

Synthesis of MFI-Type Zeolites Under Atmospheric Pressure

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Abstract—Silicalite and highly silicious ZSM-5 were synthesized using two reaction mixtures with different crystal growth environments, a dispersed low density mixture and a separated high density mixture, at 93 ± 3 °C under the atmospheric pressure. Nucleation behavior and the transformation process of two mixtures were investigated utilizing various analytical techniques such as XRD, FT-IR, TGA, SEM, and pH measurement. During the induction period, the same intermediate phase was observed in both mixtures. The presence of this phase was found to be dependent on the degree of dilution of the reaction mixture. After the induction period, a sharp increase in both the degree of crystallization and the pH of the reaction mixture was detected. This indicates that the pH change in the reaction mixture is closely related to the crystallization process. From these observations, a crystallization mechanism is proposed on the basis of the appearance of stable silicate species and the role of OH⁻ ions during the induction period. According to this mechanism, MFI-type zeolite grows by condensation reaction among the stable silicate species formed during the induction period.

Key words: ZSM-5, Silicalite, Crystallization, Low Temperature, Atmospheric Pressure

INTRODUCTION

Zeolites have been widely used in the fields of heterogeneous catalysis and adsorption/separation [Woo et al., 1987; Sie, 1994; Fajula and Plee, 1994; Connor et al., 1996; Park et al., 1997]. In recent years, ZSM-5 films and membranes have been applied to sensing of molecules and membrane separation [Oh et al., 1997; Fukui and Nishida, 1997; van de Graaf et al., 1998; Burggraaf et al., 1998]. In order to have more beneficial effects on the application of ZSM-5 films and membranes, there have been a large number of studies to control the orientation of ZSM-5 crystals, the crystal morphology and the degree of intergrowth. Some of the experimental data on zeolite synthesis are obtained from autoclave reactors at high temperatures and pressures because the process of zeolite crystallization is thermally activated [Kim et al., 1989; Chung et al., 1992]. Under these conditions, however, it is rather difficult to observe the individual steps of zeolite crystallization due to the relatively fast crystallization rate.

Cundy et al. [1990] and Kiyozumi et al. [1996] directly measured the crystal growth rate and nucleation behavior of silicalite at 368 K. They observed that nucleation was not confined to an initial induction period but carried on through the crystallization region. Kim et al. [1997, 1998] reported the synthesis and characterization of ZSM-5 prepared at low temperature and atmospheric pressure. Cundy et al. [1995] also synthesized ZSM-5 using a semicontinuous reactor and controlled over growth and nucleation by regulating the supplied nutrient. Highly effective supersaturation is accompanied by the high silica levels in the reaction sol, and this suggests that the resulting rapid increase in the nucleation rate is a primary process. At long reaction times, a tendency of broadening in cry-

stal size distribution with low gel-silica level in the sol phase may be referred to as a secondary process.

Casci and Lowe [1983] proposed a simple equilibrium model to explain the change in pH that occurred during the crystallization of high silica zeolites from gels. The model shows that the greatest increase in pH is associated with the most stable zeolite. Corkery and Ninham [1997] synthesized a stable colloidal TPA-silicalite-1 suspension at 308 K. At this relatively low temperature, the precipitated silica dissolved via slow depolymerization, and this dissolved silica was templated by the TPA⁺/H₂O structure to yield 5-10 nm germ nuclei, most of which fused syntaxially with other nuclei and grew to ca. 55 nm diameter single-crystal colloidal TPA-silicalite-1 particles. The ca. 55 nm particles were stabilized in solution by glassy surfaces rich in hydroxyl groups, and had an interfacial area indicative of much smaller constituent sub-particle (5-10 nm).

The purpose of this study is to systematically examine the crystallization process of MFI-type zeolite, and to elucidate key factors controlling the crystallization process at atmospheric pressure. Silicalite and siliceous ZSM-5 were synthesized at below 100 °C under atmospheric pressure. Under these conditions, synthesis of the MFI-type zeolite requires a longer crystallization time, and is expected to provide a good basis for identifying key factors in the synthesis.

Each of the transformation steps from an amorphous mixture to the ZSM-5 crystalline phase was investigated using various characterization techniques such as XRD, FT-IR, TGA, and SEM. In addition, the pH of the reaction mixture was measured throughout the entire course of the process.

EXPERIMENTAL

1. Materials

Aqueous mixture of the following compounds were used for the

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Table 1. The molar composition of initial reaction mixtures

Mixture	Si/Al	OH ⁻ /SiO ₂	TPA ⁺ /SiO ₂	H ₂ O/SiO ₂
Lu-200	200	0.2	0.4	34
Lu-Si	Silicalite	0.1	0.1	80

synthesis of zeolites; Ludox AS-40 (Dupont, 40 wt% colloidal silica in water), NaOH, tetrapropyl ammonium bromide (TPABr, Fluka), NaAlO₂, and distilled water.

