Modelling of Catalysts and its Relation to Experimental Problems [and Discussion]

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Modelling of catalysts and its relation to experimental problems

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We illustrate the role of both computer simulation and the evaluation of electronic structure in the study of solid heterogeneous catalysis by reference to recent work in this laboratory on (*a*) microporous materials (that have a spatially uniform distribution of accessible active sites) and (*b*) non-porous metal oxides. Computational methodologies may be used to model, first, the structure of the uniform catalysts both before and after thermal activation, second, the docking and diffusion of molecules in solids and on their surfaces; and, third, the reaction pathways of molecules at the active site. We highlight recent successes in modelling (i) the structures of zeolitic solids, (ii) the sorption of hydrocarbons within them, (iii) the protonation of small molecules at the Brønsted acid sites in uniform solid acid (zeolite) catalysts, and (iv) the reactions of small molecules on CeO_2 and MgO surfaces.

1. Introduction

Quantitative modelling is of greatest value when used directly in conjunction with experiment. It serves to confirm existing data, to interpret unusual or counter-intuitive discoveries, and to achieve aims not otherwise attainable except by synergistic use of computational techniques and experiment. The full potential of these methods has not yet been realized, but it is becoming increasingly possible to obtain information which is not in practice retrievable by experiment as well as to predict altogether new phenomena, structures and new processes.

Despite the considerable recent successes of quantitative modelling, there have not hitherto been many examples where it has been so indisputably ahead of experiment that new phenomena have been discovered through its sole deployment. Channelling of ion and atom beams in crystalline solids is one notable exception. More often, however, experiment has driven the modelling, in some instances for several decades. A good example of the latter is the 7 × 7 surface reconstruction of the silicon (111) surface which was discovered by low energy electron diffraction by Schlier & Farnsworth (1959). This reconstruction was more clearly identified experimentally by Takayanagi *et al.* (1985). It has very recently given rise to sophisticated *ab initio* total-energy calculations (Stich *et al.* 1992; Brommer *et al.* 1992), using parallel super-computers that 'predict' the details of the dimerization–adatom movements and stacking fault changes in the outermost layers of the silicon established by experiment. In reality, these sophisticated techniques do not really predict the 7 × 7 reconstruction: instead, they arrive at the same quantitative details that were first

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derived by direct experiment. Another example, symptomatic of current trends in modelling of solids is the work of O'Keeffe *et al.* (1992) on predicted new low-energy forms of carbon. Prompted by the isolation of microscopic amounts of fullerenes (in particular C_{60}) – in this case 'prediction' is quite genuine – solids of hitherto unknown structures are shown to be of lower energy than well-known stable polymorphs. O'Keeffe *et al.* used a first-principles molecular-dynamics technique to find the relaxed atomic geometries and corresponding electronic structures of several simple novel forms of three-coordinated solid carbons. One of these forms, which they termed polybenzene, was found to have a substantially lower energy (0.23 eV per atom) than C_{60}. Its isolation has not yet been reported, but is the subject of current experimental work.

In the modelling of heterogeneous catalysts, great progress may be made on those that are *uniform*, in the sense that the active sites (see below) are distributed in a spatially uniform fashion throughout the solid, which has the extra advantage – because of the zeolitic structure – of having all atoms in the bulk accessible to the reactant species which diffuse within the micropores that permeate the entire crystalline solid. Owing to the translational symmetry of these structures of uniform heterogeneous catalysts, which are also monphasic, they are much more amenable to theoretical investigation than those catalysts that are multiphasic and multi-component (Thomas 1988, 1990, 1992).

In this paper we concentrate on the application of modelling to zeolitic and metal oxide catalysts. As noted, the zeolitic, uniform heterogeneous catalysts are well suited to a variety of modelling techniques. Moreover, as we describe below, they have the extra advantage of having been the subject of extensive experimental study so that the task of blending modelling with direct experimental approaches is straightforward. Quantitative measurements have already been performed – in many instances by us and our collaborators – on a number of the properties and phenomena upon which we focus in this paper. These include the following.

