ZSM-23: A Suggested Structure

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X-Ray powder diffraction (Rietveld profile refinement) using a model derived from electron diffraction and adsorption data and space group limitations has yielded a structure for ZSM-23; it is a recurrently twinned version of theta-1 (ZSM-22).

ZSM-23 is a highly siliceous zeolite first reported[1] ten years ago. Like many other synthetic zeolites (porotectosilicates) its structure is unknown,[2] its characterising features being a well defined *X*-ray powder diffractogram, a distinctive catalytic performance, and a repeatable adsorptive capacity. Its powder diffractogram, like that of ZSM-5 (which can be prepared in a similar fashion), remains essentially the same over the range of Si/Al ratios 20 to 125, within which limits it is readily formed as thin fibres. Since no satisfactory single crystals of this material have so far been produced, its structure cannot be solved by conventional methods. In this communication we propose a structure which is consistent with all known properties of the material; the suggested structure may be regarded as a recurrently twinned variant of zeolite theta-1,[3] thought also to be identical with other synthetic zeolites, *viz.* zNu-10,[4] KZ-2,[5] ISI-1,[6] and ZSM-22.[7] Full details of the ratiocinative arguments that lead to the proposed structure will be presented elsewhere; the salient points, however, are given below.

On the basis of its adsorptive capacity to n-hexane, cyclohexane, and toluene, the main-pore aperture of zeolite ZSM-23 must be at least that associated with a 10-membered ring (ten, corner-sharing TO_4 tetrahedra, T = Si or Al). ZSM-23 is also very likely to be a one-dimensional tunnel structure. Electron diffraction patterns taken both perpendicular and parallel to the axis of the thin fibre show it to be of

