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Synthesis of Zeolite ZSM-5 from Acid Clay and Cristobalite Rock

Eiichi NARITA* and Ken-ichi AKITO
Department of Liberal Arts and Engineering Sciences, Hachinohe National College of Technology, Tamonoki, Hachinohe, Aomori 031

Zeolite ZSM-5 was easily synthesized by using acid-treated rocks such as acid clay and cristobalite rock in place of some synthetic chemicals. Although the crystal growth of existing α-quartz was also observed with the crystallization of ZSM-5, it can be inhibited by decreasing the alkalinity of a reaction mixture.

A pentasil zeolite, ZSM-5, developed by Mobil Oil Corp. has interesting applications as a catalyst in fuel and petrochemical processing.[1-3] Recently, studies on the utilization of ZSM-5 as a molecular sieve[4] and a hydrophobic adsorbent[5,6] have also been carried out. This paper describes the result for synthesis of ZSM-5 by using two natural rocks occurring in Japan. Acid clay is one of the typical phyllosilicate minerals formed from lava and volcanic ash by diagenesis, and abundant at the coast of the Japan Sea.[7,8] Cristobalite rock, mostly composed of opal-CT[9], is a siliceous hard shale and recently found in the Mena formation, Aomori Prefecture in abundance.[10] These rocks are expected to be used as a nutrient for the synthesis of highly siliceous zeolite. The synthesis of ZSM-5 has recently been carried out by using acid-treated clay[11] and zeolites[12] in the presence of an organic templating agent, and by using allophane[13,14] such as Kanuma soil without organic templates. These minerals, however, contain a large amount of Al_2O_3 and the acid-treatment is known to be quite difficult industrially. The acid-treatment of acid clay used in this study is now carried out practically. The purpose of this paper is to apply the acid clay and cristobalite rock as a starting material to prepare zeolite ZSM-5.

The acid clay from the Nakajo formation, Niigata Prefecture and the cristobalite rock from the Mena formation, Aomori Prefecture were treated with 18 N H_2SO_4 at room temperature to remove excess Al_2O_3, Fe_2O_3 and other impurities. The chemi-

Table 1. Chemical composition of acid-treated rock[a)]

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Ig. loss/ wt%	(SiO_2/Al_2O_3)[b)]
Acid clay (Niigata)	91.2	1.30	0.21	0.11	0.09	3.89	119
Cristobalite rock (Aomori)	92.9	2.55	0.26	0.15	0.18	2.38	62

a) Analyses were made by a gravimetric method and an atomic absorption spectroscopy after heating rock at 110 °C for 24 h. b) Molar ratio.

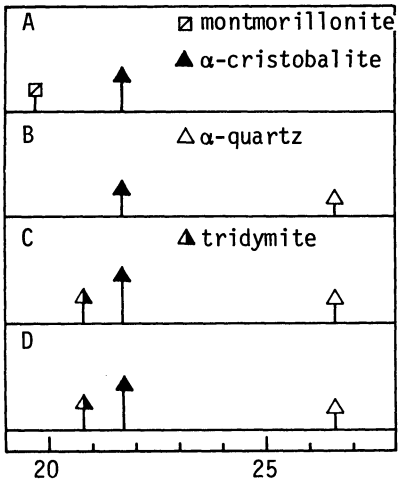

Fig. 1. X-Ray diffraction patterns of the crude rocks(A: acid clay, C: cristobalite rock) and acid-treated rocks(B: acid clay, D: cristobalite rock).

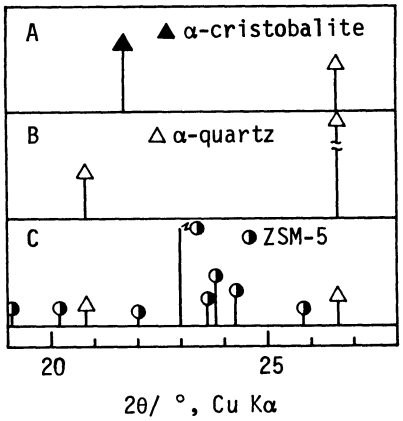

Fig. 2. X-Ray diffraction patterns of the typical products obtained in the $a(TPA)_2O$-$0.15Na_2O$-$0.0084Al_2O_3$-SiO_2-$50H_2O$ system at 170 °C. (A: a=0, 1 d, B: a=0, 3 d, C: a=0.10, 1–3 d).