1. The location, energetics and diffusivity of guest (potentially reactive) molecules inside a zeolitic catalyst or a realistic model analogue of such a catalyst (Freeman *et al.* 1991; Shubin *et al.* 1992).
2. The Brønsted acidity of the active site in zeolitic solid acid catalysts.
3. The migration of transition-metal ions, such as Ni^{2+}, that function as the locus of catalytic conversion in such processes as the cyclotrimerization of acetylene over (Ni^{2+}, Na^{+})-exchanged zeolite Y (Maddox *et al.* 1988; Couves *et al.* 1990; Thomas 1990).
4. The stability and dynamic properties of a range of germanium-containing zeolites (George *et al.* 1992*b*), where we are able to predict stability for a class of compounds that has not yet been prepared.

Our work on metal oxide catalysts is predominantly concerned with those (like many fluorite structured oxides, pyrochlores, perovskites, spinels and other relatively simple ionic-covalent oxide structures) that entail sacrificial loss of oxygen (Catlow *et al.* 1990). Experiments using isotopically labelled reactants or labelled solid catalysts reveal that structural oxygen is removed from the catalyst by the reactant, thereby rendering it, at least temporarily, a non-stoichiometric oxide. Gaseous oxygen (also a reactant) is then taken up by the catalyst, thus making good its anion deficiency. The cycle repeats itself for as long as the catalyst is active. As an example of the role of modelling in this field we describe the recent work of Sayle *et al.* (1992) which has shown how high-energy surfaces of CeO_2 may readily oxidize CO to CO_2.

We also highlight a recent study of Shluger *et al.* (1992) on the mechanism of catalytic dissociation of H_2 on the surface of MgO.

The central theme of this paper is that most of the key issues in contemporary studies of catalysis are amenable to investigation by theoretical techniques. They include the detailed *structure of the solid or surface* in or on which the reaction takes place and the way in which this is modified during the activation of the catalyst, the *nature and structure of the active site*, the *diffusion* towards and *docking* at the active site of sorbed molecules, and the *mechanisms of reaction* of the docked molecules. Moreover, as we shall show, computational techniques are able to identify the critical factors controlling catalytic performance and to guide the experimental modification of catalytic materials.

2. Methodologies

The complexity of the problems posed by catalytic systems necessitates the use of the widest possible range of computational and theoretical techniques, often in a concerted manner. Recent studies of ourselves and others have involved the full battery of *simulation techniques* (in which knowledge of electronic structure is subsumed into effective interatomic potentials). These include the following.

1. *Energy minimization*, in which the minimum energy configuration corresponding to the specified potential is obtained using an iterative numerical technique from a specified initial configuration. The method has now reached a high degree of precision in the modelling of both the crystal structures of complex inorganic materials (including microporous catalytic solids) and of surface structures: problems that are clearly of vital importance in the study of heterogeneous catalysis. Indeed, we show below that such calculations may be undertaken routinely on highly complex systems. In addition the methods may be used to simulate local structural changes around dopants and heteroatoms in solids and on surfaces and the positions and energetics of extra framework cations in microporous solids, examples of which will be given later in this paper. Another and related range of applications of minimization methods is to the location of the minimum energy site for adsorbed molecules in pores and on surfaces, and, as shown later, minimization methods may be fruitfully combined with other simulation techniques to allow such calculations to be undertaken in an automated manner.

2. *Monte Carlo*, in which ensemble averages are computed by numerical procedures which entail the generation of an ensemble of configurations by a series of random moves, with the probability of a configuration being accepted into the ensemble normally being dependent on its Boltzmann factor. The most obvious role of such methods, in the present context is in studying the distribution (and its temperature dependence) for adsorbed molecules over the available sites within a solid and on its surface, a good example of which is given in the work of Yashonath *et al.* (1988).

