

UTM-1: An Eight-Membered Ring Zeolite with the Basic Building Chains of the MFI Topology

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The structure of zeolite UTM-1 has been determined from synchrotron X-ray powder diffraction pattern by direct methods and Rietveld refinement. The framework of UTM-1 consists of pocket-like cages connected by sharing eight-membered rings forming one-dimensional channels. The structure can be completely described by the assembly of chains of 5⁸ cages. Identical chains are found in MFI topology; the zeolites UTM-1 and ZSM-5 are distinguished from each another by the way the chains are assembled.

A key element in the synthesis of new zeolites with novel pore architecture is organic molecules as structure-directing agents (SDAs). The relationships between the geometrical and chemical properties of the organic molecules and the geometry and characteristics of the cages and the pores of the zeolites are receiving much attention. However, it is known that the use of small and featureless organocations such as spherical or monocyclic molecules can direct the formation of zeolites with different topologies under a variety of synthesis conditions. Thus the recognized importance of the tight fit between the guest molecule and the framework has prompted the development of new SDAs with complex shapes.^{1,2} It is also expected that systematic explorations of the crystallization conditions of an silicate or aluminosilicate gel with a given template by carefully controlling the synthesis parameters can produce new zeolites and bring some clues to the process of zeolite formation.

The monocyclic molecule hexamethyleneimine (HMI) has been used in general as a template in the synthesis of zeolite PSH-3^{3,4} and MCM-22^{5,6} having MWW topology. During the attempted synthesis of high-silica MCM-22, we found specific conditions leading to the material, whose framework topology may be isostructural with that of MCM-35⁷ because of similarities in their XRD patterns. We referred to this material as UTM-1. In a typical synthesis of UTM-1, an aqueous solution containing NaCl and NaOH was added dropwise to colloidal silica (Snowtex-N, Nissan Chemical). After 1 h, HMI was added and the stirring was continued for 30 min. The gel thus obtained was placed in a stainless steel autoclave with a Teflon inner, the solution filling about half the reactor volume. Crystallization of zeolite UTM-1 is achieved after 7 days at 140 °C under tumbling conditions (60 rpm). The molar ratio of constituents

TABLE 1: Crystallographic Data for the Structure of Zeolite UTM-1

chemical formula	Si ₄₄ O ₈₈
space group	C2/m
cell parameters (Å)	<i>a</i> = 9.4854 (2) <i>b</i> = 30.6991 (7) <i>c</i> = 7.3150 (1) β = 91.734 (1)
cell volume (Å ³)	<i>V</i> = 2129.1 (1)
wavelength (Å)	λ = 0.850047 (4)
contributing reflections	891
$R_{wp} = [\sum \omega_i(y_{io} - y_{ic})^2 / \sum \omega_i y_{io}^2]^{1/2}$	0.048
$R_p = [\sum (y_{io} - y_{ic})^2 / \sum y_{io}^2]^{1/2}$	0.038
$R_t = \sum I_o - I_c / \sum I_o$	0.040
range of distances Si–O (Å)	1.570 < <i>d</i> _{Si–O} < 1.612
average distance Si–O (Å)	$\langle d_{Si–O} \rangle$ = 1.590
range of angles O–Si–O (°)	104.1 < O–Si–O < 114.9
range of angles Si–O–Si (°)	141.7 < O–Si–O < 174.7

in the synthesis mixture was Si: 0.0029 Al: 0.18 Na: 0.12 OH[−]: 0.06 Cl: 45 H₂O: 0.50 HMI.

After the synthesis, products were washed thoroughly with water, filtered, and dried at 120 °C for 4 h. As-synthesized form thus obtained was calcined at 550 °C for 12 h in the flow of air to obtain template-free calcined UTM-1. Details of the synthesis conditions may be found elsewhere.^{8,9} Pure and well-crystallized UTM-1 was prepared in a narrow domain of synthesis conditions. The zeolites ZSM-5, ZSM-12, and MCM-22 are found at the limits of the crystallization field of UTM-1.

We report here the structure determination of zeolite UTM-1 with direct methods from synchrotron X-ray diffraction data.

Synchrotron X-ray powder diffraction pattern of the calcined form of zeolite UTM-1 was collected on beamline BM16 at the European Synchrotron Radiation Facility (ESRF). The sample was loaded in a glass capillary of diameter 1 mm, and

