization, namely free TPA, loosely bound TPA and strongly bound TPA [Szostak, 1989]. It seems that the binding state of TPA ions on solid tend to change continuously to perfect crystal structure by the rearrangement of TPA ions inside the solid particles, even at higher crystalline states (50-97% crystallinity).

At the stage of the reaction time of around 90 hrs, seed crystals were found to be highly siliceous with Si/Al₂ ratio of higher than 600, as can be seen from the EDX analysis (Table 1). However, Si/Al₂ ratio of intermediate particles is shown to be reduced to the range of 50-120. These values are much smaller than the initial Si/Al₂ ratio of 350. Therefore, it is understood that nucleation of ZSM-5 crystals is preferentially occurred on the silica spe-

cies bound with TPA ions. As a result, silica crystals are formed at the initial stage and some Al species are gradually incorporated on the silicate structure.

Once numerous seed crystals are formed, some parts of them may be detached from amorphous solid gel and may be resolved into the reaction mixture. On the one hand, the last will survive and develop to ZSM-5 crystals, as shown in Fig. 3F. In this stage, we have observed the complex interaction among seed crystals before they grow with typical growth habit. Fig. 6A shows various types of intergrowth observed in this period. A part of the intergrowing seed crystals looks to be porous (Fig. 6B and 6C) and some parts may be in more dense state. Therefore, we speculate that the seeds which have locally-ordered structure (Fig. 6D and 6E) further grow by intergrowth mechanism and are crystallized by structural rearrangement both in the solid phase and in the solution, as similar mechanisms observed in the high temperature sintering studies of oxide materials [Kingery et al., 1976; Brinker and Scherer, 1990].

Sintering phenomena with a reactive liquid could be analogous to our system. The driving force for intergrowth among the fine particles with submicrons in size is different from that of large particles, because of the different boundary area and interfacial energy with grain size. During the intergrowth process, short-distance ordered phases can be transformed into more densified phases, viz. long-distance ordered ZSM-5 structure which is thermodynamically more stable in the liquid-solid phase. As shown in photographs of Fig. 3, most of nuclei (Fig. 3E) are shown to be spheroidal shapes and typical morphology of ZSM-5 crystals (Figs. 3F, 3G and 3H) is emerged after intergrowth stage. Therefore the intergrowth mechanisms may be partly responsible for
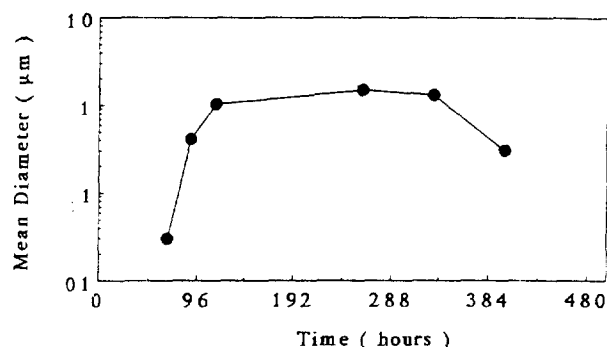
Fig. 7. Crystal size with the reaction time.

Fig. 8. The proposed crystallization process of high silica ZSM-5.

rapid growth rate of crystals observed at nucleation stage and then growth rate will be slow down, as can be seen in Fig. 7. During this period, pH in solution is increased with the similar trend of the crystallinity as shown in Fig. 1. The increase of pH at this period may be attributed to the surface dissolution of ZSM-5 crystals.

2-3. The Crystal Growth Period

At around 5 days of the reaction, the spheroidal twined ZSM-5 crystals are observed to be formed and the intermediates are also found to exist simultaneously as can be seen in Fig. 3G. Consequently, these crystals further grow over 2 μm in size, with fully-developed shapes during the following 5-6 days. At this period, it was found that Si/Al_2 ratio of the surface of the twined crystals was rapidly reduced to 308-671 (corresponding to Fig. 3G) and that of the amorphous intermediates was in the range of 52-129. Therefore, it can be said that the ZSM-5 crystals are still highly siliceous, but Si contents have been dropped with time by a factor of more than 2. This result is consistent with the expectation of the reactivity of the Si with TPA as discussed in the nucleation period.

