SYNCHROTRON X-RAY STRUCTURE OF A ZEOLITE ZSM-39 ANALOGUE.

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Introduction

The nomenclature of zeolite framework structures is based on different combinations of tetrhedrally coordinated T atom connections in aluminosilicates or aluminophosphates. The framework is microporous consisting of closed cavities in clathrasils, channels or their combinations. Clathrasils are a class of compounds in which guest molecules are trapped within cavities formed by crystalline lattice of different oxides, in the case of water such compounds are called clathrate hydrates. In this case the cavities are formed by silica around a template molecule. The structure of a high-silica zeolite ZSM-39 originally determined by powder diffraction possesses a silica clathrate structure of 12-hedra and 16-hedra formed by 5- and 6-rings of silicons (Figure 1) [1].

Crystal size of zeolites is generally small and many structural studies have been carried out using powder diffraction [2]. According to the literature the crystals prepared in systems with different template molecules have had dimensions of 0.1 – 10 μm. The use of a quaternary 1-methyl-1,3,5,7-tetra-azaadamantane-1-ium ion $[(CH_2)_6N_4CH_3]^+$ [3] as a template has made it possible to obtain crystals large enough (up to 0.07 mm) for single crystal data collection using synchrotron radiation.

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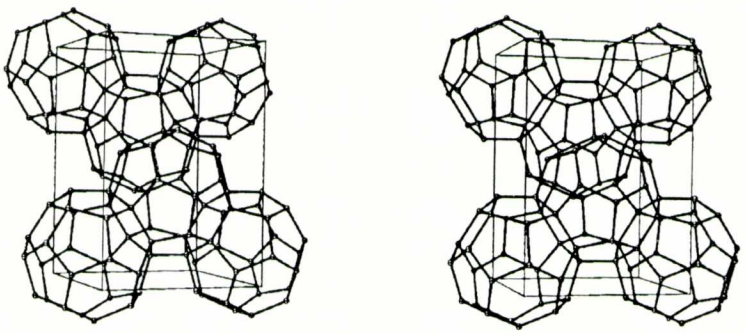

Fig. 1. The clathrate structure of ZSM39 showing the packing of 16-hedra which are tetrahedrally connected to each other through 6-rings of T-atoms. The smaller cavities are 12-hedra formed by 5-rings.

Experimental

The compound was synthesized hydrothermally in the system $[(CH_2)_6N_4CH_3]_2O$-Na_2O-SiO_2-Al_2O_3-H_2O. The silicon source was water glass (P.Q. Corp) containing 26.98% SiO_2 and 8.4% Na_2O. The template molecule 1-methyl-1,3,5,7-tetraazaadamantane-1-ium iodide was provided by R.K. McMullan. The gel formed was crystallized at 180° for 144 hours.

The crystal of dimensions 0.07x0.07x0.07 mm was selected for data collection on a Huber four circle diffractometer at the National Synchrotron Light Source beam line X-7B. The space group from the powder work was determined to be cubic *Fd3m* (no. 227), as was also found in a single crystal determination of ZSM-39 with methylamine templates [4]. In order to confirm the space group, scans were run along the reciprocal axes revealing several reflections systematically absent in the cubic space group *Fd3m*. Based on systematic absences tetragonal space group $I4_1/a$ (no. 88) was chosen. A total of 2057 reflections with $\sin\Theta/\lambda<1.0$ $Å^{-1}$ (λ=0.945 Å, Si(111) double crystal fixed exit monochromator) were collected with ω-scan methods resulting 859 unique reflections ($I > 3\sigma(I)$). Scan range was 0.1° with the stepsize of 0.001°. The scan time for each reflection was determined gating (10,000 counts/step) the number of counts from the I_0-detector.

The data was normalized using two test reflections measured at the intervals of 25 reflections. An examle of a peak profile is shown in Figure 2.

