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short communications

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M. D. Foster,[a]***** **M. M. J. Treacy,**[a] **J. B. Higgins,**[b] **I. Rivin,**[c] **E. Balkovsky**[d] **and K. H. Randall**[e]

[a]Arizona State University, Department of Physics and Astronomy, PO Box 871504 Tempe, AZ 85287-1504, USA, [b]Air Products and Chemicals Inc., 7201 Hamilton Boulevard, Allentown, PA 18195-1501, USA, [c]Temple University, Department of Mathematics, 1805 North Broad Street, Philadelphia, PA 19122, USA, [d]Rutgers University, Department of Physics and BioMaPS Institute, 136 Frelinghuysen Road, Piscataway, NJ 08854, USA, and [e]Google Inc., 2400 Bayshore Parkway, Mountain View, CA 94043, USA. Correspondence e-mail: martin.foster@asu.edu

The application of a new technique for zeolite framework structure solution is described that exhaustively enumerates every possible topology consistent with known unit-cell dimensions and space-group symmetry. It is shown that computer-generated on-line databases of hypothetical crystal structures can radically augment structure building in the pre-refinement stage.

1. Introduction

Modern powder diffraction techniques have revolutionized the determination of crystal structures from powder data. However, when materials exhibit imperfect crystallinity, small crystallite size, or other properties resulting in poor diffraction characteristics, these methods are less successful. Frequently, zeolite materials are synthesized as sub-micrometre powders containing several types of defects that degrade diffraction data. Specialized TEM and NMR analyses are sometimes useful, but often they are time consuming and seldom lead to the direct determination of atomic coordinates for a crystal unit cell. Here we report on the application of a new technique for zeolite framework structure solution that exhaustively enumerates every possible topology consistent with known unit-cell dimensions and space-group symmetry. The framework topologies are refined, and calculated powder patterns are then compared with experimental data to obtain plausible structure solutions by a process of elimination. In this work the method is applied to the long-standing problem of the structure of zeolite ZSM-10 (Higgins & Schmitt, 1996).

It is routine nowadays to use computer methods reliably to solve crystal structures directly from high-quality diffraction data. Although now used less frequently, model building as a structure-solving technique has a long and illustrious history. In 1913, W. L. Bragg determined the spatial arrangement of atoms in several alkali halides (Bragg & Bragg, 1913a), as well as the slightly more complicated arrangement of Zn and S atoms in zinc blende (sphalerite) (Bragg & Bragg, 1913b). Following the advice of Sir William H. Pope, Bragg compared experimental X-ray intensities from zinc blende with those calculated from a spherical packing model proposed by Barlow (1883). This first crystal structure analysis defined the main focus of X-ray crystallography to the present day. The technique of comparing experimental X-ray intensities with those calculated from models was used by many early crystallographers. Model building played an important role in many structure solutions, from complex biological crystals like DNA, to certain classes of inorganic materials such as zeolites, zeolite beta being a well known example (Higgins *et al.*, 1988; Treacy & Newsam, 1988). However, as more complex structures were attempted, constructing suitable models became more difficult. New techniques were devel-

oped, including heavy-atom and replaceable-atom methods, Fourier methods, Patterson synthesis, vector methods and the 'direct' statistical methods in common use today.

Today, the availability of fast computer processors and sophisticated algorithms has revitalized the model building process. There are several approaches to building hypothetical crystal structures, most of which are focused on zeolite enumeration. Almost all methods proceed by permutation of linkages between basic building elements. The earlier databases were built by hand (Akporiaye & Price, 1989; Breck, 1974; Shannon, 1993; Smith, 1988; Wells, 1977, 1979). Computer automation extends the process more reliably to more complex systems (Deem & Newsam, 1992; Delgado Friedrichs *et al.*, 1999; Fischer, 1974; Klein, 1996; Mellot-Draznieks *et al.*, 2000; O'Keeffe & Brese, 1992; Treacy *et al.*, 1997). In most instances, the computations generate graphs representing the frameworks. Plausible zeolite structures are then obtained by a separate framework-energy minimization step (Foster *et al.*, 2003; Klein, 1996; O'Keeffe & Brese, 1992; Treacy *et al.*, 1997). Despite these advances, databases of zeolite frameworks have not been extensively available until recently (Treacy *et al.*, 2004). We have created a web-based database that is freely available using the symmetry-constrained intersite bonding search (SCIBS) method (Treacy *et al.*, 1997, 2004). Presently, it contains over a million zeolite frameworks, and continues to grow.

