MOLECULAR MECHANICS STUDIES ON MFI TYPE ZEOLITES. 1. EFFECT OF *p*-XYLENE ADSORPTION ON THE ZEOLITE STRUCTURE*

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The effect of the adsorption of *p*-xylene on the all-silica MFI-structure is simulated with our molecular mechanics model. From experimental measurements it is known that the symmetry of the framework changes from monoclinic (space group $P2_1/n.1.1.$) towards orthorhombic (space group $P2_12_12_1$) upon adsorption of *p*-xylene up to eight molecules per unit cell. The experimentally observed change in the geometry of the zeolite upon *p*-xylene adsorption is compared with that calculated by molecular mechanics. For the calculations our force field for all-silica zeolites is used in combination with the MM3 force field for organic molecules. Parameters for the organic–zeolite interactions are obtained by combination of the two force fields.

Heterogeneous catalysis starts with the adsorption of molecules on the surface of the catalyst. During physical adsorption the shape of both the organic molecule and the catalyst surface are subjected to (small) changes as a response to the non-bonded interactions between adsorbate and adsorbent. It is likely that these changes can play a role in creating specific adsorption sites and in processes like diffusion and reaction kinetics. With zeolites it is even possible that these changes are required to make it possible for a molecule to enter the narrow zeolite channels. Therefore, it is important to understand these changes and to be able to predict them.

The potential of the zeolite framework to adapt to an adsorbing compound is well known from X-ray crystallographic studies[1,2] for the system ZSM-5/*p*-xylene. The ZSM-5 structure changes from monoclinic symmetry (space group $P2_1/n.1.1.$) towards orthorhombic symmetry (space group $P2_12_12_1$) upon adsorption of eight *p*-xylene molecules per unit cell. Four *p*-xylene molecules are located at the intersections of the straight and the sinusoidal channels and four molecules are in the sinusoidal channels (Fig. 1). Due to the adsorption the sinusoidal channels are

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slightly deformed to a more elliptical cross section. The deformation is due to a strictly alternating shift of adjacent (010) pentasil layers along the *c*-axis[2].

For energy calculations on systems comprising both organic molecules and a zeolite one can distinguish four kinds of interactions. (i) Zeolite interactions: all interactions present within the zeolite framework. (ii) Intramolecular interactions: the interactions within each adsorbed molecule. (iii) Intermolecular interactions: all non-bonded interactions between different molecules in the same unit cell as well as the non-bonded interactions between molecules in different unit cells. (iv) Molecule–zeolite interactions: all non-bonded interactions between the zeolite framework and the adsorbed organic molecules. In this study we use our consistent molecular mechanics force field developed for all-silica structures[3] to calculate the zeolite interactions. Both intermolecular and intramolecular interactions are calculated with the MM3 force field[4]. Parameters for the molecule–zeolite interactions are derived from the parameters of both force fields.

The MM3 force field is widely accepted to be a very good force field for all kinds of organic species. Our silica force field was recently developed and shows to be consistent in calculating the heat of formation, the vibrational frequencies (including IR intensities) and the geometry for structures ranging from the dense α-quartz structure to the open structure of faujasite[3].

CALCULATIONS

Calculations were carried out on a DEC 5000/200 workstation using DELPHI[5,6], the Delft computer program for molecular mechanics. Both Shanno's conjugate gradient method[7] and the full matrix Newton–Raphson method[6] were used in energy minimization under constant pressure. The summation of the long range interactions was in concordance with our force field tapered over the interval 0·7—1·4 nm. Partial charges were calculated using the electronegativity

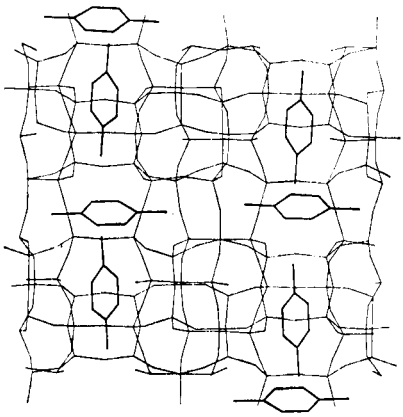

FIG. 1

Experimental location[2] of the eight *p*-xylene molecules in the MFI framework viewed along the *c*-axis

equalization method (EEM) of Mortier et al.[8] using his parameters[9] and (as a first approach) a dielectric constant $\varepsilon = 6{\cdot}2$ resulting in slightly lower charges on the zeolite atoms than the charges given in our force field.