3. *Molecular dyamics*, in which kinetic energy is included explicitly in the simulations which solve numerically the classical equations of motion of the system simulated. The technique allows us to model the detailed dynamical behaviour of the system and to simulate diffusion directly. In the work described later in this paper classical microcononical ensemble (NVE) techniques have been used on an ensemble to which periodic boundary conditions have been applied to generate an infinite system.

The quality of the interatomic potentials used in such studies is obviously of crucial importance. For ionic and semi-ionic solids, Born model potentials based on formal or partial charges have been extensively and successfully used. Short-range interactions are modelled by two and three body analytical functions, and where possible polarization effects should be included via a shell model formalism. Extensive reviews are available in Harding & Stoneham (1988) and Catlow & Cormack (1987). Molecular mechanics force fields, in which the conceptual starting point is the covalently bonded network (in contrast to the Born model which perceives the solid as an assembly of interacting ions) are being increasingly used for modelling microporous solids. Such models, which require the specification of bond-bending, bond-stretching and torsional parameters, must be used in describing the internal force field of sorbed molecules.

For both types of potential the crucial issue is parametrization. Empirical methods, which require fitting unknown parameters to the properties of model compounds, have been widely used. The availability of increasingly high quality potential energy surfaces from quantum mechanical methods using both Hartree–Fock and local density techniques (Gale *et al.* 1992; Purton *et al.* 1992; Harrison & Leslie 1992) in both cluster and periodic boundary calculations is leading to a new level of precision which has greatly extended the predictive capacity of simulations.

4. *Electronic structure* methods may use semi-empirical or *ab initio* techniques employing single and multi-determinantal Hartree–Fock procedures or local density approximation (LDA) methods. And calculations may be performed on both cluster or periodic systems. All these approaches are reviewed elsewhere in these proceedings. In the context of catalytic studies we should emphasize the following factors.

(*a*) *Semi-empirical techniques* continue to have an important role. They allow us to study large numbers of atoms, and to obtain approximate information on geometries which may then be refined by *ab initio* calculations. These are particularly helpful in assessing properties such as the Brønsted acidity of a zeolitic catalyst (see below).

(*b*) Particular care must be paid to the *embedding techniques* used in cluster calculations. It is necessary that these are such as to reproduce accurately the electric potential and fields within the cluster and that the termination effects associated with the outermost atoms are minimal. Procedures discussed by Shluger *et al.* (1992) in this volume allow us to interface simulation with quantum cluster techniques in a way which achieves accurate and consistent embedding.

(*c*) Both LDA and Hartree–Fock methods have valuable roles to play. The former may allow larger clusters to be studied at the *ab initio* level, but the latter may profit from the substantial experience gained with their use in molecular quantum chemistry.

In summary we repeat the importance of a concerted strategy in theoretical studies of catalytic materials. Simulations are the appropriate technique for studying the structure of the solid and the docking and diffusion of sorbed molecules within it. Electronic structure methods allow us to model the reaction pathways of the molecule at the active site. Simulation and quantum mechanical methods may be combined as in the calculations discussed by Shluger *et al.* (1992); and, as already noted, electronic structure methods are playing a growing role in yielding high-quality potentials for subsequent use in simulations.

Table 1. *Energies* (kJ mol^{-1} TO_2 unit^{-1}) *relative to the quartz structure for* SiO_2 *and* GeO_2 *forms of various microporous structures*

	energy	
	SiO_2	GeO_2
silicalite I	11.2	12.5
mordenite[a]	20.5	16.1
faujasite[a]	21.4	24.5

[a] Whereas silicalite may be prepared (in either of two polymorphic forms I and II or in intergrowths of the two) in the pure siliceous state, neither faujasite nor mordenite may be synthesized in the pure siliceous form. Each of them can, however, be dealuminated to Si/Al ratios in excess of 100.

3. Recent applications

(*a*) *Modelling structures*

A high degree of accuracy is now possible in crystal structure modelling using minimization methods with currently available potentials. Several examples are provided by microporous solids and include the study of the small monoclinic distortion in silicalite by Bell *et al.* (1990) and the impressive recent study of Shannon *et al.* (1991) on the new zeolite Nu87: here modelling work revealed a low symmetry distortion which allowed a full refinement of high resolution power diffraction pattern for the material which had not been refineable using previously proposed higher symmetry structures.