Two mixtures of different compositions were used and the compositions are shown in Table 1.

Jansen [1991] classified the crystal growth environments for the zeolite crystallization into four categories: (1) clear solution; (2) dispersed low density gel; (3) separated high density gel; and (4) solid phase. In this study, the reaction mixture environment of Lu-200 is near to the third category (3) and that of Lu-Si is close to the second category (2). The former was a concentrated reaction mixture (H₂O/SiO₂=34) whereas the latter was a dilute reaction mixture (H₂O/SiO₂=80). Also, the TPA⁺/SiO₂ ratio of the former is higher than that of the latter.

2. Synthesis of ZSM-5 and Silicalite-1

Ludox AS-40 was added to the basic aqueous solution of NaOH and TPABr with stirring at room temperature. After vigorous stirring for 2 h, the resulting mixture was poured into a quartz flask. The flask was connected with a condenser so that the evaporated vapor could be condensed and recycled to the flask. The Lu-200 was prepared by adding NaAlO₂ to the mixture of Ludox AS-40, NaOH and TPABr. Crystallization was carried out for 8 days in the flask heated at 93±3 °C with stirring. Samples of 15 ml were withdrawn from the flask for analysis.

3. Characterization

The pH of the samples withdrawn was measured at room temperature. After measuring the pH, the mixtures were directly dried at 110 °C because the solids in the reaction mixtures were not completely precipitated.

Phase identifications of the solids were performed by using X-ray diffractometer (Rigaku, D/max II-A) equipped with an Ni-filtered monochromatic CuK_α radiation from a tube at 45 kV and 30 mA. The degree of crystallization was evaluated from the characteristic peak heights of ZSM-5 (2θ=22-25°) in the X-ray powder diffraction (XRD) patterns [van Hoff and Roelofsen, 1991]. The reference sample was chosen as the solid sample having the highest diffraction intensity among the solids synthesized from the same reaction mixture. Thus, the crystallinity of zeolite synthesized was defined as follows:

$$\text{Crystallinity (\%)} = \frac{\text{Sum of peak heights (unknown)}}{\text{Sum of peak heights (reference)}} \times 100$$

In addition, infrared spectra of solid samples were measured with FT-IR spectrometer (Midac FT-IR) to observe the growth of ZSM-5 structure. Spectra were recorded in the range of 4,000-400 cm⁻¹ and the intensity ratio of the absorption bands at 540 and 450 cm⁻¹, respectively, was used for the measurement of the crystallinity of the samples [Condurier et al., 1982].

Scanning electron microscopy (SEM, Jeol JSMT-200) was employed to observe the morphology of the samples. Thermogravimetric analysis (TGA, Perkin-Elmer TGA7) was also performed at

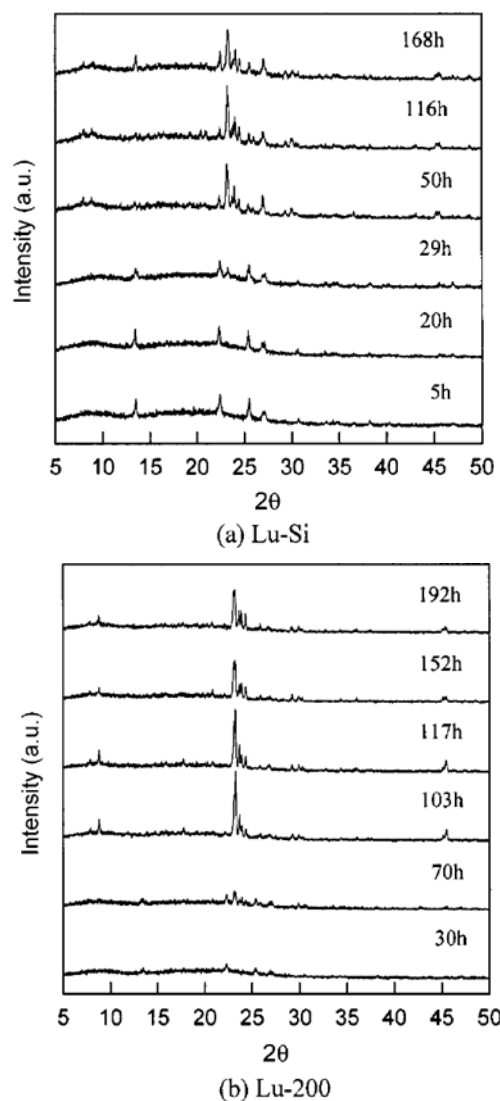


Fig. 1. XRD patterns of samples taken from the reaction mixtures at various intermediate times as the crystallization proceeds.

the range of 50-600 °C in an air flow with heating rate of 10 °C/min.