For the molecule–zeolite interactions we have used the Coulomb potential ($\varepsilon = 6{\cdot}2$) and the Hill potential. The parameters in the Hill potential were obtained by using standard mixing rules. The parameters listed in Table I give nearly identical potentials for the interactions between MM3-oxygen and the organic atoms and for the interactions between zeolite-oxygen and the organic atoms. The calculated heat of adsorption is the energy difference between the system molecule/zeolite and the systems zeolite and molecule.

RESULTS AND DISCUSSION

The parameters obtained for the molecule–zeolite interactions were checked by calculating the heat of adsorption for a number of organic molecules in the all-silica forms of the zeolites ZSM-5 (Silicalite-1, S-1) and mordenite. The results are given in Table II.

The experimental[10] and calculated values are in reasonable agreement. Note that the values obtained represent local minima on the potential surfaces as in general the global minimum can only be found by minimizing many different starting structures.

The calculations with the system S-1/*p*-xylene were carried out with two different zeolite structures. First, the energy minimized monoclinic structure (MONO) was filled with *p*-xylene (molecules set approximately on the crystallographic positions) and the structure was minimized. This structure is coded XYL-M. Second, the energy minimized high-temperature orthorhombic structure (ORTHO) was filled with *p*-xylene (the same positions as before) and minimized. This structure is coded XYL-O. Results are listed in Table III.

TABLE I

Hill potential parameters used in the energy calculations of molecules adsorbed in zeolite structures

Interaction (MM3-type)	*A* kJ/mol	*B* nm^{-1}	*C* J nm^6/mol
C(1, sp^3)–Si	18 754	27·4	1·308
C(1, sp^3)–O	46 378	32·4	1·190
H(5)–Si	14 224	30·2	0·556
H(5)–O	39 853	36·3	0·512
C(50, benzene)–Si	26 475	27·9	1·661
C(50, benzene)–O	67 040	33·1	1·517

Both minimized structures show a deviation from the experimentally found orthorhombic structure with respect to the monoclinic angle predicted. Minimization of the orthorhombic structure yields an angle of 90·18°, whereas the monoclinic angle of the monoclinic structure decreases upon energy minimization from 91·03° towards

TABLE II

Calculated and experimental heats of adsorption (kJ/mol) of organic molecules in mordenite and ZSM-5

Adsorbate	Adsorbent	Heat of adsorption, $-\Delta H_{ads}$	
		calc.	exp.[10]
Mordenite	methane	13·0	15·5—33·0
Mordenite	ethane	20·9	23·0—25·1
Mordenite	propane	28·8	33·4—37·6
Mordenite	n-butane	37·6	41·8—45·6
Mordenite	isobutane	36·8	35·5
H-ZSM-5	ethane	26·8	41·8
H-ZSM-5	propane	32·6	42·6
H-ZSM-5	n-butane	39·5	46·8

TABLE III

Energy minimization of the zeolite ZSM-5 with adsorbed *p*-xylene

Structure	Heat of adsorption kJ/mol	Lattice parameters				
		a nm	*b* nm	*c* nm	*α* deg	*V* nm³
		Calculated				
ORTHO	—	2·004	1·973	1·326	90·00	5·243
MONO	—	2·001	1·978	1·325	91·02	5·244
XYL-O	−49·4	2·007	1·971	1·331	90·18	5·264
XYL-M	−49·9	1·997	1·971	1·335	90·49	5·255
		Experimental				
ORTHO[11]	—	2·008	1·990	1·337	90·00	5·341
MONO[1]	—	2·011	1·988	1·337	90·67	5·343
ZSM-5/*p*-xylene[2]	—	2·012	1·982	1·344	90·00	5·359

90·47°. The symmetry of both structures is very close to the experimentally found space group $P2_12_12_1$.