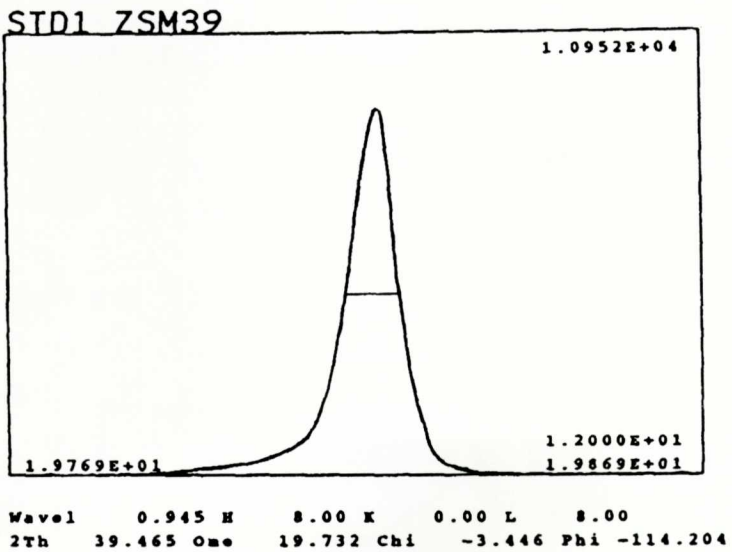

Fig. 2. An example of the scan showing the FWHM of 0.008°.

Results

Table 1. Crystal data

a	13.719(2) Å	2θ-range	3 – 85°
b	13.719(2) Å	Scan-mode	ω
c	19.410(3) Å	Space group	$I4_1/a$
V	3640.2(6) Å^3	Scan range	0.1°
μ	7.1 cm^{-1}	Step size	0.001°
λ	0.945 Å	$\text{Reflns}_{\text{measd}}$	2049
D_o	2.04 gcm^{-3}	$\text{Reflns}_{\text{obsd}}$	859
R	0.049	Nr. param.	133
Crystal size	70x70x70 _m^3		

After the refinement of the cage atoms to the R-value of 5.7%, the difference Fourier synthesis revealed several peaks in the cavities. The largest peak of magnitude 4.5 eÅ^{-1} was found in the center of the 16-hedron (point symmetry

4 bar) surrounded by several smaller peaks. This residual electron density is attributed to the disordered adamantanium ion. Based on the density measurements, elementary analyses and difference Fourier electron densities, refined occupancy factors of the water and the template molecule were found to be 0.5 and 0.125, respectively (Figures 3 and 4).

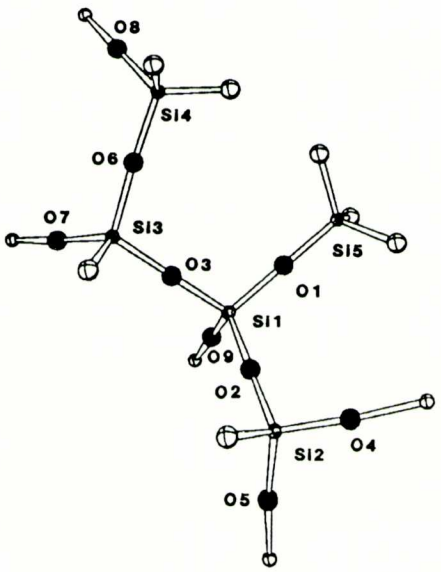

Fig. 3. The asymmetric unit of the ZSM39 framework with atomic labelling. White circles show the connections to the symmetry related atoms.

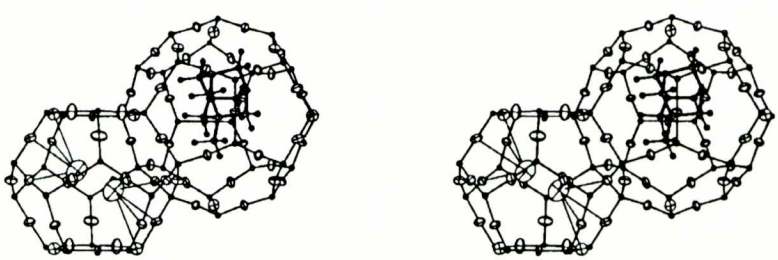

Fig. 4. A structural unit of ZSM39 inclusion compound showing the 12-hedron with the water molecule having occupancy of 0.5 and the 16-hedron with the template in one of its four orientation having occupancy of 0.125.

Table 2. Interatomic distances and angles between atoms in ZSM39

				DIST.	S.D.
Si1	–		O1	1.5183	0.0120
	–		O2	1.5563	0.0084
	–		O3	1.5594	0.0104
	–		O9	1.5653	0.0105
Si2	–		O2	1.5600	0.0087
	–		O5	1.5707	0.0089
	–		O4	1.5738	0.0028
	–		O7	1.6114	0.0089
Si3	–		O7	1.5403	0.0089
	–		O3	1.5545	0.0105
	–		O8	1.5891	0.0096
	–		O6	1.5973	0.0104
Si4	–		O6	1.5535	0.0103
	–		O8	1.5577	0.0096
	–		O9	1.5723	0.0106
	–		O5	1.5769	0.0089
Si5	–	4	O1	1.5565	0.0120
O1	–		Si1	1.5183	0.0120
	–		Si5	1.5565	0.0120
O2	–		Si1	1.5563	0.0084
	–		Si2	1.5600	0.0087
O3	–		Si3	1.5545	0.0105
	–		Si1	1.5594	0.0104
O4	–	2	Si2	1.5738	0.0028
O5	–		Si2	1.5707	0.0089
	–		Si4	1.5769	0.0089
O6	–		Si4	1.5535	0.0103
	–		Si3	1.5973	0.0104
O7	–		Si3	1.5403	0.0089
	–		Si2	1.6114	0.0089
O8	–		Si4	1.5577	0.0096
	–		Si3	1.5891	0.0096
O9	–		Si1	1.5653	0.0105
	–		Si4	1.5723	0.0106

