

Single Crystal Growth, Morphology, and Structure of ZSM-39 and Its Variation CF-4

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Abstract. Single crystals of ZSM-39 and its variation CF-4 were crystallized with various habits. The crystals had a size up to 450 μm and were hydrothermally grown over a period of 8 to 72 days from a gel system consisting of amine–alcohol– SiO_2 – H_2O at 200°C. The amines used were MA (methylamine), TMEDA (*N,N,N',N'*-tetramethylethylenediamine), TMAOH, TEAOH, isopropylamine, *tert*-butylamine, hexahydropyridine, *n*-propylamine, and *N,N*-dimethylethanolamine. The alcohols used were glycerine, ethylene glycol, and 1,3-propanediol. The highest quality crystals of ZSM-39 were grown in a system of MA– SiO_2 – H_2O , and CF-4, in the MA–glycerine– SiO_2 – H_2O system. The optical properties of these crystals were observed and crystal structures were measured from both powder and single crystal diffraction data.

Key words: Single crystal, X-ray diffraction, ZSM-39, CF-4, zeolite.

1. Introduction

The first patent on the synthesis of zeolite ZSM-39 was reported in 1981 in [1]. The following year, Schlenker *et al.* [2] deduced that ZSM-39 possessed a silica clathrate structure of 12-hedra constructed with a 5-ring and 6-ring of oxygens, which was analogous to a structure of melanophlogite, by fitting X-ray powder diffraction data [2,3]. Bibby and Parker investigated the properties of ZSM-39 prepared in some systems containing different species of amine and interpreted it as a clathrate structure in 1983 [4]. Now the synthesis and structure of ZSM-39 and its analogue is of interest to zeolite scientists and mineralogists.

According to the literature, crystals of ZSM-39 obtained in a system with pyrrolidine were 10 μm in size and those obtained from a 2-aminopropane (or 2-amino-2-methylpropane) system were only 0.1 μm in size [1,4].

In this paper, we report that large single crystals of ZSM-39 and its variation CF-4, which are uniform and are 100–450 μm in size, have been hydrothermally grown in a gel of amine–alcohol– SiO_2 – H_2O at 200°C. This work has allowed the determination of the crystal structure of ZSM-39.

2. Experimental and Results

2.1. SYNTHESIS AND CRYSTAL GROWTH

Single crystal growth was carried out at 200°C in a small autoclave (20–40 cm^3 in volume) lined with GG17 hard glass. Reagents used were silicasol, H_2SO_4 , some species of amine,

such as TMEDA (*N,N,N',N'*-tetramethylenediamine), MA (the aqueous solution of methylamine), TEAOH (tetraethylammonium hydroxide), TMAOH (tetramethylammonium hydroxide), isopropylamine, *tert*-butylamine, hexahydropyridine, *n*-propylamine, and *N,N*-dimethylethanolamine. Some alcohols, such as glycerine, 1,3-propanediol, and ethylene glycol were also used.

A certain amount of silicasol was weighed, then mixed sequentially with H_2SO_4 , and amine. The mixture was stirred at room temperature until a homogeneous reactant formed, which was poured into a small autoclave placed in an oven at a constant temperature of 200°C with an accuracy of $\pm 2^\circ\text{C}$. The product was washed, filtered, dried by IR lamp, and studied with a D/MAX-II A diffractometer. The morphology and the size of the crystals obtained were observed and measured by scanning electron microscopy or by optical microscopy with crossed nicols and a gypsum plate inserted.

2.2. GROWTH OF OCTAHEDRAL SINGLE CRYSTALS OF ZSM-39

In a synthesis experiment, it was found that some large, imperfect crystals (150–300 μm in size) of ZSM-39 could be spontaneously crystallized during a reaction period of 10–20 days at 200°C in a system of $\text{TMEDA}-\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$. The molar ratios of the reactants were as follows: $\text{TMEDA}/\text{SiO}_2 = 0.1-1$; $\text{Na}_2\text{O}/\text{SiO}_2 = 0$; $\text{H}^+/\text{SiO}_2 = 0-0.10$; $\text{H}_2\text{O}/\text{SiO}_2 = 10-30$. Although the crystals grown in TMEDA were mainly octahedral, the faces of the crystals possessed parasitic crystals, twins, and aggregates. Some phases, such as $\alpha\text{-SiO}_2$, cristobalite, and the novel zeolite CF-3 [5], having clathrate structural properties