The effect of the adsorption of *p*-xylene on the zeolite structure is visualized in Figs 2 and 3. Figure 2 shows a unit cell of the experimental monoclinic structure viewed along the [100]-direction (view into the sinusoidal channels). The arrows

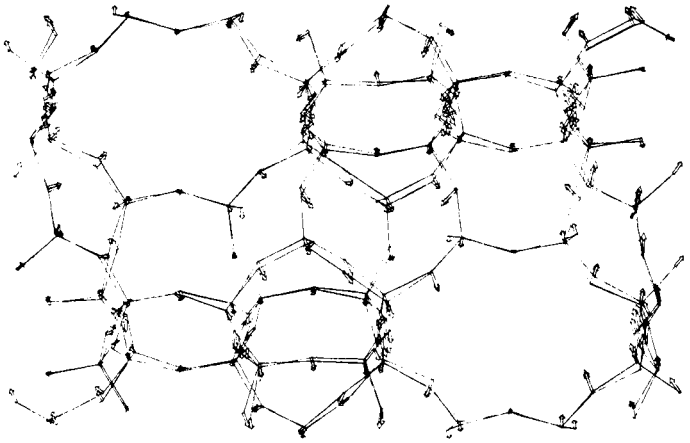

FIG. 2

Movement of the zeolite atoms of the experimental monoclinic MFI structure upon adsorption of eight *p*-xylene molecules. Viewed along [100]

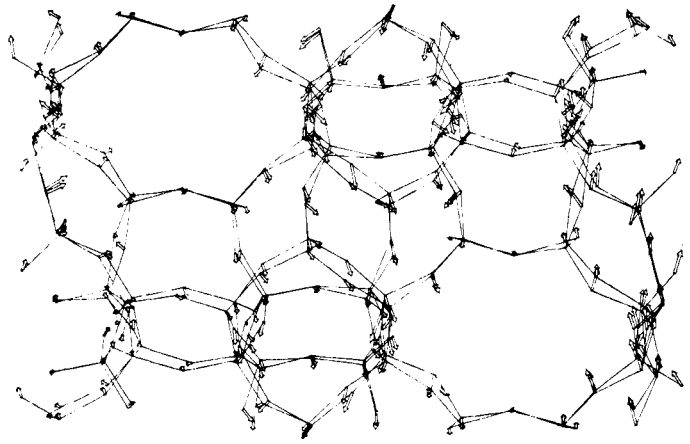

FIG. 3

Movement of the zeolite atoms of the energy minimized monoclinic MFI structure upon simulation of the adsorption of eight *p*-xylene molecules. Viewed along [100]

indicate the size and direction of the movement of the zeolite atoms upon adsorption of eight *p*-xylene molecules in the zeolite pores (experimental *p*-xylene/ZSM-5 structure minus experimental MONO structure). Figure 3 shows the energy minimized monoclinic structure and the arrows indicate the movement upon simulating the adsorption and minimizing the S-1/*p*-xylene system (minimized XYL-O structure minus minimized MONO structure).

From Figs 2 and 3 it can be seen that the effect of the adsorption of molecules on the structure of the zeolite can be predicted properly. The angle between the two vectors shown in Figs 2 and 3 is only 23° (in the 864-dimensional space!) and the ratio of the lengths is 1·1, indicating the strong resemblance of the two vectors of motion. The figures also clearly show the relative shift of the adjacent (010) pentasil layers along the *c*-direction. Except for four oxygen atoms, all atoms show a downward movement in the middle layer relative to the layers on each side of the unit cell.

With the eight *p*-xylene molecules in the MFI-framework the heat of adsorption is calculated at −49·4 kJ/mol (XYL-O; XYL-M: −49·9 kJ/mol), of which about 10% due to *p*-xylene–*p*-xylene interactions. The zeolite framework is distorted to an extent of about 7 kJ/mol *p*-xylene. The experimental heat of adsorption given by Wu et al.[12] equals −41 kJ/mol (6·1 molecules per unit cell).

CONCLUSION

Our force field for all-silica structures was successfully combined with the MM3 force field for organic molecules and extended to comprise the molecule–zeolite interactions. Effects of adsorbates on the zeolite structure were predicted quite well in the case of the system S-1/*p*-xylene.

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