A Computational Study of Zeolite Beta

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Lattice energy minimisation procedures have confirmed the structure of zeolite beta as an intergrowth of two polymorphic structures.

The aim of this communication is to show the power of modern computer simulation methods in modelling complex inorganic structures, by describing their application to the structure of zeolite beta which has been a puzzle for many years. The material, which is important owing to its catalytic application in many hydrocarbon conversion reactions, is a highly siliceous zeolite (Si/Al is typically about 25) prepared by tetraethylammonium templating. The structure has recently been investigated by Newsam and co-workers[1] using a combination of electron microscopy, powder diffraction, and distance least squares modelling techniques. Their results indicate that the structure consists of an intergrowth of two polymorphs 'A' and 'B'. Both contain similar layers constructed from the same tertiary building unit. However the layers are stacked in different ways, as shown in Figure 1, to yield the two distinct polymorphs. Newsam *et al.* suggest that the material has no particular energetic preference for either stacking sequence, hence the material will contain both in roughly equal proportions, and will also contain a very high degree of stacking disorder. It is this that has prevented the determination of the structure of zeolite beta until the present time. This communication reports our computational study of the structure and stabilities of the models proposed by Newsam *et al.* Our results, obtained using the technique of energy minimisation, support their models, although we propose refinements to the reported Si–O–Si geometry.

Our calculations were carried out using the lattice energy minimisation codes METAPOCS[2] and THBREL.[3] The interatomic potentials used were those developed by Sanders *et al.*[4] using the procedure of empirical fitting to bulk structural, elastic, and dielectric properties of alpha-quartz. The model includes a harmonic angle-bending potential applied about the O–Si–O bond. The potential has been widely and successfully used in modelling silicate and aluminosilicate systems, including a recent study of a number of zeolites.[5]

The polymorph structures proposed by Newsam *et al.* were taken as input to our energy minimisation calculations. They were assumed to be purely siliceous: an acceptable approximation in view of the very low Al content of the zeolite. Two sets of calculation were performed. In the first, cell parameters were held fixed and atomic co-ordinates were fully relaxed to equilibrium. This type of calculation yields an equilibrium structure constrained to have the reported crystallographic volume, and is hence called a constant volume calculation. In the second, or constant pressure calculation, both atomic co-ordinates and cell parameters were allowed to relax in the minimisation. In Table 1 we report the experimental and calculated cell dimensions. Clearly, the agreement is good, the maximum discrepancy being less than 2.5%.

The energy minimised structures for polymorphs A and B are shown in Figures 2 and 3, where they are superimposed on the structures proposed by Newsam *et al.* For both polymorphs the agreement is again good. For polymorph A there are no significant discrepancies.

In the case of polymorph B, there is a small but significant deviation of the calculated structure from the model proposed by Newsam *et al.* This concerns the 5-ring of the structure, in which energy minimisation has converted a non-linear Si–O–Si bridge into a linear configuration. The resulting energy minimised 5-ring structure is very close to that observed in the structure of silicalite.[6]

Of particular interest are the equilibrated lattice energies of polymorphs A and B, which are reported in Table 2. Within the limits of the numerical accuracy of the calculation, the constant pressure minimised lattice energies are the same. This result is consistent with the observation that the overall structure is an intergrowth of the two polymorphs in equal proportions.

Newsam *et al.* also suggest a third structure, 'C', based on a different stacking sequence, which they propose may be

Table 1. Observed and calculated cell dimensions.

	Observed	Calculated
Polymorph A		
a/Å	12.66	12.8
c/Å	26.41	26.9
Polymorph B		
a/Å	17.90	18.19
b/Å	17.90	18.19
c/Å	14.33	14.66
β/°	114.80	113.44
Structure C		
a/Å	12.8	13.0
c/Å	13.0	13.3

Table 2. Results of lattice energy minimisation calculations.

