

The Synthesis and Properties of Zeolite CF-3

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Abstract. The novel zeolite CF-3, with a high ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and a characteristic X-ray powder diffraction pattern, has been synthesized hydrothermally from a TMEDA- Na_2O - SiO_2 - Al_2O_3 - H_2O system at 200°C . The molar composition of CF-3 is $(0.4\text{--}0.6)\text{Na}_2\text{O} \cdot (1.5\text{--}6.3)\text{TMEDA} \cdot \text{Al}_2\text{O}_3 \cdot (80\text{--}400)\text{SiO}_2 \cdot (0\text{--}17)\text{H}_2\text{O}$. CF-3 is similar to ZSM-39 and melanophlogite, which have a clathrate-type structure.

Key words: Zeolite, CF-3, ZSM-39, melanophlogite.

1. Introduction

Studies on polymorphs of silica, with clathrate-like structures, have long intrigued mineralogists [1]. In 1965, Kamb [2] first indicated that the mineral melanophlogite was isostructural to the 12 \AA gas hydrate. Hydrocarbons could be trapped in tetrakaidecahedral cavities. Kamb's work explained the properties of melanophlogite [3], and has been confirmed by the investigation of Žak [4]. The synthesis of zeolite ZSM-39 was reported by Brace [5] in 1981. More recently Schlenker *et al.* [1] showed that the framework of ZSM-39 was isostructural with the 17 \AA cubic gas hydrate. ZSM-39 is the first example of a man-made high silica material with a structure analogous to that of the crystalline clathrate hydrate.

We now report the hydrothermal preparation of a novel high silica zeolite, which has a characteristic X-ray powder diffraction pattern, from the tetramethylethylenediamine(TMEDA)- Na_2O - SiO_2 - Al_2O_3 - H_2O system. Most properties of CF-3 are similar to those of ZSM-39 and melanophlogite.

2. Synthesis of CF-3

CF-3 was hydrothermally synthesized in a system of TMEDA- Na_2O - SiO_2 - Al_2O_3 - H_2O . The silicon source used was water glass (SiO_2 -22.33%, Na_2O -6.28%) or silica hydrosol (SiO_2 -23.60%). The alumina source was an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$ (Al_2O_3 -7.075%). TMEDA, H_2SO_4 and NaOH of reagent grade were used. The ranges of reactant composition (in molar concentrations) studied were: $\text{SiO}_2/\text{Al}_2\text{O}_3$, $75\text{--}\infty$; TMEDA/ SiO_2 , $0.3\text{--}1$; $\text{H}_2\text{O}/\text{SiO}_2$, $12\text{--}40$; OH^-/SiO_2 , $0\text{--}0.05$; H^+/SiO_2 , $0\text{--}0.02$.

When water glass was used as the silica source, a certain amount of H_2SO_4 was added to neutralize excess Na_2O . While using silica hydrosol, NaOH was added if $\text{OH}^-/\text{SiO}_2 > 0$ was needed. Otherwise, a certain amount of H_2SO_4 was added when $\text{H}^+/\text{SiO}_2 > 0$ was needed. Traces of Al_2O_3 impurity in the silicon source were not counted in the reactant composition.

The proper amount of silicon-containing material, TMEDA, and NaOH (if needed) were mixed to make gel A and a fixed amount of $\text{Al}_2(\text{SO}_4)_3$ solution, H_2O , and H_2SO_4 (if needed)

Table I. Synthetic examples^a

Example	Silica source	Molar composition of reactant mixture						Initiation of crystallization	Period of reaction (h)	Phase of product
		TMEDA	Al ₂ O ₃	SiO ₂	OH ⁻	H ⁺	H ₂ O			
1	Silica Hydrosol	0.5	0	1	0	0	30	Spontaneously	92	CF-3
2	Silica hydrosol	0.5	0	1	0.005	0	30	CDA	28	CF-3
3	Silica hydrosol	0.5	0	1	0	0	30	CDA	80	CF-3
4	Water glass	0.5	0	1	0	0	30	Seeds of CF-3	46	CF-3 and trace ZSM-39
5	Water glass	0.5	0	1	0.01	0	30	CDA	20	CF-3 and trace α -SiO ₂
6	Water glass	0.5	0	1	0	0.02	30	CDA	68	CF-3 and ZSM-39
7	Water glass	1.0	0	1	0	0.02	30	Spontaneously	144	ZSM-39 and cristobalite
8	Water glass	0.5	0	1	0	0.02	15	Spontaneously	144	α -SiO ₂ , ZSM-39 cristobalite
9	Silica hydrosol	0.5	1/100	1	0.01	0	30	Seeds of CF-3	22	CF-3, α -SiO ₂ cristobalite
10	Silica hydrosol	0.5	0	1	0	0	30	Seeds of CF-3	16	CF-3
11	Silica hydrosol	0.5	1/100	1	0	0	30	Seeds of CF-3	46	CF-3
12	Silica hydrosol	0.5	1/150	1	0	0	30	Seeds of CF-3	23	CF-3

