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A CONVENIENT METHOD FOR CRYSTALLIZATION OF ZEOLITE ZSM-5 BY USING SEED CRYSTALS IN ACETONE/WATER MIXTURE SYSTEM

Eiichi NARITA,* Keiichi SATO, and Taijiro OKABE
Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Aoba, Aramaki, Sendai 980

Zeolite ZSM-5 was easily synthesized by using ZSM-5 seed crystals as crystallization nuclei from acetone/water mixture system without any organic templates. A small amount of acetone in a reaction mixture inhibited formation of α-quartz and facilitated rapid crystallization of ZSM-5 under the mild hydrothermal conditions of 170–190 °C.

A new type zeolite, ZSM-5, developed by Mobil Oil Corp. is a silica-rich zeolite with an unique channel structure.1,2) Recently, it is known that ZSM-5 shows outstanding properties not only as catalysts but also as molecular sieves for separation of organic compounds such as xylene and creosol isomers.3) Its intrinsic hydrophobic surface also has the possibility of utilization as adsorbents for organic compounds in water.4) This ZSM-5 is hydrothermally synthesized from an aluminosilicate gel with Na-tetrapropylammonium (Na-TPA) cation in the conventional method.1) Many alternate methods characterized by using various kinds of organic compounds in place of organic ammonium ion were also proposed.5,6) However, to extend the potential usefulness of ZSM-5 in many fields, the development of further advantageous methods both in technology and in economy is indispensable. This paper describes a convenient method for crystallization of ZSM-5 by using seed crystals in aluminosilicate gel containing a small amount of acetone.

The reaction materials used for this preparation were colloidal silica (Snowtex-30 from Nissan Chemical Ind., Ltd.; 30–31% SiO_2), aluminium sulfate ($Al_2(SO_4)_3 \cdot 14{-}18H_2O$), sodium hydroxide and acetone (all Wako Pure Chemical Ind., Ltd., guaranteed reagents). ZSM-5 seed crystals were synthesized according to the patent of Mobil Oil Corp.;1) *i.e.*, the precursor was first crystallized from a gel composed of $0.12TPAOH-0.13Na_2O-0.01Al_2O_3-SiO_2-13H_2O$ at 170 °C for 3 days and then calcinated at 600 °C for 1 h to remove the obstructing organic compounds from its channel. X-Ray diffraction profile revealed that the seed crystals were ZSM-5. A mean particle size was 0.19 µm (Fig. 3-A) and SiO_2/Al_2O_3 ratio was 77.

First, 10 g of an aluminosilicate gel was mixed homogeneously with 0.36 wt% of the seed crystals and a definite amount of acetone in a polypropylene beaker and then put in a stainless-steel autoclave (20 cm^3) and maintained at 150–230 °C without agitation for crystallization. Unless otherwise stated, the reaction mixture with the composition in the molar ratios of Na_2O/SiO_2: 0.15 or 0.20, SiO_2/Al_2O_3: 100, H_2O/SiO_2: 46 was used here. The products were identified by X-ray diffractometry and their morphology were observed using a scanning electronmicroscope. The degrees of crystallization of ZSM-5 and α-quartz were estimated using X-ray diffraction as follows:

$$\%\ \text{crystallization} = \frac{\text{peak area of } 2\theta=22\text{–}25°(\text{ZSM-5}) \text{ or } 26\text{–}27°(\alpha\text{-quartz}) \text{ of solid product}}{\text{peak area of } 2\theta=22\text{–}25°(\text{ZSM-5}) \text{ or } 26\text{–}27°(\alpha\text{-quartz}) \text{ of standard samples.}}$$

Standard samples used were the products having the highest crystallinity obtained in this study.

Figure 1 shows the effect of amount of acetone added in the reaction mixture on the crystallization of ZSM-5 and α-quartz at 190 °C. It was found that the degree of crystallization of ZSM-5 increased by the presence of a small amount of acetone and was the highest at acetone contant of 4.7 wt% and a=0.15 at the synthesis time of 12 h, whereas no formation of α-quartz was observed in all runs. When the synthesis time was prolonged, α-quartz was crystallized as the another crystalline phase along with the decomposition of ZSM-5. Other kind of products except ZSM-5 and α-quartz was not observed under the conditions conducted here. In the seeded system containing acetone, rapid crystallization of ZSM-5 occurred because the seed surface provided nucleation sites and acetone inhibited the excessive gelation of the reaction mixture.