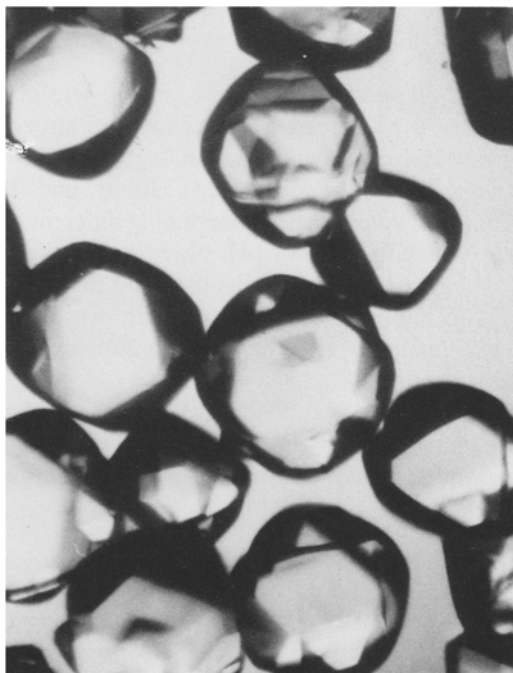


Fig. 1. ZSM-39 octahedral crystals and twins under cross polarized light, $\times 200$ (grown in the $\text{MA}-\text{SiO}_2-\text{H}_2\text{O}$ system).

like ZSM-39, were formed in the system when the composition of the reactant was out of the preferred range.

In order to obtain large single crystals of ZSM-39, the following conditions were important: controlling the number of ZSM-39 seeds added in the reactant, preventing spontaneous nucleation of ZSM-39 and other co-crystalline phases, and inhibiting coherence of crystals grown from nuclei spontaneously formed on a growing crystal surface. Therefore, a new gel system of MA-SiO₂-H₂O suitable for growing large single crystals of ZSM-39 has been selected. The molar ratios of the gel were as follows: MA/SiO₂ = 0.5–2.0; H⁺/SiO₂ = 0.10–0.15 (H⁺ was provided by adding a small amount of H₂SO₄); H₂O/SiO₂ = 12–30.

A trace of seeds (0.1 μm in size) obtained by grinding the crystals prepared in the TMEDA system was added to the reactant. While mixing, the reactant looked like a uniform sol. The seeds were dispersed in the MA-SiO₂-H₂O sol by vigorous stirring. As soon as the sol was heated in the autoclave to 200°C, it was rapidly transformed into a gel without fluidity. In this manner, an unrestricted environment for crystal growth was formed around each seed. The size of the single crystals reached 100 to 200 μm during a period of 10–20 days of hydrothermal reaction. After cooling the autoclave, the product was washed and cleaned of unreacted gel by hot distilled water. The major morphology of the crystals prepared in this way was that of an octahedron, but some cube faces occasionally appeared and twins accompanied it (see Fig. 1). The crystals were found to be isotopic.

If no seeding was done in the reaction system, the gel of MA-SiO₂-H₂O was kept for a long time without spontaneous nucleation of ZSM-39 and other crystalline phases. The

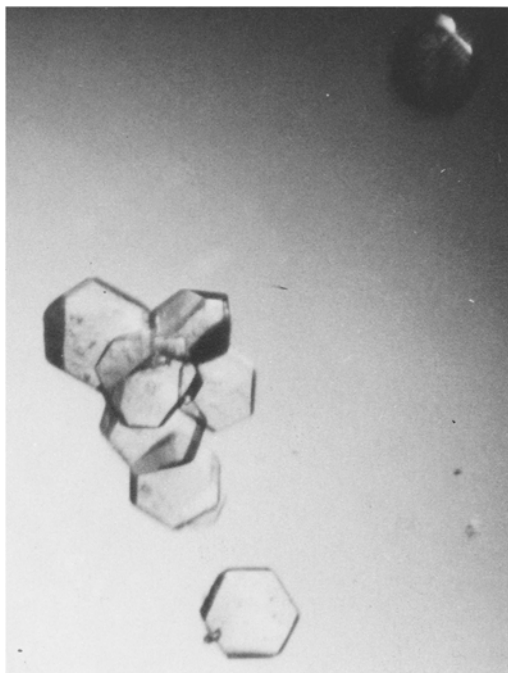


Fig. 2. ZSM-39 pseudo-hexagonal tabular crystals under cross polarized light, $\times 80$ (grown in the MA-glycerine-SiO₂-H₂O system).