ATOM1	ATOM2	ATOM3	ANGLE	SD
O1	Si5	O1	107.17	0.94
O1	Si5	O1	110.63	0.48
O1	Si5	O1	110.63	0.48
O1	Si5	O1	110.63	0.48
O1	Si5	O1	110.63	0.48
O1	Si5	O1	107.17	0.94
O1	Si1	O2	109.10	0.66
O1	Si1	O3	108.95	0.77
O1	Si1	O9	109.32	0.79
O2	Si1	O3	110.40	0.63
O2	Si1	O9	108.48	0.68
O3	Si1	O9	110.57	0.56
O2	Si2	O4	112.39	0.73
O2	Si2	O5	108.05	0.58
O2	Si2	O7	107.22	0.58
O4	Si2	O5	109.94	0.46
O4	Si2	O7	109.61	0.45
O5	Si2	O7	109.57	0.49
O3	Si3	O6	110.02	0.53
O3	Si3	O7	108.77	0.55
O3	Si3	O8	108.52	0.55
O6	Si3	O7	109.40	0.51
O6	Si3	O8	110.96	0.50
O7	Si3	O8	109.14	0.52
O5	Si4	O6	111.20	0.52
O5	Si4	O8	109.25	0.52
O5	Si4	O9	107.41	0.55
O6	Si4	O8	110.19	0.51
O6	Si4	O9	110.73	0.56
O8	Si4	O9	107.95	0.60
Si5	O1	Si1	177.67	1.01
Si1	O2	Si2	175.26	0.89
Si1	O3	Si3	179.61	0.85
Si2	O4	Si2	174.91	1.14
Si2	O5	Si4	169.35	0.69
Si3	O6	Si4	175.62	0.62
Si2	O7	Si3	170.30	0.69
Si3	O8	Si4	168.59	0.71
Si1	O9	Si4	177.10	0.94

The template molecule structure was included in the refinement as a rigid group applying to it different starting orientations and occupancy factors. The adamantanium template is distorted and non-stoichiometrically distributed in the cavity (Figure 5).

As shown in Table 2 the T-atom environments are very close to tetrahedral angles and Si – O – Si angles are exceptionally large ranging from 168 to 180°.

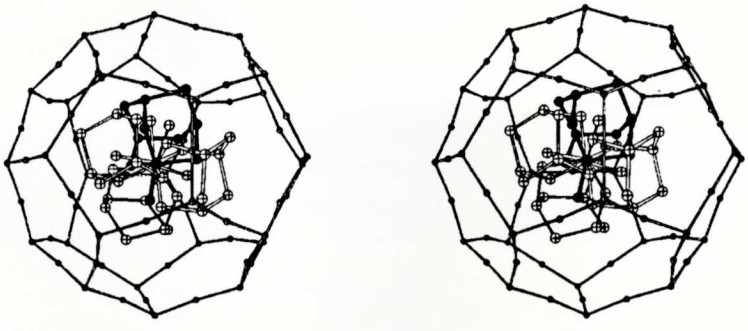

Fig. 5. Stereoscopic presentation of the 1-methyl-1,3,5,7-tetra-azaadamantan-1-ium with 4-bar symmetry applied to it in the 16-hedron.

REFERENCES

[1] J.L. SCHLENKER, F.G. DWYER, E.E. JENKINS, W.J. ROHRBAUGH, G.T. KOKOTAILO and W.M. MEIER, *Nature* **294** (1982) 340.
[2] L.B. McCusker, Acta Crystallogr. A47 (1991) 297.
[3] R. K. MCMULLAN, F. TAKUSAGAWA and T.C.W. MAK, *J. Inclusion Phenomena*, **6** (1988) 515.
[4] Y. LONG, H. HE, P. ZHENG, G. WU and B. WANG *Ibid.* 5, (1987) 355.