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Detailed Investigation of the Lattice Structure of Zeolite ZSM-11 by a Combination of Solid-State NMR and Synchrotron X-ray Diffraction Techniques

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Abstract: The lattice structure of a pure and completely siliceous sample of zeolite ZSM-11 has been investigated by a combination of high-resolution solid-state ^{29}Si MAS NMR and synchrotron-based X-ray powder diffraction techniques. The structure is temperature dependent in the range 263–363 K and a good fit to the diffraction data at 363 K is obtained with space group $I\bar{4}m2$ and $a_0 = 20.067$ (1) and $c_0 = 13.411$ (1). At room temperature the XRD data cannot be refined as the structure is intermediate and the lattice structure of the limiting low-temperature, low-symmetry form will only be deduced from data collected at 263 K.

Zeolites are porous aluminosilicates widely used as industrial sorbents, catalysts, and catalyst supports.[1–4] They can be formally described by the oxide formula **1** where there has been the replacement of some of the SiO_4^{4-} tetrahedra in silica by AlO_4^{5-} tetrahedra.

$$M^{n+}[(AlO_2)_n(SiO_2)_m]^{n-}\cdot xH_2O$$

1

Because of the difference in nuclear charge between Al and Si, a positive charge M (usually in the form of an alkali-metal cation, which could possibly be polyvalent, or as a quaternary ammonium salt) must be present for each aluminum atom to preserve electrical neutrality. The unique properties of size and shape selectivity of these materials come from their open porous framework structures which contain cavities (where the cations and associated water are usually located) interconnected by a network of channels.

In structural investigations of these materials, the ultimate aim is an understanding of the lattice structure and also the effect of elevated temperatures and/or the presence of organic molecules because of their quite unique properties as catalysts and molecular sieves. In the past, X-ray diffraction has been the most widely used technique in these investigations,[5] but it has been limited by two important factors. First, because Si and Al have almost identical scattering factors it is usually not possible to determine the distribution of Si and Al throughout the lattice, even when the framework is known, especially since the distribution is often rather random in nature. Second, although synthetic zeolites are very highly crystalline, they are usually microcrystalline, precluding the use of single-crystal techniques and necessitating the deduction of lattice structures from much more limited powder diffraction data.[6]

Recently, high-resolution ^{29}Si and ^{27}Al solid-state NMR spectroscopy has developed as a complementary technique for the investigation of these structures.[7–9] In the ^{29}Si MAS NMR spectra of low Si/Al ratio materials, five resonances may be observed and assigned to the five possible silicon environments Si[4Al], Si[Si,3Al], Si[2Si,2Al], Si[3Si,Al], and Si[4Si], giving a description of the average distribution of Si and Al in the lattice.[10] A more direct relation of the ^{29}Si spectra to the lattice structures comes from the investigation of completely siliceous systems where all of the aluminum has been removed from the lattice by chemical means (usually hydrothermal treatments) producing a perfectly crystalline, completely siliceous lattice with a structure identical with that of the original starting zeolite. For these systems, extremely narrow resonances are observed (all of which are due to Si[4Si]), whose numbers and relative intensities reflect the crystallographically inequivalent sites in the unit cell.[11,12]

Although X-ray diffraction data must ultimately be used to obtain the geometric structure directly, it is primarily sensitive to long-range orderings and periodicities, even if they are imperfect and the technique can be limited in this way. High-resolution solid-state NMR probes the local magnetic environment (geometries, ordering, symmetries, etc.) of the T-sites in the unit cell and is generally more sensitive to deviations from a general structure such as those induced by defects,[13] changes in temperature, or the presence of sorbed organic molecules[14,15] although

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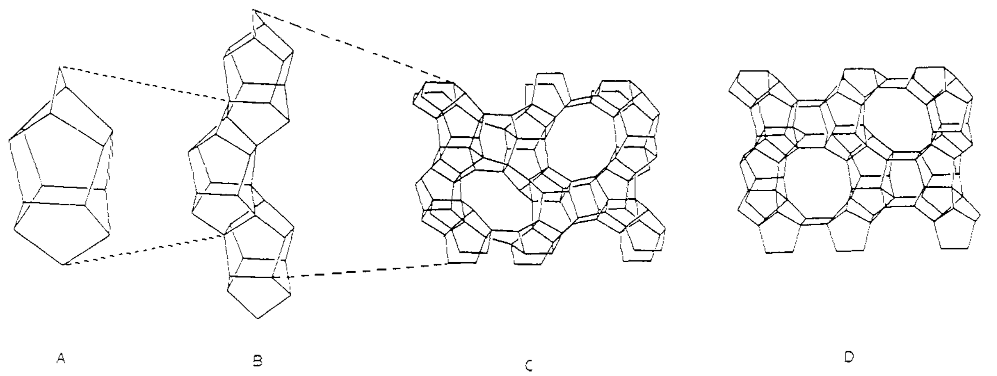