Fig. 3H illustrates typical image of the fully-developed ZSM-5 crystals taken at the reaction time of 260 hrs (about 11 days). As expected, it was found that the degree of crystallinity of this sample was in the maximum value, as shown in Fig. 1. In this stage any Al-rich amorphous intermediate was not observed, and the surface of ZSM-5 crystals was found to be in Al-rich state (Si/Al_2 ratio is in the range of 57-150, Table 1). Therefore, inferring from the observation, the disappearance of the intermediates suggests that the Al-rich amorphous phases are dissolved into the reaction mixture again, and Al components are continuously transferred to the surface of ZSM-5 crystals rather than direct transportation from the solid intermediates.

During this stage, Al contents of crystals measured by XRF, which represents bulk contents of the solid phases, have been observed to increase slowly as can be seen from Table 1. Therefore, it is difficult to say that Al-rich amorphous phases are directly transformed to ZSM-5 crystals at this period. This is not consistent with the crystallization mechanisms by the solid-solid transformation proposed previously [Ciric, 1968; McNicol et al., 1966].

In the present conditions of ZSM-5 crystallization, it is expected that the about 10-11 day is the optimum reaction time for catalyst performance and stability when conjecturing as the way reported by Suzuki et al. [1987, 1988]. In their reaction condition of 100℃ (10℃ higher than that of the present work), ZSM-5 crystals obtained with the crystallization time of 8 days have been shown to
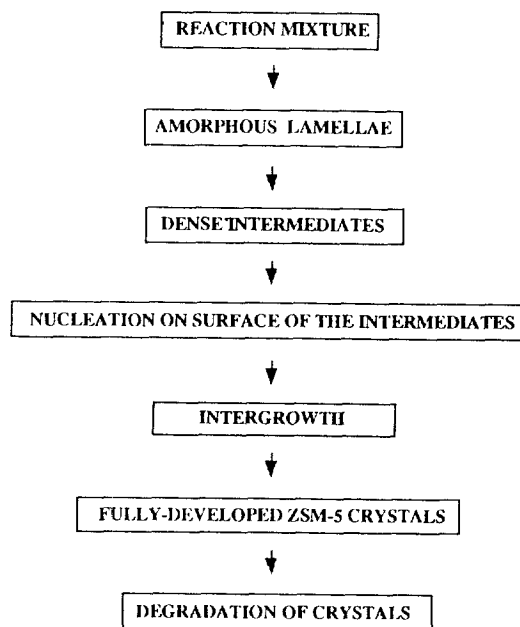
have the longest life time in the methanol conversion tests.

As the reaction proceeded further (over 260 hours), crystal size tends to decrease and shapes tend to degrade as shown in Figs. 3I and 3J. Thermodynamically, it is well known that the ZSM-5 crystals are in a metastable state. Therefore, the morphological change (Figs. 3I and 3J) with size reduction of crystals (Fig. 7) may be explained as the phase transformation process of ZSM-5 to more stable form, probably a-quartz. In summary, schematic diagram of the ZSM-5 crystallization process, based on our observation, is illustrated in Fig. 8.

CONCLUSIONS

We observed the entire crystallization process of ZSM-5 in detail at 90℃ and atmospheric pressure. From the observation of the long induction and nucleation processes during the ZSM-5 crystallization, we found that the growth mechanisms of the ZSM-5 crystals can not be limited to either the solid-solid transformation or the growth from the solution, contrary to the reported previously.

Initially, the thin lamella-like particles were formed. However, these particles were amorphous and they were soon remelted and/or destroyed. We could not notice that the lamellae played a role during crystallization in the present reaction conditions. After this stage, the dense intermediates were appeared and were found to consist of Si-rich phases. Consequently, numerous seed crystals were appeared on the Si-rich surface of the intermediates as the reaction time elapsed. Through the nucleation and early crystal growth periods, various types of intergrowth were observed. And then small ZSM-5 crystals with the normal growth habit enlarged further in the reaction mixture with no solid intermediate. It was found that the bulk ratio of Si and Al species approached that of initial reaction mixture. From the present observation, we speculate that ZSM-5 crystals manufactured under the hydrothermal synthesis conditions of elevated temperature go through similar growth steps discussed, but, very rapidly.

In addition to the normal growth of zeolite crystals, we have considered that the intergrowth among seed crystals of submicrons is also the important mode for the formation of typical ZSM-5 crystals at the nucleation and early stage of crystal growth periods. However, the mechanism of intergrowth has not been well investigated so far because of the difficulty in precise observation. Currently we are focusing attention on the relationship between the intergrowth phenomena and growth kinetics of ZSM-5 crystals.

ACKNOWLEDGMENTS

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