Simulation Studies of Reactive Molecules in Zeolites

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This paper describes the use of Mott–Littleton calculations to study hydrocarbon molecules in zeolites. The energetics and the geometry of adsorption of methanol and ethene molecules inside the pores of silicalite and ZSM-5 zeolite are reported.

Introduction

Zeolites are technologically important catalysts for hydrocarbon conversion reactions. An important current application concerns small hydrocarbon molecules such as methanol, which are highly reactive over the zeolite ZSM-5 and give rise to useful products such as gasoline and olefins. Several studies on the behaviour of small molecules inside the complex pore structures of zeolites (see fig. 1) using molecular mechanics energy calculations[1-3] and Monte Carlo calculations[4-6] have been reported. The nature of the adsorption site and the mode of activation of hydrocarbon molecules in zeolite catalysts are valuable information, assisting the design of better catalysts. Recently, atom–atom pair potential parameters have been reported for silica[7] and alumina[8] and their applicability to zeolite materials has been extensively tested. The power of energy minimisation calculations using these effective atom–atom potentials in predicting the structure of different zeolites is now clear.[9] In this paper, we report the results of simulation studies which investigate the possible adsorption sites and the geometry for the methanol and ethene molecules in ZSM-5. The methods used are closely related to those employed in Mott–Littleton[10] defect calculations.

Methodology

In the present study, calculations are performed using the generalised Mott–Littleton code CASCADE (Cray automatic system for calculation of defect energies) developed by Leslie[11] using specified interatomic potentials. The molecule is then introduced as an 'interstitial' and a region I of approximately 120 atoms is relaxed. The partially covalent nature of the zeolite crystal is modelled by incorporating a three-body potential term for O—T—O (where T = Si or Al) bond angles. Details of the potential model are given elsewhere.[7,9] The atomic positions for the unit cell of zeolite ZSM-5 were taken from the X-ray diffraction studies by Olson *et al.*[12] and they were further relaxed to obtain a zero-strain lattice. The observed relaxations were small. The different atom–atom potentials used to model the zeolite and to study the interaction of the hydrocarbon molecule with the zeolite framework are summarised in table 1.

Results and Discussion

Treatment of the Zeolite Crystal

Silicalite is the completely siliceous form of the zeolite ZSM-5. The silicon to aluminium ratio in zeolite ZSM-5 is usually in the range 35–1000. There is no conclusive evidence
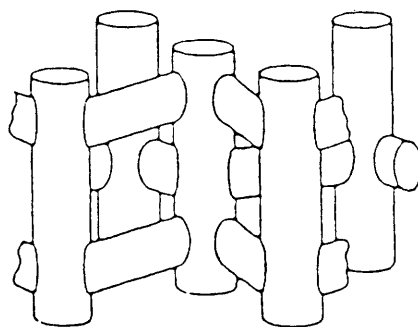
Fig. 1. The pore structure of zeolite ZSM-5 with elliptical (5.1×5.6 Å) straight channels and circular (5.4×5.6 Å) sinusoidal channels.

Table 1. The nature and the values of interatomic potentials used in the present calculation

atoms[a]	nature	A	B	C	D	ref.
O^{2-}-Si^{4+}-O^{2-}/OHO	T	6.927	109.470			7
O^{2-}-Al^{3+}-O^{2-}/OHO	T	2.070	109.470			7
Si^{4+}-O^{2-}/OHO	B	503.600	0.424	228.891		13
Al^{3+}-O^{2-}/OHO	B	498.602	0.385	0.000		13
O^{2-}-O^{2-}	B	22 764.000	0.149	46.084		13
O^{2-}-OHH	B	262.537	0.348	0.000		14
OHO-OHH	M	5.896	2.277	0.948	1.00	14
OHO-O^{2-}	L	8 388.460	18.810			15
H*-O^{2-}/OHO	L	1 557.522	5.574			16
sp$_3$C*-O^{2-}/OHO	L	11 825.615	17.661			16
sp$_2$C*-O^{2-}/OHO	L	15 118.161	22.579			16
O*-O^{2-}/OHO	L	8 388.460	18.810			15
H*-OHH	L	3.553	0.110			17
sp$_3$C*-OHH	L	2 854.571	5.844			16
sp$_2$C*-OHH	L	3 722.796	7.621			16
O*-OHH	L	1 557.522	5.574			16

