Localization of non-framework species in MFI

H. van Koningsveld *

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, Netherlands

Abstract

The MFI/sorbate structures discussed in this paper illustrate that problems involved in the localization of sorbates in MFI can sometimes be overcome. The localization of the *p*-dichlorobenzene and *p*-xylene molecules, obtained from energy minimizations, is close to the orientation found from X-ray analysis. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: MFI zeolite; Sorbate; Crystallography; Symmetry

1. Introduction

Subtle symmetry changes are frequently deduced from diffraction data. Lowering of symmetry usually increases the number of variable parameters and also increases the number of reflections which, especially with powder data, can complicate the analysis of the symmetry changes enormously because of overlapping reflections. A successful explanation of such a subtle symmetry change, caused by shearing of TO_4-layers, has been given from the single-crystal X-ray diffraction data of high-silica zeolite ZSM-5 (MFI). The structure of as-synthesized ZSM-5, containing the tetrapropyl-ammonium (TPA) ion, was described using the orthorhombic space group *Pnma* [1]. The empty, calcined framework, H-ZSM-5, shows a reversible displacive phase transition at about 340 K. The precise transition temperature is depen-

dent on the number and type of atom substituting for the framework silicon atoms [2,3]. H-ZSM-5 exhibits monoclinic symmetry below and orthorhombic symmetry above this transition temperature. The high-temperature H-ZSM-5 phase is a single crystal with the same orthorhombic *Pnma* symmetry and geometry as the as-synthesized ZSM-5 crystal (containing TPA) (Fig. 1a; [4]) and it is concluded that the template does not deform the framework significantly. Upon cooling, the empty orthorhombic *Pnma* crystal changes into an aggregate of twin domains with monoclinic $P2_1/n11$ symmetry. Rotation photographs from a H-ZSM-5 crystal at different temperatures (Fig. 2) illustrate this phase transition. At 295 K splitting of the reflection spots is observed. From these photographs and the framework topology it can be concluded that the twin formation can be ascribed to a mutual shift (a shear) of successive (010) pentasil layers along the $+c$ or $-c$ axis with equal probability (Fig. 1b; [5]). H-ZSM-5

---

* Corresponding author.

(a)

(b)

(c)

