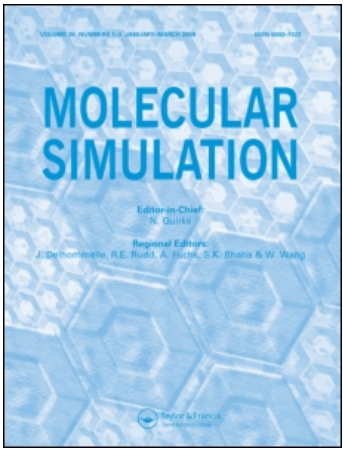

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COMPUTER SIMULATION OF THE LOCATION OF PARA-XYLENE IN SILICALITE†

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The method of atom-atom potentials has been applied to the localisation of para-xylene molecules within the channels and intersections of silicalite. Two minima were found at the intersection, with interaction energies of -82 and $-80\,kJmol^{-1}$ respectively. These two positions are in good agreement with the results of a recent, room temperature powder X-ray diffraction study. A third, slightly deeper minimum (interaction energy $-85\,kJmol^{-1}$) was located in the straight channels but was not occupied in the X-ray diffraction study. This result has been explained by considering entropic effects.

KEY WORDS: Atom–atom potentials, para-xylene, silicalite, entropic effects.

INTRODUCTION

The synthetic zeolite catalyst ZSM-5 is a member of the pentasil family of zeolites [1] and has been shown to have a wide range of industrial applications. These include the conversion of methanol to petroleum range hydrocarbons [2] and the isomerisation of xylenes to give predominantly the para isomer [3]. In order to gain an understanding of such processes it is necessary to know the location of the participating species within the channels and/or intersections of the host zeolite. Computer graphics procedures have already been used with some success in defining the positions of xenon in zeolite rho [4] and pyridine in zeolite L [5]. In the current work, we study the location of para-xylene molecules adsorbed in silicalite, the pure SiO_2 isomorph of ZSM-5.

The silicalite structure [6] consists of two different channel systems, each defined by ten-membered rings. The elliptical straight channels (approximate dimensions 5.7×5.2 Å) are parallel to [010] while the nearly circular sinusoidal channels (approximate dimensions 5.4 Å) extend along [100] and intersect the straight channels to give non-spherical cavities up to 9 Å in diameter (see Figure 1). There will be three possible generalised adsorption sites for guest molecules within the framework: the straight channels, the sinusoidal channels and the channel intersections.

Mentzen and co-workers have studied low loadings of para-xylene adsorbed in pentasil type zeolites (ZSM-5, boralite, silicalite) by X-ray powder diffraction techniques at room temperature [7–9]. They concluded that the adsorbed molecules are most likely situated at the channel intersections with the line joining the methyl groups parallel to the straight channel axis. Several different orientations of the plane of the aromatic ring to the (001) plane (defined by the angle θ in Figure 2a)) were investigated (θ = 0, 30, 60, 90, 120 and 150°) assuming that the methyl-methyl axis remained fixed, and two preferred orientations were found to be consistent with their

†Invited paper.

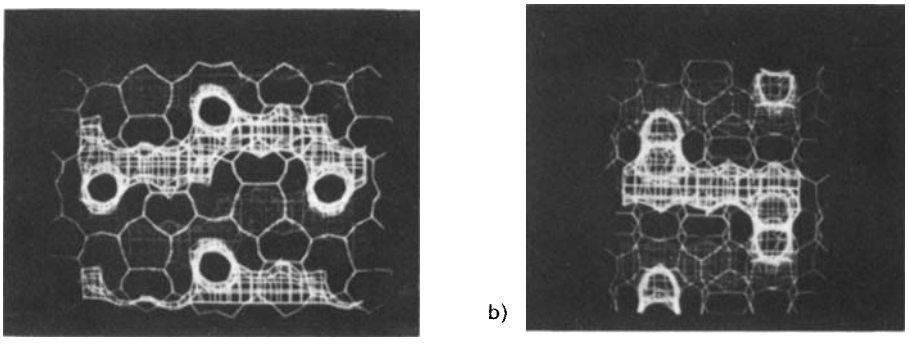

Figure 1 The channel system of silicalite viewed along a) [010], b) [100]. (See colour plate IV.)

data, at $\theta = 60°$ and 120°, suggesting a disordering of the adsorbed molecules at the channel intersections. No molecules were observed in the straight or sinusoidal channels. Adsorption of para-xylene was shown to be a physical process and the positions obtained were apparently independent of the composition of the pentasil [7].

