Surface Structure and Crystal Growth of Zeolite Beta C[**]

Ben Slater,* C. Richard A. Catlow, Zheng Liu,
Tetsu Ohsuna, Osamu Terasaki, and
Miguel A. Camblor

Zeolite Beta is a high silica zeolite that has attracted considerable experimental and theoretical investigation. In the seminal work of Newsam et al.[1] and Higgins et al.,[2] the crystal structure of zeolite Beta was deduced and three distinct polytypes were identified. Polymorph A is tetragonal and exists as an enantiomorphic pair of crystal structures. Structure B is monoclinic and achiral, whilst polytype C was predicted to be an achiral tetragonal phase. Until very recently, polymorph C had not been observed experimentally, but recent work[3] described a proven synthetic route to this phase; furthermore, using novel methods based upon electron microscopy, the crystal structure was deduced. Herein, we focus attention from the bulk to the surface properties of this topical microporous material. By a combination of computer modeling with high-resolution electron microscopy (HREM), we are able to develop detailed models for the surface termination of this material and to gain new insight into the mechanism of its growth.

The purpose of the work described here is twofold: first we report a simulation using interatomic potential techniques of the zeolite Beta C surface structure, which is able to distinguish between many numerous possible terminations and support the HREM observations reported recently by Liu et al.[3] Second, by inspection of the surface structure and analysis of the relative energies of formation using first principles methods, we present evidence that relates the growth mechanism to the external surface structure.

An interesting question that arises from addressing the surface structure of zeolites is that of how to discriminate between the relative stability of various faces and the huge number of surface terminations that could arise during crystal growth of the microporous structure. The problem is made more difficult by the fact that there are relatively few examples of purely siliceous zeolites, the majority being aluminosilicates with varied aluminum, extra-framework cation, and water content. Aside from the quite general interest in zeolite Beta C, it is also apposite in that it provides a convenient means of evaluating the surface structure of a purely siliceous material, where questions about aluminum zoning and possible cation segregation effects do not arise and for which particularly well-resolved HREM data is available.

We have used atomistic methods based upon the Born model of solids and the forcefield of Sanders et al.[4] This forcefield is particularly successful at reproducing the bulk lattice and vibrational properties of a wide range of siliceous materials, ranging in density, for example, from quartz to faujasite. The interatomic potentials are also of sufficient quality to derive surface structures and energetics as is evident from our recent work on the (111) surface of faujasite.[5]

Using this parameter set, we relaxed the Beta C unit cell and its contents to zero force until the cell was in mechanical equilibrium, using the GULP program.[6] Using a Donnay–Harker[7] approach, the (100) face is found to have the largest interlayer distance (d_{hkl}) and would therefore be expected to dominate the morphology. Large plane separations are associated with weak interlayer binding and thus slow growing, morphologically important faces. Using a two-region strategy to simulate the surfaces (using the MARVIN code as described elsewhere[8]), we are able to determine the surface energy, which can be readily used to discriminate between the stability of particular terminations and crystal faces. Using this criterion, we distinguished three possible (100) terminations as the most energetically favorable surfaces. Relaxation of four layers of the (100) face on a further four layers that are held fixed at the bulk equilibrium geometry gave essentially identical surface energies for the three different cuts (where the surface energies differed from each other by only 0.02 J m^{-2}). This result indicates that the surfaces are of equal thermodynamic stability with respect to the crystal bulk. The relaxed surface structures are shown in Figure 1, 2, and 3.

