MAXIMIZING THE IMPACT OF YOUR DATA: APPLICATIONS OF RIETVELD ANALYSIS TO INDUSTRIAL PROBLEM SOLVING

James A. Kaduk
Amoco Corporation, P.O. Box 3011 MC F-9, Naperville IL 60566

INTRODUCTION

The typical initial reaction to the suggestion that Rietveld analysis be used for industrial problem solving is "Isn't that overkill?". The advent of fast computers (especially PCs) overturns this perception, and makes this exciting analytical tool practical for even routine applications. Rietveld analysis provides a convenient and physically-meaningful way of extracting the maximum possible information from the whole diffraction pattern, including information not normally exploited.

Corporate retrenchments have resulted in more selective sample submissions to the analytical laboratory. Each sample is therefore more important, and provides a greater opportunity for the analyst to contribute value. Extracting the most information from experimental data is therefore not "overkill", but a necessity of the real world.

My aim in this paper is to illustrate the breadth of potential applications, rather than teach the details of how to do Rietveld analysis. I encourage all diffractionists to develop skills in Rietveld analysis, to be able to include it in their arsenal of tools for solving problems. Rietveld analysis forces the analyst to look at the data more carefully, so more information is obtained than from traditional diffraction techniques.

QUALITATIVE AND QUANTITATIVE PHASE ANALYSIS

Dust

In traditional qualitative phase analysis, the powder pattern is reduced to a set of d-spacings and peak heights. Using a Rietveld analysis to model the full pattern after a search/match often reveals the presence of shoulders and weak peaks, which indicate the presence of additional phases. Modelling the full pattern also indicates whether weak peaks arise from the major phases, saving the time which could be wasted trying to attribute them to additional minor phases. The refined scale factors yield a quantitative phase analysis of sufficient quality for many applications. Such a quantitative analysis is especially valuable if the appropriate reference materials are not on hand.

A sample of dust from a failed fuel filter assembly on an electric generation turbine in a gas field was subjected to a battery of tests, to determine the source of the contamination, and to see if it played any role in turbine blade erosion. The majority of the deposit was attracted to a magnet. Bulk chemical analysis indicated that the metal present in the largest concentration by far was Fe (43.0%). The sum of all the other metal concentrations was 1.68%; these other metals were those...
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expected in a corrosion deposit in a process stream, rather than from contamination by foreign material (rock or soil). The concentration of carbon was relatively high at 8.56%.

The peaks in the X-ray powder diffraction pattern were located by a second-derivative technique. A search of the peaks against the Powder Diffraction File demonstrated that the majority of the dust consisted of siderite, FeCO₃ (29-696), and that smaller concentrations of magnetite, Fe₃O₄ (19-629), and hematite, α-Fe₂O₃ (33-664), were also present. Fixed structural models of these three phases [1-3] were used in a Rietveld analysis of the pattern. All data processing was carried out using GSAS [4]. Refined were scale factors, lattice parameters, profile parameters, and background coefficients. This three-phase model of the pattern clarified the presence of many weak, broad, and shoulder peaks in the difference pattern. These peaks were located using the difference pattern, and served as the input to another search against the Powder Diffraction File. The presence of several additional phases — including goethite, α-FeOOH (29-713), pyrrhotite, Fe₇S₈ (24-220), and lepidocrocite, γ-FeOOH (8-98) — was indicated. These three phases were also included in the refinement using fixed structural models [5-7]. The quantitative analysis, based on the refined scale factors (Figure 1) was: 65% siderite, 9% magnetite, 9% hematite, 10% goethite, 5% pyrrhotite, and 2% lepidocrocite. The standard uncertainties of these concentrations are of the order of 5% relative. A few very weak peaks were not accounted for by these six phases, and indicated the presence of a trace of another polymorph of pyrrhotite. In addition, traces of ikaite, CaCO₃·6H₂O (37-416) and/or...
one or more pyroxene group silicates such as Ca(Mn,Fe)Si$_2$O$_6$ (33-292) were present. There was no evidence for the presence of amorphous material.