RESULTS AND DISCUSSION

1. XRD Analysis

The XRD patterns taken from the samples, Lu-200 and Lu-Si, collected at various intermediate times are presented in Figs. 1(a) and 1(b). At the initial stage, the same intermediate phase was observed in both of the samples. The intermediate phase was formed earlier in the mixture Lu-200 than in the Lu-Si because of the higher pH and concentrations of silicate and TPA⁺ (H₂O/SiO₂=34, TPA⁺/SiO₂=0.4). In addition, this intermediate phase did not disappear even after ZSM-5 was fully developed. In case of the dilute mixture, Lu-Si (H₂O/SiO₂=80, TPA⁺/SiO₂=0.1), this phase disappeared when silicalite-1 began to crystallize. Similar XRD patterns were observed from the silicalite synthesized by Beelen et al. [1997]. This result indicates that the intermediate phase is formed regardless of the presence of Al species in the reaction mixture and it is more

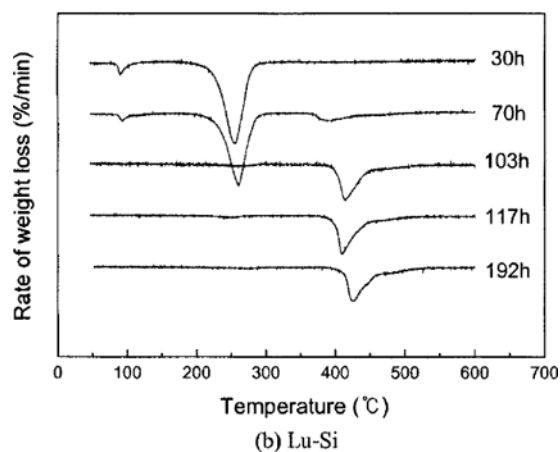
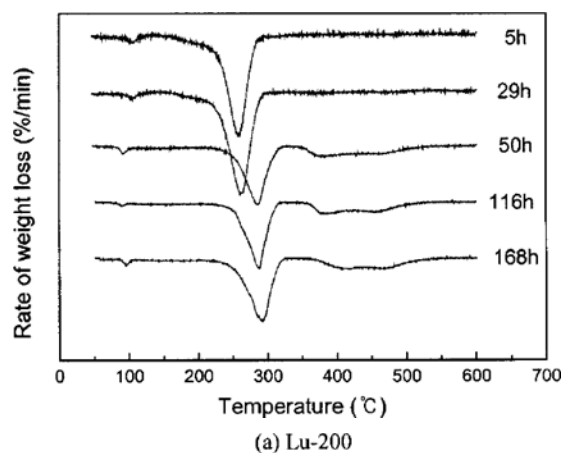


Fig. 2. DTG curves of samples taken from the reaction mixtures at various intermediate times: (a) Lu-200; (b) Lu-Si.

stable in the concentrated than in the dilute solution.

2. Thermal Analysis

Thermal gravimetric analyses conducted on the samples taken at various intermediate times are shown in Fig. 2(a) and Fig. 2(b). Information regarding the incorporation of TPA⁺ cation in the solids can be found from the literature [Scholle et al., 1985; Perez et al., 1987; Testa et al., 1997]. From these analyses weight losses at three different temperature ranges were observed: I. below 160 °C; II. 160-335 °C; and III. above 335 °C. The weight loss in the range I results from water desorption whereas the weight losses in the ranges II and III are related to the decomposition of organic materials [Derouane et al., 1981; Yi and Ihm, 1993]. In the case of Lu-Si, desorption of water (range I) and organic material (range II) from the intermediate phase was detected at the early stage (<103 h) as shown in Fig. 2(b).

The peak at low-temperature (range II) is brought about by the decomposition of loosely bound TPA⁺ cations in the intermediate phase, which neutralize silicate anions. This intermediate phase is completely changed into a silicalite phase. The desorption of organic material from the silicalite occurred at about 400 °C. These data suggest that TPA⁺ cation is occluded strongly in the silicalite. This broad decomposition peak at high-temperature (range III) is mainly ascribed to strongly bound TPA⁺ cations in ZSM-5 structure, which neutralize negative charges from Al species in the ZSM-5 framework. This implies that the intermediate phase is composed

of silicate species and TPA⁺ ion, which is confirmed by the results of XRD analysis and increase in the bond strength of the TPA⁺ with the crystallization time. Burkett and Davis [1994] observed by ¹H-Si CP MAS NMR that the close interaction between the TPA⁺ ions and silicate species was established during heating of the synthesis gel but prior to the development of long-range crystalline order.