The capability of modelling methods for structure *refinement* is therefore clearly established. More exciting applications concern the *prediction* of new structures. In this context the recent work of George *et al.* (1992*b*) is of particular note. This study examines the stability of a number of germanium analogues of zeolites. The stabilities of several GeO_2 'zeolitic' structures relative to those of the GeO_2 quartz structures are given in table 1 where they are compared with siliceous versions of the same structural types. Although there are significant differences between the relative energies of the SiO_2 and GeO_2 polymorphs, the results indicate that, in general, microporous Ge compounds should have roughly similar relative stabilities to the siliceous analogues. It would therefore be of considerable interest to attempt to synthesise these compounds. Already the synthesis and structure of a new microporous anionic derivative of GeO_2 has been accomplished in this laboratory (Jones *et al.* 1992).

Perhaps the most challenging problems concern the modelling of the structural changes during catalyst activation. A study of George *et al.* will show how detailed information may be obtained for a widely studied (Maddox *et al.* 1988) material, namely Ni-zeolite Y, for which activation is known to involve migration of Ni^{2+} ions from the hexagonal prism (S_I) sites into supercage positions as shown schematically in figure 1*a*. In a preliminary study George *et al.* (1992*a*) showed how the S_I, Ni^{2+} ion is stabilized by an extensive relaxation (0.5–0.8 Å†) of the surrounding oxygen ions: a result which nicely explains recent EXAFS data (of Dooryhee *et al.* 1990, 1991) on the dehydrated Ni-zeolite Y system. More detailed simulations were, however, able to follow the change in the energy of the Ni^{2+} as it moves out of the S_I site, through

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† 1 Å = 10^{-10} m = 10^{-1} nm.

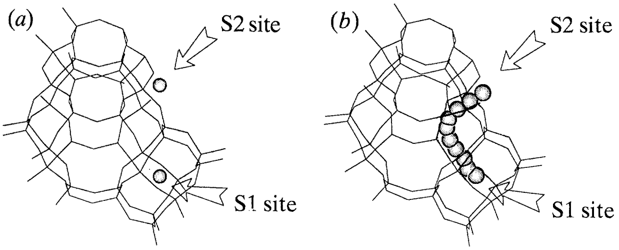

Figure 1. (*a*) S_I and S_{II} sites in zeolite Y. (*b*) Schematic trajectory of Ni ion migrating between S_I and supercage sites.

the sodalite cage and into the supercage, as illustrated in figure 1*b*. The highest energy point on this trajectory has an energy of *ca.* 2 eV relative to the S_I, Ni^{2+}, ion. Further calculations using *ab initio*, quantum mechanical techniques investigated the interaction of the Ni^{2+} ion at the saddle point with ligands including water NH_3 and acetylene situated at the neighbouring six-ring site. These molecules are known to assist (Couves *et al.* 1990) the activation of the catalyst; and the magnitude of the calculated interaction energies, which preliminary results suggest is in the range 2–3 eV indicates that such interactions are sufficient to overcome the energy barrier to motion from the S_I site supercage. The calculations have therefore allowed us both to follow the changes in ionic positions occurring during the activation of the catalyst and to understand how this is promoted by various reagents. We know from experiment, that reactant acetylene first 'draws out' the Ni^{2+} from the S_I site. Only after there are Ni^{2+} (or Ni^{+}) ions in the supercage does cyclotrimerization of the acetylene to benzene ensue.

(*b*) *Sorption, docking and diffusion*

(i) *Locating energy, minima*

The value of energy-minimization procedures in modelling the docking of molecules in zeolites was shown by the early work of Wright *et al.* (1985) who located the site occupied by pyridine in zeolite L. More recently Titiloye *et al.* (1990) reported a detailed series of energy minimization calculations on hydrocarbons in the C1–C8 range obtaining sorption energies in good agreement with experiment; these calculations also showed the important role of framework relaxation in lowering the sorption energy (*ca.* 20 kJ mol^{-1} for the larger hydrocarbons).