nucleus number in the gel depended on the seeds added. Single crystal growth only occurred on the surface of the seeds. The amount of seeds added should be closely controlled to ensure that each seed possesses enough free space in which to grow. Thus, in the growth process of the single crystals, the chemical and physical environment around the growth surface must be held constant.

2.3. SINGLE CRYSTAL GROWTH OF PSEUDO-HEXAGONAL TABULAR ZSM-39 AND CF-4

In a study on the growth of single crystals of ZSM-5, it was noted that single crystal growth could be improved by the addition of glycerine [6]. It was found that a certain amount of glycerine added to the MA–SiO₂–H₂O system caused an obvious change in morphology, and even in the optical properties of the single crystals. Some perfect and uniform ZSM-39 single crystals without visible interference colours possessing a hexagonal tabular habit and 100 to 200 μm in size (see Fig. 2) were crystallized in a system of MA–glycerine–SiO₂–H₂O with the following molar compositions: MA/SiO₂ = 1.3; glycerine/SiO₂ = 3–4; H⁺/SiO₂ = 0.05; H₂O/SiO₂ = 15. Upon increasing the ratio of H⁺/SiO₂ to 0.10 or 0.15, some large single crystals (up to 450 μm in size) with beautiful interference colours and interference lines in a cubic-octahedron habit (see Fig. 3) grew spontaneously in the reactant system over a period of 72 days. These single crystals with weak birefringence are called CF-4, a ZSM-39 variation. Evidently the formation of CF-4 was primarily related to the composition of the reactant, and especially depended on the amount of glycerine added. Some examples of experimental conditions for growing single crystals of ZSM-39 and CF-4 in MA–glycerine–SiO₂–H₂O systems are listed in Table I.



Fig. 3. CF-4 cubic-octahedral crystals under cross polarized light, $\times 80$ (grown in the MA–glycerine–SiO₂–H₂O system).

Table I. Examples of single crystal growth of ZSM-39 and CF-4 (hydrothermally prepared in the MA-glycerine-SiO₂-H₂O system at 200°C).

No.	Molar composition of reactant			Initiation of crystallization	Period of reaction (days)	Product		Maximum size of single crystals (μm)		
	MA	glycerine	H ⁺			H ₂ O	SiO ₂		Phase	Habit ^a
1	1	0	0.15	15	1	seeds of ZSM-39	15	ZSM-39	1	100-200
2	1.3	4.14	0.15	15	1	spontaneously	28	CF-4	3	100-200
3	1.3	0	0.15	15	1	spontaneously	39	ZSM-39	aggregate	—
4	1.3	2.1	0.15	15	1	spontaneously	19	ZSM-39 + CF-4	2 + 3	100-150
5	1.3	4.14	0.15	15	1	spontaneously	72	CF-4	3	450
6	1.3	4.14	0.15	15	1	seeds of CF-4	28	CF-4	3	100
7	4.0	4.0	0.15	15	1	spontaneously	48	CF-4 + Cri. ^b	3	200-300
8	4.0	0	0.15	15	1	spontaneously	28	ZSM-39	aggregate + tiny crystals	—
9	4.0	4.0	0	15	1	spontaneously	38	ZSM-39 + CF-4 + Cri.	3 + tiny crystals	300
10	1.3	4.0	0.10	15	1	seeds of ZSM-39	62	CF-4 + ZSM-39	2 + 3	100-300
11	1.3	3.0	0.10	15	1	seeds of ZSM-39	32	CF-4 + ZSM-39	3 + 2	150
12	1.3	4.0	0.05	15	1	seeds of ZSM-39	32	ZSM-39	2	150-200
13	1.3	3.0	0.05	15	1	seeds of ZSM-39	22	ZSM-39	2	100-150
14	1.3	4.0	0.10	15	1	seeds of CF-4	54	CF-4 + Cri.	3	100-300
15	1.3	3.0	0.10	15	1	seeds of CF-4	56	CF-4 + ZSM-39 + Cri.	3 + 2	150
16	1.3	4.0	0.05	15	1	seeds of CF-4	56	CF-4 + ZSM-39 + Cri.	3 + 2	200
17	1.3	3.0	0.05	15	1	seeds of CF-4	56	CF-4 + ZSM-39 + Cri.	3 + 2	120

^a Habit 1: octahedral (see Fig. 1).