X-Ray diffraction profiles shown in Fig. 2 indicate that the diffraction lines of ZSM-5 obtained in the acetone mixed system became sharp and apparently separated at 2θ, 23.0° and 23.2°, while the lines of the seed crystals were broad and overlapped. This means that the product from the acetone mixed system has the high crystallinity of ZSM-5.[7] Figure 3 shows the scanning electron micrographs

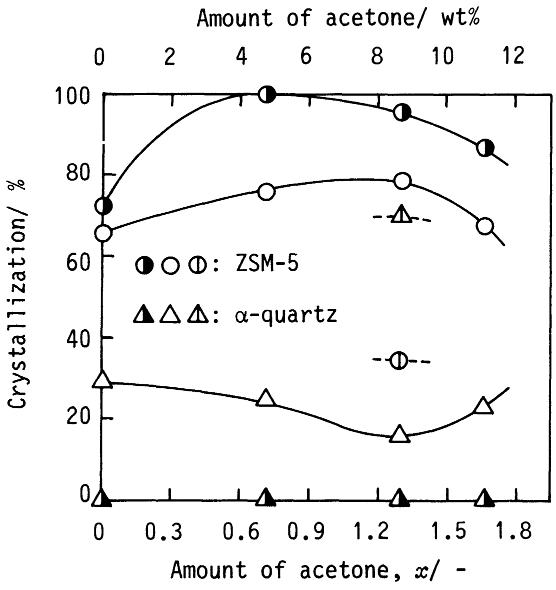


Fig. 1. Effect of amount of acetone on the crystallization of ZSM-5 and α-quartz in the $a\text{Na}_2\text{O}$-0.01Al_2O_3-SiO_2-46H_2O-xAcetone-Seed system at 190 °C.

◑ ▲ — a=0.15, time: 12 h,

○ △ — a=0.20, time: 24 h,

⦶ ◭ — a=0.20, time: 72 h.

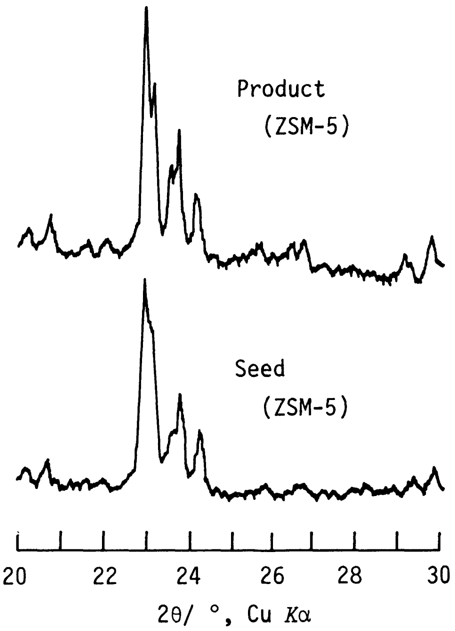
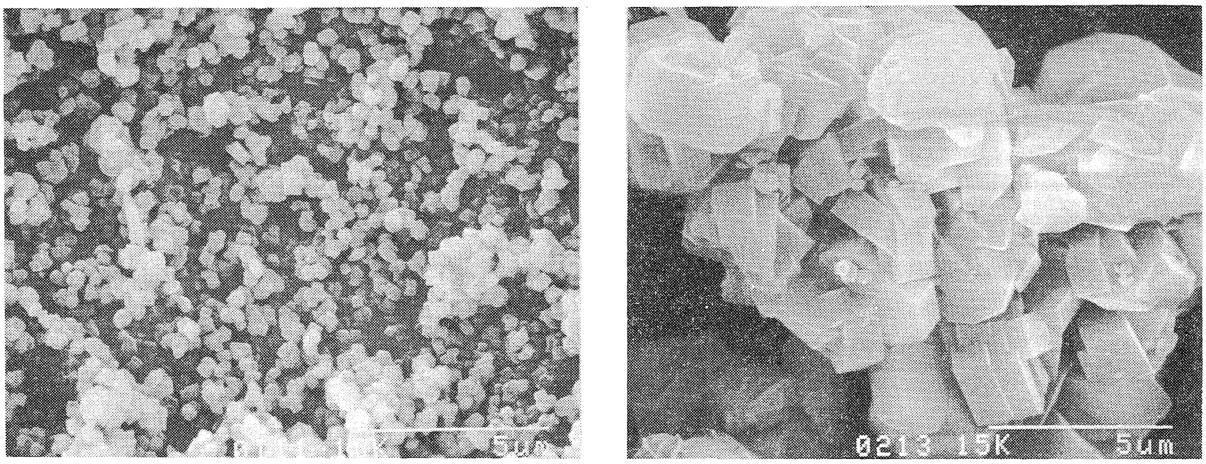


Fig. 2. X-Ray diffraction profiles of ZSM-5 seed and ZSM-5 product in the 0.15Na_2O-0.01 Al_2O_3-SiO_2-46H_2O-0.7Acetone-Seed system at 190 °C for 12 h.