(d)
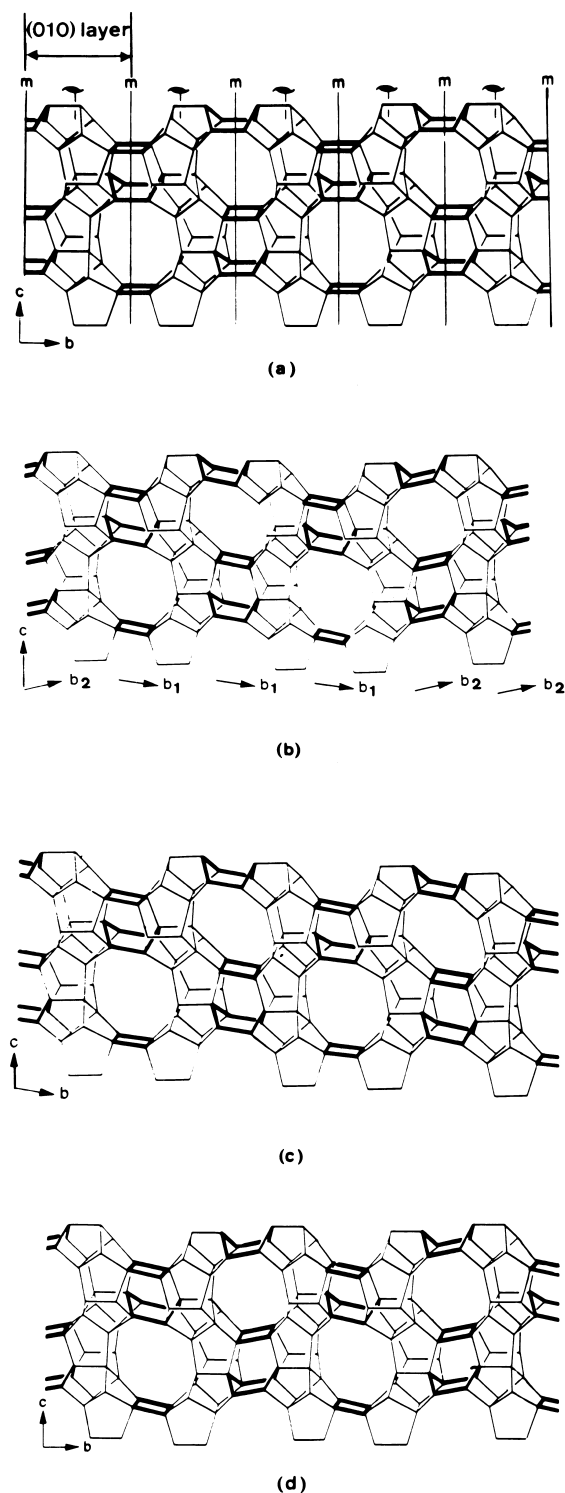
appears to be ferroelastic [6]: application of an appropriate uniaxial mechanical stress during the orthorhombic/monoclinic transition changes the population of the monoclinic twin domains and a monoclinic (nearly) single crystal can be produced (Fig. 1c; [7]). From Fig. 3 it can be seen that the intensity ratio of the intensities in the $0kl$ doublets change drastically upon application of an uniaxial mechanical stress. The volume fraction of one of the twin domains changes from 0.5 to 0.06 after application of this mechanical stress to the crystal used for structure determination [8]. At room temperature, the monoclinic/orthorhombic symmetry change can be reversibly induced by sorption/desorption of various organic molecules (e.g., *p*-xylene, *p*-diclorobenzene, *p*-nitroaniline and naphthalene [9–17]). The sorbate-loaded and sorbate-free H-ZSM-5 shows orthorhombic and monoclinic symmetry, respectively. At low sorbate loading, when there are (sufficient) sorbate molecules in the straight channels only, H-ZSM-5 exhibits the orthorhombic space group *Pnma* [9,11–14,17]. High sorbate loadings, when there are additional sorbate molecules in the sinusoidal channels, bring about