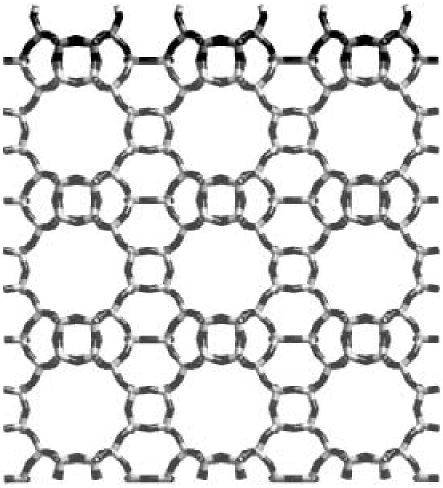

Figure 1. The type I surface of zeolite Beta C. Color code: Si: gray, O: black; H: white. The surface is shown in *cross section*. The greyed section is the zeolite surface continuum, the darker area is the growth surface.

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[*] Dr. B. Slater, Prof. C. R. A. Catlow
Davy Faraday Research Laboratory
The Royal Institution of Great Britain
21 Albemarle Street, London, W1S 4BS (UK)
Fax: (+44) 207-629-3569
E-mail: ben@ri.ac.uk

Dr. Z. Liu
CREST, Japan Science and Technology Corporation
Tohoku University
Sendai 980-8578 (Japan)

Dr. T. Ohsuna
Institute for Materials Research
Tohoku University
Sendai 980-8577 (Japan)

Prof. O. Terasaki
Department of Physics and CIR
Tohoku University
Sendai 980-8578 (Japan)

Dr. M. A. Camblor
Industrias Quimicas del Ebro
Poligono de Malpica calle D. no. 97, 50057 Zaragoza (Spain)

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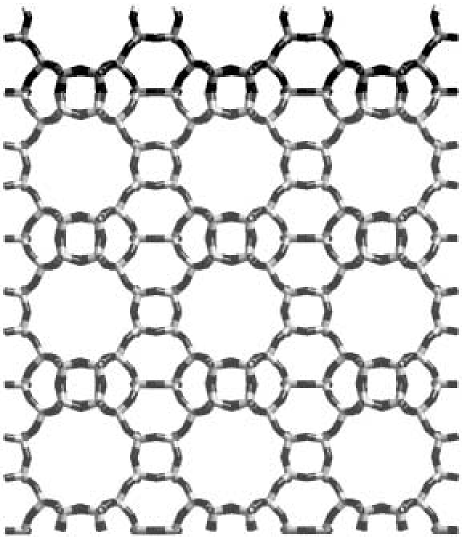

Figure 2. The type II surface of zeolite Beta C. Color code as in Figure 1.

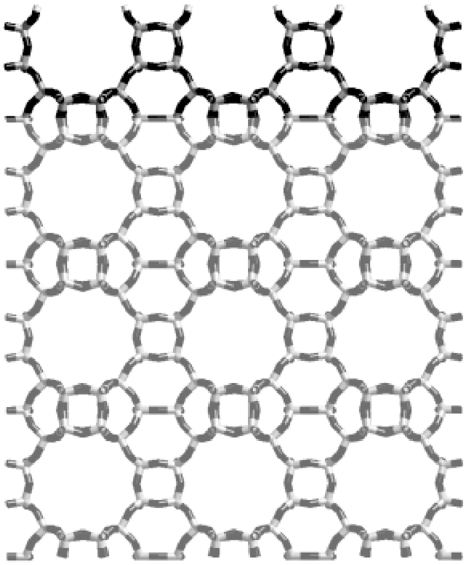

Figure 3. The type III surface of zeolite Beta C exhibiting a D4R structure. Color code as in Figure 1.

To compare these structures with our recent experimental data, we have constructed a montage (Figure 4). Figure 4a is the HREM of a single crystal of zeolite Beta C, and Figure 4b and c are magnified sections of a), exposing two distinct terminations. The simulated HREM images in Figure 4d–f have been calculated from the three relaxed terminations shown in Figure 4g, h, and i (which depict the silica framework of Figure 1, 2, and 3). What is immediately obvious by comparison with experimental HREM images shown in Figure 4b and c is that the predicted terminations agree perfectly with the measurements. Figure 1 and 4b are the type I surface proposed by us[3] which is relatively topologically smooth. Figure 3 and 4c clearly exhibit a double 4-ring (D4R) and correspond with the type III surface.