The bulk chemical analysis calculated from these phase concentrations is 54.7% Fe, 37.3% O, 6.8% C, 2.0% S, and 0.13% H. The iron concentration is comparable to the bulk chemical analysis. The calculated 6.8% C accounts for most of the measured 8.56%; gas chromatographic analysis indicated the presence of a small amount of hydrocarbons in the solid. Calculation of the bulk chemical analysis from the refined concentrations is a valuable self-consistency check on the refinement results, and is generally in good agreement with the observed bulk analysis. Microabsorption effects are, however, not eliminated by a Rietveld analysis.

Had the analysis been halted after the first search/match, 17% of the deposit would have been missed, and a very misleading picture of the nature of the solid obtained. Even though a small extra effort was required, not getting the right answer could have proved costly. The source of this deposit was a CO$_2$ pipeline. It is not unreasonable to expect iron carbonate in corrosion deposits from such a line. The mineral siderite is known to alter to goethite, magnetite, and hematite. In the presence of water, both the production of carbonate from oxides (and hydrous oxides) and the production of oxides from the carbonate seem reasonable. The particle sizes of the deposit indicated that the turbine could be protected from this corrosion deposit by suitable filters.

![Figure 2. Observed, calculated, and difference patterns of a deposit from an alkylation unit in a refinery. The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale. The bottom row of tick marks represents the FeF$_2$ peak positions; successively higher rows indicate the Fe$_2$F$_3$, 2H$_2$O and Al$_2$(OH,F)$_6$. H$_2$O peaks.](image-url)
Fluoride Corrosion Deposit

The powder pattern of a deposit isolated from the alkylation unit in one of Amoco's refineries indicated that the major phase was FeF₂ (18-638). A Rietveld refinement using a fixed structural model [8] for this phase helped to define the weak peaks better. A search of these weak peaks against the PDF indicated the presence of two additional phases: Fe₂F₅·2H₂O (28-484) and Al₃(OH,F)₆·H₂O (18-24). Addition of these two phases using fixed structural models [9, 10] to the refinement (Figure 2) yielded the quantitative phase analysis: 94(1)% FeF₂, 4(1)% Fe₂F₅·2H₂O, and 2(1)% Al₃(OH,F)₆·H₂O. A very small concentration of Na₂Fe₂F₇ (24-1098) was also probably present. The detection and unambiguous identification of small concentrations of hydrated phases led to changes in the operation of the distillation tower from which this deposit was isolated, resulting in longer tower life, and significant cost savings.

A New Polymorph of MoO₂

A common engineering practice is to place corrosion coupons in a process stream, to obtain quantitative measurement of corrosion rates, and to gain insight into the best metallurgy to use in subsequent plants. A black deposit was observed on the surfaces of several Hastelloy (a class of Ni-

![Figure 3. The powder pattern of a black corrosion deposit isolated from a Hastelloy corrosion coupon. The broad feature at low angles arises from the double-sided adhesive tape used to mount the sample.](image-url)
Figure 4. A stereo view of the akhtenskite (c-MnO₂) structure. The metal atoms are indicated by the large open circles, and the oxygens by smaller shaded circles. The view is down the hexagonal c-axis.

Figure 5. Observed, calculated, and difference patterns of a new polymorph of MoO₃. The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale. The background of the adhesive tape has been subtracted. The row of tick marks represents the MoO₃ peak positions.
Cations located at different sites would be expected to affect catalytic properties in different ways. We have studied the crystal structure of faujasite at many different stages during the preparation of a series of Ca-exchanged faujasites.

The starting material was commercial NaY (LZ-Y52), with 56 framework Al/unit cell (and thus 56 Na/cell). It was exchanged at room temperature with ammonium nitrate to reduce the sodium content to 12 Na/cell. A calcium exchange of this NH4Na-FAU was carried out at room temperature, and the product air-dried (sample 70-1). The dried product was calcined in air at 300°C to yield sample 71-4. This material was then subjected to a second calcium exchange and calcination to yield sample 63-3.

