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A study of decomposition methods for refinement of H^+-ZSM5 zeolite with powder diffraction data

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H^+-*ZSM5 Zeolite / Crystal structure*

Abstract. Profile and integrated intensity decomposition refinements have been carried out on H^+-ZSM5 X-ray powder diffractometer data (110 structural parameters). This compound is a zeolite catalyst. The SiO_4 tetrahedra were constrained towards regularity. Chemically sensible results and good fits between observed and calculated profiles and integrated intensities were obtained. It is concluded that larger structures (100–150 structural variables) can be refined from conventional X-ray powder diffractometer data with either of these methods if appropriate geometrical constraints are applied.

Introduction

Many large crystal structures of commercial interest, such as the ZSM-5 zeolite catalysts, can only be prepared as finely divided powders. In a recent survey (Taylor, 1985), it was found that few large structures (a large structure in this instance being defined as having more than 30 structural variables NP) have been refined with powder data. ZSM-5, with NP = 110 for the framework only, falls into the category of a very large structure.

In powder work especially, constraints on the molecular geometry are valuable as they effectively improve the ratio of observations to variables by refining an overall shape or unit instead of isolated atoms. The use of

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constraints, unfortunately, is not widespread but Pawley has demonstrated their value for small organic structures [e.g. see Pawley (1978)]. Constraints become progressively more important as the size of the structure increases. Baerlocher (1984) used constraints in his X-ray refinement of TPA-ZSM5 (NP = 133).

Most powder refinements are performed with the Rietveld (1969) method, but the widely-used programs (Wiles and Young, 1981; Hewat, 1973) are written for moderate sized structures and do not have the elaborate systems of constraints. The SHELX (Sheldrick, 1976) single crystal program can handle very large structures, however, and it would be an advantage to use the SHELX features in powder work.

In 1984, Toraya et al. solved and refined a large structure (NP = 113) by decomposing Weissenberg powder data into $F_0(hkl)$ with the Rietveld (1969) formula, and then using single crystal programs. Like normal Rietveld refinement, this method works on the profile. Although the two methods are different approaches, they should lead to similar results with a correct starting model. We have applied the profile decomposition method (hereafter called the PD method) in the present work to X-ray powder diffractometer profiles of H^+-ZSM5 (NP = 110), and used SHELX to refine the structure and apply constraints. Parallel refinements in which integrated intensities were decomposed to $F(hkl)$ in a similar way have also been performed.

Experimental

An X-ray pattern of H^+-ZSM5 was collected in the range $2\theta = 7° - 109°$ on a Philips powder diffractometer (1° fixed slit and graphite monochromator), with Co$K\bar{\alpha}$ radiation ($\lambda = 1.7902$ Å). The step size was 0.05° 2θ. The data were corrected for the divergence slit effect, and monochromator polarisation. Using the program of Wiles and Young (1981) and H^+-ZSM5 parameters of Olson et al. (1981), unit cell dimensions were determined as $a = 20.108(2)$, $b = 19.918(2)$, $c = 13.392(2)$ Å. The reflexions observed agreed with the space group *Pnma* of Olson (1981) and subsequent refinements did not suggest any deviation from this symmetry.

The starting refinement model was that of Olson et al. (1981). The F_{hkl} derived from either the profile or integrated intensity decomposition were input into SHELX. The soft constraints were as follows: Si−O = 1.58(5), O−O = 2.58(10) Å (corresponding to a tetrahedral angle of 109.5°), and Si−Si = 3.09(10) Å (corresponding to a Si−O−Si angle of 156°). The number of constraints was 146 (Table 1). In order to determine the optimum range of data [before, perhaps, superposition of (hkl) reflexions became too great] refinements were made with the data to 60°, 80° and 100° (536, 1099, and 1837 *hkl* respectively).

Table 1. Constraints used for framework geometry.

Si–O	1.58(5) Å (48 constraints)
O–O	2.58(10) Å (72 constraints)
Si–Si	3.09(10) Å (26 constraints)
[Tetrahedral angle 109.5°, Si–O–Si angle 155.8°]	

Total number of constraints = 146.

Table 2. Profile and instrumental parameters.