yet another symmetry change. The shift of adjacent (010) pentasil layers along *c* now strictly alternates and the H-ZSM-5 framework transforms to orthorhombic symmetry with space group $P2_12_12_1$ (Fig. 1d; [9,10,13,15]). All these symmetry changes were studied using single crystal data. It would be nearly impossible to determine these changes using powder diffraction data.

Fig. 1. (a) (100) Pentasil layer in H-ZSM-5 with orthorhombic *Pnma* symmetry. (b) (100) Pentasil layer in monoclinic H-ZSM-5 at room temperature. Random (exaggerated) shift of (010) layers along $+c$ and $-c$, leading to a twinned crystal with $P2_1/n11$ symmetry. The size of the twin domains in the actual crystal is at least about 50 unit cells (~ 1000 Å). (c) Monoclinic H-ZSM-5 after application of mechanical stress. A perfect monoclinic single crystal is shown. (d) (100) Pentasil layer showing the strictly alternating shift of successive (010) layers along *c*, leading to orthorhombic $P2_12_12_1$ symmetry.
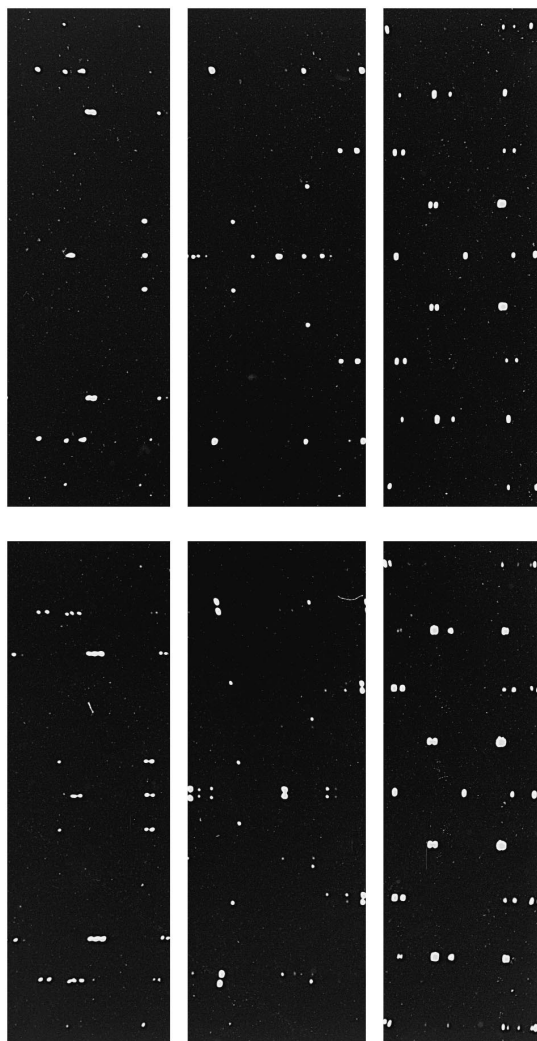
Fig. 2. Details of rotation photographs of a H-ZSM-5 crystal around [100], [010] and [001] (left to right) at 400 K (top) and 295 K (bottom). The rotation axis runs vertical in the plane of the paper.