In the sample Lu-Si, however, water desorption (range I) was not observed in the silicalite but in the intermediate phase. The states of the TPA⁺ cation in the intermediates formed from the samples Lu-200 and Lu-Si, respectively, are similar to each other because desorption temperatures are nearly the same. However, desorption temperature of TPA⁺ cation in ZSM-5 structure was lower than that in the silicalite as shown in Fig. 2(a). This indicates that the environment of TPA⁺ cation in the ZSM-5 structure is quite different

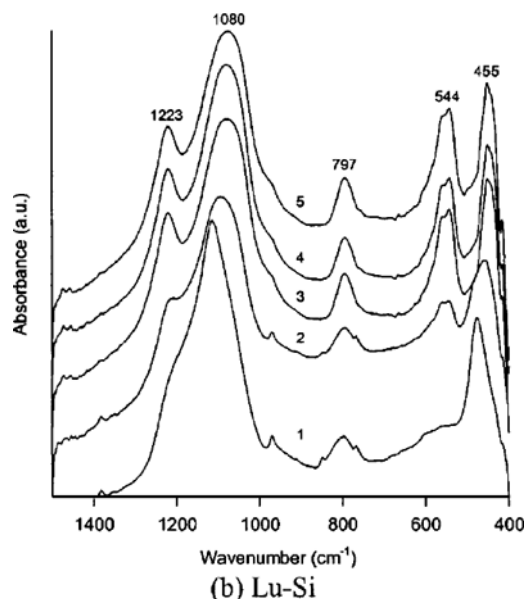
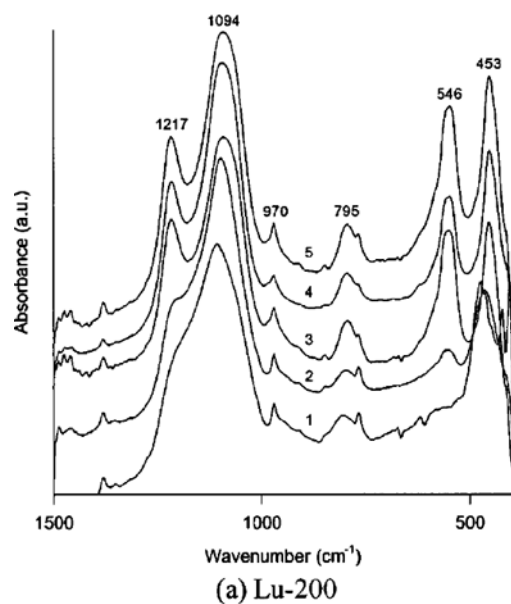


Fig. 3. The time evolution of the IR absorption spectra of samples (a) Lu-200: 1. 5 h; 2. 29 h; 3. 50 h; 4. 116 h; 5. 168 h; (b) Lu-Si: 1. 30 h; 2. 70 h; 3. 103 h; 4. 117 h; 5. 192 h.

Table 2. The degree of crystallinity and the weight loss in thermogravimetric analysis at successive crystallization times

Reaction mixture	Time (h)	Crystallinity		Weight loss		
		X-ray (%)	IR	T<160 °C	160<T<335 °C	T>335 °C
Lu-200	5	0	0.08	3.31	30.83	2.94
	29	12	0.34	3.29	32.83	5.18
	50	90	0.97	2.05	17.07	9.90
	116	100	0.73	1.35	17.62	10.10
	168	89	0.86	2.24	19.46	9.30
	Lu-Si	30	7	0.17	2.95	24.71
	70	28	0.48	2.43	20.99	5.55
	103	100	0.80	0.14	1.52	12.42
	117	98	0.78	0.18	1.31	12.34
	192	83	0.85	0.14	1.23	12.07

from that in the silicalite.

3. FT-IR

The variation in the lattice vibration of the solid products was examined by utilizing the FT-IR technique at successive crystallization times and the results are presented in Fig. 3(a) and (b). The absorption bands at 550 cm^{-1} and 450 cm^{-1} are assigned to the vi-

bration of the 5-membered rings in MFI-type zeolite and the internal vibration of silica and alumina tetrahedra, respectively [Jacobs et al., 1981]. The intensity ratio of these two bands is used as a quantitative measure of the crystallinity [Jacobs et al., 1981; Coudurier et al., 1982]. In this study, this value increased to above 0.7 as shown in the column with heading 'IR' in Table 2. This indicates that the MFI-type zeolites synthesized are composed of highly crystalline materials and the intermediate phase observed by XRD and TGA techniques may have the sub-structures of ZSM-5 crystal.