Halfwidth parameters:	U	–0.016
(Rietveld, 1969)	V	0.097
	W	0.033
Asymmetry (Rietveld, 1969)		0.23
Peak base in halfwidths		4.4
Pearson VII *m*-parameter		1.14
Monochromator 2θ angle		31°
Effective beam divergence		1.2°
Wavelengths:	Co$K\alpha_1$	1.7889 Å
	Co$K\alpha_2$	1.7928 Å

(a) Profile decomposition

A computer program was written for the point-by-point decomposition of the profile for each (*hkl*) reflexion, using the formula (Rietveld, 1969):

$$I_K(\mathrm{obs}) = \sum_j \{w_{j,k} F_K^2(\mathrm{calc.})\, y_j(\mathrm{obs})/y_j(\mathrm{calc.})\}$$

where the terms have their usual meanings for profile analysis. The α_1, α_2 doublet was treated explicitly. Peak shapes were described with the Pearson VII function. Halfwidths, Pearson *m*-parameter, instrument zero and a Rietveld (1969) asymmetry factor were chosen to give the optimum profile fit (Table 2).

(b) Integrated intensity decomposition

Some 92 graphically separable integrated intensities were observed in the range 7°–100° 2θ. The mean Co$K\bar{\alpha}$ wavelength was used to assign the various (*hkl*) reflexions to integrated intensity peaks. The doublet separation at 100° was 0.28° 2θ; however the integrated peaks selected here were 1.5 to 2° wide. Reflexions closer to a peak border than 0.09° will have one component lost to the next reflexion, but there is a compensating error at the other end of the peak. It was considered the systematic errors arising from the assumption of the mean wavelength in the integrated intensity

Table 3. Precision of profile (PD) and integrated intensity decomposition (ID) refinements with various ranges of data.

Refinement	NP	NHKL	σ(Si)(Å)	σ(O)(Å)	R_p(%)	R_F	$\bar{U}$(Å^2)
100° PD	110	1837	0.003	0.009	13.2	4.8	0.0274(3)
100° ID	110	1772	0.005	0.014	–	7.7	0.030(1)
80° PD	110	1099	0.004	0.012	13.3	5.5	0.0334(5)
80° ID	110	1033	0.008	0.023	–	8.5	0.039(1)
60° PD	110	536	0.017	0.036	13.6	8.5	0.072(2)
60° ID	110	503	0.013	0.026	–	5.4	0.062
TPA-ZSM5 (Baerlocher 1984)	133	2246	0.014	0.025	12.8	–	–

NP = number of positional parameters; NHKL = number of reflexions in range refined; R_p = profile R-factor = $\Sigma(|y_o - y_c|)/\Sigma\, y_o$; R_F = R-factor on $F = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$; $\bar{U}$ = overall isotropic temperature factor.

refinements were small. The integrated intensities were decomposed into $F(hkl)$ values with a further computer program based on the formula

$$F_i^2(\mathrm{obs}) = I(\mathrm{integ.}) \frac{m_i F_i^2}{\Sigma m_j F_j^2} \cdot \frac{\sin^2\theta \cos\theta (1 + \cos^2 2\theta_M)}{1 + \cos^2 2\theta \cos^2 2\theta_M} \cdot \frac{1}{m_i}$$

where the subscript M refers to the monochromator, and m is the multiplicity.

Results

(a) Profile decomposition refinements

The two-stage profile decomposition-constrained least-squares process gave structural and instrumental parameters which produced a good fit between observed and calculated powder pattern profiles. The profile R-factors for the 60°, 80° and 100° data sets were all in the vicinity of 13.5%, Table 3. The observed and calculated profiles are shown in Figure 1 for the refinement with data to 100° 2θ. The fit of the profile is comparable to that obtained by Baerlocher (1984) for TPA-ZSM5 (12.8%), and the scatter of the constrained distances in Table 4 suggests that the two studies are of comparable reliability. The H^+-ZSM5 and TPA-ZSM5 frameworks, and also that of Olson et al. (1981) are not directly comparable, because of differing channel contents.

Table 4 gives the framework dimensions found in the refinements. The Si–O distance found in all refinements was 1.58 Å with a mean deviation of 0.03 Å. This distance is correct for a high silica ZSM5 and is the same as found by Baerlocher (1984). The tetrahedra are close to regular (O—O = 2.58, mean deviation 0.06 Å), and the Si—Si distance, 3.09(6) Å, gives a mean Si—O—Si angle of 156°, again the same as found in TPA-ZSM5.