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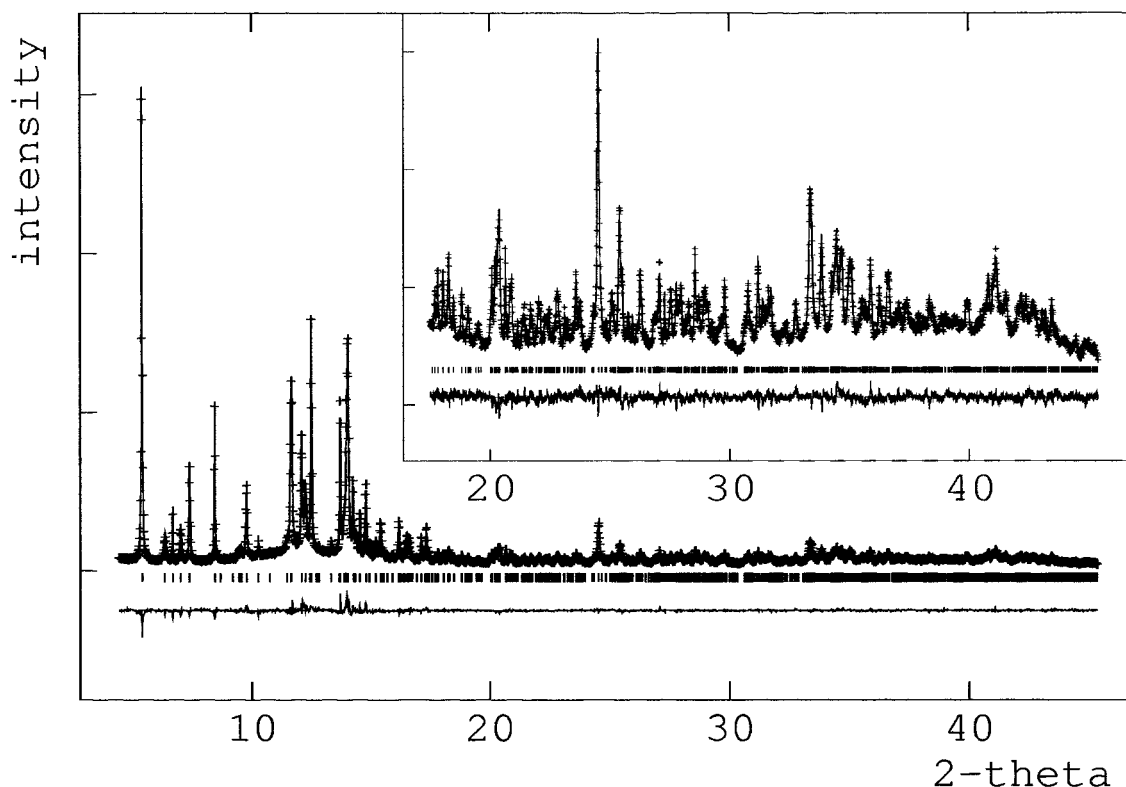


Figure 1. Experimental, calculated, and difference synchrotron powder diffraction patterns for zeolite UTM-1 using a wavelength $\lambda = 0.850047$ Å. The inset showing the high-angle part of the powder pattern has been expanded by a factor 10.

TABLE 2: Fractional Atomic Coordinates and Isotropic Displacement Parameters (\AA^2), Defined as $\exp[8\pi^2 U_{\text{iso}}(\sin\theta/\lambda)^2]^a$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Si1	.12339(36)	.04889(13)	.3678(4)	0.0180(13)
Si2	.00631(40)	.22939(13)	.2870(4)	0.0139(13)
Si3	.000000	.08317(18)	.000000	0.0158(18)
Si4	.19323(39)	.15310(13)	.8365(5)	0.0167(13)
Si5	.33898(35)	.12257(12)	.4773(5)	0.0146(12)
Si6	.30360(41)	.19760(13)	.1806(5)	0.0155(13)
O1	.1730(9)	.000000	.4005(12)	0.0208(39)
O2	.0725(6)	.05462(24)	.1582(7)	0.0186(23)
O3	.2575(6)	.08012(24)	.4076(8)	0.0265(25)
O4	.000000	.06325(32)	.500000	0.0241(38)
O5	.1605(7)	.22351(25)	.2183(8)	0.0250(26)
O6	.000000	.23525(31)	.500000	0.0192(37)
O7	.9365(7)	.27030(27)	.1925(8)	0.0161(23)
O8	.9213(8)	.18634(24)	.2432(9)	0.0244(26)
O9	.1260(6)	.11099(22)	.9222(9)	0.0190(25)
O10	.2957(6)	.17621(23)	.9857(9)	0.0244(27)
O11	.2866(6)	.13816(21)	.6729(9)	0.0204(26)
O12	.3260(7)	.16163(25)	.3338(8)	0.0244(26)
O13	.500000	.10803(35)	.500000	0.0279(39)

^a Numbers in parentheses represent the estimated standard deviations.

the acquisition was carried out at room temperature without evacuating the material, as low content of adsorbed water is expected in high-silica zeolite. The unit-cell was indexed using the program TREOR90,¹⁰ giving a monoclinic solution with a large lattice parameter **b** and systematic absences consistent with space group *C2/m* (Table 1).