Habit 2: pseudo-hexagonal tabular (see Fig. 2).

Habit 3: cubic-octahedral (see Fig. 3).

^b Cri. -impurity of cristobalite.

2.4. CRYSTALLIZATION OF ZSM-39 AND CF-4 IN SYSTEMS WITH OTHER ORGANIC SPECIES

Large single crystals of ZSM-39 of 100 to 300 μm in size were grown at 200°C during a period of 8 to 25 days in system of A-glycerine-SiO₂-H₂O with the following molar composition: glycerine/SiO₂ = 2-4; H⁺/SiO₂ = 0-0.15; H₂O/SiO₂ = 15; A/SiO₂ = 1, where A represents an amine used, such as TMEDA, TEOH, isopropylamine, *N,N'*-dimethylethanolamine, or *tert*-butylamine. The CF-4 single crystals were also prepared in a system of MA-AC-SiO₂-H₂O with the following molar composition: MA/SiO₂ = 1.3; H⁺/SiO₂ = 0.15; H₂O/SiO₂ = 15; AC/SiO₂ = 4.14, where AC is an alcohol, such as ethylene glycol or 1,3-propanediol.

2.5. STRUCTURE STUDIES BY X-RAY DIFFRACTION

The X-ray powder diffraction patterns of the octahedral and pseudo-hexagonal tabular habits, are shown in Fig. 4. They are similar to that of ZSM-39 given in the literature [1, 2]. When the diffraction angle is greater than 28°, the differences in position and number of diffraction peaks between ZSM-39 and CF-4 crystals with the cubic-octahedral habit shown in Fig. 3 become obvious (see Fig. 4).

The cell parameters of these single crystals were determined on an ENRAF-NONIUS CAD-4 four-circle diffractometer. It was shown that crystals with the octahedral habit and the pseudo-hexagonal tabular habit belong to the cubic system with cell parameters $a = 19.403 \text{ \AA}$, while CF-4 crystals with the cubic-octahedral habit belong to the tetragonal system with cell parameters $a = b = 13.65 \text{ \AA}$, $c = 19.46 \text{ \AA}$.

