12.5-2 APPLICATION OF HIGH RESOLUTION SYNCHROTRON X-RAY POWDER DIFFRACTION TO THE STRUCTURE REFINEMENT OF ZEOLITE ZSM-11. B.B. Toby, Union Carbide Corporation, Tarrytown, NY 10591, USA; M.M. Eddy, University of California, Santa Barbara, CA 93106, USA; C.A. Fyfe and G.T. Kokotailo, University of Guelph, Ontario N1G2W1, Canada; D.E.Cox*, Brookhaven National Laboratory, Upton, NY 11973, USA.

High resolution synchrotron x-ray powder data have been collected from a well-crystallized and highly de-aluminated sample of the zeolite ZSM-11 (space-group I4m2, a = 20.065A, c = 13.408A) on the dedicated triple-axis powder diffractometer X13A at the Brookhaven National Synchrotron Light Source (Cox, Hastings, Cardoso, and Finger, Materials Science Forum (1986), Vol. 9, edited by C.R.A. Catlow, 1-20 Trans Tech Publications, Switzerland). A perfect Ge(111) crystal scattering in the horizontal plane at a wavelength of 1.54155A was used as monochromator, with a flat-plate sample and a perfect Ge(220) analyzer scattering in the vertical plane. The peak shapes were symmetric and well-described by the convolution of Gaussian and Lorentzian functions, with a peak-width of about 0.04° at low angles. This is about double the instrumental resolution in this region, consistent with a mean particle size of about 0.4 μm. The high resolution of the data is illustrated in Fig. 1.

Structure analysis was accomplished by Rietveld refinement with three Gaussian and two Lorentzian half-width parameters in the following form

$$T_G = (U\tan^2\theta + V\tan\theta + W)^{1/2}$$
$$T_L = X\tan\theta + Y/\cos\theta$$

The data set contained contributions from 679 reflections. The framework topology of ZSM-11 was previously derived by distance least-squares modelling (Kokotailo, Chu, Lawton and Meier, Nature (1978) 275, 119) and contains 7 inequivalent Si and 15 inequivalent O atoms. In the final stages of refinement, 86 parameters were varied, including 54 positional coordinates and 22 individual isotropic temperature factors. Refinement converged to the following R-factors: $R_I = 0.11$, $R_{WP} = 0.22$, $R_E = 0.15$ (goodness-of-fit $S_p^2 = 2.0$). With three exceptions the Si-O bond lengths fall in the range 1.57 - 1.67A. Difference Fourier plots showed no residual features greater than about 5% of the oxygen peaks, indicating the absence of significant amounts of extra-framework species.

Rather unexpectedly, high resolution magic-angle spinning NMR spectra show more than seven resonances at room temperature, indicative of deviations from the long-range crystallographic symmetry. These disappear at 100°C, where only the expected seven resonances are observed.
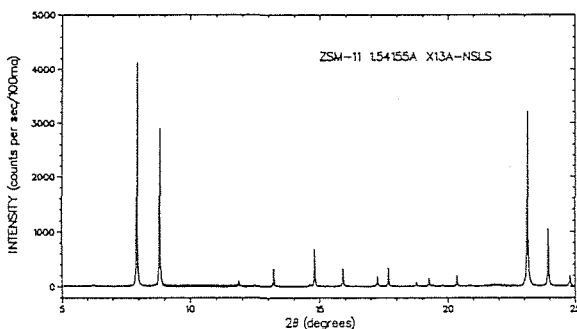
12.5-3 STRUCTURAL CHANGES ON DEACTIVATION OF ZSM5 - A STUDY BY X-RAY POWDER PROFILE REFINEMENT. By J.C. Taylor and D.M. Bibby*, Energy Chemistry Division, CSIRO, Private Mail Bag 7, Menai, NSW. 2234, *Chemistry Division, DSIR, Lower Hutt, Private Bag, Petone, New Zealand.

The framework structure of the synthetic zeolite catalyst ZSM-5, in the initial H-form and after deactivation by the deposit of coke during the conversion of methanol to hydrocarbons, has been studied by profile refinement of the X-ray powder diffraction patterns. Both the H-form and the coked ZSM-5 refine satisfactorily in the orthorhombic space group Pnma. The straight 10-ring channel parallel to b has a marked shape change on coking from nearly circular to elliptical, while the sinusoidal channel expands but remains nearly circular. As a result the unit cell volume is unchanged on coking. No diffraction effects from coke are observed so the arrangement of the coke atoms in the channels must be random.

The X-ray patterns were obtained with CoKα radiation ($2\theta_{max} = 110°$, 2240 (hkl) reflections). The analysis was carried out with soft constraints (146 in all) and a profile decomposition technique. The final profile R-factors were 0.12 and 0.13 for H-form and coked ZSM-5 respectively, with corresponding Bragg R-factors of 0.053 and 0.056. The precision of the Si and O coordinates is 0.003 and 0.007 Å respectively, and the profile refinements show shifts of up to 0.574 (9) Å in the framework atom coordinates on coking, the tetrahedral geometry around the Si atoms being unchanged.

12.5-4 X-RAY RIETVELD STRUCTURE REFINEMENT OF MONOCLINIC ZSM-5. Ch. Baerlocher, P. Schicker, Institut für Kristallographie, ETH-Z, CH-8092 Zürich, Switzerland and D.E. Cox, Brookhaven National Laboratory, Upton, N.Y. 11973, USA

X-ray synchrotron data of ZSM-5 (Si/Al >50000), calcined at 500°C, were collected at room temperature at the X13A beam line, NSLS, Brookhaven. To prevent preferred orientation the sample was placed in a 1mm glass capillary. The pattern was measured in steps of 0.01° in up to 10 sec/step to 75° 2θ (λ=1.5468Å) resulting in an overall R(exp)=19%. The LiF 400 plane was used as the analyser crystal.

The refinement with the X-ray Rietveld System (XRS-82) in space group P2₁/n progressed to an R(wp)=20%. The cell parameters are a=20.111Å, b=19.889Å, c=13.385Å, α=90.54°. Soft restrictions (distances and angles) were used, but their contribution could be reduced to a lower value than was previously necessary with conventional X-ray data, despite the very large number of 288 structural parameters.

This structure analysis can be compared with the result from a refinement of the orthorhombic structure at 500°C (P. Schicker, PhD Thesis,1987) using the same sample. The 10-rings in both, the straight and the sinusoidal channel system, do not change much. The largest shifts between the two structures are around 0.3-0.35Å for some framework oxygens and occur mainly in the framework chains. A more detailed analysis of the changes associated with the transformation to monoclinic symmetry will be presented.