	Lattice energy per SiO_2 unit/kJ mol^{-1}	
	Initial	Final
Polymorph A		
Constant volume	−11 867.3	−11 935.8
Constant pressure	−11 867.3	−11 938.7
Polymorph B		
Constant volume	−11 847.0	−11 935.9
Constant pressure	−11 847.0	−11 938.7
Structure C		
Constant volume	−11 838.4	−11 930.0
Constant pressure	−11 838.4	−11 934.8

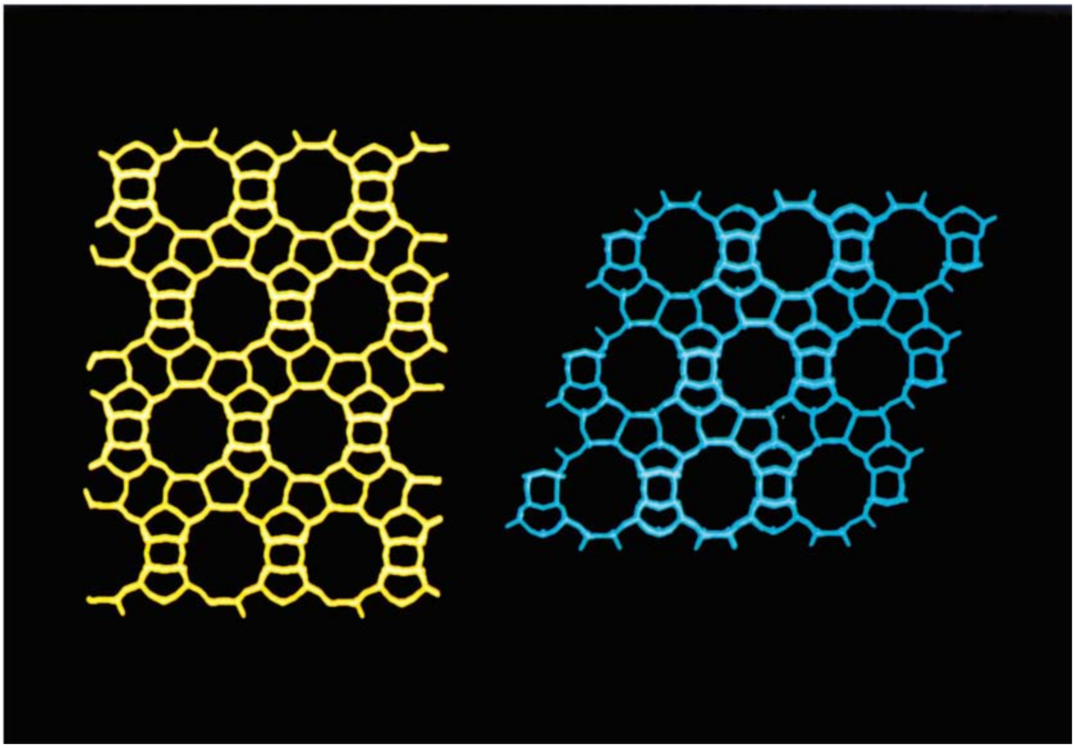

Figure 1. Structures of polymorphs A (yellow) and B (cyan).