cal composition of the acid-treated rocks is given in Table 1. These materials contain more than 90 wt% of SiO_2 and small amounts of Al_2O_3 and Fe_2O_3. The changes in crystal structure during acid-treatment are shown in Fig. 1. The montmorillonite in the acid clay was destroyed by the acid-treatment. The product was composed of a large amount of amorphous silica and small amounts of α-cristobalite and α-quartz. On the other hand, the crystal structure of the cristobalite was not changed by the acid-treatment and found to be mostly composed of α-cristobalite and tridymite with a small amount of α-quartz. The requisite amounts of the acid-treated material, tetrapropylammonium hydroxide (10% TPAOH) solution, sodium hydroxide solution and distilled water were taken in a polypropylene beaker and vigorously stirred. Then, 10 g of the resulting mixture was set in a stainless-steel autoclave (20 cm^3) and maintained at 130–170 °C under autogeneous pressure (0.5–1.0 MPa) without agitation for crystallization. After the hydrothermal reaction, the solid materials deposited in the reactor were separated by centrifuging and washed with distilled water repeatedly. Each product was dried at 110 °C for 24 h, and then examined using a X-ray diffractometer,[15] electron microscope, surface area apparatus, and chemical analysis techniques.

The X-ray diffraction patterns of the typical products obtained from the systems with or without TPA ion are shown in Fig. 2. As a nutrient, the acid-treated clay was used. It was first found that no ZSM-5 was formed from the system without TPA ion. The product in this system was identified with α-quartz. On the other hand, the product having a typical X-ray diffraction pattern of ZSM-5 was obtained from the system with TPA ion, whereas it contained a small amount of α-quartz. No other products, except ZSM-5 and α-quartz, were observed under these conditions. The same result was obtained when the acid-treated cristobalite rock was used as a nutrient. Figure 3 shows the effect of the Na_2O/SiO_2 ratio in the reaction mixture on the crystallization of ZSM-5 and α-quartz at 170 °C when the acid-treated clay

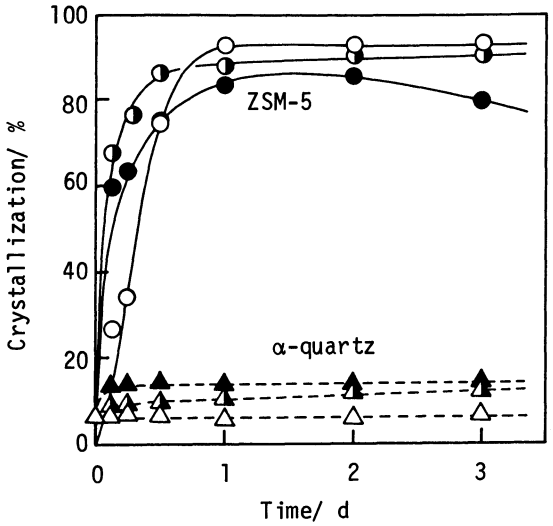

Fig. 3. Effect of alkalinity on the crystallization of ZSM-5 and α-quartz in the $0.10(TPA)_2O$-b·Na_2O-$0.0084Al_2O_3$-SiO_2-$50H_2O$ system at 170 °C. (○△: b=0, ◑◭: b=0.10, ●▲: b=0.20).

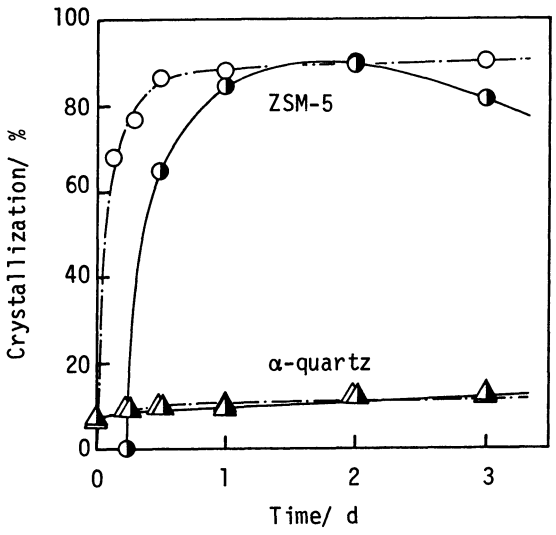

Fig. 5. Crystallization behavior of ZSM-5 and α-quartz in the $0.10(TPA)_2O$-$0.10Na_2O$-cAl_2O_3-SiO_2-$50H_2O$ system at 170 °C. (Nutrient – ◑◭: cristobalite rock, ○△: acid clay).

