

Applications of molecular graphics to zeolite catalysts

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Abstract. The use of molecular graphics procedures to simulate hydrocarbon processes in zeolites is described. Calculations of heats of adsorption, activation energies for diffusion, and the location of solute molecules are considered, and a methodology for simulating an isomerisation reaction in a shape-selective zeolite catalyst is discussed.

Keywords. Zeolite catalysts; molecular graphics; computer simulation.

1. Introduction

For several decades, zeolites have enjoyed widespread use as water softeners, cation exchangers, and molecular sieves, and more recently they have been employed as industrial catalysts, for example in catalytic cracking (Rabo 1976). Of particular interest are the new, highly siliceous zeolites, which have a high affinity for hydrocarbons and are being used as shape-selective, heterogeneous catalysts.

Zeolites have the general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]mH_2O$, where cations M , of valence n , compensate the negative charge of the zeolite framework. The latter is composed of SiO_4 and AlO_4 units, linked in such a way as to generate cages of molecular dimensions (up to ~ 11 Å), interconnected by windows, up to 8 Å in diameter (figure 1). The exchangeable cations, M , occupy a range of sites and are coordinated by oxygen atoms of the framework or by water molecules. The water can usually be driven out by heating under vacuum, leaving the cations with very low coordination numbers.

Computer graphics procedures are now being used in a variety of ways (Ramdas *et al* 1984):

- (1) to provide clear illustrations of the structural features of zeolites;
- (2) to model intergrowths and stacking faults;
- (3) to represent hydrocarbon diffusion pathways by means of energy-contoured diagrams.

Molecular mechanics models have also been developed for calculating the heats of adsorption and activation energies for diffusion of hydrocarbons in zeolites, using atom-atom potentials (Kiselev and Pham Quang Du 1981; Bezus *et al* 1984). We shall describe the applications of some of these methods to hydrocarbon adsorption and mobility in two important zeolites, faujasite and zsm-5. The former is used extensively

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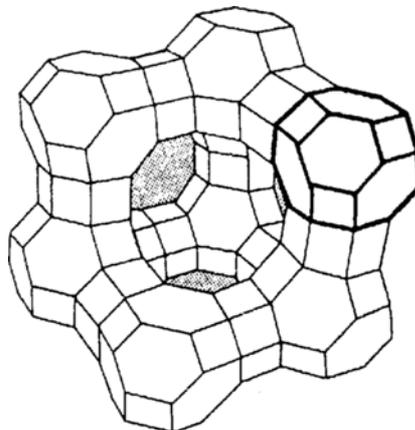


Figure 1. A view of the framework structure of zeolite-Y (faujasite).

as a cracking catalyst and the latter is being used for xylene isomerisation and the conversion of methanol to gasoline. We shall also examine the prospects for simulating catalytic reactions by using a combination of molecular mechanics and molecular orbital calculations.

2. Adsorption and activation energies

Work in this area was pioneered by Kiselev and co-workers (Kiselev *et al* 1978). The initial step involves the calculation of the interaction energy, $\phi(\text{tot})$, between the hydrocarbon and the zeolite. Several approximations are made:

- (1) the zeolite is assumed to be rigid and unperturbed by the presence of the solute molecule;
- (2) the hydrocarbon is assumed to be rigid and present in very low concentrations;
- (3) the interaction is described by a simple atom-atom potential. We have used a potential of the form:

$$\phi(\text{tot}) = \sum_{ij} \left[\frac{B}{r^{12}} - \frac{A}{r^6} + \frac{cq_i q_j}{r} \right]. \quad (1)$$

Values of A and B were determined semi-empirically (Kiselev *et al* 1978) by fitting experimental data for methane in zeolite-Y (one of the faujasite family) and the charges for the electrostatic term were obtained from molecular orbital calculations on both the hydrocarbons and the zeolites. Equation (1) must be sampled for all orientations of the hydrocarbon molecule, and at all positions in the cage, in order that the following integrations can be performed:

$$I_1 = \int_v \exp[-\phi(\text{tot})/RT] dv, \quad (2)$$

$$I_2 = \int_v \phi(\text{tot}) \exp[-\phi(\text{tot})/RT] dv. \quad (3)$$

The internal energy of adsorption, $\Delta U(\text{ads})$ can then be calculated according to the mean value theorem:

$$\Delta U(\text{ads}) = \bar{\phi}(\text{tot}) = I_1/I_2. \quad (4)$$

This gives the Boltzman-weighted interaction energy, thus accounting for entropy effects which distribute the molecule over an increasing number of sites as the temperature is increased. For example, though the minimum energy, $\phi(\text{min})$, of methane in zeolite-Y is -23.0 kJmol^{-1} , the molecule would only be expected to occupy the position with this energy at very low temperatures. At room temperature, however, $\bar{\phi}(\text{tot})$ is only -13.3 kJmol^{-1} .