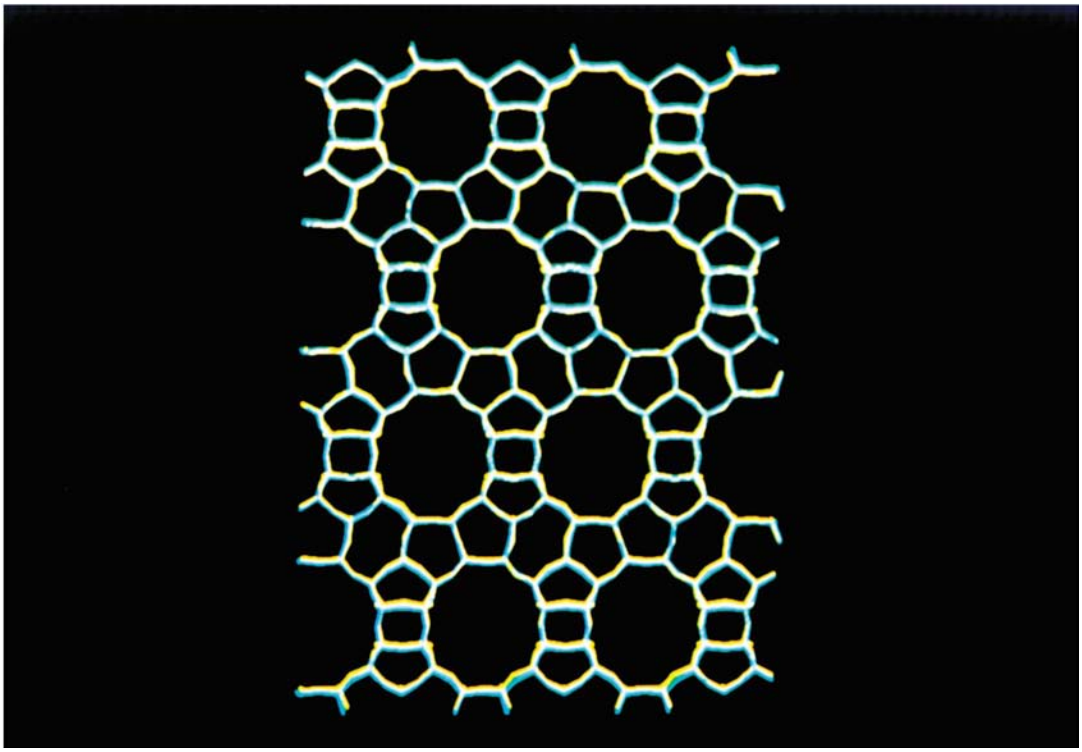

Figure 2. Energy minimised (cyan) and proposed (Newsam *et al.*) (yellow) structures of polymorph A.

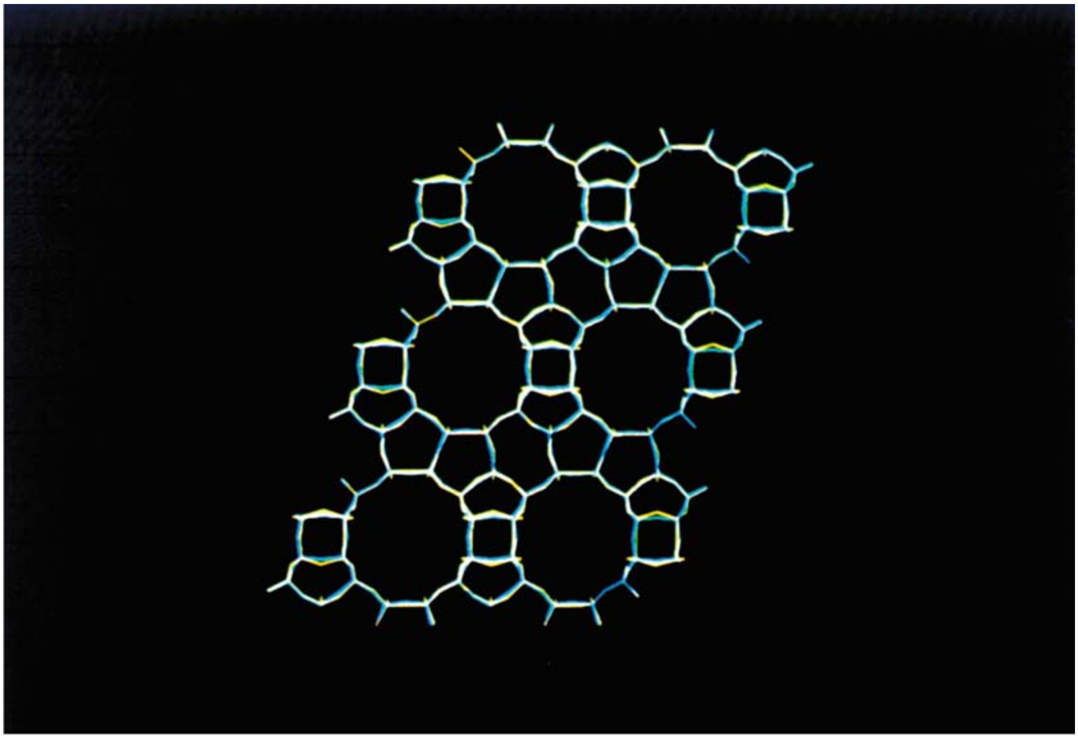

Figure 3. Energy minimised (cyan) and proposed (Newsam *et al.*) (yellow) structures of polymorph B.

