MOLECULAR MECHANICS STUDIES ON MFI TYPE ZEOLITES. 2. ISOMORPHOUS SUBSTITUTION BY ALUMINIUM*

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The molecular mechanics force field developed for all-silica structures is extended with parameters for tetrahedral aluminium. With this force field and the MM3 force field for organic molecules the effects of isomorphous substitution in the MFI framework are examined (4 Al/unit cell) with tetrapropyl ammonium (TPA) as the charge compensating cation. The results indicate a slight preference for the positions 2, 9, 5, 12, and 6 and the by mirror symmetry related positions. The differences in energy are mainly due to the differences in the zeolite framework energy.

Important aspects in heterogeneous catalysis with zeolites include adsorption, diffusion, reactivity of the reactants, flexibility of zeolite and reactant structure as a response to non-bonded interactions and the location of the catalytic sites. The potential of the zeolite ZSM-5 to deform upon adsorption of *p*-xylene molecules has been successfully simulated[1] using our all-silica force field[2] in combination with the MM3 force field (ref.[3]) for organic compounds. Heats of adsorption were also reasonably predicted.

The location of the catalytic sites in the framework is an interesting subject suitable for molecular mechanics studies. These catalytic sites are present as a result of the isomorphous substitution of silicon by another element. It is to be expected that structurally different sites will have a different degree of adaptability to accommodate non-silicon atoms due to strains within the zeolite framework.

The aluminium siting in zeolite ZSM-5 has already been examined by two quantum chemical studies[4,5] and recently by the classical shell model[6]. The orthorhombic structure of ZSM-5 exhibits 12 different crystallographic T-sites (numbered 1–12). In the monoclinic framework, where the mirror symmetry is lost, 24 crystallographically different T-sites can be distinguished (1–24 or 1–12, 1′–12′; Fig. 1).

The quantum chemical studies used fragments of the ZSM-5 structure of Olson et al.[7] (1·1 Al/unit cell) and kept this structure fixed while replacing a silicon atom by

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aluminium. The prediction of the preferential aluminium sites (sites 2 and 12) was based both on the average T—O bond length obtained from the X-ray structure and on the results obtained from the quantum chemical calculations. However, as no structure relaxation was applied, the energies may not be compared[6]. Other structure refinements of ZSM-5 samples[8,9] (3·7 and 0·8 Al/u.c., respectively) did not result in the same spread of bond lengths over the different crystallographic sites.

The work of Schröder et al.[6] (results of which were not known to us at the time we performed our substitution studies) based upon the classical shell model comprises (partial) structure relaxation using the method of defect energy calculations. The 24 different crystallographic positions of the monoclinic MFI structure are substituted (one aluminium atom per unit cell with no charge compensating cation) and energy differences are compared (maximum difference 19·5 kJ/mol Al). Position 14 (2') is found to be favoured. The calculated energy differences between positions related by mirror symmetry in the orthorhombic structure are relatively large (up to 15·2 kJ/mol Al): the three sites with highest energy have their symmetry related positions within the first five positions with lowest energy.

The calculations performed in the present work have been carried out using perfect periodicity of the framework with a repeating neutral central unit cell including four tetrapropyl ammonium cations and four aluminium atoms. In this study TPA was used as the charge compensating cation because the location of this cation is accurately known from crystallographic studies[10] and the TPA ion is generally used as template in the MFI synthesis (and possibly directs the aluminium distribution).

CALCULATIONS

Calculations were carried out on a DEC 5000/200 workstation using DELPHI[11,12], the Delft computer program for molecular mechanics. Both Shanno's conjugate gradient method[13] and the full matrix Newton–Raphson method[12] were used in energy minimization under constant pressure.

Our all-silica force field[2] was extended with parameters for aluminium (Table I). The bond energy is taken from Huheey[14] and the Al—O bond length is an average literature value for tetrahedral aluminium. The R_{13} values have been calculated using bond lengths and angles (O—Al—O angle 109·47°, Si—O—Al angle 151·6°). The force constants have been estimated

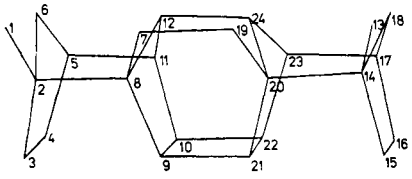

FIG. 1
The different crystallographic sites in the MFI structure (12 or 24 depending on mirror symmetry)

from IR data. The polarizability volume is obtained from the same fit on 48 minerals as those for oxygen and silicon[2].