Figure 1. Schematic representations of (A) the pentasil building unit, (B) this unit joined into chains, (C) a projection of the layers of such chains joined to form the ZSM-5 lattice (*i*-stacking), and (D) a similar projection of the layers joined to form the proposed ZSM-11 lattice (σ-stacking).

it gives no direct determination of the overall structure itself.

As indicated above, the NMR and XRD techniques are complementary and are best used together to obtain as complete a description of the structure as possible. In the present work we have optimized both of them as much as possible and applied them in a combined investigation of the lattice structure of zeolite ZSM-11. This system is a member of the family of zeolites known as pentasil zeolites, based on the pentasil unit (Figure 1A), as a basic building block. By joining these units into chains, then forming layers, and then joining the layers as indicated in the projection of Figure 1B, the lattice structure of zeolite ZSM-5, the best known of these systems is formed (*i*-stacking).[16] If the same layers are joined as indicated by the projection shown in Figure 1C so that they are related by a plane rather than a center of symmetry (σ-stacking), the general structure postulated by Kokotailo and co-workers for ZSM-11 is formed.[17] The lattice structures of ZSM-5 and ZSM-11 are thus structurally very closely related, differing in only this one projection, and this has presented problems both in synthesis and in characterization. Whereas it is relatively straightforward to prepare pure, monophasic samples of ZSM-5, it is very difficult to obtain samples of ZSM-11 free of intergrowths of ZSM-5, limiting the quality of the structural data that can be obtained.[18] The nature and degree of the intergrowths has been examined by electron microscopy and X-ray diffraction techniques, the simplest diagnostic observable being two reflections in the powder XRD pattern at $2\theta = 45°$ for ZSM-5 or intergrowths containing ZSM-5 while ZSM-11 should have a single sharp reflection at $2\theta \simeq 45°$.

Although the structure of ZSM-5 is well-defined, there is only limited structural data relating to ZSM-11.[17,19] In the present work we report the results of a detailed investigation of the structure of zeolite ZSM-11 by both NMR spectroscopy and diffraction techniques utilizing a completely crystalline, monophasic, and completely siliceous sample to obtain high-quality ^{29}Si MAS NMR spectra and with the powder diffraction data optimized by using a monochromatic synchrotron-based X-ray source. From these data a well-defined high-temperature structure has been determined and the nature of the distortions of the lattice that are present at ambient temperature identified.

Experimental Section

ZSM-11 was synthesized from aqueous silicate solutions by modifying the method reported by Chu,[20] in the presence of $PhCH_2N(CH_3)_3Cl$ and $(C_4H_9)_4NCl$ as templates using hydrothermal techniques.

A 14-day heat treatment at 170 °C yielded highly crystalline ZSM-11 material, which was dealuminated by steaming as described earlier[21] at a temperature of 770 °C for 7 days. The X-ray powder pattern obtained on a conventional diffractometer showed well-crystallized ZSM-11 with no indication whatsoever of ZSM-5 intergrowth as detailed by Perego et al.[18] Lattice parameters and systematic absences indicated a tetragonal, body-centered unit cell, indicative of a σ-stacking of pentasil layers i.e., with no intergrowths involving the *i*-stacking characteristic of ZSM-5, in agreement with the proposed structure of ZSM-11.

^{29}Si MAS NMR spectra were obtained at 79.6 MHz (proton frequency 400 MHz) with a Bruker MSL 400 spectrometer and a home-built probe.[22] Samples were spun at ~5 KHz in a 9-mm cylindrical Torlon spinner of approximately 500-μL capacity[23] and the magic angle optimized by using the ^{79}Br resonance of KBr inside the spinner as described by Frye and Maciel.[24] Temperature control was achieved with a conventional Bruker temperature controller.