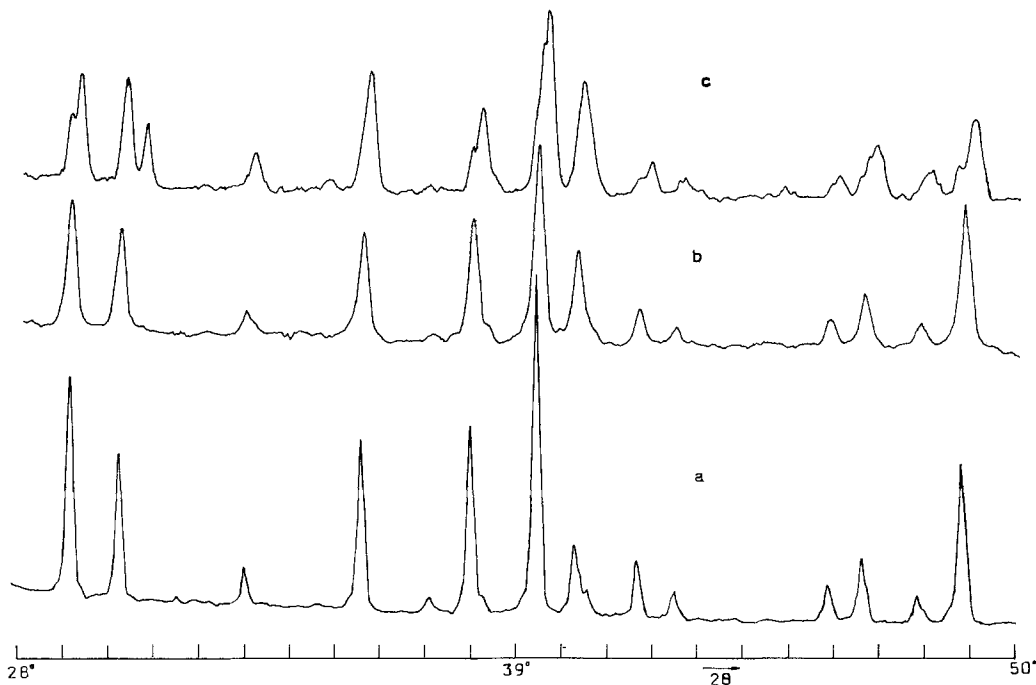


Fig. 4. X-ray powder diffraction patterns (CuK α): (a) ZSM-39 crystals with the habit shown in Fig. 1; (b) ZSM-39 crystals with the habit shown in Fig. 2; (c) CF-4 crystals with the habit shown in Fig. 3.

The structure of octahedral ZSM-39 crystals ($0.15 \times 0.15 \times 0.15 \text{ mm}^3$ in size) was determined from X-ray intensity data measured on the diffractometer. 2175 Reflections were collected in the range $2\theta < 50^\circ$ (one octant with MoK radiation) from which 181 independent observed reflections, $F^2 > 3\sigma(F^2)$, were obtained. The crystallographic parameters are as follows: crystal system, cubic; space group, $Fd3m$; cell constant, $a = 19.403(3) \text{ \AA}$; $V = 7304.5 \text{ \AA}^3$; $D_c = 1.914 \text{ g/cm}^3$; $\mu = 6.65 \text{ cm}^{-1}$; cell content, $(\text{CH}_3\text{NH}_2)_8(\text{SiO}_2)_{136}$; framework density, $18.62 \text{ T/1000 \AA}^3$. Initially, the data determined by Schlenker *et al.* [2] from X-ray powder diffractometry were used. Refinement was carried out by full-matrix least-squares procedures. A peak was found in the center of the 16-hedron on a difference Fourier map. The structure was refined to a final R value of 0.055. The result shows that the atomic parameters, listed in Table II and III, are very close to the corresponding data from Schlenker [2]. The methylamine molecules are located in the 16-hedra (hexakaidecahedra), but are disordered. The carbon atom is positioned in the center of the 16-hedron and the nitrogen atom is hydrogen bonded to the oxygen atoms in the 16-hedron. The detailed results will be reported elsewhere [7].

Table II. Atomic coordinates and temperature factors of zeolite ZSM-39

Atom	x	y	z	$B(\text{eq})$
Si(1)	0.125	0.125	0.125	1.69(9)
Si(2)	0.2165(8)	0.2165(8)	0.2165(8)	1.7(1)
Si(3)	0.1824(3)	0.1824(3)	0.3697(3)	1.97(7)
O(1)	0.170(3)	0.170(3)	0.170(3)	10.2(8)
O(2)	0.200(1)	0.200(1)	0.2930(7)	6.6(4)
O(3)	0.125	0.125	0.372(1)	4.3(4)
O(4)	0.250	0.157(1)	0.407(1)	4.8(3)
C	0.375	0.375	0.375	4(1)

Table III. Bond lengths (\AA) and bond angles ($^\circ$)

Bond	Length	Bond	Angle	Bond	Angle
Si(1)—O(1)	1.527(6)	O(1)—Si(1)—O(1)	109.5(3)	O(4)—Si(3)—O(4)	107.5(2)
Si(2)—O(1)	1.547(6)	O(1)—Si(2)—O(2)	108.5(3)	Si(1)—O(1)—Si(2)	180.0(7)
Si(2)—O(2)	1.550(3)	O(2)—Si(2)—O(2)	110.4(2)	Si(2)—O(2)—Si(3)	178.6(4)
Si(3)—O(2)	1.566(3)	O(2)—Si(3)—O(3)	109.7(3)	Si(3)—O(3)—Si(3)	177.0(4)
Si(3)—O(3)	1.576(1)	O(2)—Si(3)—O(4)	108.9(2)	Si(3)—O(4)—Si(3)	167.6(2)
Si(3)—O(4)	1.578(2)	O(3)—Si(3)—O(4)	110.9(2)		

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