A computational study on zeolite MCM-22

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Molecular-mechanics calculations show that the framework of zeolite MCM-22 minimizes to *P*6/*m* symmetry rather than to *P*6/*mmm* or *Cmmm* symmetry.

MCM-22, first synthesized in 1990,[1] has been applied as a catalyst in several hydrocarbon conversion reactions.[2] Although many studies[3–6] have been dedicated to the elucidation of the framework structure of MCM-22, no structure type code[7] has, as yet, been assigned.

Leonowicz *et al.*,[3] who used high-resolution electron micrographs and synchrotron X-ray diffraction powder data, proposed that MCM-22 comprises two independent multidimensional pore systems. Both systems are accessible through 10-membered rings of tetrahedral (T) atoms. One of the systems is defined by two-dimensional sinusoidal channels, the other consists of large supercages whose inner free diameter is defined by 12-membered rings of T atoms. The structure can be constructed by interconnecting modified dodecasil-1H (DOH) cages extended with a TO_3 cap on top $\{4^3 5^6 6^3 [4^3]\}$ and containing a framework T-atom 'buried' inside the cage. Space group *P*6/*mmm* was found to fit best and exhibits T–O–T angles of 180° (Fig. 1). Those T–O–T angles of 180° are avoided when the symmetry is reduced to *Cmmm* (Fig. 1). However, a Rietveld refinement using *Cmmm* symmetry was unsuccessful.

In this study molecular-mechanics calculations are used to get more insight into the relative stabilities of possible structures of zeolite MCM-22. The calculations were carried out on an SG Indigo workstation using the DMM force field incorporated in DELPHI.[8]

Table 1 lists the unit-cell parameters and energies of the proposed *P*6/*mmm* and *Cmmm* structures. The reduction of the symmetry from *P*6/*mmm* to *Cmmm* not only avoids T–O–T angles of 180°, but also leads to a lower energy. Energy minimization of both structures, however, converges to one and the same structure with *P*6/*m* symmetry. The energy minimized structure has T–O–T angles of 180° (as in *P*6/*mmm*) and an energy of −1817.96 kJ mol^{-1} SiO_2 (Fig. 1 and Table 1). No structure of minimum energy with *P*6/*mmm* or *Cmmm* symmetry could be found. This might indicate that the actual symmetry of MCM-22 is lower than the proposed ones.

Structures comprising T–O–T angles of 180° should always be treated with care,[9] especially when these angles are constrained to 180° by the space-group symmetry. During minimization, however, no constraints were applied. The *P*6/*m* structure represents a minimum with T–O–T angles of 180°. The question arises whether this result can be ascribed to a force-field artefact. Although the DMM force field has already been applied successfully in earlier studies,[8] a further test on the force field was done by calculating the heats of formation of BEA, FAU, LTA, MEL, MFI and TON. Table 2 shows that the calculated heat of formation of MCM-22 with *P*6/*m* symmetry is comparable with those of the other zeolites. In Fig. 2 the

