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A free energy minimisation study of the monoclinic–orthorhombic transition in MFI zeolite

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Free energy minimisation calculations of the crystal structure of the zeolite MFI are shown to reproduce the observed phase transition from monoclinic to orthorhombic symmetry.

Zeolite MFI has attracted a lot of attention, mainly since its multitude of applications in catalysis.[1] Its unit cell has 96 T sites (generally Si or Al), 192 O sites, and a number of compensating cations depending on the Si/Al ratio, which ranges from 12 to infinity. For finite Si/Al ratios, the zeolite is called ZSM-5 while the end member (pure Si) is named silicalite. The structure is orthorhombic at high temperatures, with space group *Pnma*,[2] but a phase transition to the monoclinic space group $P2_1/n.1.1$[3]† is observed on cooling below a certain transition temperature. A number of authors give different values for this transition temperature, typically between 300 and 350 K, depending on the Si/Al ratio,[4,5] although higher values have also been reported.[6] Kokotailo *et al.*[7] measured the variation of the cell parameters with temperature, using high resolution X-ray diffraction, for different Si/Al ratios in the range 35–12000 and obtained in all cases a continuous decrease of the monoclinic angle, approaching 90° at high temperatures, with no well-defined transition point. The other cell parameters remained almost unchanged on heating. The thermal behaviour of MFI was also studied with XRD by Park *et al.*,[6] who measured the thermal expansion coefficients of the zeolite and obtained a small volume-expansion rate below, and a cell contraction above, the monoclinic–orthorhombic transition temperature, which they located at about 420 K.

Computer simulations methods have enjoyed great success in studying many structural features in zeolites, although temperature effects and particularly phase transitions have not been as extensively studied. Interatomic potential based methods have been widely applied in studies of complex aluminosilicate materials, because they are able to yield acceptably good accuracy at a very low computational cost.[8] This is a clear advantage for modelling a crystal with a unit cell as large as that of the MFI, with 288 atoms. In many computer simulations of this zeolite, the orthorhombic symmetry of the crystal is used in order to reduce the number of atoms to be considered, but it has been shown that consideration of the monoclinic distortion is sometimes unavoidable, and it should be taken into account, for example, in the calculation of the distribution of Al atoms and protons.[9] The work of Bell *et al.*[10] was the first to show that, using a shell model to account for the polarization of O^{2-} ions, the monoclinic distortion of this structure can be reproduced in a calculation at 0 K. Indeed, Demontis and Suffriti,[11] using a simpler force field with rigid anions, found no evidence of an orthorhombic–monoclinic transition in a molecular dynamics study over a wide range of temperatures.

In this work we use the free-energy minimisation technique, implemented in the General Utility Lattice Program (GULP)[12] to calculate the crystal structures of MFI at temperatures between 0 and 600 K. The GULP program performs such free-energy minimisations using analytical derivatives, decreasing substantially the computational cost involved; not significantly different now to that required for calculations at 0 K.[13] This allowed us to perform our calculations on a personal computer and with a reasonable cost of CPU time. Note that the free-energy calculations we are using here are carried out in a quasi-harmonic approximation allowing the cell parameters to vary with temperature.[14] The study is performed using the zero static internal stress approximation (ZSISA),[15] in which the internal variables are optimised with respect to the internal energy, whilst only the strain variables are optimised with respect to the free energy. It has been shown that for microporous aluminosilicate materials, this approach is preferred to a full free-energy minimisation procedure.[13] Considering the large size of the real-space unit cell, only one point (the Γ point) in the Brillouin zone is used for calculating the vibrational contribution to the free energy. A set of interatomic potentials is used[16] to evaluate energies in a Born model of the solid. Two-body interactions are described by a Buckingham potential function plus a coulombic term, and for angle bending a harmonic dependence is assumed. Formal charges are used, and the shell model is adopted to account for the polarization of oxygen ions. The minimisation at each temperature point is started from the 0 K energy-minimised structure, with no symmetry constraints.

