Computer Simulation of the Monoclinic Distortion in Silicalite

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A lattice-energy minimisation calculation, performed on the ideal orthorhombic structure of silicalite, results in the simulation of the low-temperature monoclinic phase.

The success of modern computer simulation methods in modelling complex inorganic solids has recently been illustrated by studies on a variety of zeolites.[1,2] Close agreement with experimental lattice parameters, bond lengths, and interatomic angles is obtained, together with information on the relative stabilities of zeolites of different structural type and composition. Here we demonstrate that, using the technique of lattice-energy minimisation, subtle structural distortions are able to be simulated to a high degree of accuracy.

Table 1. Comparison of experimental and simulated silicalite.

	Experimental (Olsen *et al.*)[11]	Experimental (Wu *et al.*)[7]	Simulated
a/Å	20.07	20.17	19.986
b/Å	19.92	19.93	19.747
c/Å	13.42	13.42	13.324
α/°	90	90.64	90.803
β/°	90	90	90
γ/°	90	90	90
Cell volume/Å^3	5365	5394	5298
Si–O Bond lengths/Å			
Range	1.52—1.67		1.595—1.608
Average	1.59		1.601
O–Si–O Angles/Å			
Range	97.5—129.0		106.3—115.0
Si–O–Si Angles/Å			
Range	142.6—175.0		143.2—157.9
Average	155.0		148.8

Silicalite is the siliceous member of the ZSM-5 class of zeolites. These have considerable importance as catalysts, *e.g.*, in the conversion of methanol to gasoline. Their structure is characterised by two sets of interconnecting channels defined by ten-membered rings, with straight channels extending in the <010> direction and sinusoidal channels in the <100> direction. It is well established by *X*-ray diffraction and NMR measurements[3—6] that high-silica ZSM-5 undergoes a reversible phase transition between 300 and 350 K, with the low-temperature phase being monoclinic and the high-temperature phase orthorhombic (ideal space group *Pnma*). The change in symmetry is slight and has no effect on the topology of the silicate framework. Studies on samples containing residual aluminium or organic sorbates[5,7,8] suggest that the transition temperature is lowered by such impurities.

The present simulation was carried out using the lattice-energy minimisation code THBREL,[9] running on a Cray XMP-48 computer at the Rutherford–Appleton Laboratory. The interatomic potentials used were derived from empirical fitting to the bulk properties of α-quartz, and are described elsewhere.[1,10] The model included both a harmonic bond-bending potential applied to O–Si–O groupings and a 'core and shell' potential to account for the polarisability of oxygen. The energy minimisation was carried out by a Newton–Raphson method. As a starting configuration, the orthorhombic (*Pnma*) structure determined by Olsen *et al.*[11] was used. The composition of the infinitely repeating unit cell was thus $Si_{96}O_{192}$. The first stage of the calculation took the form of a constant-volume minimisation in which the atomic positions were relaxed to their minimum-energy configuration within the experimental cell dimensions. The lattice energy at this point was -12407 kJ mol^{-1} per SiO_2 unit. In the second stage the lattice parameters were additionally allowed to relax. A small gain in energy was achieved, with the final lattice energy -12408 kJ mol^{-1} per SiO_2. The accompanying relaxation of the cell dimensions however was significant in that the angle α had become 90.803° with the other two angles remaining as 90° *i.e.*, a monoclinic-type distortion had been simulated in the same plane as that observed experimentally in the low-temperature phase. The good agreement between the simulated and experimental structures is clear from Table 1.

Three points regarding the simulation should be borne in mind. First, the simulation has in effect been undertaken at 0 K, and therefore it is expected that the minimum-energy structure should resemble the low-temperature phase. This factor also accounts for the slightly smaller calculated cell dimensions. Secondly, the simulation shows that the formation of the monoclinic phase is not caused by the presence of any impurity. Thirdly, the monoclinic-type unit cell is only predicted when the oxygen ions are allowed to polarise. Using a rigid-ion model (*i.e.*, unpolarisable ions) throughout the calculation, the unit cell remains orthorhombic.

In summary we have illustrated that, using a sufficiently detailed and accurate potential model and necessarily exploiting some of the most modern supercomputer technology, structural effects which are themselves close to the limits of experimental detection may be predicted accurately.

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