The symmetry change in all-silica MFI has also been studied by energy minimization [18,19] and by molecular dynamics [20,21]. The force fields used by de Vos Burchart et al. [19] and by Yamahara et al. [21] both predict energy minima for the monoclinic and orthorhombic structure. The energy minimization study [19] describes the direction of the vector that connects the atomic coordinates in the monoclinic and orthorhombic structure quite well but overestimates its length by almost a factor of two. The

molecular dynamics study [21] reports a transition temperature between 225 and 275 K, which is low compared to the experimental value.

2. Localization of non-framework species

A crystallographic problem inherent to zeolite structure analysis is the localization of non-framework species. The often high symmetry of the framework is rarely obeyed by the guests such as templates, adsorbed molecules or cations leading to partial occupancies, disorder and pseudo-symmetry. In nearly all zeolite structures presently studied, the occluded material is disordered. When the point group symmetry of the site where the guest molecule resides is much higher than the symmetry of the guest molecule itself, the induced disorder is many fold and an accurate determination of the position and geometry of the extra-framework molecules becomes very difficult. If, in addition, the occluded material partially occupy two or more positions not related by a symmetry operation of the space group, the electron density of the atoms is spread over many sites within the zeolite and the localization of the material becomes nearly impossible.

No serious order/disorder problems are involved in several H-ZSM-5/sorbate systems. Single crystals of H-ZSM-5 (MFI) have been successfully loaded with several organic molecules. The structure of a single crystal of low-loaded H-ZSM-5, containing about three molecules *p*-dichlorobenzene (pdcb) per unit cell, has been determined in the orthorhombic space group *Pnma* [14]. The sorbed pdcb molecules prefer the position at the intersection of channels (Fig. 4a,b). Although the symmetry of the pdcb molecule is compatible with the site symmetry of the framework it turns out that the molecular mirror plane perpendicular to the Cl–Cl axis does not coincide with the crystallographic mirror plane and a 2-fold positional disorder around the mirror plane occurs. How-
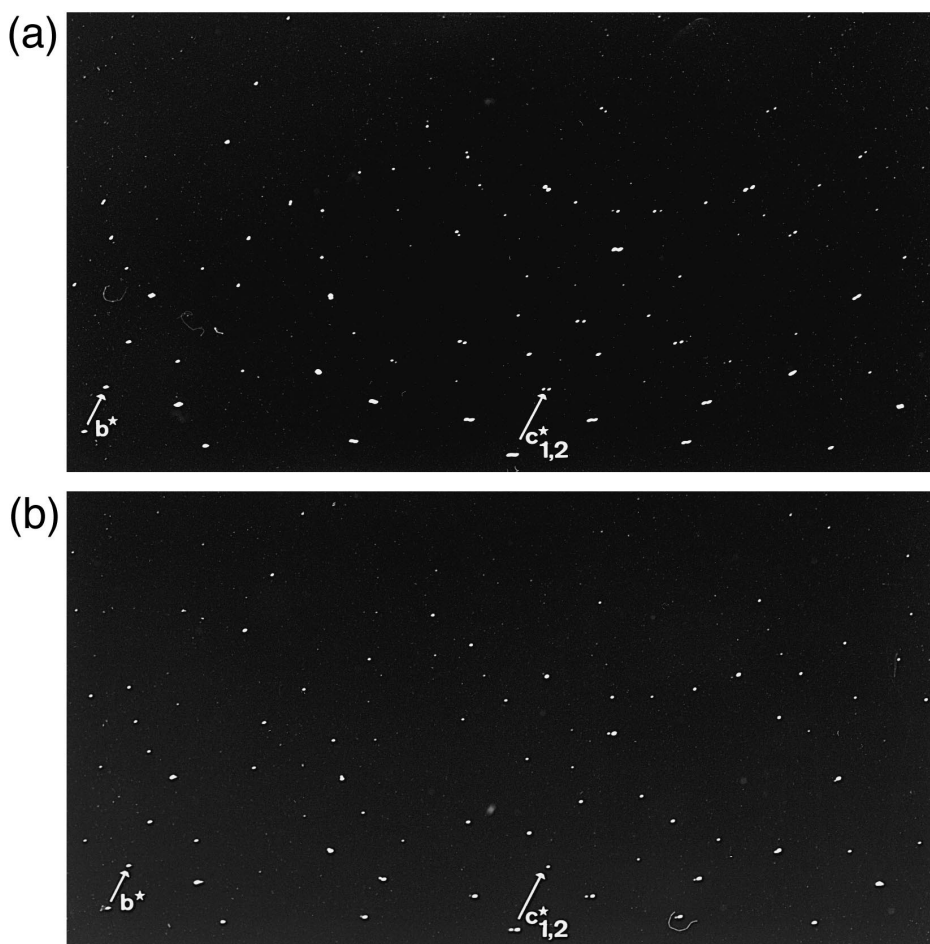
Fig. 3. $0kl$-Weissenberg photographs before (a) and after (b) application of an appropriate uniaxial mechanical stress on a H-ZSM-5 crystal.

ever, this causes no serious problem. The orientation of a relaxed pdcb molecule, obtained from energy calculations, using the Biosym Catalysis and Sorption Software [23], is close to the orientation found from the X-ray analysis. The location and rotational orientation of the sorbate at the intersection can, in a first approximation, be described by the fractional coordinates (x, y, z) of its molecular centre and the angle α between the positive a-axis and the vector normal to the aromatic ring plane (Fig. 4a; Table 1).