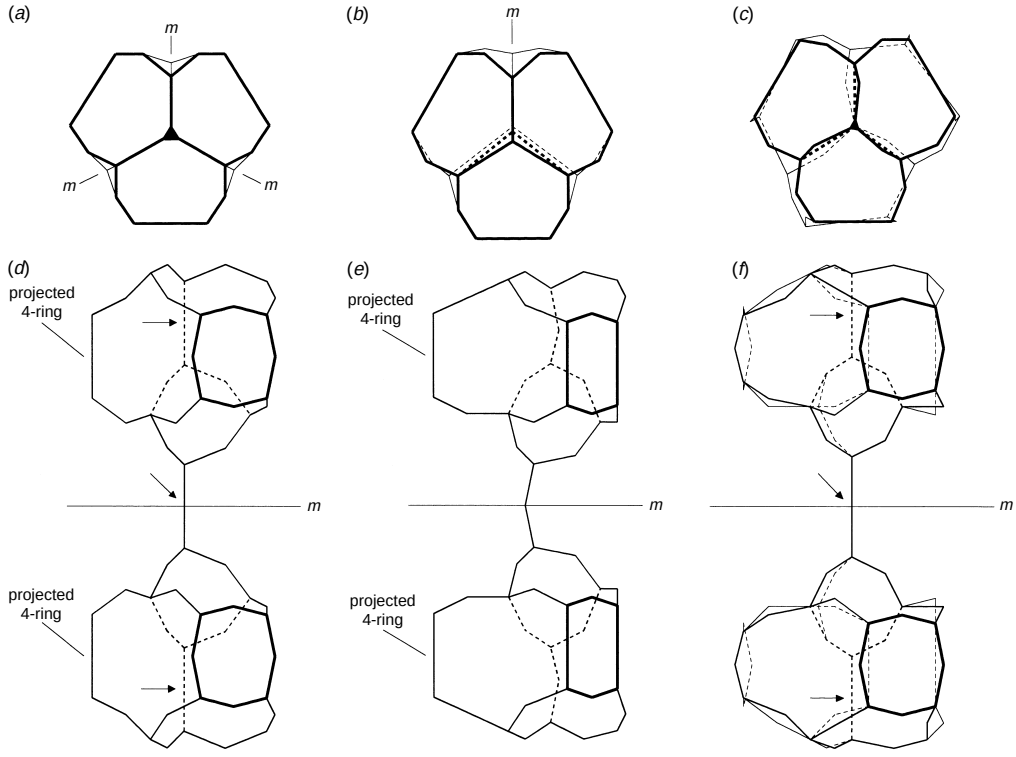

Fig. 1 Top view (*a*)–(*c*) and side view (*d*)–(*f*) of the $\{4^3 5^6 6^3 [4^3]\}$ cages in the MCM-22 structures exhibiting *P*6/*mmm*, *Cmmm* and *P*6/*m*, respectively. Some symmetry elements are indicated. The cages in structures with *P*6/*mmm* and *P*6/*m* symmetry contain T–O–T angles of 180° (indicated by arrows). In *Cmmm* the corresponding T–O–T angles deviate from 180°.

Table 1 Unit-cell parameters and energies of the proposed (single-point energy calculations) and minimized structures

	Proposed[3] *P*6/*mmm*	Proposed[3] *Cmmm*	Minimized *P*6/*m*
a/Å	14.1145	24.4470	14.3101
b/Å	14.1145	14.1145	14.3101
c/Å	24.8822	24.8822	24.9940
γ/°	120.0	90.0	120.0
ΔE/kJ mol^{-1} SiO_2	−1787.27	−1815.82	−1817.96

Table 2 Calculated heats of formation in kJ mol^{-1} SiO_2

Zeolite	$\Delta_f H$
BEA[10]	−870.47
FAU[11]	−868.82
LTA[12]	−869.52
MEL[13]	−871.78
MFI[14]	−872.02
TON[15]	−873.46
MCM-22 with *P*6/*m*	−869.96

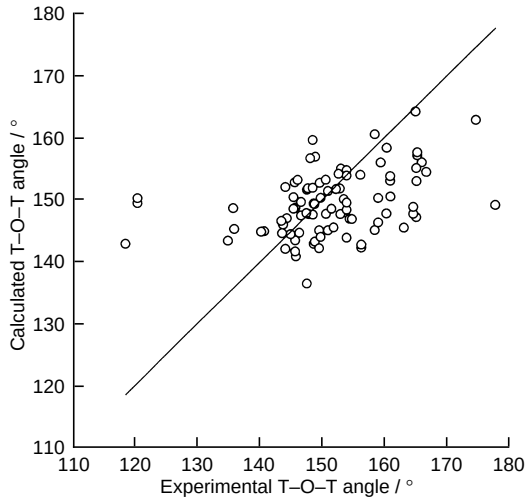

Fig. 2 Calculated *vs.* experimental[10–15] T–O–T angles: (○) calculated T–O–T angles; (——) $y = x$

calculated T–O–T angles are given as a function of the experimental ones.[10–15] From this figure it is evident that the force field does not tend to overestimate the T–O–T angles. The range of predicted values is smaller than the range of experimental values, which indicates that the 180° angle might indeed be caused by the framework topology. A force-field artefact seems very unlikely and the *P*6/*m* structure might exist.

The calculated XRD patterns in Fig. 3 are only slightly different, which means that very accurate experimental data are necessary to elucidate the precise symmetry and topology. Owing to the size and the shape of the MCM-22 crystals, such an accurate XRD pattern might be difficult to obtain.

In conclusion, the molecular-mechanics calculations show that zeolite MCM-22 having the framework topology as proposed by Leonowicz *et al.*,[3] has *P*6/*m* symmetry. The proposed *P*6/*mmm* and *Cmmm* structures seem to be unstable

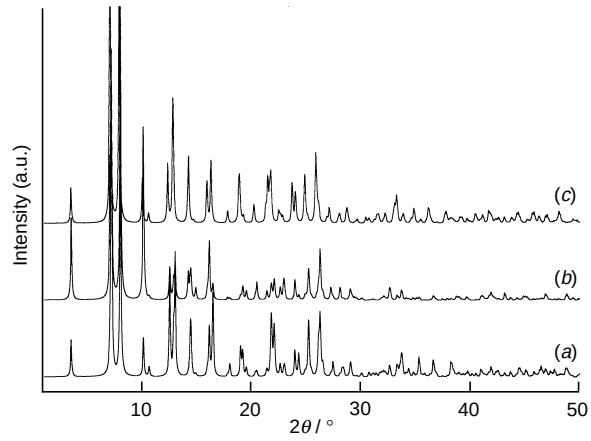

Fig. 3 Calculated XRD patterns excluding extraframework atoms: (*a*) proposed *P*6/*mmm*;[3] (*b*) proposed *Cmmm*;[3] (*c*) calculated *P*6/*m*

systems. Zeolite MCM-22 might indeed comprise T–O–T angles of 180°.

Footnote

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