In the table below, we compare the calculated and experimental adsorption energies for a series of hydrocarbons in zeolite-Y. As the molecules become larger, the energies increase. These values correspond to the energies of isolated molecules and are only valid at infinite dilution when intermolecular interactions can be ignored. We are currently working on the calculations at higher hydrocarbon loadings.

Activation energies are also of interest since they provide a means of rationalising some of the factors that control hydrocarbon diffusion in zeolites. Bezus *et al* (1984) calculated E by taking the difference between the minimum energy position, $\phi(\text{min})$, and the lowest barrier. Given that the molecules have only a low probability of occupying this site at ambient temperatures, the approach seems to be over-simplistic. We have chosen to take the difference between $\bar{\phi}(\text{tot})$ and the weighted-average energy of the molecule as it passes through the ring into the next cage, $\bar{\phi}(\text{ring})$. In the case of propane in zeolite-Y, the predicted value of the activation energy is 13 kJmol^{-1} , compared with the experimental value of $9.8 \pm 1.5 \text{ kJmol}^{-1}$ (Pfeifer 1981). One of the interesting conclusions that emerge from such calculations is that high activation energies often stem from large values for the heat of adsorption, rather than high ring barriers. A comparison of diffusion rates for 1,3,5-trimethylbenzene and its trimethyl-aniline analogue, in zeolite-Y, provides an interesting example. The sizes and shapes of the two molecules are almost identical, but their experimental activation energies are 38 and 71 kJmol^{-1} , respectively. Our calculation shows that much of this difference stems from the stronger interaction of the more polar amine molecule with the zeolite framework, leading to a substantially more negative value for $\bar{\phi}(\text{tot})$.

3. Experimental location of guest molecules

The treatment described in §2 provides a basis for predicting not only the energetics of adsorption, but also the location of adsorbed molecules. We have seen that, at ambient

Table 1. Internal energy of adsorption of hydrocarbons in zeolite-Y/ kJmol^{-1} .*

	Calcd.	Exptl.
CH ₄	13.3	15.2
C ₂ H ₆	21.5	23.3
C ₃ H ₈	30.1	32.3
C ₄ H ₁₀	35.2	37.4

* A K Nowak and A K Cheetham (unpublished results)

temperatures, the molecules are likely to be distributed over several sites, but their positions at low temperatures provide a useful test for the molecular graphics calculations since they should correspond to the positions of $\phi(\min)$. There have been no single crystal diffraction studies of zeolite-adduct complexes, but, recently, several studies by high resolution powder neutron diffraction have been reported. These include the location of Xe in zeolite- ρ (Wright *et al* 1984), CO in zeolite-A (Adams and Haselden 1984), benzene in zeolite-Y (Fitch *et al* 1985), and pyridine in zeolite-L (Wright *et al* 1985). In the latter instance, the molecule occupies a single site in the main channel, at 4K, coordinated to a potassium ion through the nitrogen of the pyridine ring (figure 2). Molecular graphics calculations (figure 3) predict the location and orientation of the molecule within 0.2Å of the observed position, thus lending credence to the validity of both the experiment and the simulation.

4. Shape-selective catalysis in zsm-5

A great deal of recent interest has focused on the catalytic properties of the synthetic zeolite, zsm-5, first reported in 1972 (us patent 1972). Like most other zeolites, it owes its catalytic activity to the presence of Brønsted acid sites (protons attached to framework oxygen atoms) and its specificity to the shape and size of its channels (figure 4). One of the reactions for which it is used extensively is the isomerisation of xylenes (figure 5). An interesting feature of this reaction is that the useful product, paraxylene, which is used in the manufacture of polyesters, is significantly more mobile than the meta-derivative. A molecular graphics study of the mobility of *p*- and *m*-xylenes in zsm-5 reproduces this behaviour by means of a colour-contoured, potential

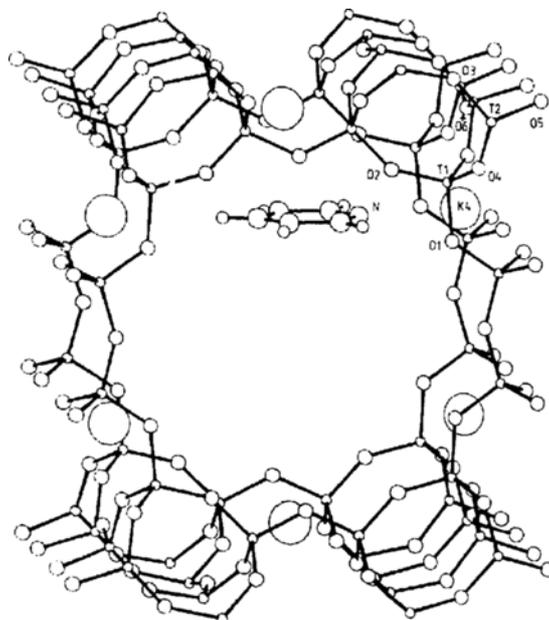


Figure 2. The location of pyridine in the main channel of potassium zeolite-L.

