Calculation of the Morphology of Silica Sodalite

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The morphology of all-silica sodalite is calculated using surface simulation techniques, and is found to compare favourably with the experimentally observed morphology.

The importance of morphology and particle size is well established for the application of microporous solids to catalysis, adsorption, separations and new applications. In the case of particle size, methodologies exist for the preparation of larger crystals[1,2] and more recently colloidal materials.[3] The influence of size on physical properties is well known and has been clearly demonstrated for a number of well defined experimental systems. However, morphological effects are less well defined and have received little detailed study apart from empirical observations which can be readily found in the zeolite literature.[4] With the growing emphasis on microporous solids as materials for advanced applications, it is important to understand better the control of morphology of particulate zeolites and to prepare materials which express a particular face or morphology.

Recent developments in the modelling of crystalline ionic systems allow the prediction of crystal morphologies from a knowledge of the crystal structure parameters and the relative energies of defined Miller plane surfaces. The technique has been applied to a number of different crystal systems, including $CaCO_3$,[5] $BaSO_4$,[6] and Cr_2O_3,[7] with good agreement between the calculated and observed crystal morphologies.

The purpose of this communication is to describe the key parameters involved with the prediction of zeolite crystal morphologies. Using all-silica sodalite as an example, we have applied the techniques of lattice energy minimization, (used extensively to model accurately the crystal structure of zeolites),[8] and surface relaxation to predict the likely morphology. This is the first attempt to predict the crystal morphology of a zeolite. All-silica sodalite was chosen because of the large amount of experimental data relating to is synthesis conditions. It is synthesised in the presence of ethylene glycol, with one ethylene glycol molecule found to be encapsulated in each sodalite cage.[9] The all-silica form crystallises in the cubic space group *Im*3*m*, with a lattice parameter of 8.83 Å. This structure was used as a starting point for the calculations. Comparable calculations were also carried out starting from a more general structural model,[10] which gave the same structure.

In common with studies on ionic solids, the initial stage of the calculation is to minimize the bulk crystal structure under conditions of constant pressure, allowing the coordinates of the ions and shells to relax completely, with the lattice parameters also allowed to vary to remove any remaining strain. The silicons are assigned a formal charge of +4, with the oxygen ions a total formal charge of −2, partitioned between the core and massless shell. The lattice energy minimization procedure was carried out using a newly developed program GULP,[11] using standard two and three body potentials, listed in Table 1.[12] The ethylene glycol molecule was not included in this study.

Having generated a completely relaxed model of the all-silica sodalite framework, this structure is then used as a starting model for the calculation of the relative surface energies. This procedure, carried out using the newly developed code MARVIN,[13] which utilises a two region approach, similar to MIDAS,[14] where the ions and shells defining the surface are allowed to relax explicitly, in contrast to the bulk ions which are kept fixed to represent the bulk crystal structure.

Although, in principle, the surface may be cleaved through any plane of ions coincident with the required Miller plane, in practice the total system must be charge neutral without a perpendicular dipole. To achieve this the surface planes are cleaved through layers of oxygens, which must then be terminated in a chemically meaningful and consistent manner. In this study the oxygens are terminated with hydrogens, creating a complete hydroxy surface. The hydroxy oxygens and hydrogens are then assigned partial charges, consistent with a formal charge of −1 for each of the hydroxy groups. These charges and the required O–H bonding potential are listed in Tables 1 and 2. These have been widely used in previous studies of hydroxy-containing systems.

The size of the surface region is increased, until the ions in the interface area do not alter their position during the minimization. The size of the bulk region is automatically set to allow convergence of the summation of the long range coulombic interactions. Only small perturbation of the basal ions due to surface relaxation was observed beyond 5 unit cells. The three low index Miller planes were selected as these are known to be expressed in the observed morphology, and are therefore of primary importance for the purposes of verifying the theoretical approach. These Miller planes are degenerate as the relaxed bulk structure retains the cubic space group, thereby reducing the number of surfaces which need to be treated.

The surface energies are calculated as in eqn. (1).

$$E_{\mathrm{surf}} = \frac{(E_{\mathrm{R1}} - n^{*}E_{\mathrm{bulk}} + E_{\mathrm{corr}})}{\text{Surface Area}} \tag{1}$$

where, E_{R1} is the total energy of the surface region, n is the number of repeats defining the size of region one and E_{bulk} is the total energy of the relaxed bulk structure. The surface energy is corrected to take account of the reaction of the surface with water to form terminal surface hydroxyls.

$$E_{\mathrm{corr}} = \{n_{\mathrm{OH}}{}^{*} - 2.69\ \mathrm{eV}\} \tag{2}$$

The calculated energies of the relaxed, hydrogen terminated surfaces of all-silica sodalite are listed in Table 3.

