Postulated Mechanism for Faulting in Zeolite Beta

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Molecular modelling methods have been used to predict the locations and orientations adopted by 1,1-dibenzyl-1,1-dimethylammonium template ions in zeolite beta and hence to rationalise the extensive crystallographic faulting in this industrially-important material.

Zeolites are crystalline, cage-structured aluminosilicates which possess microporous channels of molecular dimensions. This feature has given them many important industrial applications as, for example, ion exchangers, molecular sieves and catalysts.[1–3] However, these materials may be prone to crystallographic faulting which can affect their catalytic and sorption properties.

Zeolite beta, first reported in 1967 by Wadlinger *et al.*,[4] has been shown to be a highly faulted system.[5] It is a three-dimensional large-pore zeolite with straight 12-membered ring channels running in the *a*- and *b*-directions and a more tortuous 12-membered ring channel system running parallel to the *c*-direction. The faulting arises from random translations of layers or sheets of the framework by $\pm\frac{1}{3}$ of the lattice repeat in the *a*- and *b*-directions. This does not block channels, or alter the topology of the straight channels, but it does affect the tortuosity of the channels in the *c*-direction. The end-member which shears with alternating translations is referred to as polymorph A (ABABAB... sequence), while that which arises from shears in the same direction, is referred to as polymorph B (ABCABC... sequence). These are shown in Fig. 1.

Despite the extensive faulting, zeolite beta has found use in several hydrocarbon conversion processes including cracking,[6,7] hydrocracking,[8] dewaxing,[9] and dealkylation.[10] The synthesis of pure polymorph A is an extremely attractive target because the chiral nature of its channel system suggests that this structure could be used in separation processes or catalytic reactions involving chiral compounds.[5,11]

Organic molecules referred to as 'templates' have played significant roles in directing the synthesis of many novel zeolites. Several templates have been used in the synthesis of beta.[4,12,13] These molecules are included in the reaction mixtures of silica and alumina gels and are occluded into the zeolite structure as the framework crystallises. The aim of this

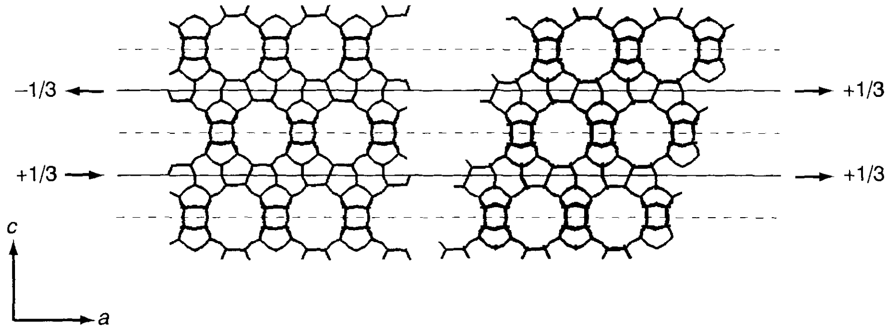

Fig. 1 Representation of the two ordered end-members polymorphs A and B, *via* regular ordered translations of framework sheets