The zeolites were mixed with known concentrations of a quartz internal standard, and the powder diffraction patterns were measured at beamline X3B1 at the National Synchrotron Light Source at Brookhaven National Laboratory, using a wavelength of approximately 1.15 Å. The Rietveld refinements were begun including just the framework atoms, and difference Fourier techniques were used to locate the extraframework sites. Patterns were measured on hydrated sieves at ambient conditions (to calibrate other analytical techniques) and on dehydrated samples at a catalytically-relevant temperature of 300°C.
The cation site occupancies change considerably with ion exchange and with changes in temperature (Table 1). In the air-dried CaNa-FAU 70-1, Ca occupy sites I', II, and V. Site II' contains too much electron density to be accounted for by all of the Na, so it seems to be populated by both Ca and Na. When this material is dehydrated by heating to 300°C, and the pattern measured in situ, the Ca move to site I (in the center of the D6R), and site II' becomes vacant. The electron density at sites I' and II corresponds to just the right number of Na and Ca to account for the bulk chemical analysis. When this material is cooled back to room temperature (and rehydrated), the Ca move to sites I', II, and II', and the Na back at II'. The Ca at site I' are coordinated directly to the framework, while those at II' and II are hydrated, and bonded indirectly. The Ca at site II are coordinated directly to the framework. On further Ca exchange, the extra Ca go to sites I', II, and V, and the occupation of site II' decreases. If a Ca occupies site I, it precludes a Ca from occupying two adjacent sites I'. At high Ca loadings, site I' is preferred over site I. At 300°C, the Ca move from V to I'. In the Ca-FAU 63-3, the site I' occupancy corresponds to 2 Ca/sodalite cage. In all cases, the cation composition calculated from the refined site occupancies agrees with that determined by bulk chemical analysis. The detailed understanding developed in this study helped interpret spectroscopic data, and rationalize patterns of catalytic activity.

<table>
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<tr>
<th>Sieve / Description</th>
<th>I</th>
<th>I'</th>
<th>II'</th>
<th>II</th>
<th>V</th>
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<tr>
<td>70-1, CaNaY, air dried</td>
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<td>10 Na</td>
<td>7 Ca</td>
<td>2 Ca</td>
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<tr>
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<td>12 Ca</td>
<td>10 Na</td>
<td>6 Ca</td>
<td>trace Ca</td>
<td></td>
</tr>
<tr>
<td>70-1, CaNaY, in situ, 300°C</td>
<td>10 Ca</td>
<td>6 Ca</td>
<td>-</td>
<td>6 Ca</td>
<td>-</td>
</tr>
<tr>
<td>63-3, CaY, calcined @ 300°C, ambient</td>
<td>13 Ca</td>
<td>10 Ca</td>
<td>5 Ca</td>
<td>2 Ca</td>
<td></td>
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<tr>
<td>63-3, CaY, in situ, 300°C</td>
<td>1 Ca</td>
<td>20 Ca</td>
<td>6 Ca</td>
<td>7 Ca</td>
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Dimethyl-2,6-naphthalenedicarboxylate (NDC)

Many materials of practical importance are difficult or impossible to isolate as single crystals for structure determination. It is therefore necessary to determine the crystal structure ab initio using only powder diffraction data. Knowledge of the crystal structure provides a framework for understanding and predicting the properties of materials, and for characterizing the solid itself, avoiding extensive sample preparation.

Very little is known about the crystal structures of 2,6-disubstituted naphthalenes, for it is
very difficult to grow the single crystals "necessary" for structural characterization by diffraction techniques. Molecular modelling techniques have advanced to the point that they are useful in solving crystal structures from powder data [18].