4. Crystallinity Versus Composition of the Reaction Mixture

The changes in the crystallinity and pH of the mixtures Lu-200 and Lu-Si with the synthesis time are shown in Fig. 4(a) and (b), respectively. Initially, the gel formed in the mixture is dissolved by the action of OH^- anion [Iler, 1972], and the concentration of dissolved silicate anions increases while the OH^- anions are consumed. When equilibrium is established between the gel and the silicate anion [Szostak, 1989], the pH of the reaction mixture is kept constant (cf. Fig. 4(a)). If ZSM-5 structure starts to grow from the nuclei, the pH of the reaction mixture is slightly increased (cf. Fig. 4(b)). The zeolite synthesis mixtures are mainly composed of heterogeneous mixture, in which at the early stage, the gel and silicate anions are at quasi-equilibrium state, while at the later stage, the intermediate phase is transformed into ZSM-5 type structure, and as a result the pH of the mixture increases. This heterogeneous mixture may be considered as the reactants pool. The trend of pH variation appears to be dependent upon the dissolution rate of gel as well as the condensation rate of intermediate phase in the reactants pool. This period from the dissolution of the gel to the starting point of condensation in the intermediate phase is the induction period of zeolite synthesis.

After the induction period, sharp rises both in the crystallinity and in the pH of the reaction mixture are observed. A similar feature was also noticed by Casci and Lowe [1983] during the crystallization of zeolite EU-1. They explained that the incorporation of SiO_2 units into the zeolite framework determined the ['free base']/[silica] ratio in the remaining reaction mixture and thus the pH of the mixture was elevated. The condensation reaction between the nucleophilic deprotonated silanol group and a neutral species produces OH^- ions and brings about the formation of nuclei as well as the growth of crystals. These OH^- ions make the gel dissolve by means of the nucleophilic $\text{S}_\text{N}2$ mechanism and form silicate spe-

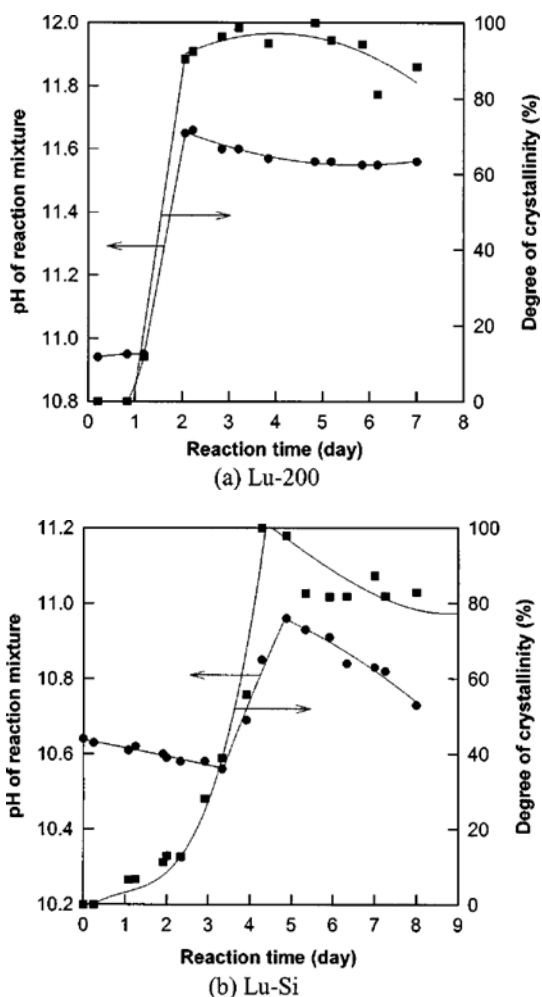


Fig. 4. The variations in the pH of solutions and the degree of crystallinity of solid products against the reaction time.

cies [Feijen et al., 1994]. After the induction period, condensation sets about between the relatively stable intermediate phase and nuclei, and the quasi-equilibrium state of the reactants pool is broken. These changes are accompanied by the increase in the concentration of OH^- ion.

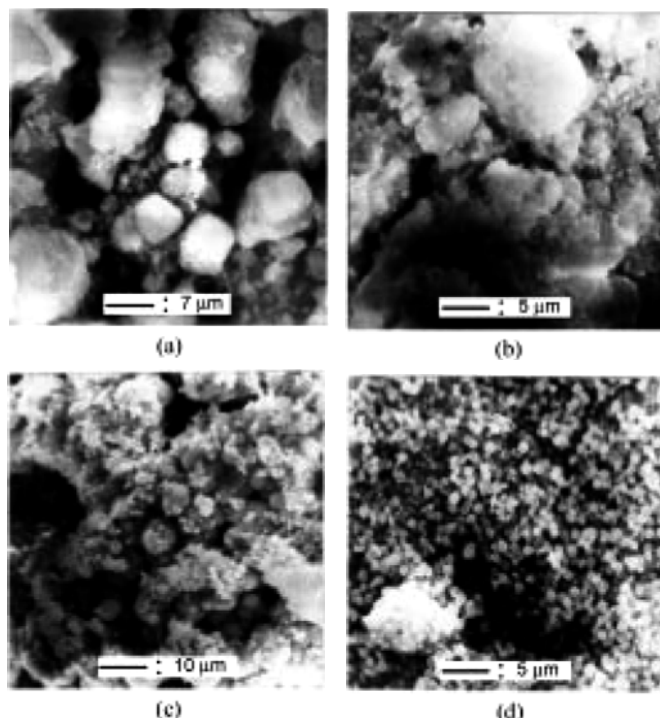


Fig. 5. SEM of the solid products taken from Lu-200 at successive times; (a) 20 h; (b) 29 h; (c) 50 h; (d) 116 h.