(A) ZSM-5 seed (B) ZSM-5 product

Fig. 3. Scanning electron micrographs of ZSM-5 seed and ZSM-5 product in the $0.15Na_2O-0.01Al_2O_3-SiO_2-46H_2O-0.7$Acetone-Seed system at 190 °C for 12 h.

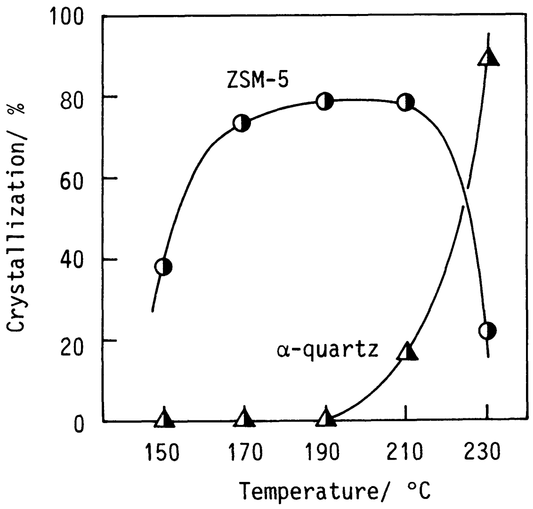


Fig. 4. Effect of synthesis temperature on the crystallization of ZSM-5 and α-quartz in the $0.20Na_2O-0.01Al_2O_3-SiO_2-46H_2O-1.3$Acetone-Seed system for 12 h.

of the seed crystals(A) and the ZSM-5 product having the highest crystallinity (B). Although there was no differences in the morphology, the mean particle size of the product (2.5 μm) became large compared with that of the seed crystals (0.19 μm). As can be seen in Fig. 1, ZSM-5 was also crystallized from the seeded system without acetone. However, the crystallinity of the product was lower and the particle size was quite ununiform.

The effect of synthesis temperature on the crystallization of ZSM-5 and α-quartz was shown in Fig. 4. ZSM-5 was observed as the single crystalline phase and its degree of crystallization increased with increasing synthesis temperature in the range of below 190 °C. At temperatures above 210 °C, α-quartz was also crystallized and its degree of crystallization increased proportional to the decrease in ZSM-5 one.

The effect of SiO_2/Al_2O_3 ratio in the reaction mixture on the chemical composition of ZSM-5 product is given in Table 1.

Table 1. SiO_2/Al_2O_3 ratio of starting gel and ZSM-5 product in the $0.15Na_2O-bAl_2O_3-SiO_2-46H_2O-0.7$Acetone-Seed system at 190 °C for 12 h

Run	*b*	SiO_2/Al_2O_3 molar ratio	
		Starting gel	ZSM-5 product
1	0.02	50	39
2	0.01	100	64
3	0.005	200	104

When SiO_2/Al_2O_3 ratio was changed as 50–200, ZSM-5 was crystallized in a similar manner as described above and SiO_2/Al_2O_3 of ZSM-5 product was governed by the initial SiO_2/Al_2O_3 ratio in the reaction mixture as reported by Ueda *et al.* on the syntheses of analcime8) and mordenite.9) However, in the aluminium-free system, ZSM-5 or silicalite (the aluminium-free analogue of ZSM-5) was not crystallized. All seed crystals were decomposed. This indicates that the presence of aluminium ion appears to be essential for the crystallization of ZSM-5 structure without organic templates. On the other hand, it was also found that methylethyl ketone and cyclohexanone exhibited the same effect as does acetone here and the degree of the effect was acetone ≃ methylethyl ketone > cyclohexanone in order. One of the reason for the acceleration of ZSM-5 crystallization by these ketones is thought to act as an inhibitor of excessive gelation of the reaction mixture. However, definite reason is as yet unclear.

Although the use of seed crystals for the synthesis of ZSM-5 has been reported by some earlier workers,10,11) the synthesis without using organic templates has been performed only by Mobil Oil Corp. using mixtures of alcohols with ammonium hydroxide.10) As we tried the crystallization of ZSM-5 according to this patent10) and compared the result with that described above, the crystallinity of ZSM-5 in acetone/water system was higher than that in ethanol-ammonia/water system.

These results clearly demonstrate the significance of crystal size and shape uniformity on ZSM-5 crystallization, and provide a practical and economical method without the use of any organic templates and the calcination process.

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