Intensity data of a powder sample were collected at beam line X13A at Brookhaven National Laboratory, Brookhaven, NY [$\lambda = 1.3151$ Å, Ge(111) monochromator; Ge(220) analyzer; scanning interval 0.01° 2θ; range 5–70° 2θ].[25] Experiments were carried out at both ambient temperature and 100 °C using a capillary sample. Diffuse scattering was observed at around 15, 21, and 25°, related to amorphous material, and above 55°, related to the sample heater. Intensities from these regions were suppressed for the refinement process.

Results and Discussion

The high-resolution ^{29}Si MAS NMR spectra obtained at 5° intervals from 268 to 373 K are presented in Figure 2. The sharpness of the resonances (the line widths at half-height of resolved peaks being ~0.2 ppm) confirms the highly siliceous nature of the sample and its monophasic nature. The most striking feature of the spectra is their temperature dependence. Thus, there is little change in the spectra above 333 K and below 278 K, given that small gradual shifts may be expected due to changes in local T-site geometries from lattice expansion. However, between 283 and 323 K there are changes not only in resonance positions but also in the number and intensities of the signals, the most noticeable being in the range 313–323 K. These changes must involve a change in the symmetry and pose problems for structure investigations at ambient temperature where the system has not quite reached the limiting low-temperature form.

The limiting high-temperature spectrum may be deconvoluted in terms of six resonances of approximate relative intensities 1:4:2:1:2:2 as shown in Figure 3. This is in good agreement with

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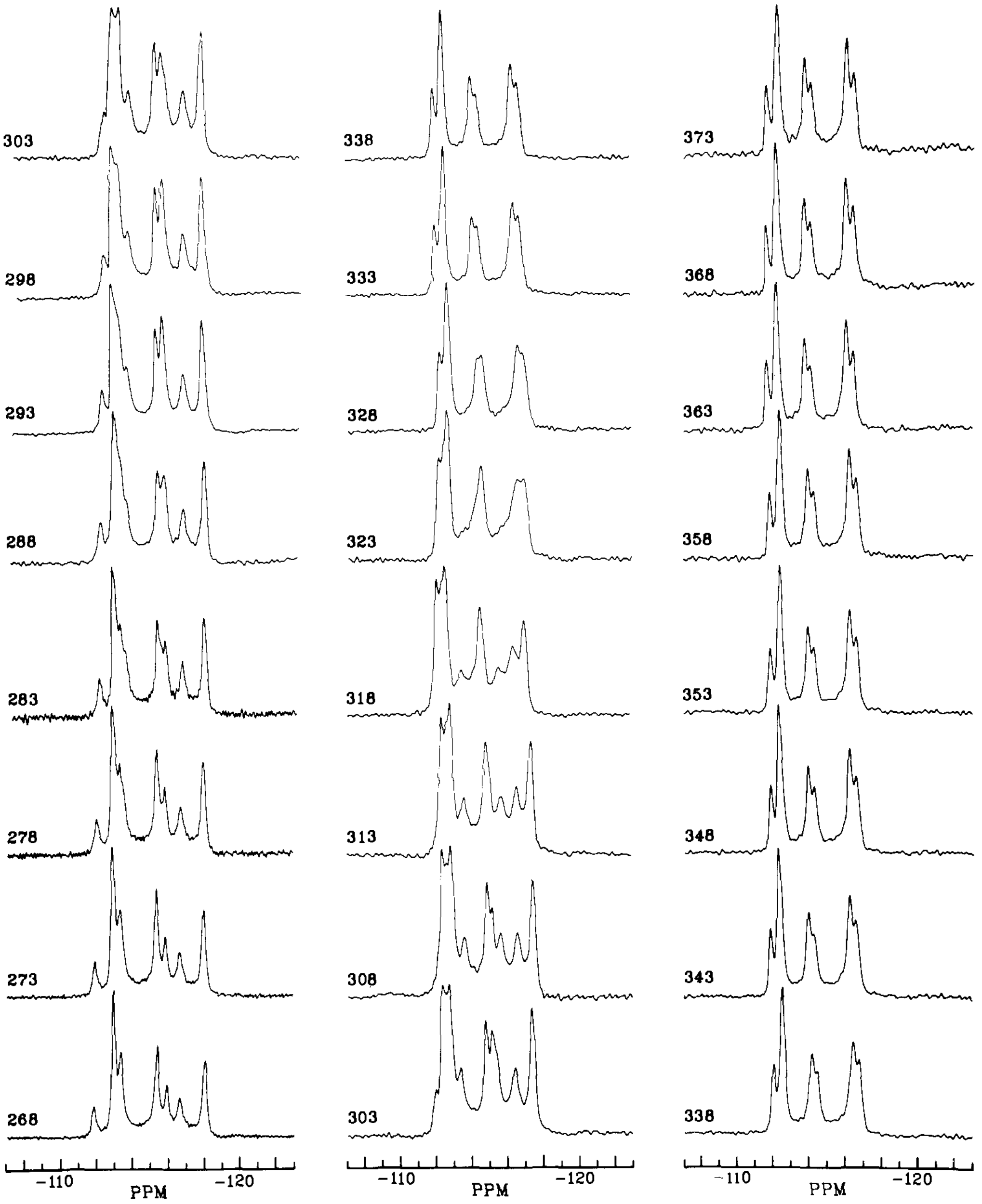