[a] An asterisk denotes atoms of hydrocarbon molecules; OHO, oxygen in the hydroxyl group; OHH, hydrogen in the hydroxyl group. T = Three-body potential evaluated as: $V(R) = 1/2A(C-B)^2$, where A are the bond bending force constants (eV rad^{-2}), B are the equilibrium bond angle (degrees), C are the bond angles in the crystal (degrees). B = Buckingham potential evaluated as: $V(R) = A \exp(-R/B) - C/R^6$, where units for A are in eV, B are in Å, C are in eV Å^6. L = Lennard-Jones potential evaluated as: $V(R) = A/R^{12} - B/R^6$ where units for A are in eV Å^{12}, B are in eV Å^6. M = Morse potential evaluated as: $V(R) = A\{1 - \exp[-B(R-C)]\}^2 - A - DQ_1Q_2/R$, where units for A are in eV, B are in Å^{-1}, C are in Å, D are in eV Å e^{-2}.

to assign the site at which silicon is replaced by aluminium, although there are speculations based on n.m.r.[18] and quantum-mechanical[19] studies. Based on these results, we represent the ZSM-5 structure, by substituting the Si^{4+} at the T_2 site by Al^{3+}. The O^{2-} ion bridging the T_2 and T_8 sites is replaced by an OH$^-$ ion and thus the charge neutrality is preserved. Indeed it is the introduction of these protons that causes the Brønsted acidity of the zeolite which is vital for its catalytic activity.
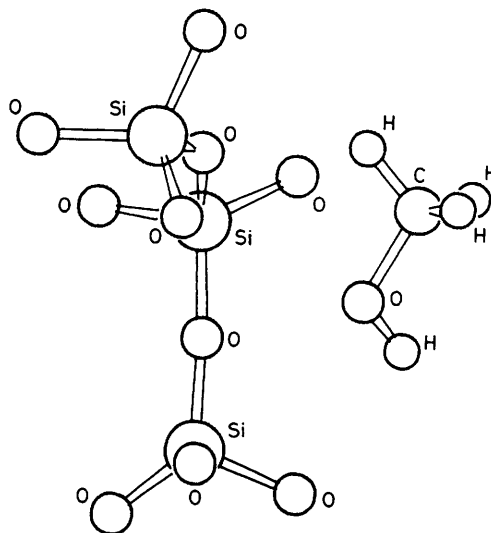
Fig. 2. The final position of methanol in silicalite with respect to the nearest framework atoms.

Treatment of Hydrocarbon Molecule

In the present calculations, the geometry of the molecules was held rigid during the process of relaxation of the hydrocarbon molecules to a minimum-energy configuration. We study the geometrical and electronic variations within the hydrocarbon molecules by quantum-mechanical calculations once the adsorption sites are located. The geometry assumed for the hydrocarbon molecules is the optimised configuration obtained by *ab initio* calculations and the formal charges on individual atoms deduced from a Mulliken population analysis were used in the present calculation.

Methanol in Silicalite

Defect energy calculations were performed for methanol inside the silicalite framework. To begin with, the methanol molecule was placed at the centre of the 10-membered ring of the straight channel where it opens into the sinusoidal pores. There is an attractive coulombic interaction between the hydrogen atoms of the methanol molecule and the oxygen atoms in the framework. The molecule relaxed towards the T_2 site in the framework. The 'defect energy' which corresponds to the adsorption energy, is calculated as -0.96 eV. The final energy minimised configuration of methanol with respect to the three nearest SiO_4 groups of the framework is shown in fig. 2. The distances of the atoms of the methanol molecule from the lattice ions in the final configuration are shown in table 2. The long-range (electrostatic) interactions between the methanol molecule and the silicalite framework are found to be attractive, while the short-range forces are repulsive. Experimental studies[20] reveal that the methanol molecule undergoes dissociation and further reactions that are highly exothermic processes. However, there is no precise value available for the heat of adsorption. We observe that there is a considerable amount of distortion of the framework atoms in the vicinity of the methanol molecule. As discussed in ref. 21, such effects can only be treated by the present procedures and are not included in many molecular modelling packages.