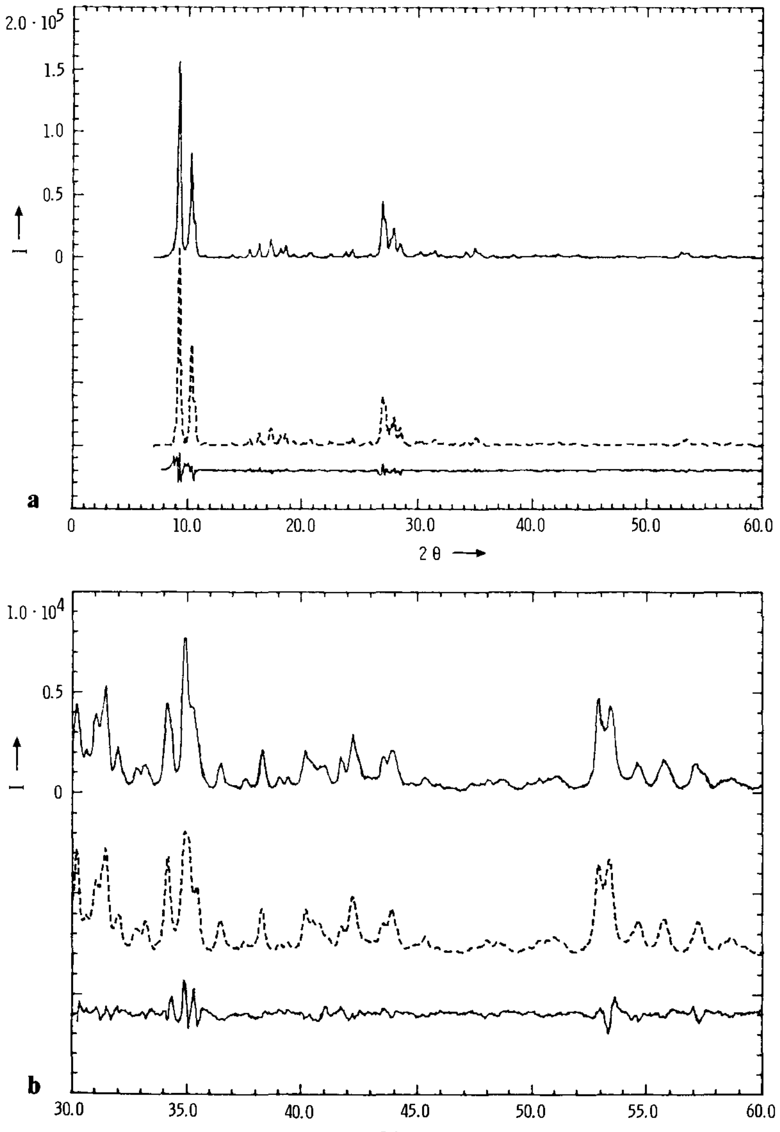

Fig. 1. Observed (unbroken line) calculated (dotted line) and difference X-ray powder diffraction patterns for H^+-ZSM5 (a) to 60° 2θ (b) from 30° to 60° 2θ and (c) from 60° to 100° 2θ, for profile decomposition coordinates.

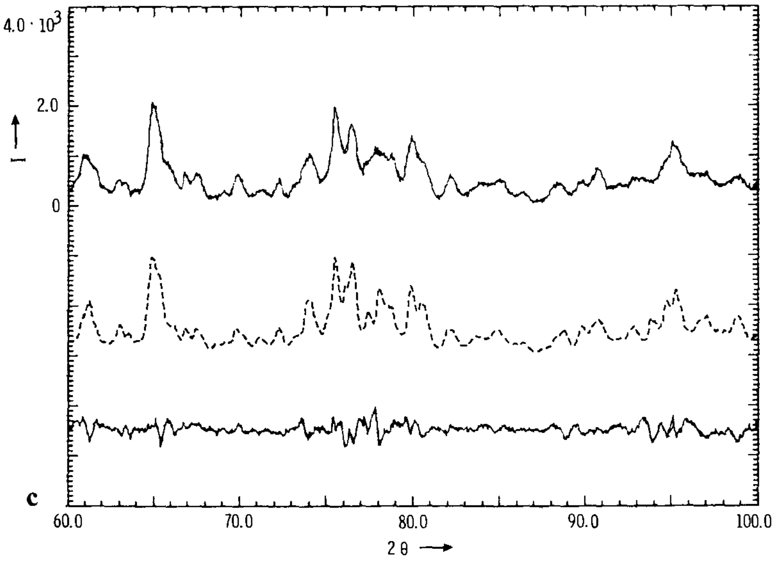

Fig. 1

Table 4. Ranges of Si – Si, Si – O, and O – O for the profile decomposition and integrated intensity refinements of the H^+-ZSM5 data.