Figure 2. ^{29}Si MAS NMR spectra (79.6 MHz) of zeolite ZSM-11 recorded at 5° intervals at the temperatures indicated.

the previously proposed structure where the 96 T-atoms in the unit cell are distributed over seven crystallographically inequivalent sites of relative populations 1:2:2:2:1:2:2. It should be noted, however, that the "room-temperature" spectrum at 303 K cannot be fitted in terms of this symmetry, a minimum of nine peaks being needed. Figure 4 shows the deconvolution of the limiting low-temperature spectrum at 263 K. From the intensity of the highest field resonance, which from the temperature variation is known to respresent two T-sites, the total number of T-sites in the asymmetric unit can be deduced to be 12. Eight peaks are required for the deconvolution, but their relative intensities now approximate to 1:3:2:1:1:1:1:2, implying a lowering of the unit cell symmetry, but with at least eight inequivalent T-sites in the asymmetric unit.

With these results in mind, we can now discuss the refinement of the synchrotron X-ray diffraction data. In assessing the success of the refinements, particular attention was paid not only to the resulting "R factors" but also to the reasonableness of the resulting structures, particularly in terms of the Si–O distances and Si–O–Si bond angles, the former being known to vary very little in well-defined crystalline silica phases.[26]

At 100 °C, excellent data are obtained with very sharp reflections due to the monochromatic nature of the synchrotron radiation. The data are presented in Figure 5 together with the theoretical fit from the refinement and an estimate of the general correctness of the fit in terms of the difference between observed and calculated diffraction patterns. There is no splitting of peaks or weak additional intensities indicative of stacking faults. The peak shapes are intermediate between Lorentzian and Gaussian and can be fitted very well by a convolution of the two functions in a pseudo Voight approximation.[27]

The structure refinement was performed with a modified Rietveld–Hewat program.[28] The total number of peaks included in the refinement was 678; the number of parameters was 85, 54 of which were positional parameters, 22 were isotropic temperature factors, and 5 were profile parameters. The refinement of all 85 parameters in space group $I\bar{4}m2$ and cell parameters $b = 20.067$ (1) and $c = 13.411$ (1) Å converged for the silica framework at $R_p = 0.13$ ($R_p = \sum|y(\text{obsd}) - (1/C)y(\text{calcd})|/\sum|y(\text{obsd})|$). The final atomic coordinates, thermal parameters, and standard deviations are given in Table I, with the numbering of the atoms

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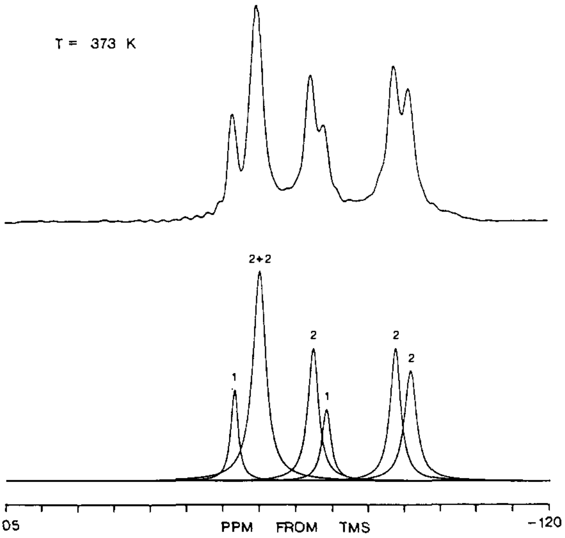

Figure 3. Limiting high-temperature ^{29}Si MAS NMR spectrum of ZSM-11 (373 K) and its deconvolution in terms of Lorentzian curves as indicated.