A substantial technical development was reported by Freeman *et al.* (1991), whose approach has been exploited and extended recently by Shubin *et al.* (1992). This novel method involves a combination of molecular dynamics (MD) Monte Carlo (MC) and energy minimization (EM) methods. The MD of the isolated molecules is undertaken in order to generate a library of low energy conformational states; each of these is then introduced randomly into the zeolite, and the resulting configuration is retained if its energy falls below a specified threshold value. All accepted configurations are then submitted to energy minimization. In the initial study of Freeman *et al.* (1991) the framework was constrained to be rigid, but in the more recent work of Shubin *et al.* (1992) framework relaxation was included.

Freeman *et al.* (1991) considered the topical case of the sorption of butene isomers in ZSM-5, which catalytically converts but-1-ene into isobutene (which is subsequently used in synthesis of the methyl tertiary butyl ether (MTBE) blending

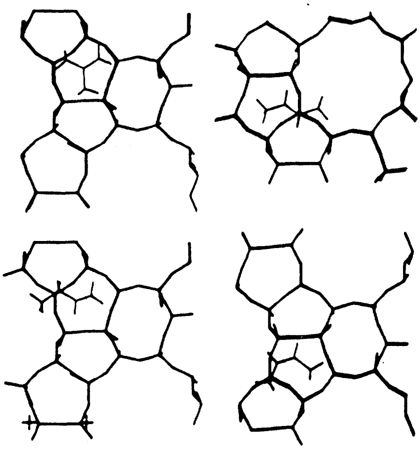

Figure 2. Low energy configurations for the four isobutene isomers in silicalite.

Table 2. *Butene isomer binding energies in silicalite*

isomer	calculated minimum energy/(kJ mol^{-1})	calculated average energy/(kJ mol^{-1})	relative minimum energy/(kJ mol^{-1})	relative average energy/(kJ mol^{-1})
2-methyl propene	−38.58	−28.09	0	0
but-1-end	−54.30	−44.41	−15.72	−16.30
cis-but-2-ene	−45.45	−31.64	−6.87	−3.55
trans-but-2-ene	−48.76	−38.44	−10.18	−10.35

agent). Their results for the four isomers are presented in table 2 which gives the minimum energy configurations (illustrated in figure 2) and the average energies of the docked minimized structures. By both criteria it is clear that isobutene is the least strongly adsorbed of the isomers: a result which is fully consistent with it being the dominant product in the isomerization. Moreover, the automated nature of these techniques would permit their use in a routine manner to screen modified or different zeolites to maximize the shape-selective discrimination between the different isomers.

The work of Shubin *et al.* (1992) explored the sorption of butanols in silicalite H-ZSM-5, following earlier experimental catalytic studies of Williams *et al.* (1990) and Stepanov *et al.* (1992). The results are summarized in table 3 while in figure 3 we display two of the energy minima. The calculations reveal that for all four butanol isomers, the predicted adsorption energies are only slightly different from one another. Second, the total adsorption energy increases only by 6–15 kJ mol^{-1} in H-ZSM-5 which is less than the expected value of 25–30 kJ mol^{-1}. This may be due to pore-confinement effects in the adsorption of C4 alcohols in H-ZSM-5. It seems that it is difficult to find any conformation for the C4 alcohol in the vicinity of the bridging OH-group in H-ZSM-5 without increasing the internal strain of the alcohol molecule and of the zeolite lattice. For *iso*-butanol, we can explain the similar adsorption energies in both silicalite and H-ZSM-5 as this is a bulky isomer while for both butanol-1 and butanol-2 and also for *tert*-butanol it is easier to optimize their positions for each within one of the zeolite channels. We also note, that, as a rule, for adsorption on both silicalite and H-ZSM-5, the energy values obtained for

