

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  $I4m2$ ,  $a = 20.065\text{\AA}$ ,  $c = 13.408\text{\AA}$ ) 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  $1.54155\text{\AA}$  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  $0.04^\circ$  at low angles. This is about double the instrumental resolution in this region, consistent with a mean particle size of about  $0.4\ \mu\text{m}$ . 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

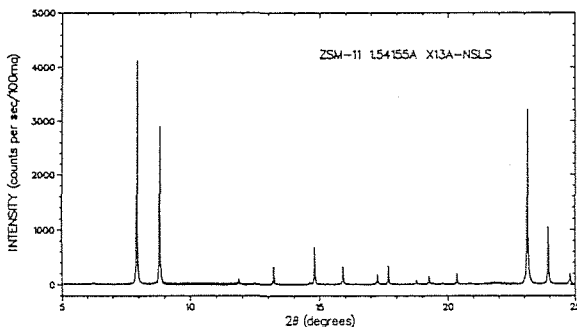
$$I_G = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

$$I_L = X \tan \theta + Y / \cos \theta$$

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  $S^2_p = 2.0$ ). With three exceptions the Si-O bond lengths fall in the range  $1.57 - 1.67\text{\AA}$ . 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  $100^\circ\text{C}$ , where only the expected seven resonances are observed.

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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  $\text{CoK}\alpha$  radiation ( $2\theta_{\text{max}} = 110^\circ$ , 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  $0.007\text{\AA}$  respectively, and the profile refinements show shifts of up to  $0.574(9)\text{\AA}$  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-2, 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  $500^\circ\text{C}$ , 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  $0.01^\circ$  in up to  $10\text{ sec/step}$  to  $75^\circ 2\theta$  ( $\lambda = 1.5468\text{\AA}$ ) resulting in an overall  $R(\text{exp}) = 19\%$ . The LiF 400 plane was used as the analyser crystal.

The refinement with the X-ray Rietveld System (XRS-82) in space group  $P2_1/n$  progressed to an  $R(\text{wp}) = 20\%$ . The cell parameters are  $a = 20.111\text{\AA}$ ,  $b = 19.889\text{\AA}$ ,  $c = 13.385\text{\AA}$ ,  $\alpha = 90.54^\circ$ . 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  $500^\circ\text{C}$  (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  $0.3 - 0.35\text{\AA}$  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.