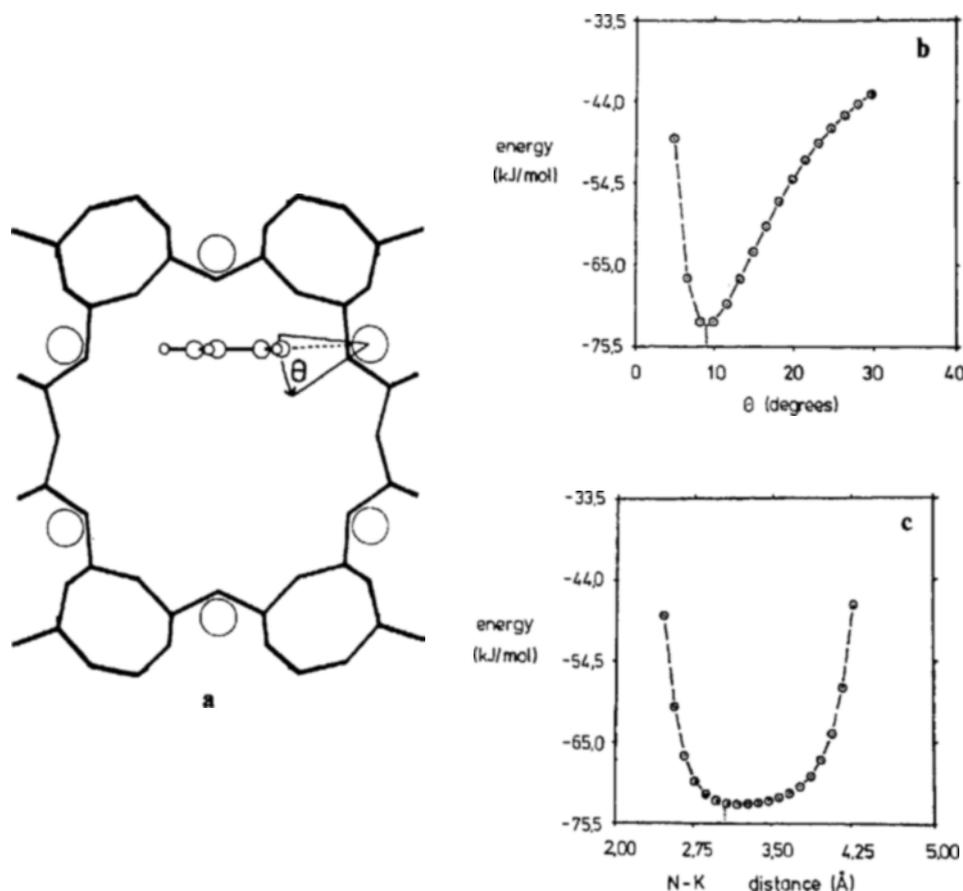


Figure 3. (a) A view of the pyridine molecule down [001] showing the angle θ which was varied for the calculations presented in (b). (b) The interaction energy between pyridine and zeolite-L as a function of angle θ , the observed angle is indicated by a dotted line. (c) The interaction energy as a function of the K(4)-N distance at $\theta = 8.8$; the observed position is again indicated.

energy diagram, which shows the variation of $\phi(\text{tot})$ as a function of the angular orientation and position of the molecule in the zeolite channel.

But perhaps the ultimate goal of the molecular graphics work is the simulation of a catalytic reaction by means of a combination of molecular graphics procedures, described here, and off-line molecular orbital calculations. We have now developed a methodology for this procedure and can illustrate it with some preliminary results on the xylene isomerisation. The initial step of the reaction, which is assumed without comment in other theoretical treatments (Corma *et al* 1979; Nebot *et al* 1981), is shown in figure 6. We have performed molecular orbital calculations (GAUSSIAN 80) on the four species A-D (for $X = \text{OH}$), and calculated the interaction energies, A-B and C-D, as described in §2. On this basis, the estimated activation energy for this initial step is

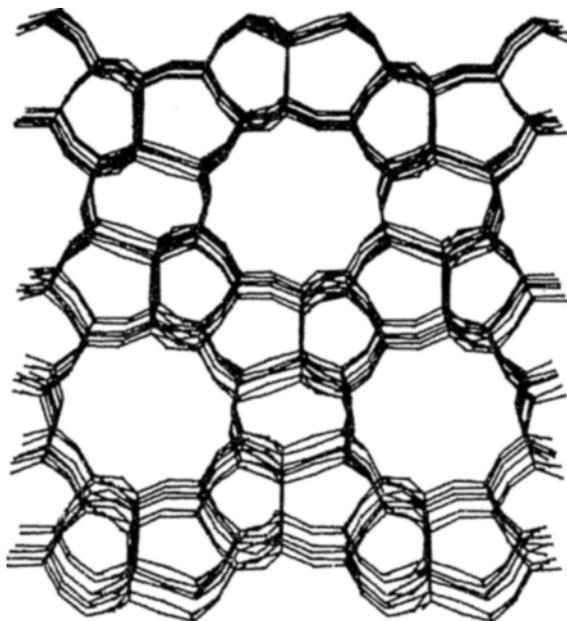


Figure 4. The framework structure of ZSM-5, viewed down [010].