COMPUTATIONAL TECHNIQUES

The method of atom-atom potentials has been used to calculate adsorbate-framework interaction energies, following the work of Kiselev *et al.* [10]. Pairwise interaction energies are calculated using the Lennard-Jones potential, equation 1.

$$\phi_{i,j} = \frac{B}{r^{12}} - \frac{C}{r^6} \tag{1}$$

where r is the distance between two atoms i and j. B and C are the repulsion and dispersion attraction constants calculated from the reported polarizabilities and van der Waals radii of the O, C(sp^2), C(sp^3) and H atoms which are assumed to be independent of the atom valence state. The values of B and C are given in Table 1 and have already been employed with some success in a study of the adsorption and diffusion of benzene and toluene in the zeolites silicalite and theta-1 [11].

The atom–atom potentials are then summed to give the total interaction energy of the molecule with the framework at a given position:

$$\phi_{tot} = \sum_{i,j} \phi_{i,j} \tag{2}$$

Several approximations have been made in calculating ϕ_{tot}:

1. The framework is rigid and unperturbed by the adsorbate.

Table 1 Lennard-Jones parameters, B and C.

	B ($kJ\text{Å}^{12}mol^{-1}$)	C ($kJ\text{Å}^{6}mol^{-1}$)
O–H	149978.0	536.74
O–C_{sp^3}	1138724.0	1700.67
O–C_{sp^2}	1444997.8	2158.09

2. Only adsorbate-oxygen atom-atom potentials are calculated. Thus, interactions due to silicon atoms are ignored in the calculation.
3. The silicalite framework is neutral and, therefore, no electrostatic terms need be included in the calculation.
4. The adsorbate molecule is assumed to be rigid in its equilibrium geometry.
5. No adsorbate-adsorbate interactions have been calculated and so the results will apply to a low loading of adsorbate molecules at absolute zero.

The calculations described above were performed within the 'Chem-X' suite of programs [12]. The zeolite structure was generated from crystallographic data [13] and the adsorbate molecule placed in a channel intersection. A portion of the structure, over a radius of about 10 Å from the centre of the intersection and containing approximately 190 oxygen atoms, was isolated and the adsorbate-framework interaction energy calculated for a range of molecular orientations. The energetics involved in placing the para-xylene molecule in the straight and sinusoidal channels were also examined.

To assist with these calculations the program contains a minimisation routine that allows the interaction energy about a particular starting position to be optimised, giving a local minimum energy position. Variables, such as translation of the adsorbate along the x, y and z axes and rotation about these axes through a specific point, for example, the centre of mass of the molecule, are specified and the minimisation is performed with respect to these. Any combination of such variables may be taken. Thus, the adsorbate may be positioned at a series of different points within the framework and the local minima calculated. In this way the optimum energy positions of the molecule within the intersection and channels may be predicted.

RESULTS AND DISCUSSION

Initially we examined the rotational freedom of an adsorbed para-xylene molecule about the straight channel axis. The centre of mass of the molecule was that calculated by Mentzen (Table 3) with the line joining the methyl groups parallel to the straight channel axis in 5° steps and the interaction energy minimised at each point with respect to (001) was $\theta = 0°$. The molecule was rotated through 180° about the channel axis in r° steps and the interaction energy minimised at each point with respect to translation along the x, y and z axes and rotation about the x and z axes through the centre of mass of the molecule. Figure 3 shows the energy profile obtained. Two well-defined minima are present at $\theta = 65$ and 155°, with interaction energies of $-80\,\text{kJmol}^{-1}$ and $-82\,\text{kJmol}^{-1}$ respectively. The barrier to rotation between these two minima is approximately $9\,\text{kJmol}^{-1}$.

The interaction energy is much less favourable for orientations between $\theta = 0$ and 45°, peaking at $\theta = 20°$ where the interaction energy is $-59\,\text{kJmol}^{-1}$. This is a manifestation of the elliptical shape of the 10-rings defining the straight channel. When the plane of the aromatic ring lies along this short axis of the 10-ring at $\theta = 20°$ the interactions of the ring hydrogens with several framework oxygens become unfavourable because of the atoms approach too closely. The shortest H–O distances are then in the range 2.3 to 2.4 Å (Table 2). The activation energy for rotation about the straight channel axis at the intersection can be estimated as the difference in energy between the maximum and minimum energy points in figure 2 and is approximately