In single crystals of H-ZSM-5 loaded with four molecules naphthalene [12] or four molecules p-nitroaniline [17] per unit cell, both exhibiting orthorhombic *Pnma* symmetry, the organic molecules at the intersection are in an analogous orientation as in the low-loaded H-ZSM-5/pdcb system (Fig. 4b–d; Table 1). In H-ZSM-5, fully loaded with eight molecules p-xylene per unit cell, the adsorbate has been found to be orderly located in the orthorhombic space group $P2_12_12_1$, allowing its packing determination (Fig. 5a; [10]). One of the p-xylene molecules lies at the intersection of the straight and sinusoidal channels with its long molecular axis nearly parallel to (100) and deviating about $8°$ from the straight channel axis. The second p-xylene molecule is in the sinusoidal channel. Its long molecular axis is practically parallel to (010) and deviates almost $6°$ from [100]. An analogous orientation of the two independent
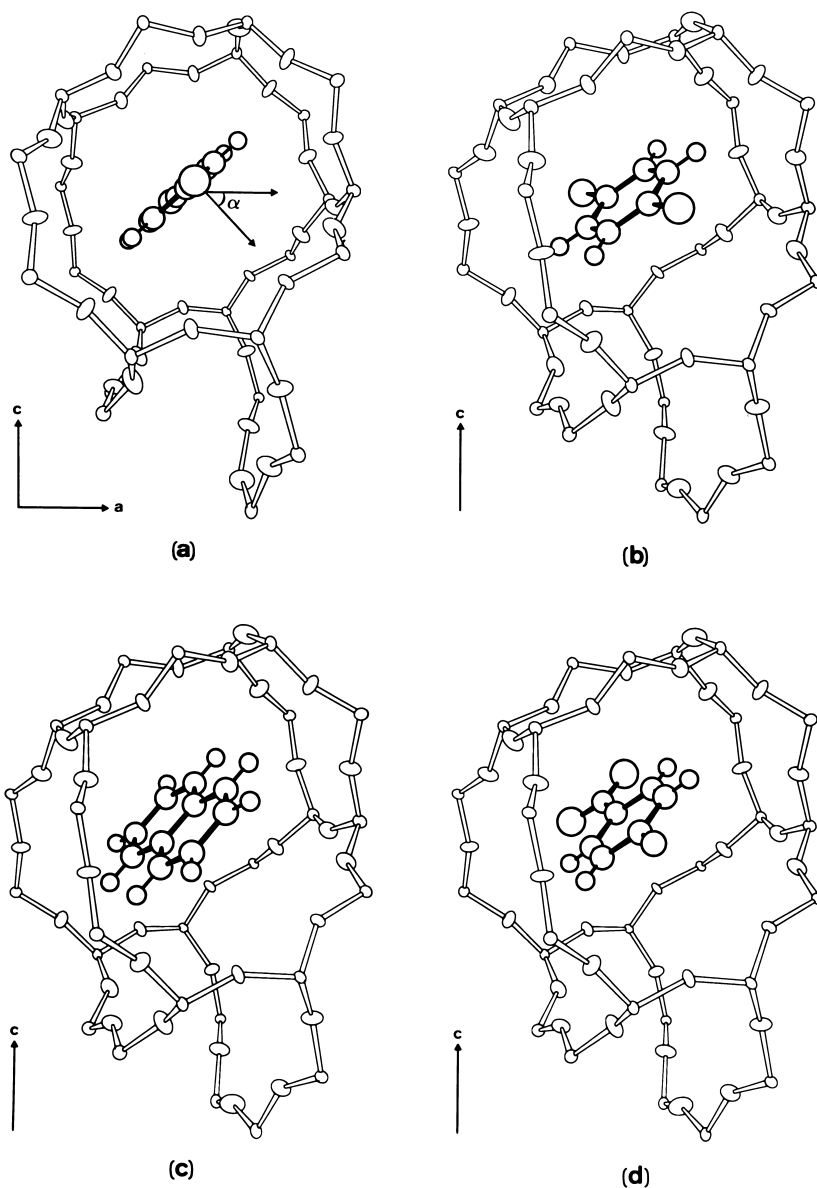
Fig. 4. ORTEP drawings [22] of the position and orientation of adsorbed molecules at the intersection of channels in low-loaded H-ZSM-5. Open bonds connect framework atoms and solid bonds connect atoms in adsorbed molecules. (a) *p*-Dichlorobenzene molecules in H-ZSM-5/2.6 *p*-dichlorobenzene, viewed down the straight channel axis. Definition of α. (b) As in (a), but viewed down an axis inclined 20° with the straight channel axis. (c) Naphthalene molecules in H-ZSM-5/3.7 naphthalene, viewed as in (b). (d) *p*-Nitroaniline molecules in H-ZSM-5/4.0 *p*-nitroaniline, viewed as in (b).

p-xylene molecules is obtained from energy minimization procedures [24]. The structural aspects of H-ZSM-5 loaded with eight *p*-dichlorobenzene (pdcb) molecules per unit cell [15] are in all details comparable to those in the

high-loaded H-ZSM-5/8 *p*-xylene system (compare Fig. 5a and b).

The phase transition from *Pnma* to $P2_12_12_1$ can be connected to a sudden increase in ordering of the sorbed phase with increasing cover-