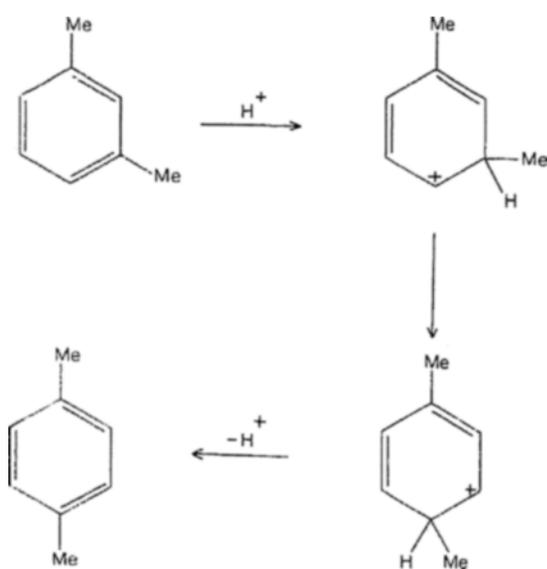


Figure 5. The isomerisation of xylenes.

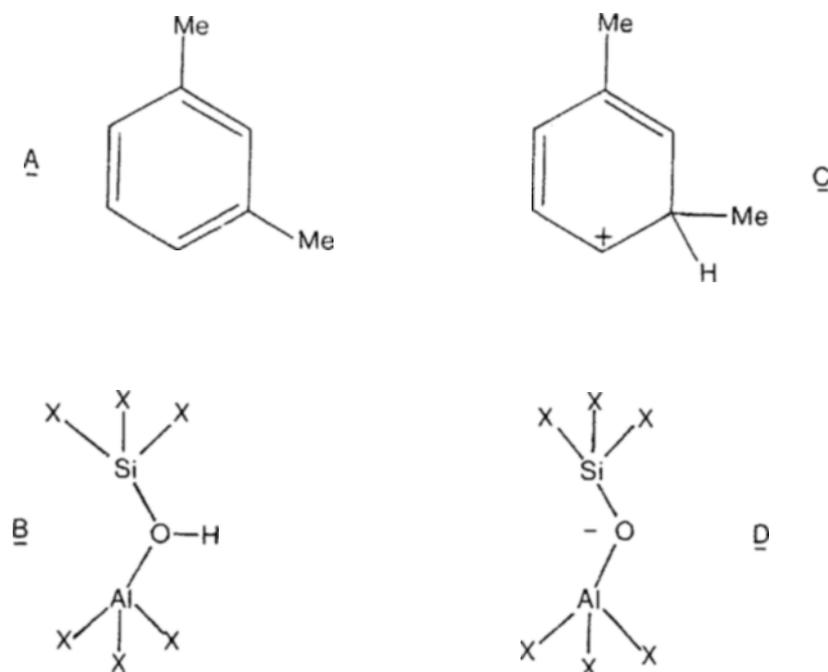
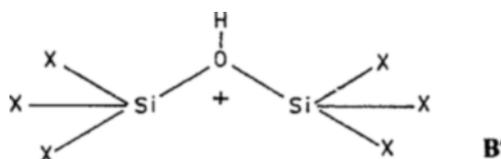


Figure 6. Species involved in the first step of isomerisation $A + B \rightarrow C + D$.



$\sim 634 \text{ kJmol}^{-1}$! If, however, we consider an acid site, B' , in which Al is replaced by Si, the O–H bond strength is much weaker, i.e. the acidity is much greater, and the activation energy is reduced by $\sim 540 \text{ kJmol}^{-1}$ to $\sim 90 \text{ kJmol}^{-1}$. The molecular orbital calculations require refinement by means of energy minimisation, but if the preliminary findings are confirmed, the results will have interesting implications in zeolite catalysis.

5. Conclusions

Recent work has shown that molecular graphics can play a vital role in enhancing our understanding of catalytic processes in zeolites, but a great deal remains to be done. Future work must explore some of the approximations that are currently being made, in particular the rigidity of both the framework and the guest molecules, but the techniques that are necessary to achieve this have been applied elsewhere and rapid progress can be anticipated.

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