Table 2. Interatomic distances in silicalite–CH_3OH adsorbed complex[a]

atoms: framework-methanol	distances/Å
O_{13}–H_1	2.94
Si_8–H_1	2.07
O_7–H_1	2.68
Si_2–O_2	2.87
O_{13}–O_2	2.70
O_2–O_2	2.93
O_1–O_2	2.87
O_1–C_3	2.97
Si_2–H_5	2.96
O_2–H_5	2.41
O_1–H_5	2.71
O_1–H_4	2.89

[a] Framework atoms labelled after Olson *et al.*[12] Methanol atoms labelled as:

$$H_5 \diagdown$$
$$H_4 - C_3 - O_2 \diagup H_1$$
$$\diagup$$
$$H_6$$
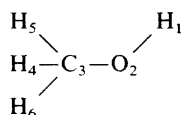
Methanol in ZSM-5

In the second set of calculations, silicon at the T_2 site was replaced by aluminium and the oxygen bridging the T_2 and T_8 sites was replaced by an O—H group to model ZSM-5 zeolite, as described earlier. Again, the methanol molecule was allowed to relax from the centre of the straight channel pore where it opens into the sinusoidal pore. The final energy minimised configuration of methanol with respect to the three nearest TO_4 groups (where T = Si or Al) is shown in fig. 3. The distances of the atoms of the methanol molecule from the lattice ions in the final configuration are shown in table 3. It is well known from the experimental studies[22] that this hydroxyl group, which is the source of Brønsted acidity in the zeolite catalysts, is the active centre for the conversion of methanol to gasoline. The adsorption energy calculated for this configuration is −0.64 eV. More realistic values of adsorption energy could be obtained only from electronic structure calculations using quantum-mechanical methods. Results of such studies for the final configurations will be reported elsewhere.[23] There is a subtle difference between the final configurations shown in fig. 2 and 3. The fact that the hydroxyl group is the active site for the methanol conversion is emphasised from the results of present calculations. From neutron spectroscopic study, Jobic *et al.*[24] speculated that there is an adsorbed methanol species where there is a freedom of rotation along the O—C bond and the same is true with the final configurations predicted from these calculations.

    Finally, to avoid the possibility of obtaining a local minimum in the energy-minimisation calculations, we started the calculation with different orientations of the methanol molecule (*i.e.* C—O bond lying parallel and perpendicular to the straight and sinusoidal pores) in the starting configuration and confirmed that the reported configuration is energetically preferred.

Adsorption of Ethene in Silicalite and ZSM-5

The mechanism of formation of C—C bonds in the conversion of the C_1 compound (methanol) to C_n compounds (gasoline) is not yet conclusively established. Ethene is
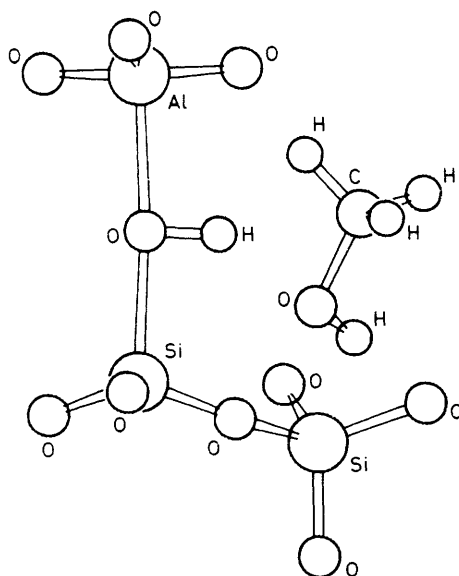
Fig. 3. The final position of methanol in ZSM-5 with respect to the nearest framework atoms.