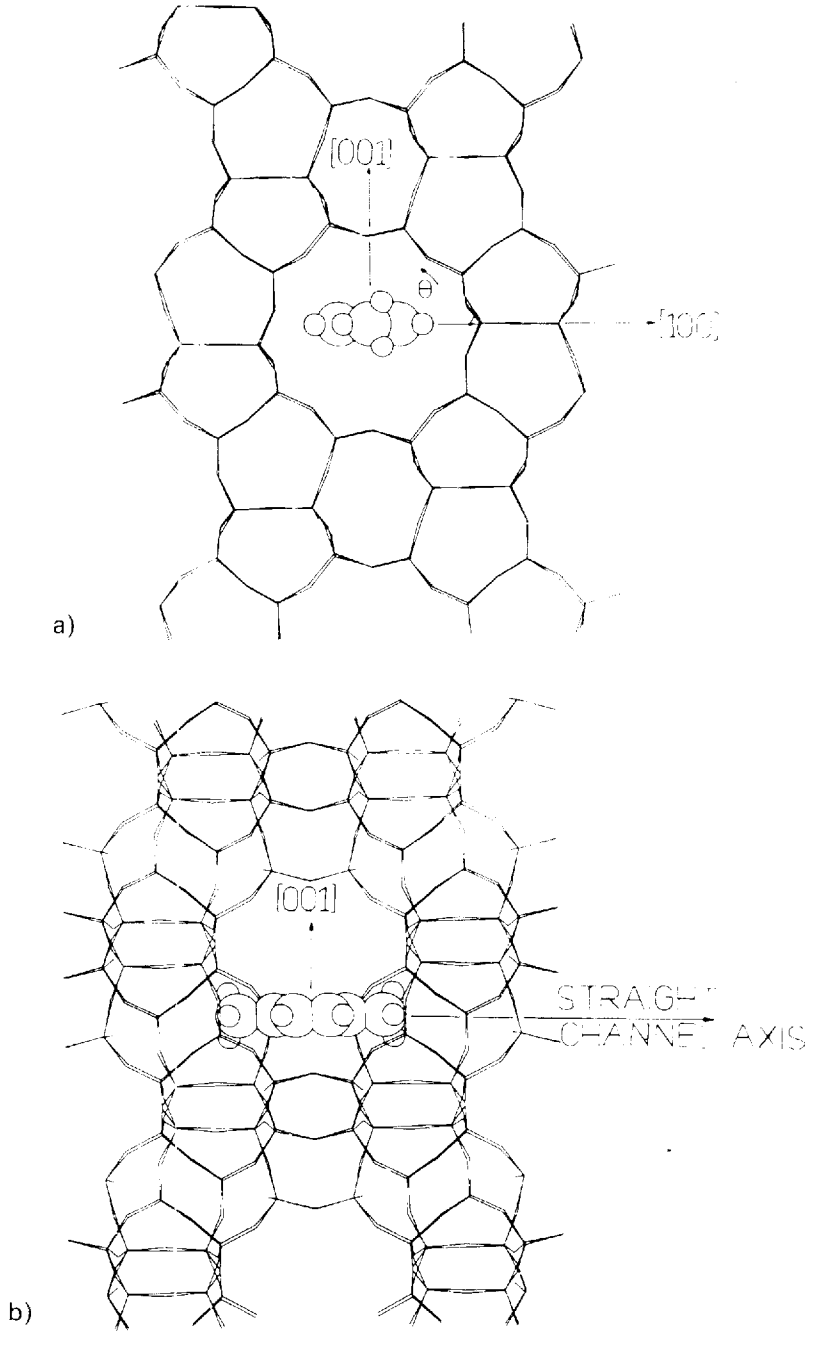

Figure 2 The starting position of para-xylene at the intersection, a) along [010], showing the angle θ. b) along [100].