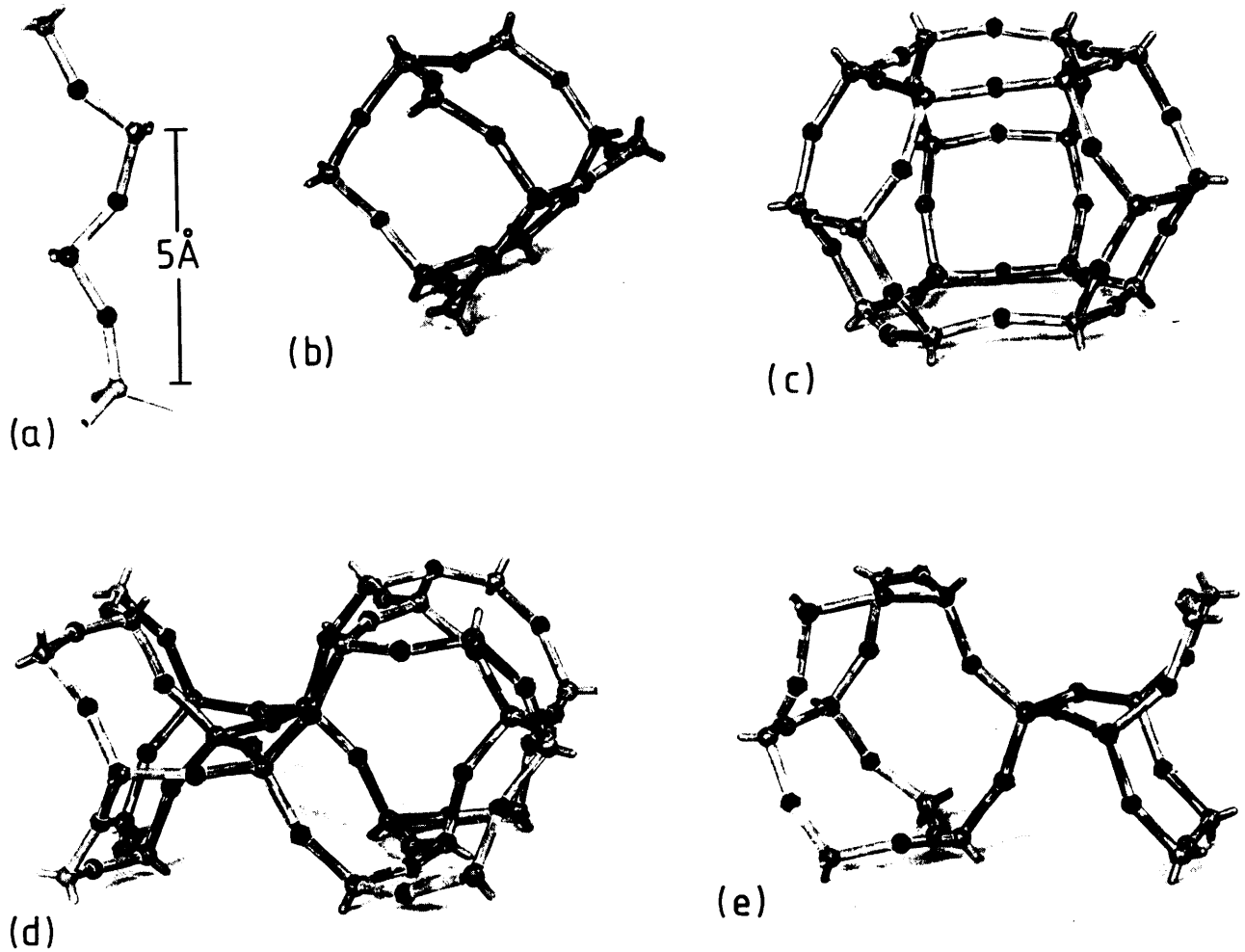

Figure 1. (a) Primary (zig-zag) building unit for the minerals cristobalite, bikitaite, and cancrinite as well as for θ-1 and other synthetic zeolites. The repeat distance (*ca.* 5 Å along the chain of TO-atoms (T = Si or Al), is indicated. Secondary building units, comprised of linked zig-zag chains, are shown in (b) cristobalite, (c) cancrinite, (d) theta-1, and (e) bikitaite.

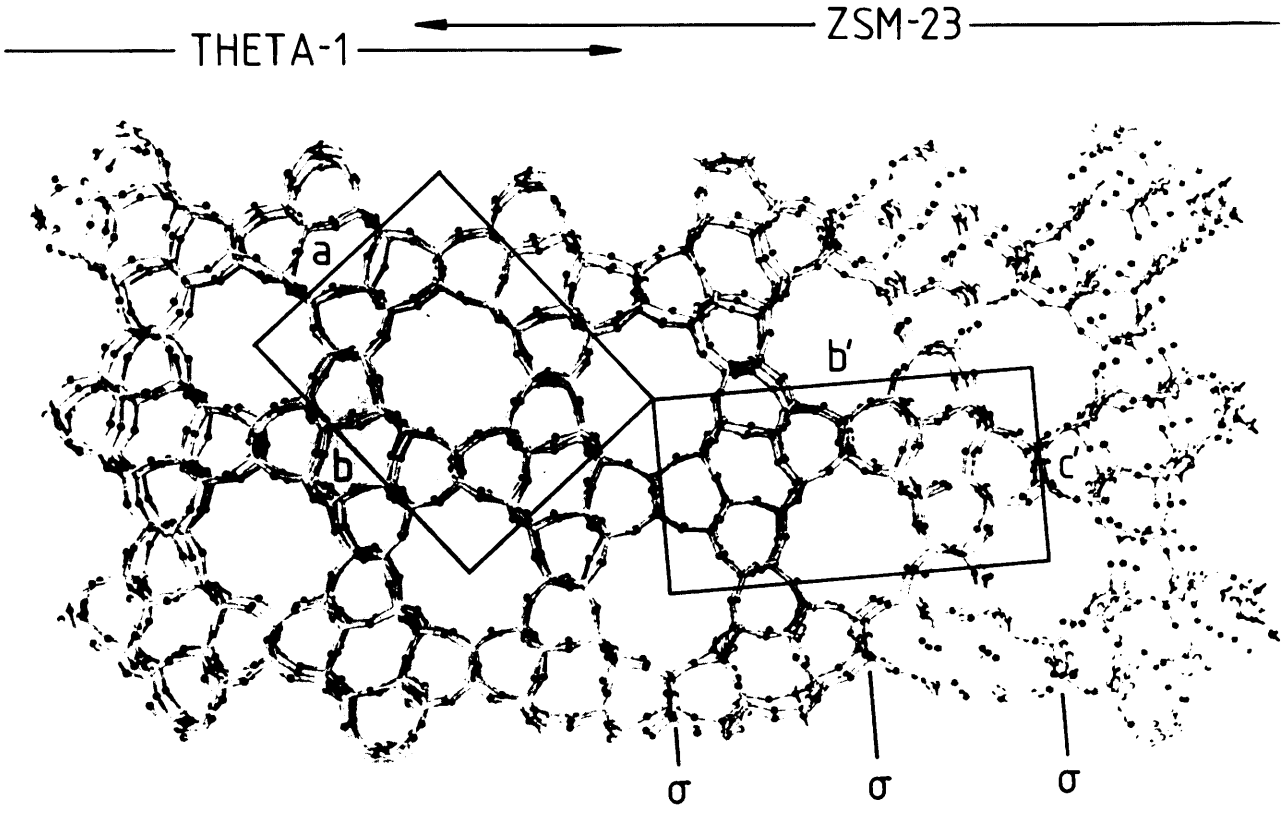

Figure 2. Photograph of a model of theta-1 (unit cell *a*, *b*) intergrown with ZSM-23 (unit cell *b'*, *c'*). ZSM-23 is seen to be generated by twinning across successive equivalent {110} planes of the theta-1 structure.