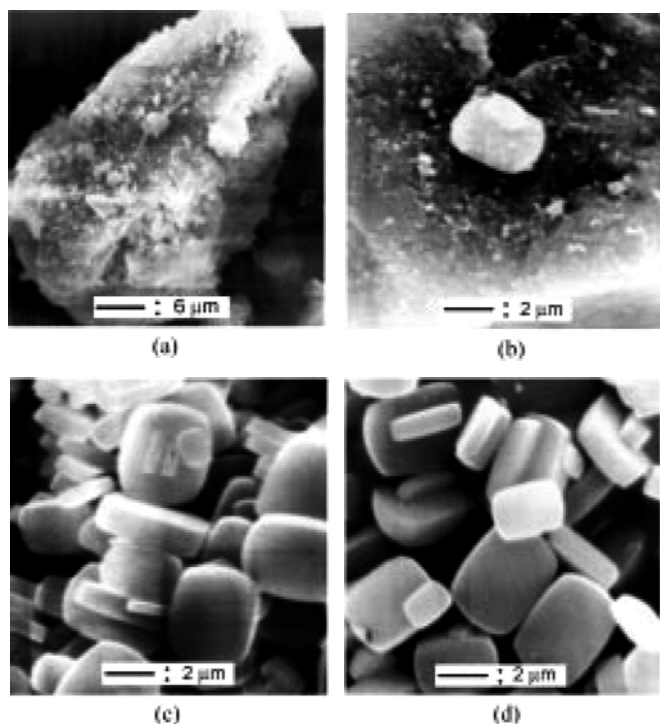


Fig. 6. SEM of the solid products taken from Lu-Si at successive times; (a) 30 h; (b) 70 h; (c) 103 h; (d) 117 h.

5. Changes in the Morphology of the Solid Phase

The shapes of the crystals are shown in Figs 5 and 6. In case of the sample Lu-200, a large amorphous intermediate phase is observed at the earlier stage (*cf.* Fig. 5(a)). The gel is a reservoir of source materials for zeolite formation and its solubility controls the composition of the crystallization solution. Silicate species are produced by the action of OH^- ions. Such an increase in the local concentration of silicate species leads to the formation of crystal nuclei of zeolite and the intermediate phase [Jansen et al., 1989]. At this stage, the condensation reaction proceeds without change in the pH value as noted in Fig. 4(a).

As the reaction proceeds further, ZSM-5 crystals are formed and begin to grow by the condensation reaction (*cf.* Fig. 5(b)). The evolved OH^- ions produce additional silicate species. Consequently, the condensation reaction is accelerated with the increased silicate species and this is well represented by the sharp increase in the crystallinity as shown in Fig. 4(a). During the course of the sharp rise in the pH value, the solid product is transformed to the ZSM-5 crystals as shown in the parts (c) and (d) of Fig. 5.

For the sample Lu-Si, the dried intermediate phase is shown in part (a) of Fig. 6. Silicalite crystals and dried gel can be discriminated as shown in part (b) of Fig. 6. Although the particle size of sol in the sample Lu-Si is much smaller than that of gel in the sample Lu-200, the silica sol particles disappear and only large MFI-type zeolite crystals are resulted as shown in parts (c) and (d) of Fig. 6.

CONCLUSIONS

ZSM-5 was synthesized using two reaction mixtures under different crystal growth environments, a dispersed low density mixture and a separated high density mixture, at $93 \pm 3^\circ\text{C}$ under the atmospheric pressure. The gel formed in both mixtures was found to be almost the same amorphous gel phase. The silicate is dissolved by the action of OH^- anions and the concentration of dissolved silicate anions increases while the OH^- anions are consumed. When equilibrium is established between the gel and the silicate anion, ZSM-5 structure starts to grow from the nuclei and the pH of the reaction mixture increases slightly. The trend of pH variation turns out to be dependent upon the dissolution rate of gel as well as the condensation rate of intermediate phase in the reactants pool. The TPA^+ cations in the intermediate phase are loosely bound and the TPA^+ cations occluded in the silicalite are strongly bound. This indicates that the intermediate phase is composed of silicate species and TPA^+ ion, and that the environment of TPA^+ cation in the ZSM-5 structure is quite different from that in the silicalite.