A sample of commercial material was ground in a McCrone micronising mill, using corundum grinding media and ethanol as the milling liquid. The laboratory diffractometer pattern could be indexed [19] on a high-quality primitive monoclinic unit cell having \(a = 13.404, b = 6.169, c = 7.170\) Å, and \(\beta = 100.36^\circ\). The systematic absences unambiguously determined the space group to be \(P2_1/c\). The density is such that \(Z = 2\), and thus that the molecule resides on a center of symmetry. The \(b\) and \(c\) lattice parameters are very similar to two of the cell dimensions of 2,6-dimethylnaphthalene, providing evidence that the stacking of the naphthalene cores is similar in the two structures. The \(a\) lattice parameter indicates that the long axis of the molecule is aligned roughly in this direction. A set of structure factors \((d > 1.60\) Å) obtained from a LeBail extraction was used as input to a direct methods [20] calculation. This calculation indicated a preference for the orientation of the planar molecule with respect to rotation about the \(b\) axis, but no other clear indication of the crystal structure.

All of this information was used to guide manipulation of the molecule in Cerius\(^2\) TM [21], while monitoring the calculated diffraction pattern and assessing its similarity to the observed pattern, as well as monitoring intermolecular contacts. The problem was made more complex by the fact that there are two potential centrosymmetric conformations of the molecule. While plausible structures could be found using one conformer, none of them could be refined successfully, and the molecules did not really pack together very well. Changing to the other conformer quickly resulted in identification of a promising low-energy structure, one which refined well in a Rietveld refinement.

Although the structure was solved using laboratory powder data, the final refinement was carried out using a pattern collected at beamline X3B1 at the National Synchrotron Light Source at Brookhaven National Laboratory. Initial refinements with laboratory data used an 8-atom rigid body consisting of half the naphthalene core and the carboxyl group. After this converged, a difference Fourier map was calculated. The two strongest peaks were located near the bridgehead carbons, but the third strongest peak was in a reasonable location for the methyl carbon C8, in agreement with the orientation derived using Cerius. The final refinements treated the 5-atom half naphthalene core as a rigid body, and used extensive soft constraints in the center of the molecule and in the ester linkage. Hydrogen atoms were included in calculated positions, which were updated during the course of the refinement. A common isotropic displacement coefficient was refined for the core carbons, and a separate thermal parameter was refined for the ester group. The isotropic displacement coefficient of the hydrogens was fixed at 0.08 Å\(^2\).

This sample contained a corundum impurity, a contaminant from the grinding media. Corundum was included in the refinement using a fixed structural model. Scale factors and the lattice parameters for both phases were refined. The NDC peaks exhibited preferred orientation, consistent with the layered structure. Second-order symmetrized spherical harmonic coefficients were refined. The profiles were described by pseudo-Voigt functions. The profiles were dominated by strain broadening. For NDC, the gaussian \(U\) and cauchy \(Y\), and \(L_x\) anisotropic strain broadening parameters were refined; only the \(Y\) profile parameter was refined for corundum. The background
Figure 7. Observed, calculated, and difference patterns of dimethyl-2,6-naphthalenedicarboxylate (NDC). The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale. The bottom row of tick marks represents the NDC peak positions; the top row indicates the peaks of a corundum impurity.

Figure 8. The NDC molecule, indicating the atom numbering scheme. The heavy atoms are represented by 50% probability spheroids, and the hydrogens by small circles of arbitrary radius.
from the capillary was described by a 10-term real space pair correlation function, with fixed characteristic distances of 0.716, 3.883, 4.000, and 4.771 Å.

The final refinement of 49 variables using 15683 observations yielded the residuals \( wR_p = 0.1152, R_p = 0.0912, \chi^2 = 9.011, \) and \( R(F) = 0.1855. \) The agreement of the observed and calculated patterns (Figure 7) is good. The largest errors are in the description of the asymmetry of the low-angle peaks. The largest peak in the final difference Fourier map was 0.61 e\( \cdot \)Å\(^3\), and the largest difference hole was -0.67 e\( \cdot \)Å\(^3\). A normal probability plot indicated that the standard uncertainties are underestimated by a factor of 2.3. The refined structural parameters are reported in Table 2.