Figs. 1 and 2 show the calculated variation of the cell parameters with temperature for the structure with no Al atoms (Si/Al = ∞), compared to the experimental measurements of Kokotailo *et al.*[7] in ZSM-5 with Si/Al = 12000. Our calculations show that the monoclinic angle α decreases with temperature, gradually approaching 90°, whilst the other two angles remain almost exactly at right angles, in agreement with the results of Kokotailo *et al.*[7] The cell parameters *a*, *b* and *c* are also almost constant, with values $a \approx 20.0$ Å, $b \approx 19.8$ Å and $c \approx 13.4$ Å, although all of them increase slightly with temperature, yielding, in combination with the approach of α to 90°, in a small increase of the cell volume with temperature over the temperature range calculated. In the calculation the monoclinic angle is overestimated by around 0.2° with respect

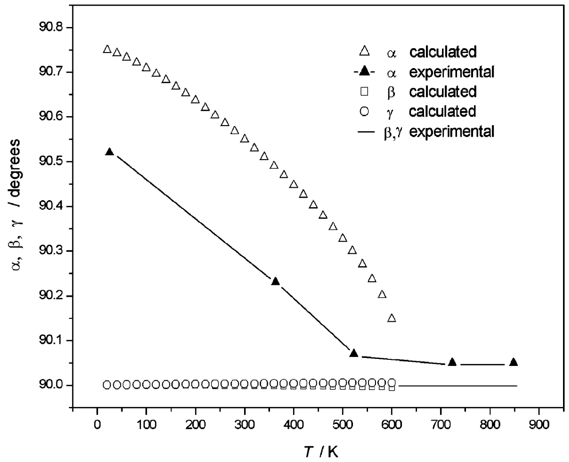

Fig. 1 Calculated variation with temperature of unit cell angles, in comparison with the experimental results in ref. 7. α is the monoclinic angle. In the experimental work β and γ are exactly 90°.

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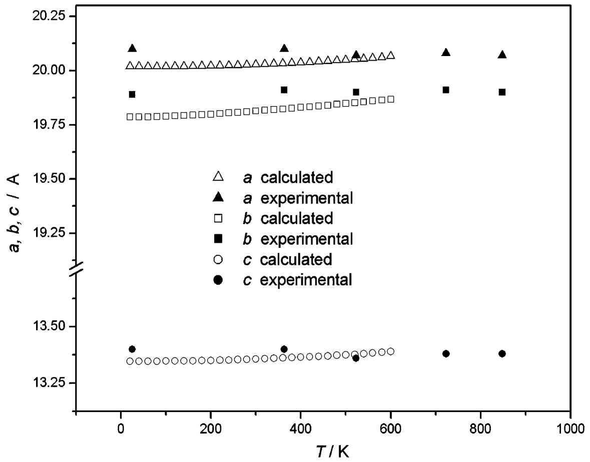

Fig. 2 Calculated behaviour of cell parameters in comparison with the experimental results in ref. 7.

to the experimental values in ref. 7, through the temperature range. However, the transition from the monoclinic to the orthorhombic cell is clear. To our knowledge, this is the first work where this transition is theoretically reproduced. Unfortunately, for temperatures above 600 K, the method fails to converge to a free-energy minimised structure. At high temperatures the quasi-harmonic approximation involved in the calculation is no longer valid, as the harmonic nature of the atoms vibration is largely lost at temperatures near to half of the melting temperature (or, as here, close to half of the decomposition temperature). Although this behaviour is a limitation for the general use of the technique, it is worth noting that the temperature interval for which calculations are reliable is, at least in principle, large enough to study displacive phase transitions occurring in many zeolites.[17]

In order to check the evolution of the crystal symmetry when increasing temperatures, we also calculated an 'orthorhombicity index', which was defined as the maximum deviation (in Å) of the atomic positions from those required by the *Pnma* space group symmetry. This index showed the same behaviour that the monoclinic angle, and in fact, a strong linear correlation (R = 0.998) was found between these two crystal properties.

The behaviour of the cell length parameters in the calculations is also in agreement with the experimental results of Park *et al.*[6] Table 1 shows the volume and linear expansion coefficients calculated from our results, in comparison with values given by those authors. The calculated values have the same sign and order of the experimental ones, except for α_{33} in the first temperature interval. However, the experimental measurements refer to the as-synthesized zeolite, with the organic template included, and therefore are not directly comparable with our results. For the calcined zeolite, they observed a small increment of all the cell length parameters below the transition point, leading to a volume expansion coefficient of 27.7 × 10^{-6} K^{-1} (with a standard deviation of 22.3 × 10^{-6} K^{-1}), which compares well with our calculated value of 18.1 × 10^{-6} K^{-1}.