The type II surface (Figure 2) is not observed in the experimental HREM image. However on energetic grounds, this surface would be expected to be stable.

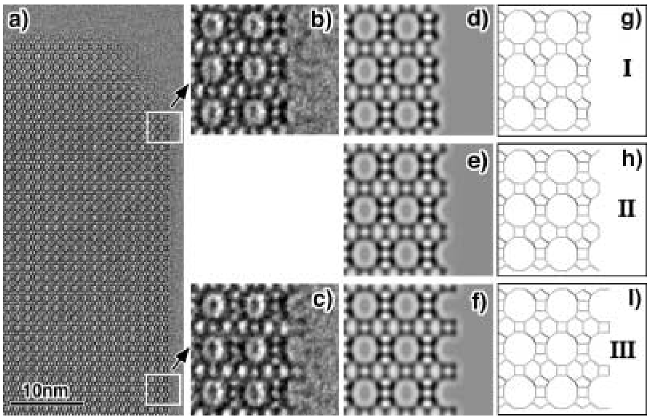

Figure 4. a), b), c) Composite of HREM images.[3] d), e), f) Simulated HREM images from relaxed surface structures g), h), and i), respectively, corresponding to a 90° rotation of the type I, II, and III surfaces shown in Figure 1, 2, and 3, respectively.

Upon inspection, the type II surface is related to the type I and type III terminations by the addition or removal of a single silicon 4-ring (S4R), respectively (by a condensation reaction). Intuitively, one recognizes that the terminations form part of a sequence that corresponds to a crystal growth process. To resolve this apparent discrepancy between theory and experiment, we assessed the feasibility of crystal growth by reacting elementary siliceous growth units with the type I surface, to form the type II and type III terminations.

We performed density functional theory, total energy pseudopotential calculations using the CASTEP[9] code on a single layer of the (100) face, starting from the type I termination. Details of the parameters used and simulation conditions are available as Supporting Information. We initially considered two possible mechanistic routes leading to the formation of the two observed terminations. In the first strategy shown in Figure 5, we consider direct condensation of a S4R on the type I surface to give the type II surface (reaction A), followed by further condensation of a S4R, to give the type III surface (reaction B). Figure 6 depicts the direct condensation of a D4R unit on the type I surface, resulting in the formation of the type III surface (reaction C). In each instance, the total energies of formation for the reactant and products in their ground state were used to calculate the net change in enthalpy.

Reaction A is calculated to be an endothermic process. As an additional check on the reliability of this key result, we performed the same calculation but with a broken 4-ring (B4R), which has been shown previously[10] to possess a higher condensation energy than the S4R. The direct condensation of monomers and dimers was also considered. In each case, reaction A was found to be endothermic which suggests that the reaction does not proceed or it occurs by a different reaction pathway. Irrespective of this evidence, if termination II is formed by whatever pathway, reaction B (calculated with respect to a S4R) is thermodynamically favorable and therefore termination II is thermodynamically and probably kinetically unstable with respect to termination III. By contrast, reaction C is predicted to be only slightly energeti-