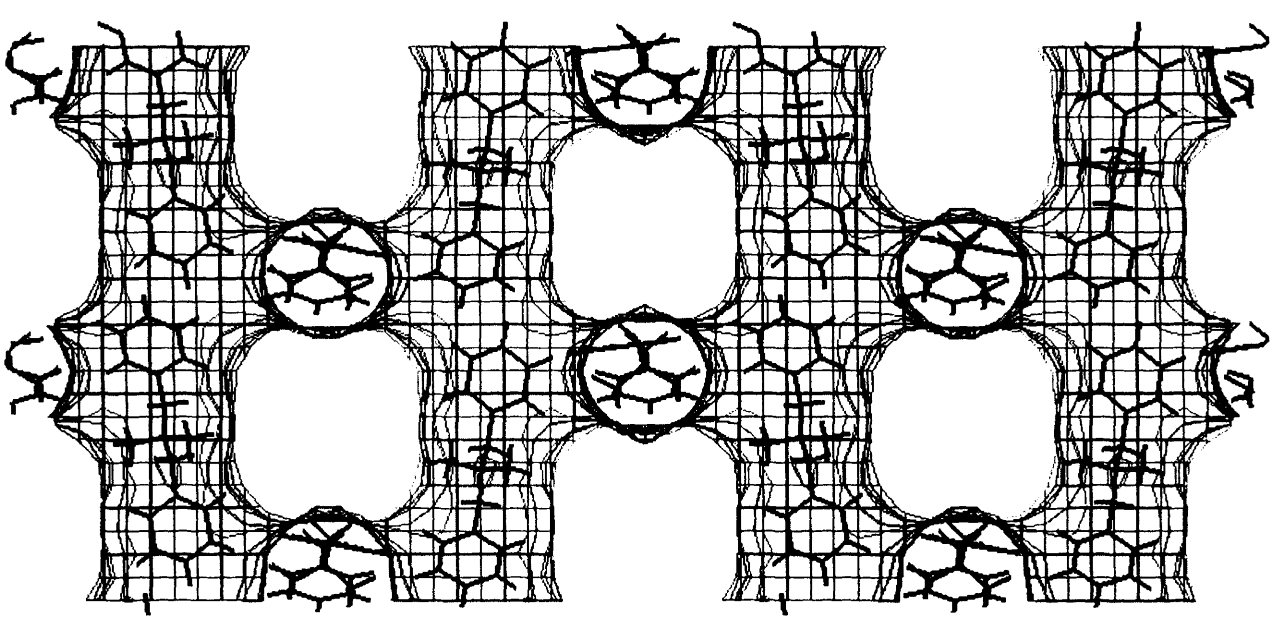

Fig. 2 Results of the combined Monte Carlo/Simulated Annealing docking studies on the chiral polymorph A (ABABAB sequence). A pore map of the channel system is superimposed to show the extensive void filling.

investigation has been to predict the location of one of these templates, the 1,1-dibenzyl-1,1-dimethylammonium ion[13] (DBDM), in the beta channel system. This particular template was chosen because initial docking studies, using a molecular graphics approach, suggested a high void-filling of the zeolite pore system by the DBDM ions, a feature indicative of a strong templating effect. Although all structural studies on zeolite beta have used material derived from the smaller tetraethylammonium ion, it is reasonable to expect that the level of faulting from the DBDM route will be very similar (*i.e.* ≈ 50%). This assumption is based on the *d*-spacing for the first peak in the XRD pattern which is the same for both preparations;[4,13] a characteristic known to be sensitive to the exact ratio of the two polymorphs in the product.[5]

The complex nature of the beta structure means that direct experimental determination of the location and conformation adopted by the templates occluded within the framework is not easily attained. However, molecular modelling techniques can offer an effective method of study[14–16] and a two-stage Monte Carlo/Simulated Annealing [MC-SA] computational approach has been used.[17] Essentially, the Monte Carlo part of the calculation is an automated technique used to locate potential docking sites by placing a guest molecule into the zeolite framework at a random location and orientation.[18] The interaction energy between the template and framework is calculated using a molecular mechanics technique, employing the CVFF force field, within the program Discover.[19] If this is below a specified threshold value, then the configuration is accepted. However, if the calculated energy is higher then the procedure is repeated until a successful configuration is obtained. This is continued until as many templates as possible have been successfully packed within the framework. Simulated Annealing is then used in order to optimise the location and conformation of each template in the framework, by simulating them at high temperature (1000 K) and then slowly cooling to 0 K in order to obtain low energy configurations. Periodic boundary conditions are included throughout both stages in order to simulate an infinite array. The coordinates of the zeolite framework are held fixed throughout the run.

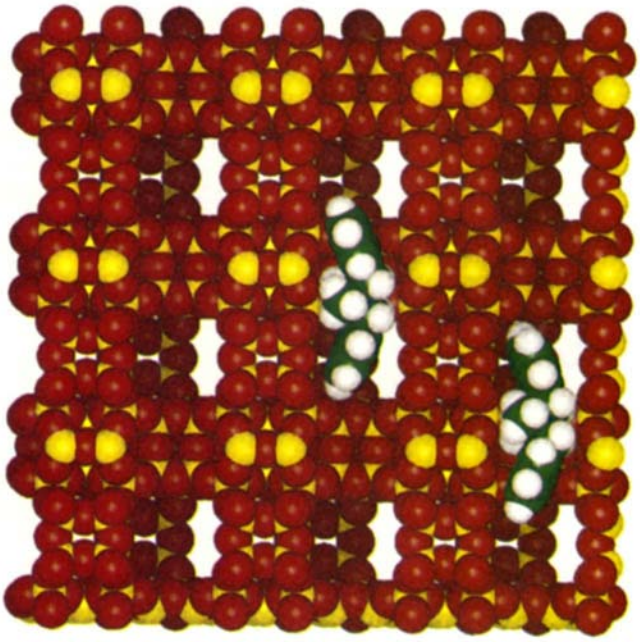

Fig. 3 Representation of the two possible template orientations that can be adopted about the 'surface holes' of the beta lattice