Parameters for the Hill potential are listed in Table II. The treatment of the long range interactions and charges is handled the same as in the preceding article of our molecular mechanics studies on MFI type zeolites[1]. For the intramolecular interactions nitrogen MM3 type 8 was used with one positive charge added.

In this study the structure described by van Koningsveld et al.[10] (0·3 Al/u.c.) was used as the initial geometry in our calculations. Their first TPA coordinates were used. The location of the TPA ions (at the intersections of the straight and sinusoidal channels) in the energy minimized structure with lowest total energy is shown in Fig. 2. In each calculation four of the 96 silicon atoms of the X-ray structure were replaced by aluminium on one of the crystallographic sites (the 24 sites of the monoclinic symmetry, Fig. 1).

TABLE I

Parameters for aluminium added to the all-silica force field

Morse potential: Al—O bond

$D_0 = 471{\cdot}75$ kJ/mol

$R_{12}^0 = 173{\cdot}0$ pm $\qquad a = 14{\cdot}5\ \mathrm{nm}^{-1}$

Urey–Bradley potential

R_{13}^0(Si—O—Al) = 322·0 pm $\qquad R_{13}$(O—Al—O) = 282·5 pm

k_{13}(O—Al—O) = 87·1 N/m

k_{13}(Si—O—Al) = 123·3 N/m

Hill potential: Al

α	$0{\cdot}74\ \mathrm{cm}^{-24}$
van der Waals radius	212 pm

TABLE II

Additional Hill parameters for calculations on the system TPA–[Al]-ZSM-5

Interaction (MM3-type)	A kJ/mol	B nm^{-1}	C J nm^6/mol
C(1)–Al	14 799	27·3	1·060
H(5)–Al	11 108	30·0	0·447
N(8)–Si	20 694	28·1	1·247
N(8)–O	52 734	33·3	1·138
N(8)–Al	16 289	28·0	1·008

RESULTS AND DISCUSSION

Energy minimization of the substituted structures yielded the energies and lattice parameters listed in Table III. The relative energies for the zeolite interactions (*Z*) are given as well as the inter- and intramolecular interactions of the TPA ions (*O*), the molecule–zeolite interactions (*Z–O*), and the total relative energy. From Table III it can be seen that all pairs of positions which are related by mirror symmetry in the orthorhombic structure have nearly equal energies (maximum difference in total energy 0·42 kJ/mol Al) and lattice parameters, which is not unexpected as the distortion in the monoclinic symmetry is small compared with the orthorhombic structure. It seems inconceivable that the energy calculated for the positions related by mirror symmetry in the orthorhombic structure can be influenced to a great extent by the type of force field used or the choice of parameters therein. Thus it seems allowed to discuss all 24 positions as 1 – 12 positions. All minimized structures deviate from the orthorhombic symmetry. The smallest monoclinic angle is found for position 12.

The order in total relative energy is largely determined by the differences in zeolite framework energy, in particular differences in bonding energy, bending energy and van der Waals energy. Differences in Coulomb energy are only small (maximum difference zeolite 0·8 kJ/mol Al, zeolite-TPA 0·6 kJ/mol Al) indicating that a (small) change in partial charges would not influence the results.

The positions 2, 9, 5, 12 and 6 are preferred to the other seven positions. There is a difference of 4·3 kJ/mol Al in the zeolite energy between these first five and the last seven positions and a difference of 3·6 kJ/mol Al in total relative energy. The order found is not in harmony with the results found with the quantum chemical studies[4,5] (although positions 2 and 12 were found to be preferred) nor with the results found

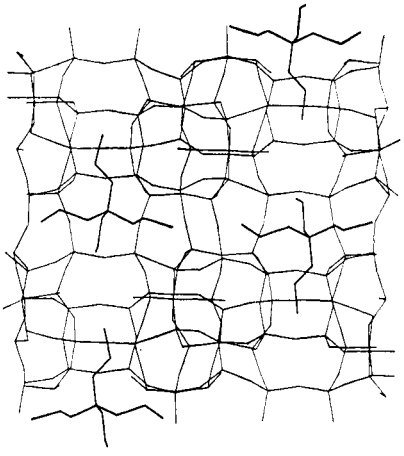

FIG. 2

The location of the TPA ions in an energy minimized structure (Al atoms located at sites 2) viewed along *c*

with the classical shell model[6] (position 2′ preferred, but position 2 one of the highest energies). For position 2 the vibrational frequencies were calculated, resulting in three zero-eigenvalues for the Hessian matrix, indicating that the extreme found with the Newton–Raphson method indeed represents an energy minimum.