The powder pattern shows significant anisotropic line broadening depending on the *hkl* indexes typical of microstructural effects.¹¹ The crystallites have a platelike morphology with the smaller dimension along the **b** axis. A Le Bail structure factor extraction¹² was performed in the 2θ range between 2° and 45° and the reflections were used as input data for the direct methods

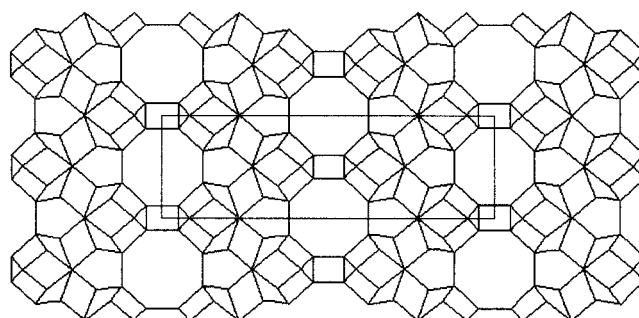


Figure 2. Framework topology of zeolite UTM-1 viewed down the pores in the *c* direction. The unit-cell edges are superposed on the structure.

program SIRPOW,¹³ yielding a solution using the default parameters. The silicon atoms were identified and the framework structure was completed by KRIBER.¹⁴ The atomic coordinates were optimized by the program DLS-76.¹⁵ The structural model was refined by the Rietveld method from the synchrotron data using the GSAS software package.¹⁶ The anisotropy of the line broadening was modeled using the Lorentzian Scherrer broadening option in GSAS.

The final atomic position and thermal parameters are given in Table 2. There are six independent tetrahedral atoms and 13 oxygen atoms in the structure, making UTM-1 one of the most dense zeolites, $FD = 20.7 \text{ T/nm}^3$. Figure 1 shows the observed and calculated profiles, together with their difference curve for the final Rietveld refinement. The distances between atoms are typical of distances observed in high-silica zeolites and clathrasils.

UTM-1 is formed from two types of cages, small (5^8) cages composed of eight five-membered rings and large ($4^25^86^28^4$) cages. The 16-sided cages are unusual cages as they contain four eight-membered rings, two with a regular shape and two

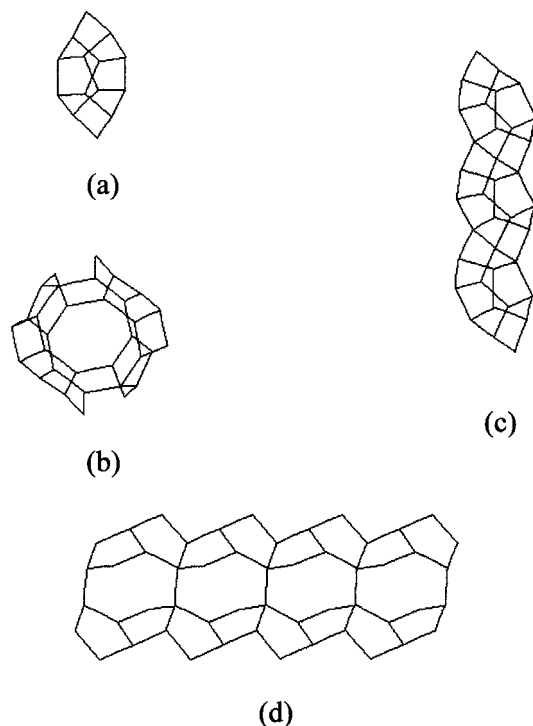


Figure 3. (a) Small (5^8) cage and (b) large ($4^2 5^8 6^2 8^4$) cage found in zeolite UTM-1, (c) interconnection of (5^8) cages along the pore direction forming the basic building chains of the structure, (d) interconnection of the pocket-like cages along the **c** direction forming the one-dimensional channels, view of the channel along the **b** axis showing the distorted eight-membered rings.

strongly distorted. The cages are connected through the well-shaped eight-membered rings and form one-dimensional channels running along the **c** axis (Figure 2). The oxygen atoms of the eight-membered rings are nearly coplanar as no atoms deviate from the average plan by more than 0.2 Å. The aperture, with a free diameter varying from 3.6 to 4.1 Å, is relatively regular compared to many other eight-ring structures.¹⁷ The largest diameter of the UTM-1 cage, i.e., between the two opposite four-membered rings, is ca. 9 Å.

A complicated pore network, accessed through the puckered eight-membered rings, connects the channels. This second pore system, containing seven-membered loops, is however blocked by six-ring windows not allowing the diffusion of molecules from one strait channel to another. This confined volume can

be described as two lateral ($5^4 6^6 8$) nonconcave cavities connected to the UTM-1 cages, which increase the diameter of the cages in the direction perpendicular to the channel axis. But their access is probably limited because of the strong distortion of the eight-membered ring openings.

The smaller (5^8) cages form chains running parallel to the one-dimensional channels by sharing three vertexes (Figure 3). The structure may be completely described as an assembly of chains of (5^8) cages. The MFI topology is also constructed entirely by the same chains of (5^8) cages. Both the zeolites UTM-1 and ZSM-5 are distinguished one from the other by the way the chains are assembled. It is worth noting that ZSM-5 is obtained as impurity as the Si/Al ratio of the gel decreases.

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