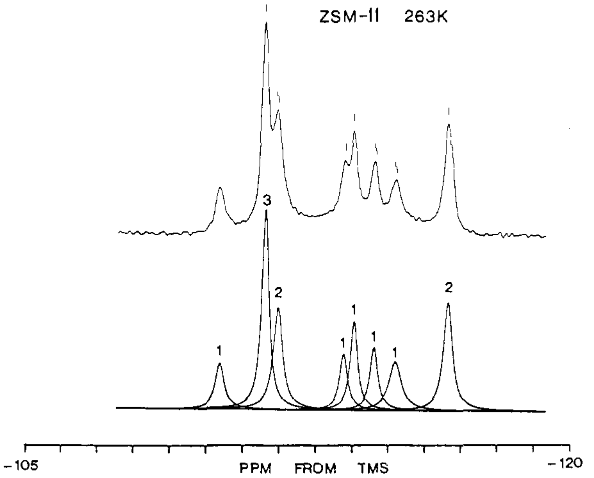

Figure 4. Limiting low-temperature ^{29}Si MAS NMR spectrum of ZSM-11 (263 K) and its deconvolution in terms of Lorentzian curves as indicated.

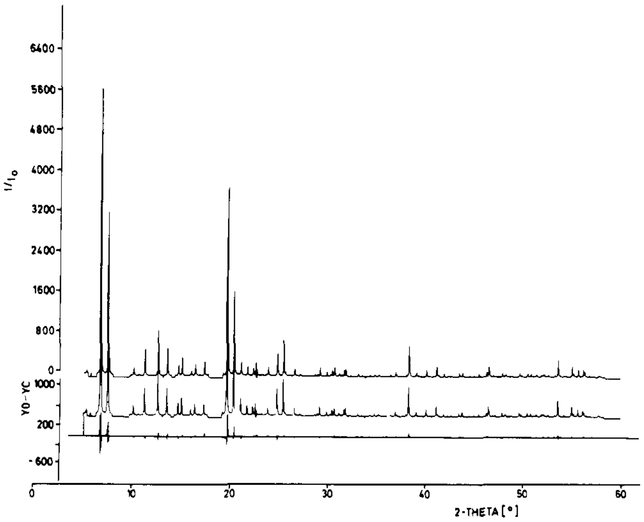

Figure 5. Synchrotron X-ray diffraction pattern of ZSM-11 together with the theoretical fit from a Rietveld structure refinement and the difference between the observed and calculated patterns.

Table I. Positional Parameters of Powder Refinements of ZSM-11 (100 °C) in Space Group $I\bar{4}m2$

				B_{eq} values
Si(1)	0.077 (6)	0.0777 (6)	0.0	0.34 (48)
Si(2)	0.1212 (6)	0.1860 (6)	0.1451 (8)	1.64 (36)
Si(3)	0.0775 (5)	0.2219 (6)	0.3569 (11)	1.29 (34)
Si(4)	0.2801 (5)	0.1882 (7)	0.1403 (9)	0.39 (30)
Si(5)	0.3053 (8)	0.0768 (5)	-0.0079 (6)	0.28 (33)
Si(6)	0.1938 (7)	0.1938 (7)	0.5	1.10 (35)
Si(7)	0.0761 (5)	0.3819 (5)	0.3589 (8)	-0.20 (26)
O(1)	0.0873 (17)	0.0	0.0279 (27)	3.30 (1.26)
O(2)	0.1067 (12)	0.1179 (12)	0.0975 (16)	2.83 (77)
O(3)	0.0926 (9)	0.1856 (13)	0.2550 (15)	1.71 (71)
O(4)	0.2018 (10)	0.1993 (11)	0.1506 (13)	1.79 (46)
O(5)	0.3309 (15)	0.1186 (11)	0.0889 (15)	1.62 (63)
O(6)	0.3003 (19)	0.0	0.0247 (19)	0.77 (71)
O(7)	0.3095 (13)	0.1905 (12)	0.25	3.27 (98)
O(8)	0.1204 (9)	0.1931 (15)	0.4478 (14)	0.24 (53)
O(9)	0.2511 (10)	0.1927 (14)	0.4252 (14)	1.43 (57)
O(10)	0.0905 (9)	0.3010 (11)	0.3497 (13)	1.16 (55)
O(11)	0.0	0.2090 (22)	0.3875 (23)	3.49 (1.14)
O(12)	0.0	0.3960 (15)	0.3871 (20)	-0.34 (88)
O(13)	0.0926 (11)	0.2437 (11)	0.0900 (15)	1.59 (71)
O(14)	0.1295 (10)	0.4078 (11)	0.4348 (14)	0.03 (62)
O(15)	0.0875 (8)	0.4125 (8)	0.25	-1.59 (82)