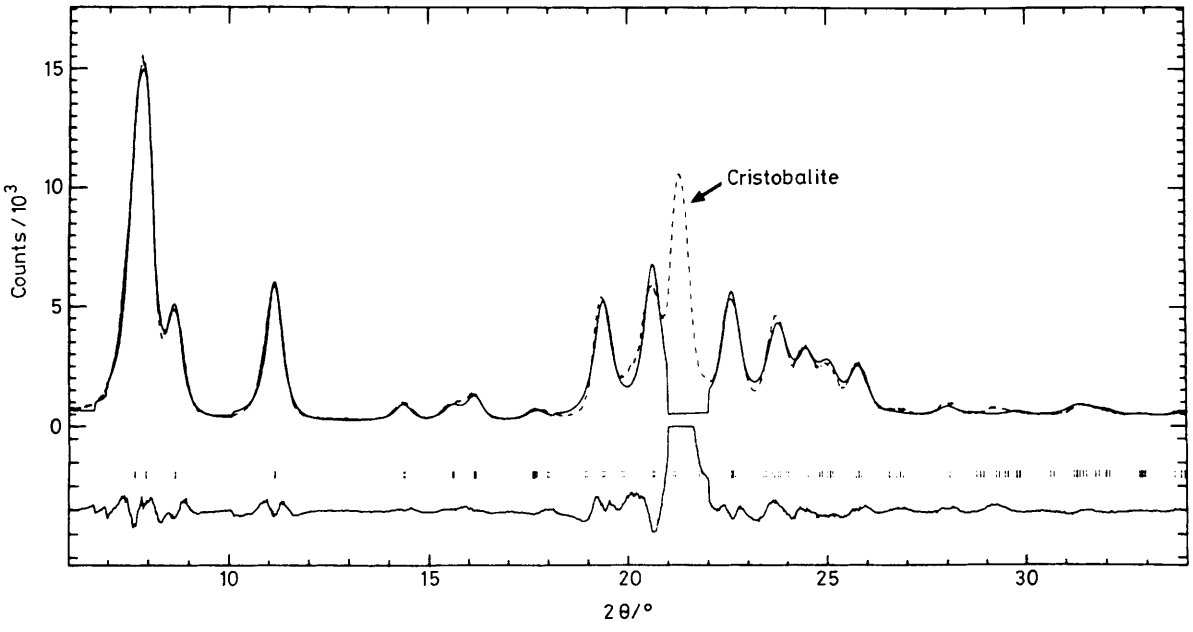

Figure 3. *X*-Ray powder pattern of ZSM-23 (with some cristobalite impurity) at 350 °C, and Rietveld-fitted curve (weighted profile R_{wp} = 18.2), with residue below. The cristobalite peak is not fitted. The space group used is *Pmmn* and the co-ordinates of tetrahedral atoms were the only structural parameters varied. The refinement is underdetermined with respect to the positions of the oxygen atoms.

orthorhombic symmetry, space group *Pmmn* or $P2_1mn$, unit cell dimensions 5.2, 21.7, and 11.2 Å; the cell dimensions are in line with, and permit the indexing of, the *X*-ray powder diffractogram. Preliminary high-resolution electron microscopic studies[8,9] also support these facts and are consistent with the idea that ZSM-23 has a one-dimensional tunnel structure. Recognizing that the short axis repeat (*ca.* 5 Å) occurs also in the minerals bikitaite, cancrinite, cristobalite, and the synthetic zeolite theta-1, we concluded that the same 'zig-zag' chain (see Figure 1) occurs in all these structures.

(We note in passing that some cristobalite is almost always present in all synthesized samples of ZSM-23.) Working on the assumption that recurrent unit-cell twinning of the theta-1 structure could occur, we arrive at a plausible model, consonant with the space-group operations (Figure 2). In excess of 50 or so possible models can, in principle, be constructed from zig-zag chains with 5 Å repeats but only one, that shown in projection in Figure 2, satisfies all available criteria. From a three-dimensional (to scale, 'ball and stick') version of this model, co-ordinates were enumerated for the atom positions. Using the Rietveld *X*-ray profile fitting procedure (a version[10] of that made available by Young and Wiles[11]), and approximating the shape of the diffraction peaks in terms of intermediate Lorentzians, the structure was refined so as to yield a good match (Figure 3) between the observed and calculated diffractograms. The relative ease with which this profile refinement could be conducted encourages the view that the structure shown in Figure 2 is a plausible model for ZSM-23. In view of the fact that the structures of theta-1 and ZSM-23 are closely related and readily cohere (as seen in Figure 2) we predict that, just as there exists[9,12—14] an infinite family of porotectosilicates with ZSM-5 and ZSM-11 end members, there should exist an infinite family of zeolite structures consisting of regular intergrowths of theta-1 and ZSM-23. Likewise, just as with ZSM-5/11, non-recurrent structures[14] may be expected with theta-1/ZSM-23 components.

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