2. Method

The SCIBS model-building approach was applied to the long-standing problem of ZSM-10, a poorly crystalline zeolite that was originally synthesized in the late 1960s, for which a tentative framework topology was proposed by Higgins & Schmitt (1996). Those authors determined that the ZSM-10 framework is consistent with hexagonal $P6/mmm$ space-group symmetry, with unit-cell dimensions of $a \simeq 31.575$, $c \simeq 7.52$ Å. The space group and unit-cell dimensions were determined by single-crystal electron diffraction. The framework density suggested there were six unique tetrahedral atoms (T atoms). They conjectured that the structure was related to the hexagonal framework of zeolite L (IZA code **LTL**), since zeolite L can cocrystallize. Two models were obtained manually by applying simple modifications to the triple-cell setting of the **LTL** cell. Poly-

hedral representations of their models, A and B, are shown in Figs. 1 and 2. Each model has three T-atoms in the x, y, z general position, and three T atoms on the $x, y, 0$ mirror plane. Rietveld refinement of model A achieved an R_{wp} value of 0.15, which was inconclusive. This was most likely due to the inability to locate the 40% of the original K cations that could not be ion-exchanged from the pore system (Higgins & Schmitt, 1996), and not necessarily because the framework model was inappropriate. Although Higgins and Schmitt favored model A, it was not clear how many more viable models might exist. In order to be certain, the challenge is to identify every topology consistent with the known structural details. The SCIBS method is ideal for structural problems of this type.

The SCIBS method has been described in detail elsewhere (Treacy *et al.*, 1997, 2004). The method enumerates every possible four-connected graph that is consistent with a given space-group symmetry and the number of unique T atoms, N_T. For $N_T = 6$ in space group $P6/mmm$, 18 400 408 zeolite graphs were found. Of these, 289 662 graphs had three of the T atoms in the x, y, z general position, and three on the $x, y, 0$ (or $x, y, 1/2$) mirror plane, dramatically extending the possibilities beyond the original two models. Those two models, A and B, were present in our list, as well as the triple-cell setting of **LTL**. For thoroughness, all 18.4 million graphs were annealed using a simple cost function that favours ideal tetrahedral T-atom arrangements, ignoring oxygen atoms (Treacy *et al.*, 1997). The low-cost graphs with unit-cell dimensions close to those of ZSM-10 [$a = b = 31.0$ (2), $c = 7.5$ (1) Å] were then refined further using a more sophisticated cost function, BGB, developed for SiO_2 compositions (Boisen & Gibbs, 1993). Graphs with energies within 3.0 eV/T-atom of the value for quartz were retained, and further refined by the *General Utility Lattice Program* (*GULP*) (Gale, 1997) to determine a thermodynamic feasibility factor relative to quartz, following procedures outlined by Foster *et al.* (2003). *GULP* performs interatomic potential methods to refine a structure. The potential parameters we used are those of Sanders *et al.* (1984) with a modified oxygen shell charge by Schröder *et al.* (1992). The graph generation and refinement process took about eight weeks of continuous running on a 32-processor computer cluster. This effort distilled 493 graphs that had framework energies within 0.4 eV/SiO_2 of quartz, according to the *GULP* program. Similarly, graphs for $N_T = 3$, 4 and 5 in $P6/mmm$ were also enumerated and refined, extending the total to 543 viable low-cost frameworks with unit-cell parameters corresponding to ZSM-10.