Table 1 Volume (β) and linear (α_{ii}) expansion coefficients (in units 10^{-6} K^{-1}) calculated in this work, in comparison with the XRD data of ref. [6]. Values are averages for the given temperature intervals and standard deviations are in parenthesis in all cases

T/K	Data	β	α_{11}	α_{22}	α_{33}
120–298	Calc.	12.4 (3.2)	2.4 (0.9)	6.3 (1.0)	3.5 (1.1)
	Exp.[a]	5.3 (4.4)	4.6 (2.5)	4.7 (4.4)	−4.0 (3.1)
298–348	Calc.	18.1 (0.7)	4.2 (0.2)	8.1 (0.2)	5.6 (0.3)
	Exp.[b]	27.7 (22.3)	> 0	> 0	> 0

[a] Values obtained in as-synthesized silicalite, including the organic template molecule TPA-OH. [b] Values measured in the calcined zeolite. Linear coefficients not given but said to be positive.

We also repeated the calculations with a structure containing one Al atom and one proton per unit cell (Si/Al = 95), forming the catalytically active Al–OH–Si acid site. The Al atom and the proton were placed at the most probable positions according to our previous computer simulation study of acid sites in H-ZSM-5,[9] and the potential parameters used for interactions with the OH group were the same used in that work. The results, however, did not show any significant variations from those obtained for silicalite. It is obvious that lower Si/Al ratios should be considered to study the effect of the Al content on the phase transition behaviour.

Note that the potentials used here were originally derived to reproduce the room temperature properties of quartz, which may account for the transition temperature not being reproduced exactly. However, we have demonstrated that these methods do, indeed, reproduce the subtle structural changes that occur at this phase transition. It is also worth noting that an improved treatment of the vibrational term of the free energy is currently being developed in GULP (J. D. Gale, personal communication), which, although not expected to change the qualitative picture of the results, may lead to improved agreement with the experimental results.

Our present results show how the model and methodologies used are able to reproduce many features of the observed thermal behaviour of complex materials, even when, as in this case, very subtle effects are involved.

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Notes and references

† The nonstandard setting with the *a* axis unique is used for easy comparison with the orthorhombic framework, with space group *Pnma*.

1 S. T. Sie, in *Advanced Zeolite Science and Applications*, ed. J. C. Jansen, M. Stöcker, H. G. Karge and J. Weitkam, ; *Stud. Surf. Sci. Catal.*, 1994, **85**, 587.
2 H. van Koningsveld, J. C. Jansen and H. Van Bekkum, *Acta Crystallogr., Sect. B*, 1987, **43**, 127.
3 H. van Koningsveld, J. C. Jansen and H. Van Bekkum, *Zeolites*, 1990, **10**, 235.
4 D. G. Hay and H. Jaeger, *J. Chem. Soc., Chem. Commun.*, 1984, 1433.
5 C. A. Fyfe, G. J. Kennedy, G. T. Kokotailo, J. R. Leyrla and W. W. Flemming, *J. Chem. Soc., Chem. Commun.*, 1985, 740.
6 S. H. Park, R.-W. Große, H. Graetsch and H. Gies, in *Progress in Zeolite and Microporous Materials*, ed. H. Chon, S.-K. Ihm and Y. S. Uh, *Stud. Surf. Sci. Catal.*, 1997, **105**, 1989.
7 G. T. Kokotailo, L. Riekert and Tisslert, in *Zeolites as Catalysts, Sorbents and Detergent Builders*, ed. H. G. Karge and J. Weitkamp, Elsevier, Amsterdam, 1989, p. 821.
8 *Modelling of Structure and Reactivity of Zeolites*, ed. C. R. A. Catlow, Academic Press, London, 1992.
9 R. Grau-Crespo, A. G. Peralta, A. R. Ruiz-Salvador, A. Gómez and R. López-Cordero, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5716.
10 R. G. Bell, R. A. Jackson and C. R. A. Catlow, *J. Chem. Soc., Chem. Commun.*, 1990, 782.
11 P. Demontis and S. Suffriti, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1657.
12 J. D. Gale, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 629.
13 J. D. Gale, *J. Phys. Chem. B*, 1998, **102**, 5423.
14 S. C. Parker and G. D. Price, *Adv. Solid State Chem.*, 1989, **1**, 295.
15 N. L. Allen, T. H. K. Barron and J. A. O. Bruno, *J. Chem. Phys.*, 1996, **105**, 8300.
16 M. J. Sanders, M. Leslie and C. R. A. Catlow, *J. Chem. Soc. Chem. Commun.*, 1984, 1271.
17 K. D. Hammonds, V. Heine and M. T. Dove, *J. Phys. Chem. B*, 1998, **102**, 1759.