The crystal structure of dimethyl-2,6-naphthalenedicarboxylate contains discrete centrosymmetric molecules (Figure 8). Since a rigid body and soft constraints were used, all distances and angles fall within the expected ranges. The naphthalene core and the ester linkage are

Table 2. Structural Parameters of dimethyl-2,6-naphthalenedicarboxylate (NDC)

\[
P2_1/c, \quad a = 13.41931(14), \quad b = 6.14869(5), \quad c = 7.15257(5) \text{ Å}, \quad \beta = 100.400(1)^\circ, \quad V = 580.47(1) \text{ Å}^3
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{iso} ) Å(^2)</th>
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<td>-0.1874(4)</td>
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<td>0.1450(6)</td>
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<td>C4</td>
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<td>0.2294(3)</td>
<td>0.0536(3)</td>
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planar; the ring carbons C1-C5 are within 0.0003 Å of the mean plane, and the atoms of the ester group (C7, C8, O1, and O2) are within 0.02 Å of the mean plane. The ester group is twisted out of the core plane; the C3-C2-C7=O1 torsion angle is 16°, the C1-C2-C7-O2 torsion angle is 24°, and the angle between the mean planes is 20°.

The crystal structure (Figure 9) consists of layers perpendicular to the a-axis. The aromatic rings stack parallel to c, with "side-to-side" interactions along b. The molecules pack in a herringbone fashion in these directions, resulting in an interlocking layer. These layers interact only loosely with their neighbors along a, with only end-to-end contacts between the layers. This packing accounts for the platy morphology and the pronounced preferred orientation in flat plate samples, even after extensive grinding. There are no close intermolecular contacts; the packing is dominated by van der Waals interactions. This refinement illustrates the structural detail which can be obtained in a Rietveld refinement. The crystal structure can be used to rationalize the observed crystal morphology, and provides the basis for understanding how to modify and control the morphology.

"TRADITIONAL" POWDER DIFFRACTION APPLICATIONS

Rietveld analysis provides a convenient way to use only a portion of the information in a powder pattern, if that is what is required to answer a particular question. The crystal structure serves as a "constraint" on the least squares refinement, making it possible to extract information inaccessible to traditional analyses.

Lattice Parameters

Substitution for silicon by various trivalent heteroatoms (such as Al, B, or Fe) in crystalline
molecular sieves leads to negatively-charged frameworks. This charge is balanced by extraframework cations, of which the proton is most important, since it yields an acid catalyst. The framework heteroatom concentration is thus a direct measure of the concentration of acid sites in a molecular sieve, and an important parameter in catalyst characterization. A Si-O bond distance in a tetrahedral framework is 1.60 Å, while an Al-O distance is 1.74 Å, and a B-O distance 1.48 Å. Thus, incorporation of B into a molecular sieve framework leads to a contraction of the unit cell, while Al leads to cell expansion.

Development of a correlation between unit cell parameters or volume using carefully-prepared materials is valuable in catalyst characterization. Such correlations between orthorhombic (or monoclinic) unit cell volume and framework heteroatom concentration have been developed for B- and Al-MFI [22] (Figure 10). Although the Al-MFI are generally quite highly crystalline, the borosilicates in general have broader peaks, which are more difficult to locate accurately by standard methods. With the use of an internal standard, Rietveld refinement can permit accurate (± 0.01 Å) and precise lattice parameter determinations even from catalysts containing only a few percent of poorly-crystalline sieve. In addition, the quality of the fits make it easy to detect peak splittings that indicate lowering of the symmetry from orthorhombic to monoclinic. With a template file, the calculation is as fast as traditional methods of determining individual peak positions and refining the cell dimensions using only the positions. Rietveld analysis is helpful in cases in which there is extensive peak overlap, especially in mixtures.