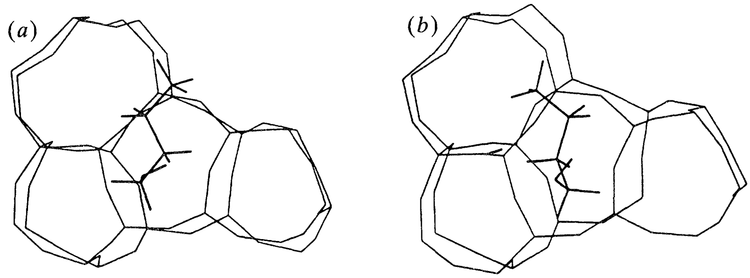

Figure 3. Examples of final butanol-1 positions in relaxed framework structure. (*a*) Butanol-1 in zig-zag channel of silicalite and (*b*) butanol-1 and bridging hydroxyl group (shown in bold lines) at position (19, 43, 4) in H-ZSM-5 [10].

Table 3*a*. *Low sorption sites and energies for butanol isomers in silicalite*

(All sorption energies are with respect to the zeolite and molecules at infinity and are given in kJ mol^{-1}. Channels: s, straight; si, straight near intersection; z, zig-zag; zi, zig-zag near intersection.)

butanol-1	butanol-2	*tert*-butanol	*iso*-butanol
−132.25 (z)	−117.47 (z)	−114.18 (z)	−121.31 (s)
−117.44 (z)	−111.69 (s)	−113.85 (s)	−119.87 (z)
−117.37 (s)	−102.67 (z)	−111.56 (z)	−119.79 (si)
−116.47 (si)	−102.27 (zi)	−109.54 (si)	−118.11 (si)
	−100.58 (zi)	−108.93 (zi)	−108.04 (zi)

Table 3*b*. *Low energy sorption sites and energies for butanol isomers on H-ZSM-5* (kJ mol^{-1})

(A cross (×) marks positions for which the lattice relaxation calculations were unsuccessful due to excessive distortions in the framework structure.)

crystallographic position of OH[a]						
Al	O	Si	butanol-1	butanol-2	*tert*-butanol	*iso*-butanol
2	13	8 (s)	−115.09	−112.93	−116.67	×
7	17	16 (z)	×	×	−129.06	−119.10
20	33	19 (si)	−119.52	−126.50	−124.32	−119.88
7	7	8 (si)	×	×	×	×
19	43	4 (z)	−138.42	−126.83	−120.37	−114.57
16	17	7 (z)	−120.42	−109.18	−105.09	×
14	32	18 (z)	−127.36	×	−110.98	−117.20
1	1	2 (s)	×	−113.08	×	×

[a] Using notation of Schröder *et al.* (1992*b*).

positions in straight and zig-zag channels and channel intersections are not very different. At all but the lowest temperatures, we would therefore expect the butanols to be distributed over a variety of sites.

Modelling methods may therefore predict sorption sites and energies both routinely and reliably. We now consider the more demanding problems posed by simulating dynamical behaviour.

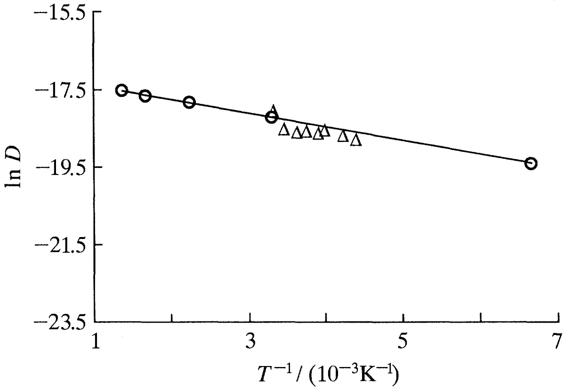

Figure 4. Calculated Arrhenius plot of CH_4 in silicalite obtained using MD simulations by Kawano *et al.* (1922).