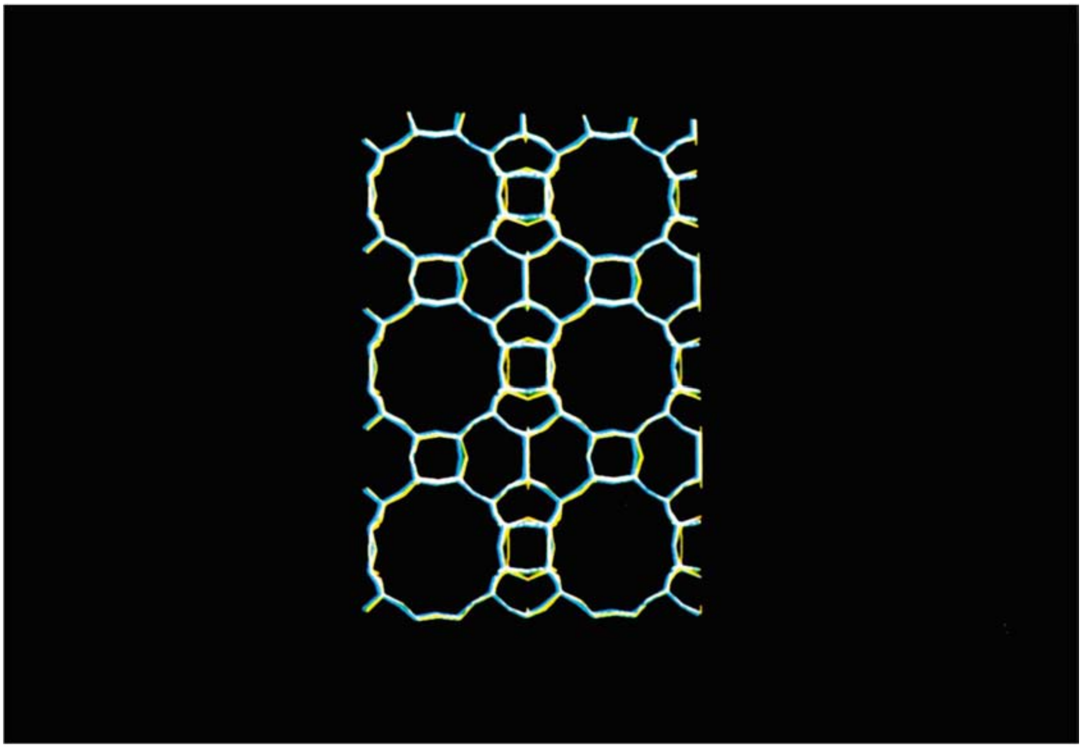

Figure 4. Energy minimised (cyan) and proposed (Newsam *et al.*) (yellow) structures of structure C.

stable. The energy minimised and proposed structures are shown in Figure 4. Again, there is a generally good agreement except for the change in the geometry of the Si–O–Si bond of the 5-ring on minimisation. The calculated lattice energy is less than the lattice energy of polymorphs A and B by approximately 5 kJ mol^{-1} (see Table 2). Structure C would therefore be expected to be marginally less stable, but given different preparative conditions it may be possible to synthesise this structure.

In summary, energy minimisation procedures confirm the stability of the polymorph structures for zeolite beta proposed by Newsam *et al.* The calculated lattice energies are fully consistent with their proposal that the structure consists of intergrowths of the two polymorphs. The results when taken together with those reported in reference 5 demonstrate the viability of the currently available modified Born model potential for SiO_2 in reproducing structural properties of complex zeolites.

We are grateful to Drs J. Newsam and M. Treacy for communicating their structural models for zeolite beta prior to publication.

Received, 31st January 1990; Com. 0/00463D

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