Table 1 Charges

	Si_{core}	O_{core}	O_{shel}	O_{oh}	H_{oh}
q_i	4.00	+0.86902	−2.86902	−1.426	0.426

Table 2 Buckingham potentials

	A/eV	ρ/Å	C/eV Å^6
Si_{core}–O_{shel}	1283.907	0.32052	10.66158
Si_{core}–O_{oh}	983.5566	0.32052	10.66158
O_{shel}–O_{shel}	22764.0	0.149	27.88
O_{shel}–O_{oh}	22764.0	0.149	27.88
O_{shel}–H_{oh}	311.97	0.25	0.00

Long range cutoff = 20 Å

Morse potential:

	D/eV	α/Å^{-1}	r_0/Å
O_{oh}–H_{oh}	7.0525	2.1986	0.9485

Three-body potential:

	k/eV rad^{-1}	θ_0/deg
O–Si–O	2.09724	109.47

The morphology of the crystal can then be deduced by substituting the relative surface energies into Wulff's theorem, $h_i = \lambda k_i$, where h is the surface normal energy and k is a surface normal vector from the face to a point within the crystal. The resultant crystal morphology can then be viewed using computer graphics.[15]

It is found that the low index miller planes are ordered in terms of increasing stability 100 < 111 < 110. The fact that the 110 surface is preferentially stabilised with respect to the other modelled surfaces, is found to dominate the predicted crystal morphology, shown in Fig. 1. However, the differences in the calculated surface energies are not sufficient to rule out the likely effect of environmental factors.

Table 3 Relaxed surface energies

Miller Plane	Surface Energy/ Jm^{-2}
100	6.81
110	5.27
111	5.75

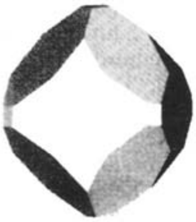

Fig. 1 The calculated morphology of silica sodalite

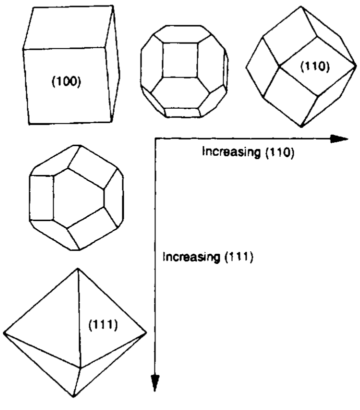

Fig. 2 The relationship between the different possible morphologies based on expression of the (100), (110) and (111) faces

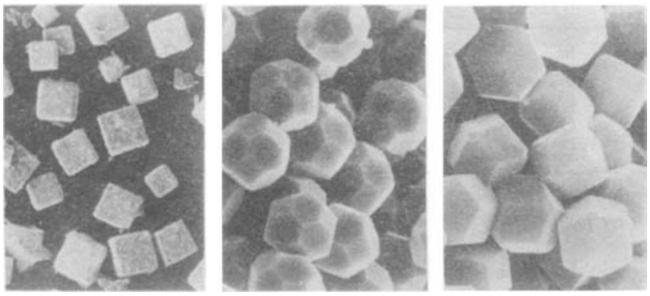

Fig. 3 Corresponding experimental morphologies

Bibby *et al.* reported that the morphology of the silica sodalite was based on a cubic morphology with octahedral and dodecahedral modifications. Both of these can be regarded as modifications of the cubic morphology arising from different relative expressions of the (110) and (111) faces. Typical SEM images of all-silica sodalite samples, and their relationship in terms of relative expression related faces are shown in Fig. 2 and 3. These clearly illustrate the importance of the (100) and (110) faces in determining the morphology. Not only is the calculated morphology observed,but slightly different expressions of these other faces lead to different morphologies. These morphologies occur as a consequence of the influence of crystallising conditions (*e.g.* gel composition) and indicate that the morphology is controlled by a number of factors, of which the relative surface energies is one.

These results indicate that it is possible to use advanced computational techniques to predict the morphologies of covalent inorganic solids, such as zeolites. There is good agreement between the calculated and observed morphology, given that in the experimental situation a number of factors (*e.g.* mineralisers, solvent and structure directing agents) have an influence on the overall morphology. We are currently investigating some of these factors and are extending this approach to other zeolitic systems.

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