Profile Shapes

Carbon-supported Pd hydrogenation catalysts are useful in several commercial processes. The fresh catalyst ideally contains atomically-dispersed Pd, so no metal is detectable. The diffraction

![Graph showing the cell volume of MFI-structure molecular sieves as a function of framework heteroatom concentration.](image)

**Figure 10.** The cell volume of MFI-structure molecular sieves as a function of framework heteroatom concentration [22].
Figure 11. The powder pattern of a used Pd/carbon hydrogenation catalyst. The broad features at 2θ = 23 and 44° arise from the carbon support.

pattern of a used catalyst (Figure 11) contains Pd peaks, indicating the sintering which is a major cause of catalyst deactivation. Occasionally, Pd₃S is observed, indicating poisoning as a second mechanism of deactivation. A third deactivation mechanism is plugging of the top of the bed. For many years, we measured Pd crystallinity in the traditional way using a reference catalyst, and determined the average crystallite size from the integral breadths using the Scherrer equation.

The closer examination forced by Rietveld analysis has led to new insight into catalyst deactivation. The scattering of the carbon support can be described adequately by a combination of graphite and a real space pair correlation function. Refining the cubic Pd lattice parameter yielded 3.896(2) Å, in excellent agreement with the 3.889 Å of pure Pd. The Pd peaks, however, could not be described by a simple pseudo-Voigt profile; shoulders on the low-angle sides of each Pd peak were prominent in the difference pattern. The best explanation of these shoulders is the presence of a fcc Pd alloy with an expanded unit cell of 3.986(6) Å. Analytical electron microscopy detected pure Pd particles, but also grains containing Pd and Sb and/or Pb. Alloys such as Pd₃Pb have been reported. Including such an alloy in the model led to an excellent fit (Figure 12). The detection of alloy formation in the Rietveld analysis led to the discovery of a fourth mechanism of catalyst deactivation, with important practical consequences.

If a large enough range of the pattern is measured, it can be seen that the peaks of the Pd and
Figure 12. Observed, calculated, and difference patterns of a used Pd/carbon catalyst. The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale. The bottom row of tick marks represents the carbon (graphite) peak positions, the middle row indicates the Pd peaks, and the upper row the peaks of the fcc with an expanded unit cell compared to that of pure Pd.

The alloy contains size and strain contributions. The average crystallite sizes determined from the Scherrer equation are thus underestimates. In this case, the refined profile coefficients indicate average Pd crystallite sizes as large as 400 Å, compared to the 120 Å obtained from the Scherrer equation. The accuracy of such results can be confirmed by transmission electron microscopy. The alloy peaks exhibit larger strain than the Pd peaks.

**Anisotropic Peak Broadening**

Although the widths of peaks in the powder diffraction pattern are frequently used to quantify crystallite size and strain, the information conveyed by the anisotropy of the broadening is less commonly used. Rietveld analysis provides a simple way to interpret this broadening in a physically-meaningful way.

Amoco obtained a patent for a "novel phosphorous-vanadium catalyst having a characteristic X-ray diffraction pattern" [23]. This composition of matter was defined by the stoichiometry (VO(HPO₄) · ½H₂O) and the characteristic X-ray powder pattern. The pattern exhibits some similarities in peak positions to that of VO(HPO₄) · ½H₂O (Figure 13), but the relative peak heights in the two patterns are very different. A close examination of the raw pattern reveals that the line
An additional demonstration of the utility of anisotropic peak broadening is provided by the pattern of 2,6-naphthalenedicarboxylic acid (Figure 15). Knowledge of the crystal structure [18] made it possible to determine that this pattern also exhibits anisotropic size broadening, characteristic of domains approximately $150 \times 150 \times 600$ Å. The observed crystal morphology did not, however, correspond to that expected from the crystal structure, and provided insight into the degree and nature of faulting in this material.