After the induction period, a sharp increase in the degree of crystallinity is observed and this is accompanied by an abrupt change in the pH of the reaction mixture. Morphologies of both samples are in different forms due to the different compositions of reaction mixtures. Apparently, the key factors in the crystallization of MFI-type zeolites are the presence of intermediate phase and nuclei, and the action of OH^- ions to dissolve the silicate species. The crystals of MFI-type zeolites grow by the condensation reaction of the stable silicate species.

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REFERENCES

- Beelen, T. P. M., Dokter, W. H., van Garderen, H. F. and van Santan, R. A., in Ocelli, Mario L., and Kessler, H. (Eds.), "Synthesis of Porous Materials: Zeolites, Clays, and Nanostructures," Marcel Dekker, Inc., New York, 59 (1997).
- Burggraaf, A. J., Vroon, Z. A. E. P., Keizer, K. and Verweij, H., "Permeation of Single Gases in Thin Zeolite MFI Membranes," *J. Membr. Sci.*, **144**, 77 (1998).
- Burkett, S. L. and Davis, M. E., "Mechanism of Structure Direction in the Synthesis of Si-ZSM-5 - An Investigation by Intermolecular ¹H-Si-29 CP MAS NMR," *Phys. Chem.*, **98**, 4647 (1994).
- Casci, J. L. and Lowe, B. M., "Use of pH-Measurements to Monitor Zeolite Crystallization," *Zeolites*, **3**, 186 (1983).
- Chung, K.-H., Kim, K.-S. and Seo, Gon, "The Rate of Nuclei Formation of ZSM-5 Zeolite," *Korean J. Chem. Eng.*, **9**, 144 (1992).
- Connor, C. T. O., Van Steen, E. and Dry, M. E., "New Catalytic Applications of Zeolites for Petrochemicals," in Chon, H., Woo, S. I. and Park, S.-E. (Eds.), "Recent Advances and New Horizons in Zeolite Science and Technology," *Stud. Surf. Sci. Catal.*, **102**, 323 (1996).
- Corkery, R. W. and Ninham, B. M., "Low-Temperature Synthesis and Characterization of a Stable Colloidal TPA-Silicalite-I Suspension," *Zeolites*, **18**, 379 (1997).
- Coudurier, G., Naccache, C. and Verdrine, J. C., "Uses of I.R. Spectroscopy in Identifying ZSM Zeolite Structure," *J. Chem. Soc. Chem. Comm.*, 1413 (1982).
- Cundy, C. S., Lowe, B. M. and Sinclair, D. M., "Direct Measurements of the Crystal-Growth Rate and Nucleation Behavior of Silicalite, a Zeolitic Silica Polymorph," *J. Cryst. Growth*, **100**, 189 (1990).
- Cundy, C. S., Hentry, M. S. and Plaisted, R. J., "Zeolite Synthesis Using a Semicontinuous Reactor, Part 1: Controlled Nucleation and Growth of ZSM-5 Crystals having Well-defined Morphologies," *Zeolites*, **15**, 379 (1995).
- Derouane, E. G., Detremmerie, S., Gabelica, Z. and Blom, N., "Synthesis and Characterization of ZSM-5 type Zeolites. 1. Physico-Chemical Properties of Precursors and Intermediates," *Appl. Catal.*, **1**, 201 (1981).
- Fajula, F. and Plee, D., "Application of Molecular Sieves in View of Cleaner Technology. Gas and Liquid separation," in Jansen, J. C., Stcker, M., Karge, H. G. and Weitkamp, J. (Eds.), "Advanced Zeolite Science and Applications," *Stud. Surf. Sci. Catal.*, **85**, 587 (1994).
- Feijen, E. J. P., Martens, J. A. and Jacobs, P. A., "Zeolites and their Mechanism of Synthesis," in Weitkamp, J., Karge, H. G., Pfeifer, H. and Holderich, W. (Eds.), "Zeolites and Related Microporous Materials: State of the Art 1994," *Stud. Surf. Sci. Catal.*, **84**, 3 (1994).
- Fukui, K. and Nishida, S., "CO Gas Sensor Based on Au-LaO Added SnO Ceramics with Siliceous Zeolite Coat," *Sensors and Actuators B*, **45**, 101 (1997).
- Iler, R. K., "The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry," John Wiley & Sons, New York (1972).
- Jacobs, P. A., Derouane, E. G. and Weitkamp, J., "Evidence for X-ray-Amorphous Zeolites," *J. Chem. Soc. Chem. Commun.*, 591 (1981).