Table 4. *Calculated diffusion coefficients* ($cm^2\ s^{-1}$) *for hydrocarbons in silicalite*
(Numbers in parentheses indicate concentration in molecules per unit cell.)

molecule type	D (10^7)	molecule type	D (10^7)	molecule type	D (10^7)	molecule type	D (10^7)
methane (1)	410	methane (2)	1340	ethane (1)	692	ethane (2)	620
propane (1)	56.3	propane (2)	68	butane (1)	7	butane (2)	14
hexane (1)	14.4	hexane (2)	9.6				

(ii) *Molecular dynamics simulation of diffusion*

Recent studies (see, for example, Pickett *et al.* 1988; Demontis *et al.* 1988; Goodbody *et al.* 1991) have demonstrated the power of MD techniques in directly simulating diffusion of adsorbants in zeolites. The value of such studies in revealing both quantitative and qualitative information on diffusion rates and mechanism is shown by recent work of Kawano *et al.* (1992) and Hernandez *et al.* (1992*a*, *b*). These calculations, which included full framework flexibility were performed using standard microcanonical ensemble (NVE) MD. The results for methane are summarized in figure 4 in the form of an Arrhenius plot, which shows the excellent measure of agreement between calculated and measured diffusion coefficients.

Calculated diffusion coefficients for C1–C6 hydrocarbons are given in table 4. The values obtained for ethane and propane are in good agreement with experimental measurements obtained with the single-step frequency response (SSFR) (Den-Begin *et al.* 1989), and pulsed-field gradient (PFG) NMR techniques (Den-Begin *et al.* 1989; Caro *et al.* 1985). As noted by Den-Begin *et al.* (1989), values obtained with the PGF NMR techniques are approximately five times as large as those obtained with the SSFR method. Our values are compatible with both experimental measurements. The results for butane compare very well with those reported by Shen *et al.* (1991) measured with the SSFR technique, but those for hexane are higher than the reported experimental values of Den-Begin *et al.* (1989).

Analysis of the molecular trajectories shows that the molecules diffuse by means of 'jumps' whose distance is approximately equal to 0.5 lattice units (*ca.* 10 Å). For paraffins the channel intersections are energetically less favourable so that the molecules tend to reside in either the straight or the sinusoidal channels, and diffusion along a given channel will consist of a series of jumps across the channel

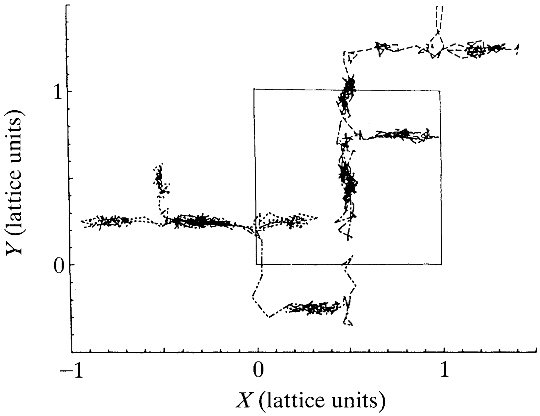

Figure 5. Trajectory plot for ethane in silicalite (at 300 K) illustrating movement of molecule between different channel systems.

intersections. However, a molecule that was originally diffusing along a straight channel can leave it through the sinusoidal channel. Examples of this kind of motion have been identified in our trajectory plots (as shown in figure 5).

A decrease in the diffusivity with increasing concentration of adsorbed molecules has been observed experimentally (Den-Begin *et al.* 1989; Caro *et al.* 1985) and predicted by simulation (June *et al.* 1990; Goodbody *et al.* 1991). As pointed out by Den-Begin *et al.* (1989), when the diffusion takes place by means of jumps, there are two possible mechanisms to explain this behaviour: (*a*) a reduction in the mean molecular jump length and/or (*b*) a decrease in the frequency of jumps. In our simulations we see no decrease in the mean jump length, though we cannot discount this type of mechanism at higher loadings.

The computational demands of such calculations should not be underestimated. It is necessary to run the simulations for long periods (>100 ps) if reproduceable data are to be obtained. Such calculations are, however, becoming increasingly feasible with the new generation of parallel architectured machines which offer exciting opportunities for these types of investigation.