Table II. Bond Distances (Å) and Angles (deg) of ZSM-11, $I\bar{4}m2$ (100 °C)

Bond Distances			
Si(1)-O(1)	1.61 (2)	2×	1.625
Si(1)-O(2)	1.64 (2)	2×	
Si(2)-O(13)	1.49 (3)		1.563
Si(2)-O(2)	1.54 (3)		
Si(2)-O(3)	1.58 (2)		
Si(2)-O(4)	1.64 (2)		
Si(3)-O(3)	1.58 (2)		1.605
Si(3)-O(8)	1.60 (2)		
Si(3)-O(10)	1.61 (2)		
Si(3)-O(11)	1.63 (1)		
Si(4)-O(7)	1.59 (1)		1.598
Si(4)-O(4)	1.59 (2)		
Si(4)-O(9)	1.60 (2)		
Si(4)-O(5)	1.61 (3)		
Si(5)-O(14)	1.55 (2)		1.598
Si(5)-O(5)	1.55 (2)		
Si(5)-O(6)	1.61 (1)		
Si(5)-O(13)	1.68 (3)		
Si(6)-O(9)	1.53 (2)		1.580
Si(6)-O(8)	1.63 (2)		
Si(7)-O(14)	1.57 (2)		1.605
Si(7)-O(12)	1.60 (1)		
Si(7)-O(15)	1.60 (1)		

Bond Angles			
Si(1)-O(1)-Si(1)	149.8 (2.5)	Si(6)-O(9)-Si(4)	158.5 (2.0)
Si(2)-O(2)-Si(1)	146.6 (1.7)	Si(3)-O(10)-Si(7)	157.1 (1.3)
Si(3)-O(3)-Si(2)	151.0 (1.8)	Si(3)-O(11)-Si(3)	145.3 (2.5)
Si(4)-O(4)-Si(2)	161.0 (1.6)	Si(7)-O(12)-Si(7)	145.6 (2.0)
Si(5)-O(5)-Si(4)	147.4 (1.6)	Si(2)-O(13)-Si(5)	165.3 (1.6)
Si(5)-O(6)-Si(5)	147.5 (1.9)	Si(5)-O(14)-Si(7)	165.1 (1.6)
Si(4)-O(7)-Si(4)	152.0 (1.9)	Si(7)-O(15)-Si(7)	160.2 (1.4)
Si(3)-O(8)-Si(6)	144.1 (1.6)		

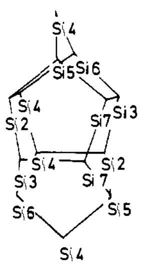

Figure 6. Numbering of the T atoms of the pentasil unit used in refinement of the synchrotron data (Table I).

shown in Figure 6. Selected Si–O distances and Si–O–Si angles are listed in Table II. The overall Si–O distance ⟨d⟩ = 1.60 Å and Si–O–Si angle ⟨∠⟩ = 154° are in good agreement with those from known dense and porous silica phases.[26] Variations of d(Si–O) (in the range of 1.53–1.63 Å) and ∠(Si–O–Si) (in the range

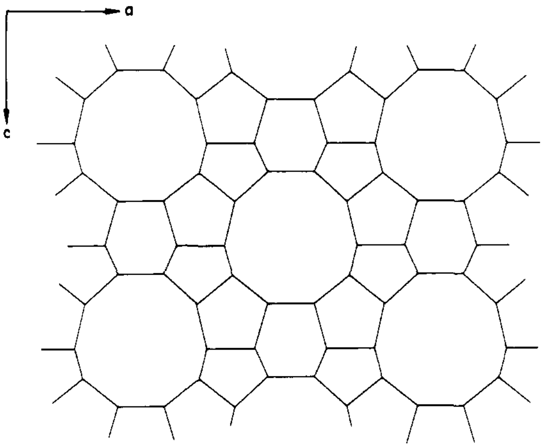

Figure 7. Representation of the ZSM-11 structure projected on *a,c* from the structure refinement of the high-temperature XRD data (373 K).