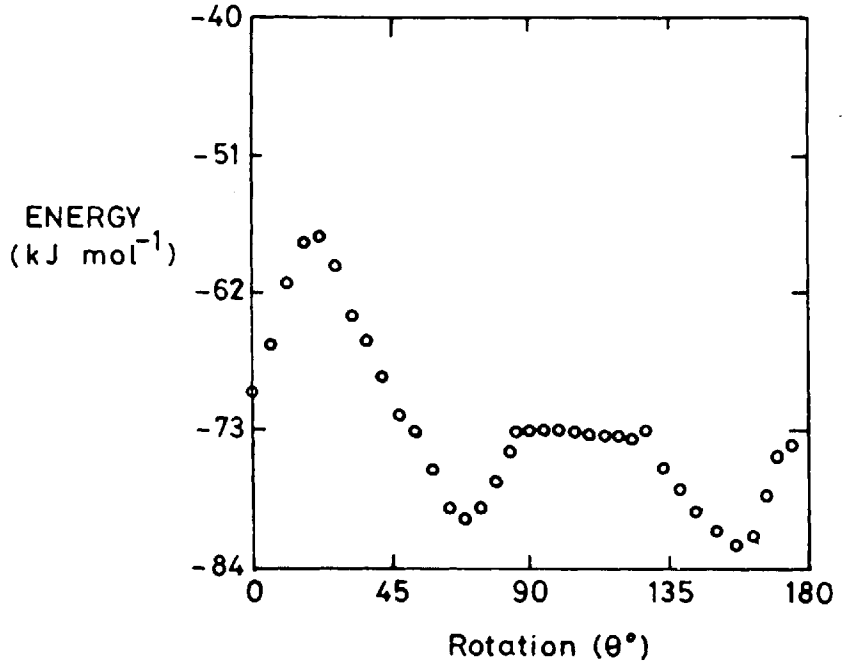

Figure 3 Minimised interaction energy plotted against the angle θ in Figure 2a.

23 kJmol^{-1}. However, if the molecule is restricted to rotation between $\theta = 50$ and 180°, this activation energy drops appreciably to about 9 kJmol^{-1}.

The results above suggest that minima may be located about orientations of $\theta = 65$ and 155°. The para-xylene molecule was then allowed to minimise around these two positions with respect to rotation about the straight channel axis as well as the 5 variables specified above. The two minima obtained at orientations of $\theta = 64.8$ and 154.8° with interaction energies of -80 and -82 kJmol^{-1} respectively, are close to those calculated above.

In order to ensure that the molecule was allowed to sample the entire potential energy surface of the intersection, a para-xylene molecule was allowed to minimise with respect to the six variables used above. Starting orientations were such that the line joining the methyl groups was no longer parallel to (001) but perpendicular to it. Several such orientations were investigated and one notable minimum was located with an interaction energy of -76 kJmol^{-1} (Figure 4). Several other minima were also located with interaction energies below -70 kJmol^{-1}.

Investigation of the para-xylene molecule located within the straight and sinusoidal

Table 2 Short H–O distances (Å) at $\theta = 20°$

H2–025	2.373
H2–018	2.321
H3–018	2.305
H5–025	2.395
H5–020	2.307
H6–020	2.300

Table 3 Observed and calculated centre of mass in fractional coordinates, and the total observed shift from the Mentzen position (Å).
(a = 20.07 Å, b = 19.92 Å, c = 13.42 Å [13])

θ	x/a	y/b	z/c	*Total shift (Å)*
65°	0.5309	0.2504	0.9718	0.66
120°	0.4825	0.2689	0.9706	0.51
155°	0.4820	0.2768	1.0173	0.92
Mentzen	0.4982	0.2488	0.9687	0.00

channels enabled us to locate the global minimum energy position i.e. the lowest interaction energy anywhere within the structure. This position, shown in Figure 5, is in the straight channel and has an interaction energy of $-85\,\text{kJmol}^{-1}$. The minimum energy position in the sinusoidal channel has an interaction energy of $-77\,\text{kJmol}^{-1}$.

The first conclusion that can be drawn from these results is that the computer simulations yield two well-defined minima in the channel intersection, close to those reported by Mentzen *et al.* In common with the diffraction results, our simulations show that the methyl groups lie approximately parallel to [010]. The minimum at $\theta = 65°$ is very close indeed to that at $\theta = 60°$ reported by Mentzen; the discrepancy in the centre of mass coordinates of the molecule is less than 0.1 Å along *b* and *c* (Table 3), and the larger discrepancy along *a*, approximately 0.7 Å, brings the molecule closer to the framework in the simulation. The calculated position at $\theta = 155°$ is not in such good agreement with Mentzen's value of 120°, but the centre of mass coordinates still agree to within less than 0.7 Å in *a*, *b* and *c*. The shifts along the *a* and *c* axes again bring the molecule closer to the framework, increasing the adsorbent-adsorbate interaction energy. It must be remembered that in calculating the positions at $\theta = 60$ and 120°, Mentzen allowed no variation in the centre of mass of the para-xylene molecule after the initial localisation.