age [10,25,26]. This commensurate crystallization of molecules within the H-ZSM-5 framework is assumed to be stabilized by establishing contacts at the channel intersection between adjacent molecules (See Fig. 5; [27]). However, the methyl(H) $\cdots$ aromatic ring interactions in H-ZSM-5/8 *p*-xylene are replaced by Cl $\cdots$ ring(C,H) interactions in H-ZSM-5/8 pdcb, which are substantially weaker. The importance of these interactions in stabilizing the guest structure within the zeolite host framework might therefore need reconsideration. The ring(C,H) $\cdots$ framework(O) contacts, which are the same in both structures, might be important in stabilizing the actually observed packing arrangement. The longest dimension of the adsorbed molecule, being commensurate to the length of the straight channel axis, very probably determines the commensurate crystallization by a flexible response of the channel pores in the zeolite host framework. The rotational orientation of pdcb in the low-loaded system differs $73.3°$ ($= 47.1 + 26.2$) and $78.2°$ ($= 47.1 + 31.1$) from the rotational orientation of the pdcb and *p*-xylene molecules trapped at the intersection in the high-loaded H-ZSM-5/sorbate systems (see Table 1). These two rotational orientations correspond to the directions of the two maximal pore dimensions observed in the clover-like
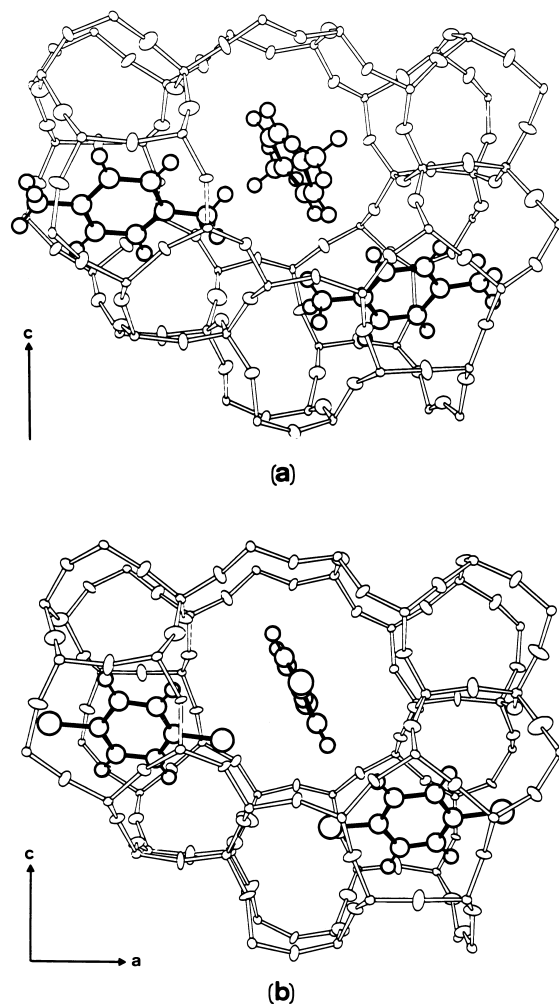

(a)

(b)

Fig. 5. Position and orientation of adsorbed molecules in high-loaded H-ZSM-5. (a) *p*-Xylene molecules at the intersection of channel and in the sinusoidal channel in the high-loaded H-ZSM-5/8 *p*-xylene system. The angle between the view direction and the straight channel axis is 15°. (b) As in (a) with *p*-xylene replaced by *p*-dichlorobenzene and viewed down the straight channel axis.

window in the empty H-ZSM-5 framework at 350 K [4].

3. Conclusions

The molecular centre (disregarding the oxygen atoms) of the adsorbed molecule is approximately in the same 'off-intersection centre' position in all structures. The same type of disor-

Table 1
Orientation of adsorbates at the intersection of channels in H-ZSM-5

	Code[a]				
	PDCB1	NAPH	PNAN[b]	PXYL	PDCB2
x	0.4860	0.4860	0.4858	0.4894	0.4824
y	0.2400	0.2366	0.2332	0.2379	0.2439
x	−0.0188	−0.0352	−0.0260	−0.0180	0.0175
α[c]	47.1	40.5	44.3	−31.1	−28.2

[a]CODES are as follows: PDCB1: H-ZSM-5 containing 2.6 molecules *p*-dichlorobenzene/u.c.; NAPH: H-ZSM-5 containing 3.7 molecules naphthalene/u.c.; PNAN: H-ZSM-5 containing 4.0 molecules *p*-nitroaniline/u.c.; PXYL: H-ZSM-5 containing 8.0 molecules *p*-xylene/u.c.; PDCB2: H-ZSM-5 containing 8.0 molecules *p*-dichlorobenzene/u.c..
[b]Molecular center calculated disregarding the oxygen atoms.
[c]The angle α is defined in the text and illustrated in Fig. 4a.

der is observed in all low-loaded systems. Refinements of the low-loaded systems show that the start orientation of the sorbate molecule may be rather far away from its minimized orientation as long as its geometry is reasonable and its molecular centre is not too far away from the minimized value. The examples illustrate that sorbed molecules can be located within the zeolite framework by single-crystal X-ray diffraction methods when the symmetry of the adsorption site is compatible with the symmetry of the sorbed molecule and also in some cases when these symmetries do not coincide and disorder occurs.