3. Discussion

Simulated powder patterns of these frameworks were compared visually with the data for calcined ZSM-10. Visual inspection shows unambiguously that the original model A gives the best fit to the data by far (see Fig. 3). Three other possibilities are labelled B to D. The pattern comparison for D is also respectable below 15°, but overall the pattern for model A matches the data the best. The low-angle intensity data for ZSM-10 are strongly attenuated compared with all of the models. This attenuation is likely due to occlusion of the zeolite channels with extraframework material, especially K cations and associated water molecules, as well as the small crystallite size as indicated by uniformly broadened peaks. Adding K cations to the centers of the cancrinite cages and the centers of the 8-rings between cancrinite cages significantly enhances the fit, as shown in Fig. 3.

A comparison of framework energies is instructive (see Table 1). For model A the calculated framework energy is low, 0.1829 eV/SiO_2,
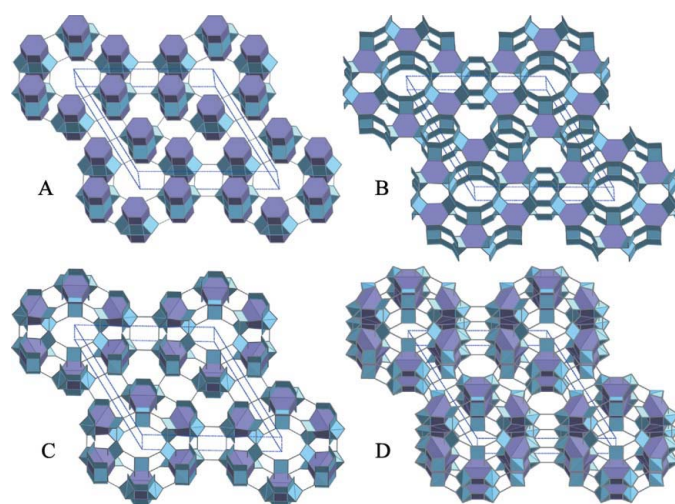
Figure 1
Polyhedral representation of four of the models examined. These frameworks share the same projection down the hexagonal c axis. Many additional topologies with the same c-axis projection were observed. In the database, the models A, B, C and D correspond to: 191_6_10432993, 191_6_10387515, 191_6_9978149 and 191_6_10014924, respectively. Model A is the correct ZSM-10 framework.
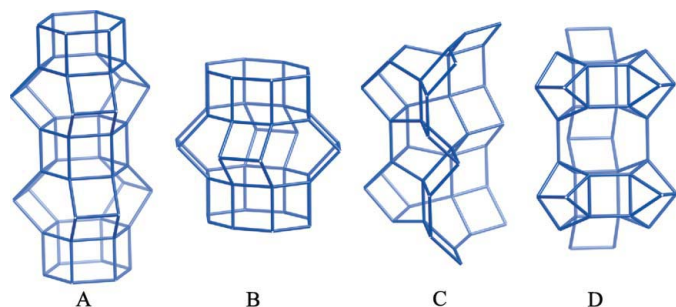
Figure 2
Fragments from the frameworks A–D illustrating their connectivity along the c axis.
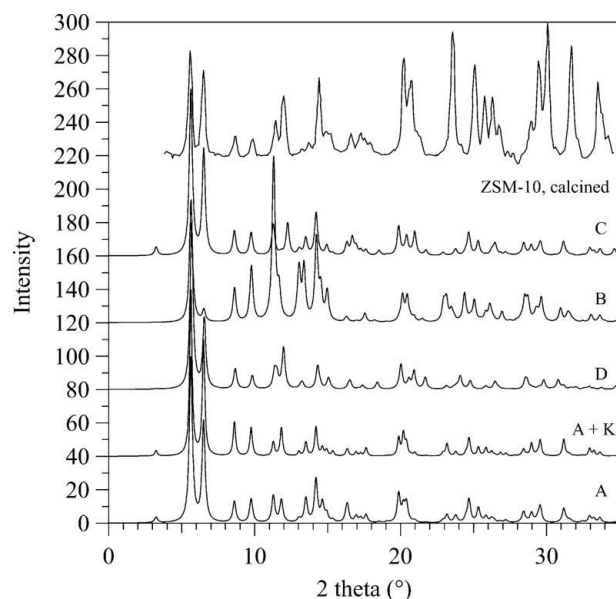
Figure 3
Computed powder patterns for models A–D assuming an SiO_2 composition and a wavelength $\lambda = 1.5418$ Å. The data for calcined ZSM-10 matches model A the best. The fit improves when K cations are added (A + K). Intensities at low angles are suppressed in the data probably because of residual extraframework material remaining in the zeolite channels.