^a Hydrothermally reacted at 200°C.

were used to obtain solution B. Then A and B were stirred to get a homogeneous gel. The gel was then poured into a small autoclave lined with GG 17 glass and was crystallized at 180 to 220°C for 2 to 6 days under hydrothermal conditions. The volumes of the autoclaves used were 20, 40 or 200 cm³. The reaction product was filtered, washed, and dried by an IR lamp and then identified by X-ray powder diffraction.

Use of a crystallization directing agent (CDA) or CF-3 seeds led to a more pure CF-3, better reproducibility, and a decrease in the period of crystallization. The molar composition of the CDA was as follows: Al₂O₃/SiO₂, 0; TMEDA/SiO₂, 0.5; OH⁻/SiO₂, 0; H⁺/SiO₂, 0; H₂O/SiO₂, 30. The reaction mixture was hydrothermally reacted at 200°C for 20 to 40 h, then cooled, and a gel of CDA was formed.

Examples of the syntheses are shown in Table I. It was found that the formation of co-crystallized phases, such as ZSM-39, α-SiO₂, and cristobalite, was related to reactant composition, silica source, and method of initiating the crystallization.

3. The Properties of CF-3

3.1. MORPHOLOGY AND OPTICAL PROPERTY

Scanning electron microscopy showed cylindrical aggregates of CF-3 up to the size of 10–20 × 20 × 30 μm consisting of small plates with a thickness of 0.5 μm (see Figure 1). On investigation by microscopy with crossed nicole and gypsum plates inserted, a weak birefringence of CF-3 was found.

3.2. X-RAY POWDER DIFFRACTION

Table II gives the characteristic X-ray powder diffraction data of CF-3. The CF-3 samples prepared from reaction mixtures with different silica/alumina ratios (such as examples 10, 11, 12 in Table I) have similar diffraction patterns.

3.3. CHEMICAL COMPOSITION

Analysis of samples 10, 11, and 12 gave results as shown in Table III. Although no Al₂(SO₄)₃ was added to the reaction mixture, the amount of Al₂O₃ in the product of sample 10 was 0.50% due to an impurity of Al₂O₃ in the silica hydrosol used. From Table III, the typical oxide formula of CF-3 may be expressed as follows:



The high silica percent and low density of CF-3 are similar to that of ZSM-39 and melanophlogite:

	SiO ₂ %	Specific gravity
CF-3	93–94	2.02 ± 0.03 (25°C)
melanophlogite	92.4	2.05 ± 0.013 [3]
	94.6	2.00 [4]
ZSM-39	92.9	1.92 ± 0.02 [6]

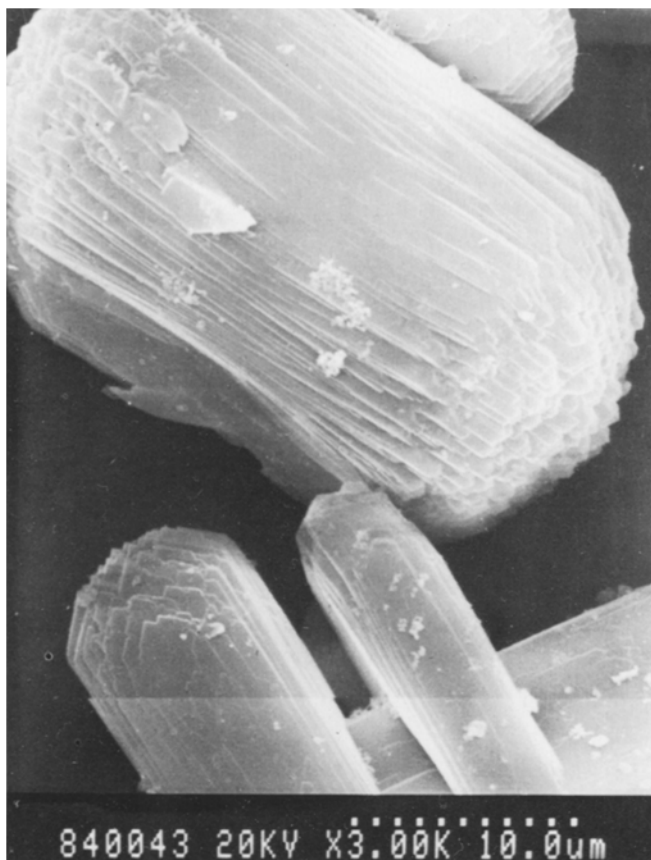


Fig. 1. Scanning electron photomicrograph of CF-3 aggregates.