Refinement	Si – Si(Å)			Si – O(Å)			O – O(Å)		
	mean	range	mean deviation	mean	range	mean deviation	mean	range	mean deviation
100° PD	3.09	2.98 – 3.21	0.06	1.58	1.50 – 1.71	0.03	2.58	2.44 – 2.76	0.06
100° ID	3.09	2.96 – 3.19	0.04	1.58	1.48 – 1.68	0.03	2.58	2.38 – 2.75	0.06
80° PD	3.09	2.99 – 3.20	0.05	1.58	1.52 – 1.70	0.03	2.58	2.44 – 2.75	0.06
80° ID	3.09	2.98 – 3.19	0.04	1.58	1.50 – 1.67	0.03	2.58	2.41 – 2.73	0.06
60° PD	3.10	2.90 – 3.24	0.06	1.59	1.51 – 1.64	0.03	2.59	2.33 – 2.81	0.07
60° ID	3.09	2.98 – 3.25	0.05	1.58	1.47 – 1.66	0.03	2.58	2.43 – 2.76	0.05

PD = Profile decomposition; I = Integrated intensity decomposition.

In this H^+-ZSM5 study, there are 110 positional parameters and 6 instrumental variables, whereas in Baerlocher's TPA-ZSM5 study (1984) there are 133 positional parameters, 48 isotopic *B*-factors, and 9 profile parameters. As the refinement methods and conditions were different, it is difficult to comment on the e.s.d.'s in the two studies, because it is well known that different powder refinement methods give different e.s.d.'s for the same data [see Taylor (1985)].

Table 5. Internal consistency between various refinements of the H^+-ZSM5 data.

Refinement 1	Refinement 2	Δ(Si) (Å)	Δ(O) (Å)	
100° PD	7– 80° PD	(a) 0.008	0.015	
		(b) 0.024	0.047	
80° PD	7– 60° PD	(a) 0.025	(a) 0.023(x, y)	0.049(z)
		(b) 0.068	(b) 0.060(x, y)	0.153(z)
100° ID	7– 80° ID	(a) 0.003	(a) 0.007	
		(b) 0.008	(b) 0.025	
80° ID	7– 60° ID	(a) 0.010	(a) 0.014(x, y)	0.017(z)
		(b) 0.030	(b) 0.040(x, y)	0.064(z)
100° PD	7–100° ID	(a) 0.016	(a) 0.017(x, y)	0.032(z)
		(b) 0.050	(b) 0.052(x, y)	0.109(z)
100° PD	7– 80° ID	(a) 0.017	(a) 0.016(x, y)	0.027(z)
		(b) 0.045	(b) 0.060(x, y)	0.082(z)
100° PD	7– 60° ID	(a) 0.020	(a) 0.019(x, y)	0.027(z)
		(b) 0.060	(b) 0.066(x, y)	0.067(z)

(a) = Mean difference between comparable coordinates.
(b) = Largest difference between comparable coordinates.

The powder studies of H^+-ZSM5 and TPA-ZSM5, which feature the use of constraints, appear more accurate than other studies without constraints. In fact, the framework geometry in H^+-ZSM5 and TPA-ZSM5 would appear to be as well-defined as in the single-crystal studies of ZSM5-type zeolites (Olson et al., 1981; Chao et al., 1986). (Admittedly these single-crystal studies are less accurate than normal because of non-ideal crystallinity.)

(b) Integrated intensity decomposition refinements

Tables 3 and 4 show that the H^+-ZSM5 framework can also be refined with integrated intensity data, to reasonable R_F, $\bar{U}$, σ(Si) and σ(O) values. The Si–Si, Si–O and O–O ranges are much the same as with the profile decomposition.

Discussion

(a) Comparison of decomposition methods

In Table 5, differences in atomic coordinates between pairs of refinements for different 2θ ranges and decomposition techniques are given. These are given as mean differences together with the largest individual difference, the largest difference usually being about three times the mean difference.

Table 6. Final coordinates[a], H^+-ZSM5[b].