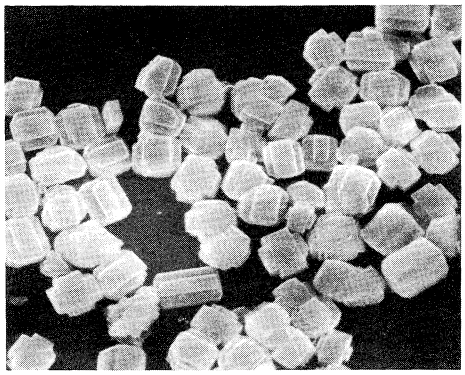

Fig. 4. Scanning electron micrograph of the ZSM-5 product.

was used. It was found that there is no induction period for starting the crystallization of ZSM-5 in all cases and ZSM-5 crystallized immediately. This is because cristobalite particles may act as heterogeneous nuclei for ZSM-5 crystallization. The other important feature is that the crystallization rate of ZSM-5 was affected by the Na_2O/SiO_2 ratio and maximized when the ratio was 0.10. When the Na_2O/SiO_2 ratio was 0, crystal growth of α-quartz did not occur, whereas it increased with an increase in the Na_2O/SiO_2 ratio because of the increased solubility of SiO_2 in water. The synthesis experiments of ZSM-5 were also carried out at 130 °C and 150 °C under the same conditions, and the Arrhenius plots for the crystallization rate of ZSM-5 were made. From the result, the apparent activation energy for crystallization was calculated as 50.3 kJ mol^{-1}. Figure 4 shows the SEM photograph of the ZSM-5 product obtained at the $(TPA)_2O/SiO_2$ and Na_2O/SiO_2 ratios of 0.10. The particle was found to be twin having uniform crystal shape and size (2 μm). Figure 5 shows the crystallization behavior of ZSM-5 and α-quartz at 170 °C when the acid-treated cristobalite rock was used as a nutrient. It should be noted that an induction period of 6 h was observed. The crystallization rates of ZSM-5 and α-quartz were, however, similar to those when the acid-treated clay was used.

The effects of variations in the reaction mixture on the percent of ZSM-5 and

Table 2. Effect of chemical composition of reaction mixture on the degree of ZSM-5 and α-quartz crystallization, the SiO_2/Al_2O_3 ratio and B.E.T. surface area of the solid product

Run	Mineral	Reaction mixture[a)] a	Reaction mixture[a)] b	Degree of crystallization /% ZSM-5	Degree of crystallization /% α-quartz	SiO_2/Al_2O_3 ratio	B.E.T. s.a. $m^2\ g^{-1}$
1	acid clay	0.10	0.20	83.3	13.6	62	286
2		0.10	0.10	89.0	9.3	85	327
3		0.10	0	92.6	5.5	110	328
4		0.05	0.10	89.4	9.0	99	342
5		0.05	0	80.9	6.2	109	296
6*	cristobalite rock	0.10	0.10	84.7	8.2	82	256

a) Reaction mixture: $a(TPA)_2O$-bNa_2O-cAl_2O_3-SiO_2-$50H_2O$, temperature: 170 °C, time: 24(*; 48) h.

α-quartz crystallization, the SiO_2/Al_2O_3 ratio and the B.E.T. surface area of the solid product are summarized in Table 2. The crystallization degree of ZSM-5 increased with a decrease in the Na_2O/SiO_2 ratio, whereas the formation of α-quartz was inhibited. It was also found that the SiO_2/Al_2O_3 ratio of the solid product became larger with a decrease in the Na_2O/SiO_2 ratio. The high crystallinity of ZSM-5 was achieved even at the smaller $(TPA)_2O/SiO_2$ ratio such as 0.05. The solid products having a high degree of ZSM-5 crystallization were found to have a B.E.T. surface area of over 300 $m^2\ g^{-1}$. Accordingly, the prepared ZSM-5 will be used as a catalyst and an adsorbent.

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