3.4. HEATING CF-3 IN AIR

Differential thermal analysis of CF-3 at $10^{\circ}\text{C min}^{-1}$ in air showed two wide exotherms at 500 and 870°C . Since no phase change was detected by X-ray powder diffraction for samples of CF-3 heated at 500 or 870°C , these two exotherms were probably associated with the oxidation of organic species. The DTA of ZSM-39 gives wide exotherms up to 900°C [6] which are comparable with those of CF-3. The endotherm to free water below 200°C was not obvious. It might be explained by a small amount of water trapped in small cavities of CF-3 which was difficult to liberate rapidly upon heating.

Like ZSM-39 [6] and melanophlogite [3,4], on heating at 600°C for 48 h, CF-3 samples also turned brown. This indicated that residues of organic matter were trapped in the zeolite cages. After calcining at 900°C for 24 h, samples became white and there was no change in the X-ray powder diffraction pattern. This showed that the thermally stable white products were the carbon-free form of CF-3.

Table II. X-ray powder diffraction data^a of CF-3

2θ (deg)	d (Å)	Relative intensity	2θ (deg)	d (Å)	Relative intensity
7.20	12.26	2	26.61	3.34	8
7.89	11.06	100	27.22	3.27	10
9.56	9.24	9	27.55	3.23	4
11.68	7.56	4	28.45	3.13	2
12.90	6.85	2	28.99	3.07	1
14.16	6.24	2	29.52	3.02	2
14.81	5.97	2	29.73	3.00	2
15.18	5.83	2	30.62	2.91	1
15.99	5.53	2	31.01	2.88	1
17.39	5.09	1	31.44	2.84	1
17.94	4.94	1	32.31	2.76	4
18.59	4.76	1	32.63	2.74	1
19.16	4.62	18	33.28	2.68	3
19.84	4.47	11	34.46	2.60	1
20.60	4.30	33	34.93	2.56	2
21.71	4.09	2	35.59	2.52	4
22.28	3.98	14	36.51	2.45	2
23.57	3.77	5	36.92	2.43	1
24.09	3.69	51	37.56	2.39	2
24.85	3.57	10	38.94	2.31	2
25.99	3.42	3	39.33	2.28	2

^a Rigaku diffractometer, $\text{CuK}\alpha$ radiation.

Table III. Chemical composition of CF-3

Samples	Wt%					Mol%				
	N	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O	TMEDA	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O
10	0.86	0.23	94.21	0.50	1.49	6.30	0.40	320	1	16.90
11	0.75	0.60	93.21	1.81	1.27	1.51	0.54	87	1	3.97
12	0.82	0.46	94.30	1.24	0.30	2.41	0.61	129	1	1.37

3.5. TEST OF CATION EXCHANGE

Sample 11 was calcined at 900°C for 24 h and then exchanged with 0.2 M HCl (ratio of solid/liquid = 0.05 g/ml) at 95°C for 3 times. The residue of Na₂O as analyzed by atomic absorption spectrometer was 0.28%. The degree of exchange for Na⁺ was 53%. It might indicate that the Na⁺ trapped in small cages of CF-3 was difficult to exchange with H⁺. Similarly, the cation exchange of ZSM-39 was also incomplete under mild conditions [6].

3.6. INFRARED ABSORPTION SPECTROSCOPY

The IR spectra of CF-3 and ZSM-39 were performed with a NICOLET FT-IR-50X IR Spectrometer at a scanning range of 400 to 1400 cm⁻¹. Discs of KBr and CF-3 or ZSM-39 powder were used. The IR spectra of CF-3, ZSM-39, and melanophlogite [4] are shown in Figure 2. The ZSM-39 used was synthesized in MA(methylamine)-SiO₂-H₂O gel [7]. There