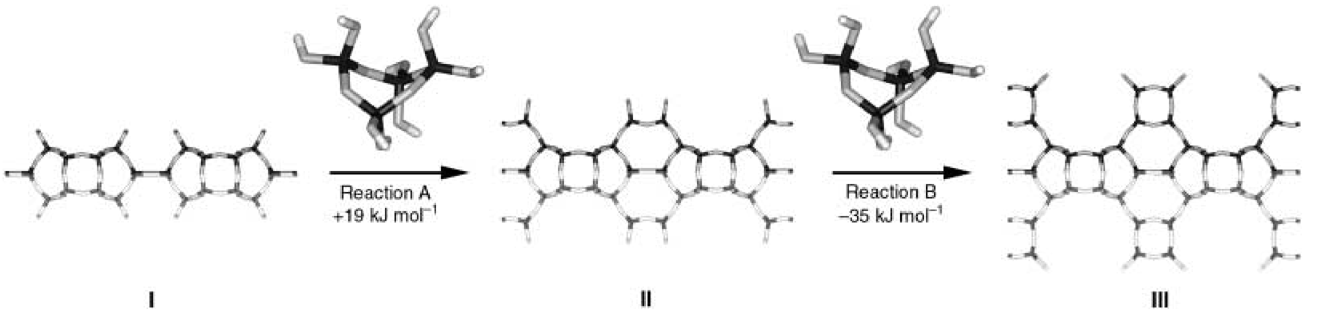

Figure 5. The S4R-mediated reaction pathway. The reaction proceeds by the addition of an S4R to the type I surface, giving the type II surface and further S4R condensation to give the type III surface. Color code as in Figure 1.

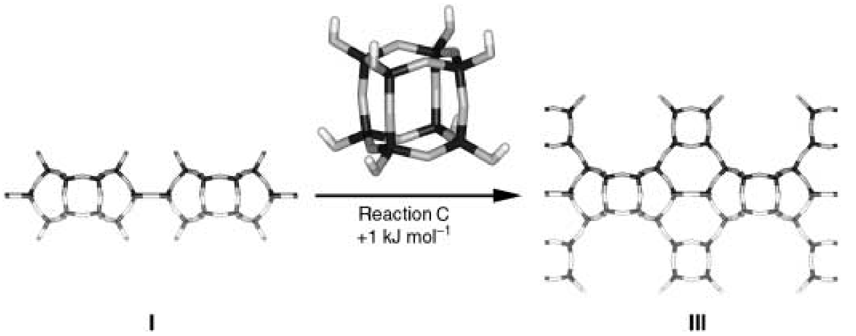

Figure 6. The D4R-mediated reaction pathway. The reaction proceeds by a one-step condensation of a D4R species onto the type I surface to give the type III surface. Color code as in Figure 1.

cally unfavorable but even at relatively moderate temperatures, this reaction would be expected to proceed.

Given these findings, the evidence suggests that termination II, the surface structure expected to be stable on the grounds of surface energy, but not observed by HREM,[3] is either not formed, or quickly reacts to give the D4R-terminated surface. By contrast, condensation of a D4R unit on the type I surface is predicted to occur under reaction conditions. The addition of this unit gives a route from the type I to type III surface, which does not require formation of the type II surface and therefore may also explain why the type II surface is not observed. Given recent synthetic findings, the process of condensation which gives rise to the D4R unit is clearly accelerated by the presence of fluoride ions. We speculate that the fluoride ion lowers the activation barrier that separates reagents from the D4R unit and other products but will address this point directly in future work.

In summary, we have demonstrated that relatively simple interatomic potential calculations are able to reproduce the surface structures observed by using HREM imaging. Additionally, direct assessment of the crystal growth process reveals that one possible termination is not formed or is likely to be a short-lived intermediate that accounts directly for its absence in HREM imaging experiments. More fundamentally, the results provide evidence that the nanoscopic surface structures arise not simply from optimal packing of silicate tetrahedra but from the complex reactions of siliceous oligomers with the zeolite surface.

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Pd-Catalyzed Decarbonylative Olefination of Aryl Esters: Towards a Waste-Free Heck Reaction**

Lukas J. Gooßen* and J. Paetzold

Dedicated to Dr. Manfred Jautelat
on the occasion of his retirement

Over the last years, the Heck reaction has found widespread use in preparative laboratories and in industrial applications as a mild and efficient method for the regioselective attachment of side chains to aromatic rings.[1] Besides the standard aryl halides, various aryl sources such as aryl triflates,[2]

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[*] Dr. L. J. Gooßen, J. Paetzold
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-2985
E-mail: goossen@mpi-muelheim.mpg.de

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