However, we must also ask why the X-ray study locates the molecules at the channel intersection whereas our energy calculations predict that the global minimum lies in the straight channel. The most important point here is that our calculations refer to absolute zero. The difference in energy between the minimum in the straight channel and that at the intersection is small, $3\,\text{kJmol}^{-1}$, which is approximately equal

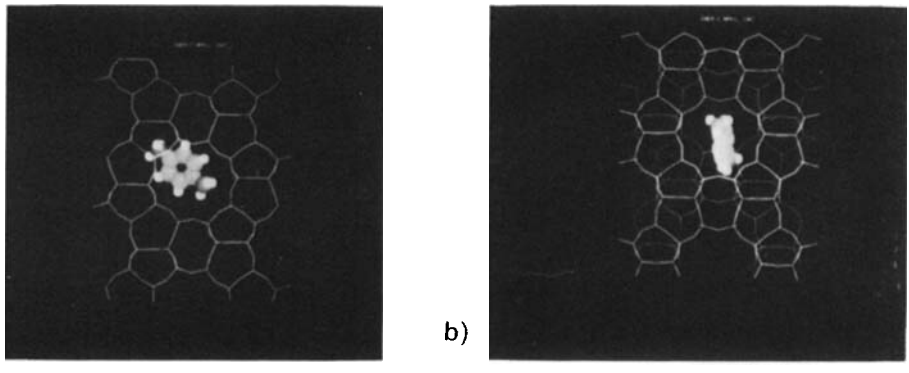

Figure 4 Local minimum energy position for para-xylene at the intersection, interaction energy = $-76\,\text{kJmol}^{-1}$, a) along [010], b) along [100]. (See colour plate V.)

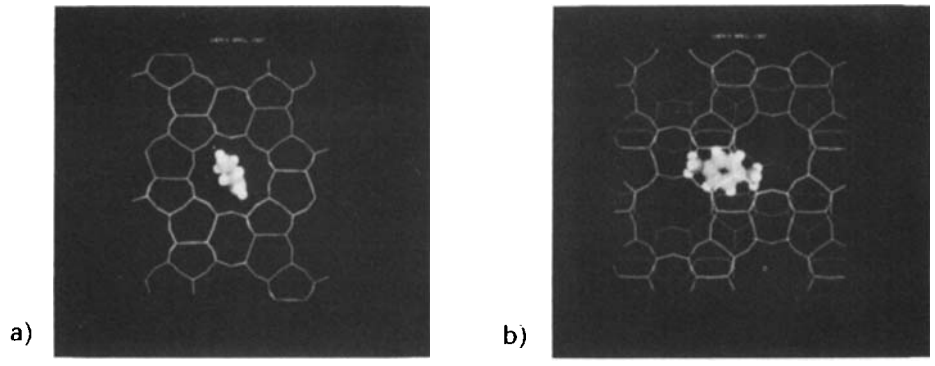

Figure 5 Minimum energy position of para-xylene in the straight channel, interaction energy = −85 kJ-mol^{-1}, a) along [010], b) along [100]. (See colour plate VI.)

to the value of RT at room temperature. Also, within the intersection the molecule has a much greater orientational freedom, being able to rotate quite freely around the channel axis between $\theta = 50$ and 180°. Such a rotation is much more constrained within the straight channel, the dimensions of the molecule matching the dimensions of the channel more closely than they do in the intersection. Consequently, entropic effects will play a crucial role in determining the preferred locations of adsorbed molecules at room temperature. We would therefore propose that, at lower temperatures, para-xylene molecules should be seen to migrate into the straight channels, as long as thermodynamic equilibrium can be maintained. Indeed, a recent powder neutron study of deuterobenzene molecules in ZSM-5 at 77 K [14] revealed molecules located within the straight channels as well as at the channel intersections.

Simulations, such as those described above, can help further our understanding of zeolite catalysis. With respect to xylene isomerisation, it can be assumed that the reaction will most likely occur at the channel intersections. The results above suggest that at temperatures usually employed in such reactions the adsorbed molecules will be situated mainly at the channel intersections. The size of the straight and sinusoidal channels, which restrict the orientational freedom of xylene molecules within the channels, will also hinder protonation to form a bulkier intermediate, again favouring the channel intersections as likely reaction sites. In future studies we will attempt a computer simulation of the xylene isomerisation reaction within pentasil type zeolites, exploring these factors in greater detail.

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