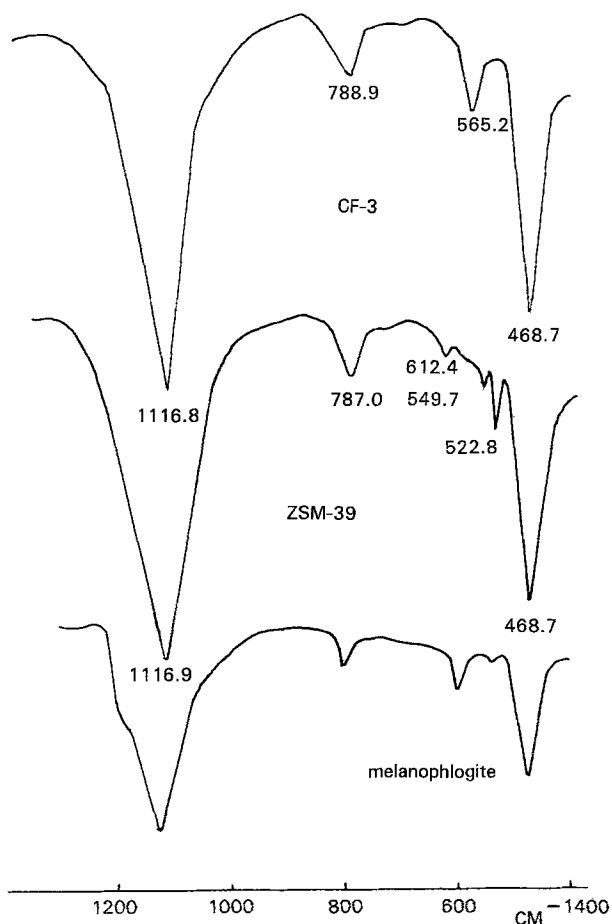


Fig. 2. Infrared spectra of CF-3, ZSM-39 and melanophlogite.

are striking resemblances in both position and intensity of the main absorption bands, especially between CF-3 and melanophlogite. The strongest bands at about 1120 cm^{-1} and 470 cm^{-1} are assigned to the internal tetrahedron vibrations. The medium bands at about 790 cm^{-1} are assigned to the symmetric stretch of the external linkages of the tetrahedral atoms. In the range of $500\text{ to }650\text{ cm}^{-1}$, which is related to the presence of the double rings or a larger polyhedral unit in the framework structure [8], there is a medium band at 565 cm^{-1} for CF-3. In comparison with CF-3, the spectrum for melanophlogite in this region shows two bands, and for ZSM-39, bands at $522.8(\text{m})$, $549.7(\text{w})$ and $612.4(\text{w})\text{ cm}^{-1}$ are found. The framework of ZSM-39 consists of 16-hedra and 12-hedra, which are composed of face-sharing layers. In ZSM-39, these layers are stacked in an ABC sequence. The framework may also be viewed as 16-hedra linked tetrahedrally through common six rings [1]. In the framework of melanophlogite, the 12-hedra are isolated and 14-hedra are linked directly by common six rings in a more simple fashion. Therefore, the IR absorption bands for ZSM-39 and melanophlogite in the range $500\text{ to }650\text{ cm}^{-1}$ may be associated with the linkage of polyhedra. The CF-3 crystal structure will reveal whether the linkage of polyhedra in the CF-3 framework is simpler than that in melanophlogite.

3.7. ABSORPTION ON CF-3

The sorption behavior of CF-3 calcined at 900°C for 24 h has been studied and data are presented in Table IV. The uptake of small molecules such as water or methanol at normal temperature and pressure is very low (less than 1 wt%). Samples exposed to water vapor at 200°C and 15 kg pressure for 24 h sorbed 2.6 to 5.5 wt% of water. The desorption of water on samples having maximum sorption capacity has been investigated by means of TG. The weight loss between 220 and 480°C is 3.4 wt%. The other 2.1 wt% of water is slowly liberated during prolonged calcination at 600°C. The absorption and desorption behavior of water on CF-3 suggest that the pore size of CF-3 may be similar to ZSM-39, which is about 2.7 Å with six oxygen rings. It can also be considered to have a clathrate structure like ZSM-39 and melanophlogite in which the molecules are trapped in cages.

Table IV. Absorption of H₂O and CH₃OH on CF-3

Absorbent	Pressure (mm Hg)	Temperature (°C)	Time (h)	Absorption (Wt%)
Methanol (4.4 Å)	39.5	25	1.25	0.28
	100.9	25	1.50	0.40
	122.6	25	1.75	0.78
H ₂ O (2.7 Å)	20	25	2.0	0.70
	760	120–130	3.0	0.43
	15 (Kg)	200	24–72	2.6–5.5

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