**Preferred Orientation**

While analysts generally take pains to avoid preferred orientation, there are times when it can yield useful information. Amoco manufactures over $5 \times 10^9$ pounds of purified terephthalic acid per
Figure 14. Observed, calculated, and difference patterns of "Modified Phase A". The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale.

Figure 15. Observed, calculated, and difference patterns of 2,6-naphthalenedicarboxylic acid. The crosses represent the observed data points, and the solid line the calculated pattern. The difference pattern is plotted at the same vertical scale.
Figure 16. Observed, calculated, and difference patterns of unground (top) and milled (bottom) purified terephthalic acid. The crosses represent the observed data points, and the solid lines the calculated patterns. The difference patterns are plotted at the same vertical scale as the corresponding observed patterns. The bottom rows of tick marks represent the peaks of polymorph I, and the upper rows indicate the peaks of polymorph II.
year, and sells both unground and milled grades to meet customer requirements. The flat plate powder patterns of unground and milled TA differ (Figure 16). The patterns can be described quite well, and the difference lies in the degree of preferred orientation. Both polymorphs have complex crystal morphologies [25], leading to complex preferred orientation, which cannot be described adequately by a uniaxial March-Dollase model. Describing the orientation is possible using spherical harmonics. Since both polymorphs are triclinic, only second-order harmonic coefficients were refined. Analysis of the coefficients yields a texture index, which correlates very well to the asphericity of the particles, as determined by optical microscopy. Analysis of the preferred orientation thus yields useful information about particle morphology.

STUDIES AT NONAMBIENT CONDITIONS

To obtain the detailed structural information necessary to solve practical problems, it is sometimes necessary to make nonstandard measurements. Studies of extraframework sites in zeolites sometimes lead to ambiguous results, since the X-ray experiment is sensitive only to electron density. The exact identification of a "blob" of electron density is sometimes not clearcut. A good example is provided by a Zn-exchanged Na-FAU - a continuation of the study discussed above.

We used Zn as a diamagnetic analog of catalytically-interesting first-row transition metal cations. Using a single laboratory or synchrotron dataset, the cations could not be identified unambiguously. At wavelength nears the Zn absorption edge (1.28 Å), the scattering factor of the Zn can be varied by about 25%. By simultaneous refinements using datasets measured both far from the Zn K-edge and near it, we could unambiguously establish the site occupancies. The data were very clear about indicating which of several possible cation distributions was correct.

In air-dried (hydrated) ZnNa-FAU, the Zn occupy sites II' and II, with the Na at site I' (Figure 6). There is significant density at the center of the sodalite cage (site U). While it is possible that this density represents extraframework Al (produced by dealumination of the framework), the Zn-U distances are about right for Zn-O distances. I believe that this density represents an O coordinated to the hydrated Zn ions at site II'. The Zn at site II are also hydrated. At 300°C, Zn move to site I', and the Zn at site II' moves closer to the framework, indicating direct coordination. The Na are displaced to site II in the supercage. The central oxygen density is still present. This resonant study determined the occupancies unambiguously. These cation occupancies correspond to those in a preliminary communication by Wilkinson and Cheetham [26].

Xe$^{129}$ NMR spectroscopy is commonly used to characterize pore sizes and to quantify diffusion rates in molecular sieves. To help interpret the NMR results, it was of some interest to locate the Xe atoms in a sieve. A sample of Na-FAU in a capillary was carefully dehydrated at 110°C, and cooled to room temperature in a vacuum line. The sieve was then equilibrated with Xe at atmospheric pressure, and the capillary sealed. The powder pattern was measured at beamline X3D1 at NSLS at 20 K. The right number of Na (56/cell) were observed at sites I', II', and II. Additional electron density was detected at two additional sites in the supercage - one near site III, a van der Waals contact from the framework O and the Na, and another site near the middle of the supercage. These Xe sites were reasonable, and correspond to a population of 7 Xe/cell.
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