Atom	$10^4 x$	$10^4 y$	$10^4 z$
Si(1)	4264	0581	−3396
Si(2)	3096	0297	−1814
Si(3)	2755	0603	0350
Si(4)	1198	0617	0287
Si(5)	0699	0253	−1862
Si(6)	1884	0593	−3273
Si(7)	4263	−1707	−3284
Si(8)	3138	−1280	−1759
Si(9)	2697	−1752	0366
Si(10)	1186	−1744	0356
Si(11)	0728	−1288	−1786
Si(12)	1929	−1734	−3098
O(1)	3733	0565	−2449
O(2)	3090	0604	−0728
O(3)	1977	0488	0212
O(4)	0949	0589	−0850
O(5)	1208	0560	−2668
O(6)	2421	0569	−2405
O(7)	3777	−1534	−2264
O(8)	3076	−1623	−0720
O(9)	1933	−1568	0359
O(10)	0926	−1579	−0743
O(11)	1241	−1531	−2635
O(12)	2498	−1554	−2356
O(13)	2994	−0495	−1728
O(14)	0804	−0525	−1670
O(15)	4207	1275	−3816
O(16)	4050	0018	−4180
O(17)	3974	−1315	−4268
O(18)	1893	1288	−3762
O(19)	2001	−0003	−4029
O(20)	2016	−1277	−4119
O(21)	−0038	0463	−2139
O(22)	−0004	−1504	−2077
O(23)	4237	−2500	−3436
O(24)	2001	−2500	−3293
O(25)	2749	−2500	0657
O(26)	1048	−2500	0579

[a] For each atom, the set of (x, y, z) coordinates is from the 100° profile decomposition refinement. The equivalent positions are those of Olson et al. (1981).

[b] Precision of the coordinates is given in Table 3.

In the profile decomposition (PD) refinements, the coordinates are much the same for the refinements to 80 °C and 100 °, the mean differences between Si and O positions being 0.008 and 0.015 Å respectively. This suggest that no further advantage is gained by adding data over 100 °, where the superposition is becoming severe. The data to 60 °, however, appears to be insufficient, on comparing the PD refinements to 80 °C and 60 °. Similar conclusions are obtained for the intensity decomposition refinements.

The coordinates for the profile and integrated intensity refinements show agreement. The best comparison is between the 100 ° profile and 80 ° integrated intensity refinements, where the mean differences in the atomic positions are 0.02–0.03 Å. The integrated intensity coordinates are more likely to suffer from systematic errors than the profile refinements coordinates for reasons given above. There is a tendency in some cases for the differences to be larger for the *z*-coordinates. The differences are listed for (x, y and z) coordinates separately when these are significantly different.

In Table 5, for the 100 ° PD and 80 ° ID comparison, $\bar{\Delta}(\mathrm{Si}) = 0.017$ and $\bar{\Delta}(\mathrm{O}) \doteqdot 0.025$ Å. This agrees with $\sigma(\mathrm{Si}) = 0.014$ and $\sigma(\mathrm{O}) = 0.025$ for the TPA-ZSM5 analysis (Baerlocher, 1984), and suggests that the precision of the H^+-ZSM5 100 ° PD refinement is about the same as that of the TPA-ZSM5 refinement.

(b) E.s.d.'s

Powder refinements are usually not as good as single-crystal refinements, because the individual reflexions are not observed. In decomposition methods, use is made of the current structural model and either the profile or the integrated intensities in extracting the $I(hkl)$ for each reflexion. The definition of the number of data points being the number of observations is artificial in the Rietveld method, because they can be varied at will from zero to infinity by varying the step size (Scott, 1983), the e.s.d.'s becoming zero at infinity. Rietveld datapoints are also somewhat interconnected by the fact that the underlying (hkl) intensities have a Gaussian or some other shape. These difficulties caused by superposition make interpretation of the computed e.s.d.'s more difficult with powder than with single crystal methods.

Conclusion

The present results suggest that, with constraints, the framework geometry of a structure with 100–150 structural parameters can be refined by decomposition methods and a reliable starting model. The refinements here are of comparable precision to a constrained Rietveld refinement of another ZSM5 derivative (Baerlocher, 1984). The success of the refinements appears to be more due to the application of the constraints, rather than which refinement method is adopted. Thus, while the number of points in a Rietveld or profile decomposition refinement appears to be much greater than the number of separable integrated intensity peaks, the advantage is only apparent and not actual, because of the variability of step size and correlation of scan points mentioned above. The separate $F(hkl)$ are not measured directly in any of these powder techniques, unlike single-crystal methods.

Despite the limitations in interpreting the calculated e.s.d.'s, it appears that useful information can be extracted from complex powder patterns with these techniques. Higher resolution would lessen, but not entirely remove, the superposition problem. With powerful, logical constraints, and a correct model, either profile or integrated intensity methods should converge to a chemically reasonable solution for large structures.

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