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Table 1
Calculated structures and energies of models A–D relative to quartz.

Model	BGB energy (eV/SiO$_2$)	GULP energy (eV/SiO$_2$)
Model A	0.0462	0.1829
Model B	0.0486	0.1975
Model C	0.0588	0.1731
Model D	0.1170	0.2952

Table 2
Coordinates for model A refined with the BGB method [$P6/mmm$ (191), a = 31.4750 Å, b = 31.4750 Å, c = 7.3893 Å].

Atom	x	y	z
Si1	0.28981	0.09588	0.28654
Si2	0.38633	0.09697	0.28507
Si3	0.48391	0.19392	0.28536
Si4	0.20753	0.05440	0.00000
Si5	0.42658	0.05463	0.00000
Si6	0.52535	0.15284	0.00000
O1	0.28109	0.08328	0.50000
O2	0.30535	0.15267	0.25353
O3	0.33322	0.08670	0.21462
O4	0.23969	0.06048	0.17915
O5	0.38365	0.08601	0.50000
O6	0.42713	0.15362	0.24601
O7	0.40088	0.06112	0.17958
O8	0.49487	0.19614	0.50000
O9	0.49470	0.24735	0.21673
O10	0.51936	0.17895	0.17933
O11	0.15935	0.00000	0.00000
O12	0.19066	0.09533	0.00000
O13	0.41978	0.00000	0.00000
O14	0.48444	0.09509	0.00000
O15	0.57940	0.15881	0.00000

relative to quartz, making this an attractive candidate. This energy compares favorably with the value of 0.1872 eV/SiO$_2$ for the pure SiO$_2$ form of the triple-cell **LTL** framework. Model D, which had the next best visual fit to the powder pattern, has a significantly higher framework energy, 0.2952 eV/SiO$_2$, making it a less plausible candidate. A few marginally lower energy frameworks were identified, but their powder patterns disqualify them as candidates for the ZSM-10 framework. Based on our comprehensive survey of every possible topology consistent with ZSM-10, it emerges by elimination that model A is the most plausible framework for ZSM-10. Coordinates for model A, obtained by distance least-squares fit, were given by Higgins & Schmitt (1996), along with a detailed description of the framework. Coordinates for the SiO$_2$ composition obtained by the GULP program, along with all the other topologies considered, can be found on our website, http://www.hypotheticalzeolites.net. Table 2 gives the coordinates for model A for the BGB refinement; further coordinates are available in the supporting information.[1]

GULP refinements using a pure SiO$_2$ composition can result in significantly lower a cell dimensions than those of the ZSM-10 material. For example, the GULP refinement of model A has a = 30.96, c = 7.52 Å, whereas ZSM-10 has a = 31.575, c = 7.52 Å. ZSM-10 is synthesized with an Si/Al ratio of 0.22. Incorporation of Al with a

partial occupancy of 0.22 over all the T sites increases the a cell dimensions to a = 31.35 Å when refined under GULP, due in part to the distortion from the ideal tetrahedral geometry by Al atoms. Work by Simperler et al. (2004) confirms that a SiO$_2$ energy evaluation relative to quartz can alone give a satisfactory indication of zeolite feasibility without probing the ideal composition.

As this study shows, computer-generated on-line databases of hypothetical crystal structures can radically augment structure building in the pre-refinement stage. In cases where a (low-R-factor) Rietveld refinement is unattainable, we show that a plausible zeolite framework determination can be made by ruling out all other possible topologies. The benefits of databases are not limited to topology determination. With additional analysis tools for pore size and shape determination, such databases will be indispensable for identifying promising synthetic targets for industrial applications.

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[1] Supplementary data are available from the IUCr electronic archives (Reference: ZM5033). Services for accessing these data are described at the back of the journal.