of 144.1–165.3°) are within the standards of the experimental technique. However, the distances Si(2)–O(13) and Si(5)–O(13) (1.49 and 1.68 Å, respectively) deviate considerably. With d(Si(2)–Si(5)) = 3.15 (2) Å and an average d(Si(2,5)–O(13)) = 1.58 Å, it seems likely that the O(13) position is slightly distorted. Attempts to resolve the problem during the refinement procedure failed, always yielding O(13) in the position reported.

The high-temperature structure is thus well-defined and can be described in terms of the [SiO_4] tetrahedra as primary building units being corner linked to build a three-dimensional, four-connected net in the sense of Wells.[29] 15[SiO_4] tetrahedra form the fundamental polyhedron [5^8] characteristic for the polytypic series of pentasil-type zeolites. Each [5^8] is linked to two neighboring units via common edges to form chains as schematically outlined in Figure 7, where two chains in a layer are related by a mirror plane. The 10-membered ring channels run perpendicular to the pentasil layers. As indicated by the space group symmetry $I\bar{4}m2$, identical layers occur in the $\vec{a},\vec{c}$ and $\vec{b},\vec{c}$ plane sharing chains of pentasil units. In ZSM-11, two neighboring layers are connected such that they are related by a mirror plane. To complete the three-dimensional four-connected net, additional four-membered ring units are introduced, as shown in a projection of the structure along $\vec{c}$ (Figure 8).

A data set obtained at ambient temperature showed sharp reflections. As found in a refinement of a room-temperature flat plate data set,[19] no deviation from the body-centered symmetry of the unit cell was found. Thus, the long-range ordering of the structure appears high. However, the structure would not refine smoothly, either in a lower symmetry space group or by starting with the high-temperature structure and letting the atomic positions vary. Although the refinement led to "satisfactory" *R* factors, Si–O distances deviated considerably from expected values. This was particularly true for the two Si atoms on special sites (Si(1) and Si(6)) in the four-membered ring shown in Figure 7, with the Si–O distances varying between ~1.4 and ~1.7 Å compared to the usual Si–O distance of 1.6 Å. This indicates that considerable deviation from the high-temperature structure is occurring and that the deformation primarily involves distortion of the four-membered ring systems. From the NMR data, this behavior is understandable, and it is anticipated that a proper refinement of the lower symmetry, low-temperature structure will be possible only if data are collected at −10 or −20 °C.

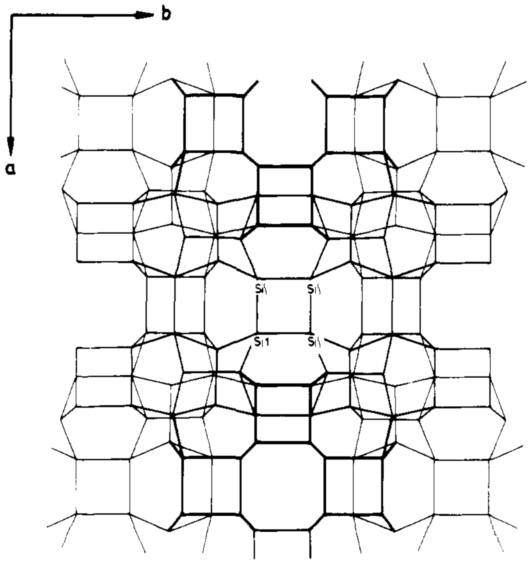

Figure 8. *a,b* projection of the same data showing the location of the four-membered rings in the structure.

Conclusions

The present work has shown that it is possible to prepare monophasic, intergrowth-free zeolite ZSM-11. The ^{29}Si MAS NMR spectra indicate that the lattice structure is temperature dependent, changing from a high-temperature form to a lower symmetry form below ambient temperature. Rietfeld refinement of synchrotron powder X-ray diffraction data collected at 100 °C proceeds smoothly in space group $I\bar{4}m2$, giving a well-defined structure similar to that previously proposed. It was not possible to refine room-temperature data in the same way, however, and the NMR results suggest that synchrotron data will have to be collected at −20 °C to obtain the limiting low-temperature structure.

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