CONCLUSIONS

We have examined the individual crystallographic sites in the MFI structure with respect to aluminium substitution in the presence of TPA^+. Preference is found for

TABLE III

Relative energies and lattice parameters for the zeolite ZSM-5 with four silicon atoms of one type substituted with aluminium and with TPA as charge compensating cation

Si No.	Relative energy, kJ/mol Al, TPA				Lattice parameters					
	Z	*O*	*Z–O*	total	*a* nm	*b* nm	*c* nm	*α* deg	*β* deg	*V* nm^3
2	0·02	2·51	1·73	0·00	1·999	1·993	1·335	88·7	90·0	5·316
14	0·00	2·62	1·74	0·09	1·999	1·993	1·335	91·3	90·0	5·316
9	1·39	2·18	2·80	2·11	1·995	2·001	1·329	88·9	90·0	5·302
21	1·42	2·24	2·83	2·24	1·995	2·001	1·329	91·1	90·0	5·302
17	3·31	2·67	1·54	3·25	2·004	1·993	1·330	88·8	90·0	5·312
5	3·34	2·74	1·56	3·38	2·004	1·993	1·330	91·2	90·0	5·312
12	1·69	5·67	0·33	3·44	2·007	1·990	1·335	90·0	89·8	5·332
24	1·69	5·68	0·33	3·45	2·007	1·990	1·335	90·0	89·8	5·332
6	3·02	3·04	1·73	3·54	1·999	1·993	1·335	89·2	90·0	5·315
18	3·02	3·09	1·74	3·59	1·999	1·993	1·335	90·8	90·0	5·316
10	7·89	0·59	2·99	7·21	2·002	1·997	1·330	89·2	90·0	5·314
22	7·89	0·69	2·97	7·29	2·002	1·997	1·330	90·8	90·0	5·314
20	7·64	5·55	0·00	8·93	2·004	1·992	1·333	89·8	89·7	5·322
8	7·68	5·49	0·02	8·93	2·004	1·992	1·333	90·2	89·7	5·322
13	11·30	0·00	4·20	11·24	2·015	1·993	1·330	90·3	89·7	5·339
1	11·28	0·03	4·22	11·27	2·015	1·993	1·330	89·7	89·7	5·339
16	9·29	5·24	1·07	11·34	2·003	1·992	1·333	89·5	89·9	5·317
4	9·31	5·22	1·11	11·38	2·003	1·992	1·333	90·5	89·9	5·318
7	10·16	3·86	2·17	11·92	2·006	1·997	1·331	89·3	89·9	5·332
19	10·19	3·82	2·20	11·95	2·006	1·997	1·331	90·7	90·0	5·332
23	10·85	4·44	1·80	12·82	2·007	1·993	1·331	90·5	89·4	5·325
11	11·00	4·80	1·69	13·24	2·008	1·992	1·332	89·5	89·5	5·330
3	9·18	6·21	2·58	13·72	2·007	1·985	1·340	89·6	89·9	5·339
15	9·16	6·27	2·58	13·75	2·007	1·985	1·340	90·4	89·9	5·339

the positions 2, 9, 5, 12, and 6, but energy differences found are small. Comparison with other work shows that the order in energies strongly depends on the calculation method. Prior to drawing conclusions about the aluminium substitution, consensus must be reached with respect to the force field and the parameters. However, our method seems more promising than the quantum chemical studies (no structure relaxation) and the classical shell model (large energy differences for the mirror symmetry related positions). To obtain information about the aluminium distribution in the MFI framework it is necessary to calculate many different structures with a different distribution of aluminium atoms over the individual crystallographic sites. It seems interesting to perform Monte Carlo-like calculations to investigate this aluminium distribution. Schemes to avoid energy minimization for each distribution are necessary as to minimize the amount of CPU-time needed.

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