The orientation of *p*-dichlorobenzene and of *p*-xylene, obtained from energy minimizations, is close to the orientation found from X-ray analysis. The present force fields describe reasonably well subtle symmetry changes induced in MFI. However, the force field can still be improved. Changes in lattice symmetry and geometry, reviewed in this paper, might be of use in future force field parametrizations.

References

[1] H. van Koningsveld, H. van Bekkum, J.C. Jansen, Acta Crystallogr. B 43 (1987) 127.
[2] Z. Gabelica, J.L. Guth, Angew. Chem. 101 (1989) 60.
[3] A. Lopez, M. Soulard, J.L. Guth, Zeolites 10 (1990) 134.
[4] H. van Koningsveld, Acta Crystallogr. B 46 (1990) 731.
[5] H. van Koningsveld, J.C. Jansen, H. van Bekkum, Zeolites 7 (1987) 564.
[6] K. Aizu, Phys. Rev. B 2 (1970) 754.
[7] H. van Koningsveld, F. Tuinstra, J.C. Jansen, H. van Bekkum, Zeolites 9 (1989) 253.
[8] H. van Koningsveld, J.C. Jansen, H. van Bekkum, Zeolites 10 (1990) 235.
[9] B.F. Mentzen, J. Appl. Crystallogr. 21 (1988) 266.
[10] H. van Koningsveld, F. Tuinstra, H. van Bekkum, J.C. Jansen, Acta Crystallogr. B 45 (1989) 423.
[11] B.F. Mentzen, M. Sacerdote-Peronnet, J.F. Berar, F. Lefebvre, Zeolites 13 (1993) 485.
[12] H. van Koningsveld, J.C. Jansen, Microporous Mater. 6 (1996) 159.
[13] B.F. Mentzen, M. Sacerdote-Peronnet, Mater. Res. Bull. 28 (1993) 1161.
[14] H. van Koningsveld, J.C. Jansen, A.J.M. de Man, Acta Crystallogr. B 52 (1996) 131.
[15] H. van Koningsveld, J.C. Jansen, H. van Bekkum, Acta Crystallogr. B 52 (1996) 140.
[16] G. Reck, F. Marlow, J. Kornatowski, W. Hill, J. Caro, J. Phys. Chem. 100 (1996) 1698.
[17] H. van Koningsveld, J.H. Koegler, Microporous Mater. 9 (1997) 71.
[18] R.G. Bell, R.A. Jackson, C.R.A. Catlow, J. Chem. Soc., Chem. Commun. (1990) 782.
[19] E. de Vos Burchart, H. van Bekkum, B. van de Graaf, Zeolites 13 (1993) 212.
[20] P. Demontis, G.B. Suffritti, S. Quartieri, A. Gamba, E.S. Fois, J. Chem. Soc., Faraday Trans. 87 (1991) 1657.
[21] K. Yamahara, K. Okazaki, K. Kawamura, Catal. Today 23 (1995) 397.
[22] C.K. Johnson, ORTEP Report ORNL-3794, Oak Ridge Natl. Lab., Oak Ridge, TN, 1965, revised June 1970.
[23] Biosym Catalysis and Sorption Software, Version 3, Biosym Technologies, San Diego.
[24] E. de Vos Burchart, B. van der Linden, H. van Bekkum, B. van de Graaf, Collect. Czech. Chem. Commun. 57 (1992) 675.
[25] P.T. Reischman, K.D. Schmitt, D.H. Olson, J. Phys. Chem. 92 (1988) 5165.
[26] R.E. Richards, L.V.C. Rees, Zeolites 8 (1988) 35.
[27] H. Thamm, J. Phys. Chem. 91 (1987) 8.