

07.9-2 SYNTHESIS AND CRYSTALLOGRAPHIC DATA ON A NEW SILICA ZEOLITE, SILICA-ZSM-48. By R.P. Cunawardane, Department of Chemistry, University of Peradeniya, Sri Lanka & H.Gies, Mineralogy Institute, Kiel University, West Germany.

A high silica zeolite ZSM-48 has been synthesized (Schlenker, J.L. et al., Zeolites, 1985, 5, 355-8) from silica solutions containing trace amounts of aluminium. In the present study the aluminium-free end member of the zeolite ZSM-48 i.e. silica-ZSM-48, has been crystallized hydrothermally at 160° - 200°C from a pure silicic acid solution in the presence of polyamines as templates. Triethylenetetramine, tetraethylenepentamine, 1,5,8,12-tetraazadodecane etc act as efficient templates in this synthesis. Microprobe analysis of the product confirmed the absence of aluminium in the framework.

The X-ray powder diffraction pattern was indexed on the basis of an orthorhombic cell and the least square refinement using X-ray powder data gave the unit cell parameters  $a = 14.21(4)$ ,  $b = 20.09(5)$  and  $c = 8.40(3)$  Å. Powder reflections indicate C or I centering suggesting Immm, Imma, Cmcm and Cmmm symmetries. HRTEM studies on silica-ZSM-48 confirmed the lattice parameters obtained from X-ray powder data. All specimens investigated by TEM show weak reflections indicating the space groups Pmmm or P2<sub>1</sub>mm. Disregarding the weak reflections the space group Immm is found to be the most plausible. Twinning of silica-ZSM-48 is a common feature and the twin plane is perpendicular to [001].

It is apparent from these data that a structure based on ferrierite sheets linking via oxygen atoms located on mirror planes and consisting of 1-D channel systems may be visualized for silica-ZSM-48. The 10-T ring channels are running parallel to the c axis. Its framework topology appears to be closely related to that of ZSM-23 and ZSM-22. Further work is in progress to grow single crystals in order to confirm the structure by single crystal structure refinement.

07.9-3 HYPOTHETICAL FRAMEWORK STRUCTURES RELATED TO MOBIL ZEOLITE ZSM-48. By J. L. Schlenker and W. J. Rohrbaugh, Mobil Research and Development Corporation, Research Department, Paulsboro, NJ 08066, USA. ZSM-48 is a high-silica zeolite whose structure has been proposed to be a disordered linking of ferrierite sheets via bridging oxygen atoms located on mirror planes. The proposed framework topology was based on agreement between observed and calculated x-ray powder diffraction patterns. The Smith plot in best agreement was obtained from a disordered intergrowth of two ideal framework structures with Cmcm and Imma symmetries. Because x-ray and electron diffraction data seem to indicate an orthorhombic lattice with pseudo-I or pseudo-C-centering, attention was initially restricted to the formulation of hypothetical centered structures. With lattice parameters of  $a=14.24$  Å and  $b=20.14$  Å, and a C- or I-centered orthorhombic lattice, the ferrierite sheet has only four independent T-atoms, each of which may point up (U) or down (D) in order to link with other sheets. Alternating the orientation of these independent T-atoms yields twenty-eight closely related hypothetical framework structures, e.g. UDD-Cmcm, UDUD-Imma, etc.

07.9-4 A SINGLE CRYSTAL STRUCTURE OF ZEOLITE ZSM-39. By J. Macicek, V.P. Vulchev, G.N. Kirov, Institute of Applied Mineralogy, BAS, Sofia, Bulgaria.

Octahedrally shaped crystals of the zeolite up to 0.7mm in size were grown hydrothermally from a gel with a composition  $33\text{Na}_2\text{O} \cdot 16(\text{TMA})_2\text{O} \cdot 16(\text{TrMA})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 110\text{SiO}_2 \cdot 7300\text{H}_2\text{O} \cdot 22\text{H}_2\text{SO}_4$  for 7 days at 473 K. A spherically ground transparent crystal with  $r = 0.19\text{mm}$  was investigated on a CAD4SDP diffractometric system. Crystal data: (Na,TMA)<sub>4.4</sub>Al<sub>4.4</sub>Si<sub>131.6</sub>O<sub>272</sub>, Mr = 8337,

cubic, Fd3m,  $a = 19.396(1)$  Å,  $V = 7297(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.897$  g.cm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,

$\mu = 6.8$  cm<sup>-1</sup>,  $F(000) = 4180$ ,  $T = 291$  K. From 8998 total ( $\theta < 35^\circ$ ) and 316 unique ( $R_{\text{int}} = 0.033$ ) 298 reflections with  $I > 3\sigma(I)$  were used in calculations. Final  $R(F) = 0.035$  by full-matrix least-squares. Residual max.  $\Delta(\rho) = 0.09$  e.Å<sup>-3</sup>.

The ZSM-39 topology, known from the powder data study (Schlenker J.L. et al., Nature, 1981, v. 294, 340-2) was confirmed. Besides, disordered Al, Na and TMA were localized in the 16-hedral cage. The Al-atom occupies a tetrahedron which shares face with another, currently vacant SiO<sub>4</sub>-tetrahedron from the framework. The apical oxygen atom of AlO<sub>4</sub> is pointed to the centre of the cage, where both the Na and TMA are disposed. The electron density peak near the centre of the 12-hedral cage is presumably a water-oxygen.

07.9-5 ABOUT CRYSTAL STRUCTURES OF ZSM-11 AND ZSM-39. By A. Hardy, K. Ahmadi, M. Benjdir, P. Graveriau, A. Ouali and J.L. Guth\*, Laboratoire de Cristalochimie Minérale, Université de Poitiers, 40 av. Recteur Pineau, F - 86022 Poitiers cédex, France, \*Laboratoire de Chimie Minérale Générale, E.N.S.C.M., 3 rue Alfred Werner, F - 68093 Mulhouse cédex, France,

Single crystals of zeolites were synthesized in size large enough to study their crystal structure especially ZSM-11 (MEL) and ZSM-39 (MTN) known up to now only by their powder X-ray diffraction diagrams. One MEL single crystal measuring  $94 \times 54 \times 54 \mu\text{m}^3$  with {100} and {001} faces allowed us to assign it to space group P4<sub>2</sub>2<sub>1</sub>2 in place of I4m2 suggested by Kokotailo et al. (Nature, 1978, 275, 119-20). Cell parameters are  $a=b=19.93(1)$  Å,  $c=13.35(1)$  Å,  $V=5304(9)$  Å<sup>3</sup>. Independent reflections were collected using CAD.4 diffractometer allowing us to index ZSM-11 powder diagram without any ambiguity and confirming a non-centered space group. The Kokotailo framework hypothesis must be called into question.

A quasi-spherical single crystal of MTN,  $544 \mu\text{m}$  in diameter, was prepared and studied with MoK $\alpha_1$ . Faces are {100}, {111} and {211}, space group Fd3m and unit cell parameter  $a=19.43(1)$  Å. Data and refinements confirm the framework hypothesis given by J.L. Schlenker et al. (Nature, 1981, 294, 340-2) from powder X-Ray diffraction data.