The results from the MC-SA calculations on the DBDM–beta system show that four templates are accommodated into the unit cell, extensively filling the void-space of the pore channel system. The minimum energy configuration obtained from a series of MC-SA runs is shown in Fig. 2 for an alternating stacking sequence of sheets (polymorph A). We note that the benzene rings of the DBDM templates are located at channel intersection positions, with the molecule spanning the fault plane, oriented to the left or right, depending on the shear direction. Energetically, each of these four sites is found to be equivalent, with the filled pore system appearing identically packed irrespective of whether the system is viewed along the *a*- or *b*-direction.

The role of the DBDM template in producing beta samples with extensive crystallographic faulting can be understood when considered in terms of Vaughan's extended structure approach.[20] This proposes that primary cations in the reaction mixture (*e.g.* Na^+), direct the formation of framework sheets from extended building units, whilst secondary cations (template molecules, *e.g.* DBDM) direct the combination of these sheets to form the completed structure. The growing surface of beta consists of a framework sheet that possesses surface holes at the 'channel intersection' sites. The modelling results suggest that a DBDM molecule approaching the growing surface will locate one of its rings at a surface hole site, with the rest of the template having an equal probability of rotating either side about the hole (Fig. 3). Once located, the length of the DBDM template corresponds to approximately $\frac{2}{3}$ of the lattice repeat distance. Thus, when the next layer is linked above with its surface hole site located around the other benzene ring in the DBDM molecule, a shear of $\pm\frac{1}{3}$ for the layer is obtained,

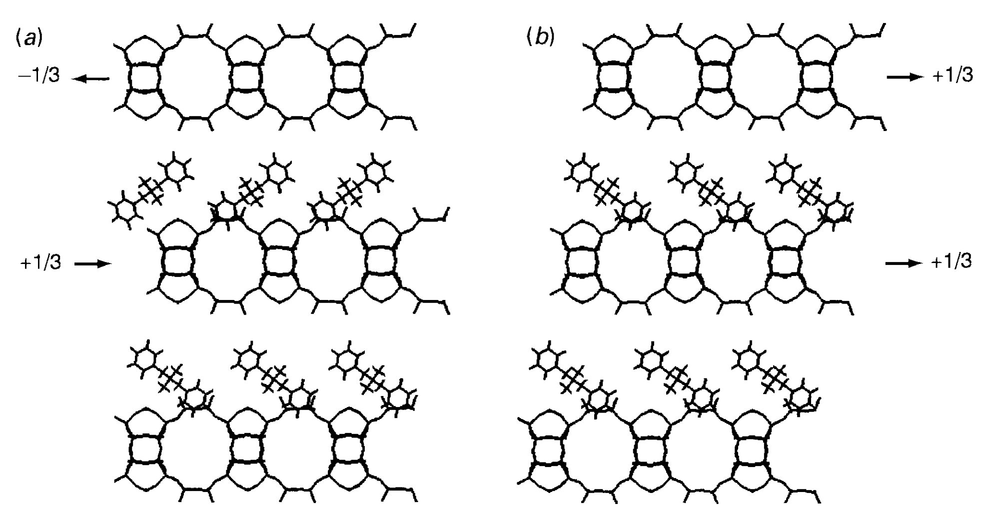

Fig. 4 Exploded diagram demonstrating the growth of (*a*) layers with ($+\frac{1}{3}$, $-\frac{1}{3}$ shears in the *a*-direction (polymorph a) and (*b*) layers with $+\frac{1}{3}$, $+\frac{1}{3}$ in the *a* direction (polymorph b)

depending on which of the two energetically equivalent orientations is adopted by the DBDM molecule (Fig. 4). Once one molecule in each layer adopts one orientation then all the others are likely to follow suit, since this maximises favourable zeolite–template interactions.

Previous experimental and theoretical studies have demonstrated the importance of template shape in directing zeolite synthesis.[14,17,21,22] Knowledge of the locations adopted by DBDM molecules and their role in the faulting process may help lead to the design of a template molecule which will direct formation of pure polymorph A. We note that the high symmetry of the DBDM template (C_{2v}) appears to be responsible for the observed crystallographic faulting. This would explain why some success has been reported in using chiral molecules to produce samples with an enriched content of polymorph A.[11] On the basis of the present work, another potentially interesting approach would be *via* the use of a rigid molecule that lies across two fault planes, effectively 'locking' sheets at one site. The DBDM template appears to be an ideal building block for the design of either type of molecule.

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