Table 3. Interatomic distances in
ZSM-5–CH_3OH adsorbed complex[a]

atoms: framework–methanol	distances/Å
$H–H_1$	2.52
$O_7–H_1$	2.40
$O_{25}–H_1$	2.58
$Si_7–H_1$	3.00
$H–O_2$	2.41
$Si_8–O_2$	2.96
$O_8–O_2$	2.76
$O_7–O_2$	2.83
$O_2–H_5$	2.98
$H–C_3$	2.90

[a] Framework atoms labelled after Olson *et al.*[12]
Methanol atoms labelled as:

$$H_4—C_3—O_2$$

with H_5, H_6 on C_3 and H_1 on O_2
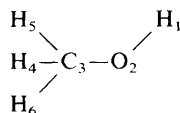
the first molecule with a C—C bond to be formed as the product of the primary reaction in the conversion of methanol to gasoline. Hence we are interested to study the adsorption behaviour of ethene and to identify its adsorption sites in both silicalite and ZSM-5 cages. The ethene molecule is placed at the centre of the 10-membered ring of the straight channel, where it opens into the sinusoidal pore in the all siliceous framework, namely the silicalite lattice. Since ethene is a more symmetrical and less polar molecule than methanol, it remained almost at the centre of the channel. The displacement of the molecule from the original position was less than *ca.* 0.2 Å; the adsorption energy
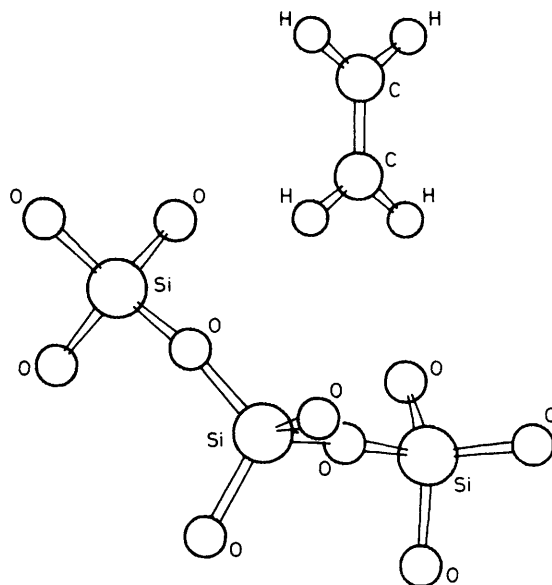
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Fig. 4. The final position of ethene in ZSM-5 with respect to the nearest framework atoms.

Table 4. Interatomic distances in ZSM-5–C_2H_4 adsorbed complex[a]

atoms: framework-methanol	distances/Å
O_5–H_3	2.63
O_{21}–H_3	2.77
O_5–C_1	3.26
O_5–H_5	3.36
O_{19}–C_1	3.48
O_{14}–H_5	3.14
Si_5–H_3	3.02
Si_5–H_5	3.49
Si_6–H_3	3.41

[a] Framework atoms labelled after Olson *et al.*[12]
Ethene atoms labelled as:

$$\begin{matrix} H_3 & & H_4 \\ & \diagdown \quad \diagup & \\ & C_1 = C_2 & \\ & \diagup \quad \diagdown & \\ H_5 & & H_6 \end{matrix}$$
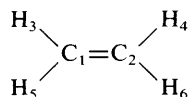
of ethene was found to be −0.97 eV. However, when one of the silicons is replaced by aluminium to represent the ZSM-5 lattice, the molecule undergoes a displacement of *ca.* 1.5 Å and the adsorption energy for this configuration was found to be −0.32 eV. In contrast to the behaviour of the methanol molecule, ethene moves away from the hydroxyl group and towards the T_5 and T_6 site with maximum interaction with the oxygen (O_5) which bridges them. The final adsorption site predicted by the present calculation is shown in fig. 4 and the distances are given in table 4.

Conclusions

The calculations reported here are an efficient way of identifying the adsorption sites for hydrocarbon molecules in zeolites. From these preliminary results, it appears that the Brønsted acid sites are the active sites for the primary C—C bond formation but that the ethene molecule does not interact strongly with the Brønsted acid site.

The present calculations simulate a situation where there is a low concentration of adsorbates present in the largest channel. Studies pertaining to the behaviour of these hydrocarbon molecules at larger concentrations and allowing occupancy of the smaller channels and cages of the zeolites will take us closer to the real situation. These modelling studies are now well within the range of Mott–Littleton like procedures. Once geometries have been identified in these methods, quantum-mechanical techniques may be used for studying the accurate electronic structure.

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