- Jansen, J. C., Engelen, C. W. R. and van Bekkum, H., "Crystal Growth Regulation and Morphology of Zeolite Single Crystals of the MFI Type," in M. L. Ocelli and H. E. Robson (Eds.), "Zeolites Synthesis," ACS Symp. Ser., Am. Chem. Soc., Washington, DC., **398**, 257 (1989).
- Jansen, J. C., "The Preparation of Molecular Sieves, A. Synthesis of Zeolites," in van Bekkum, H., Flanigen, E. M. and Jansen, J. C. (Eds.), "Introduction to Zeolite Science and Practice," *Stud. Surf. Sci. Catal.*, **58**, 77 (1991).
- Kim, G.-J., Ahn, W.-S., Cho, B.-R. and Kwon, L.-M., "Synthesis of ZSM-5 and Silicalite-I (II)-Effect of pH on Crystallization," *HWAHAK KONGHAK*, **27**, 198, (1989).
- Kim, W. J., Lee, M. C., Kim, J. W. and Ha, J. M., "The Crystallization of ZSM-5 at Low Temperature and Atmospheric Pressure," *J. of Korean Ind. & Eng. Chem.*, **8**, 320 (1997).
- Kim, W. J. and Lee, M. C., "The Effect of Various Alkali Cations on the Crystallization of ZSM-5 at Atmospheric Pressure and Low Temperature," *J. of Korean Ind. & Eng. Chem.*, **9**, 38 (1998).
- Kim, W. J., Lee, M. C. and David, H. T., "Synthesis of ZSM-5 at Low Temperature and Atmospheric Pressure in a Pilot-scale Batch Reactor," *Micropor. Mesopor. Mater.*, **26**, 133 (1998).
- Kiyozumi, Y., Shin, S., Shul, Y.-G., Ihm, S.-K. and Koo, K.-K., "Crystal Growth of High Silica ZSM-5 at Low Temperature Synthesis Conditions," *Korean J. Chem. Eng.*, **13**, 144 (1996).
- Oh, H.-S., Kim, M.-H. and Rhee, H.-K., "Synthesis of Zeolite Membrane on the Inner Surface of a Ceramic Tube," in Chon, H., Ihm, S.-K. and Uh, Y. S. (Eds.), "Progress in Zeolite and Microporous Materials," *Stud. Surf. Sci. Catal.*, **105**, 2217 (1997).
- Park, J.-W., Hahn, H.-S., Kim, J.-W., Ha, J.-M. and Park, H.-Y., "Physico-Chemical Characteristics of the ZSM-5 Crystallized at Atmospheric Pressure and Conversion of Propene on the ZSM-5," *HWAHAK KONGHAK*, **36**, 369 (1998).
- Perez-Pariente, J., Martens, J. A. and Jacobs, P. A., "Characterization of Intermediate TPA-ZSM-5 type Structures During Crystallization," *Appl. Catal.*, **31**, 35 (1987).
- Scholle, K. F. M. G. J., Veeman, W. S., Frenken, P. and van der Velden, G. P. M., "Crystallization Mechanism of Zeolite Beta from (TEA)₂O, Na₂O, and K₂O Containing Aluminosilicate Gels," *Appl. Catal.*, **17**, 233 (1985).
- Sie, S. T., "Past, Present and Future Role of Microporous Catalysts in the Petroleum Industry," in Jansen, J. C., Stcker, M., Karge, H. G. and Weitkamp, J. (Eds.), "Advanced Zeolite Science and Applications," *Stud. Surf. Sci. Catal.*, **85**, 587 (1994).
- Szostak, R., "Molecular Sieves: Principles of Synthesis and Identification," Van Nostrand Reinhold, New York (1989).
- Testa, F., Szostak, R., Chiappetta, R., Aiello, R., Fonseca, A. and Nagy, J. B., "Crystallization of MFI and MEL Zeolites from Clear Solutions," *Zeolites*, **18**, 106 (1997).
- van de Graaf, J. M., Kapteijn, F. and Moulijn, J. A., "Methodological and Operational Aspects of Permeation Measurements on Silicalite-1 Membranes," *J. Membr. Sci.*, **144**, 87 (1998).
- van Hoff, J. H. C. and Roelofsen, J. W., "Techniques of Zeolite Characterization," in van Bekkum, H., Flanigen, E. M. and Jansen, J. C., (Eds.), "Introduction to Zeolite Science and Practice," *Stud. Surf. Sci. Catal.*, **58**, 241 (1991).
- Yi, K.-H. and Ihm, S.-K., "Crystallization Mechanism for Atmospheric

Synthesis of High Silica ZSM-5; *Microporous Materials*, **1**, 115 (1993).
Woo, M.-U., Kim, M.-H., Rhee, H.-K. and Lee, W.-Y., "Synthesis and

Characterization of ZSM-5 Zeolite Catalyst; *HWAHAK KONG-HAK*, **25**, 427 (1987).