(*c*) *Modelling of active sites and reaction mechanisms*

In this, the most challenging of the fundamental problems posed by catalytic studies, electronic structure techniques clearly become necessary, although simulation methods still have a considerable role to play, as is illustrated by recent studies both by Brønsted acid sites in zeolites and of CO oxidation on CeO_2.

(i) *Brønsted acid sites and protonation reactions in zeolites*

A simplifying feature of zeolite catalysis is the fact that in many reactions the dominant active site is well defined, i.e. the protonated oxygen neighbouring a tetrahedral Al atom (or AlOH complex). Many studies using both quantum mechanical and simulation techniques have been reported of the fundamental properties of this centre (see, for example, Sauer 1992; Sim *et al.* 1991; Cheetham *et al.* 1984; Schröder *et al.* 1992*b*).

Recent studies of Schröder *et al.* (1992*a*, *b*) have demonstrated the value of simulation techniques in this field. Using lattice energy minimization methods based on effective potentials they investigated the Brønsted acid site in both faujasite and

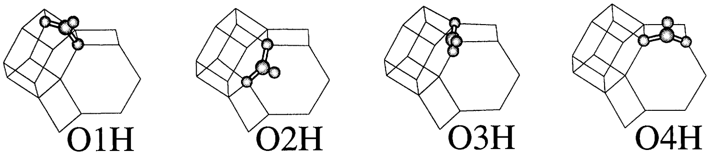

Figure 6. Brønsted acid sites in zeolite Y.

ZSM-5. The former is relatively simple as there is only one crystallographic T site, although there are four distinct types of oxygen site (see figure 6).

The calculations identify the O3 and O1 sites as being the most favoured for protonation (but with a small energy difference of *ca.* 5 kJ mol^{-1}). Calculations of the deprotonation energies indicate that the protonation of the O1 group results in slightly higher acidity. The calculations yield detailed information on the geometry of the AlOH group, showing, in particular, that the Al–O bond is surprisingly long (*ca.* 1.9 Å); they also yield vibrational frequencies that accord well with experiment. Moreover, the results from the simulation studies are in good agreement with earlier quantum mechanical calculation of Sauer *et al.* (1989). They establish the reliability of simulations (with carefully chosen potential parameters) in modelling the structures and properties of this type of acidic site.

The work of Schröder *et al.* (1992*b*) examined the more difficult problems of the location of the AlOH complex in ZSM-5, in which there are 12 crystallographically distinct T sites. They found that there are only small differences between the energies of the complex at different sites and, indeed, the results would lead us to expect a distribution that is close to random. These predictions contrast with those of previous studies (Derouane & Fripiat 1985); the latter work, however, was shown to be inadequate due to the omission of framework relaxation, which can be straightforwardly included in simulation studies.

Having identified the nature of the Brønsted acid site, the next stage is to study the mechanisms of the protonation reactions. Recent work has been undertaken in this field by J. D. Gale who has used both semi-empirical and *ab initio* techniques to investigate the protonation of small molecules (H_2O, NH_3, CH_3OH) at the Brønsted acid site in zeolites. The calculations used clusters which allows interactions of the molecule with both edge and face configurations to be studied. The results obtained on H_2O and NH_3 indicate the intriguing possibility of the protonated forms of these molecules docking above the face of the AlO_4 tetrahedron as illustrated for the case of NH_3 in figure 7. The stability of these configurations was supported by *ab initio* studies, although their energies with respect to the AlOH complex and the unprotonated molecules are still somewhat uncertain.

Further calculations are in progress aimed at examining the interaction of the Brønsted acid sites with organic molecules. The combination of the use of semi-empirical techniques for exploring a wide range of conformations with the use of *ab initio* techniques to refine the information on low energy structures is, we consider, a powerful strategy in catalytic studies.

(ii) *Oxide surfaces*

Again we find an important role for both simulation and quantum chemical methods in studying reactivity on oxide surfaces. As an example of the former, we cite the recent work of Sayle *et al.* (1992) who studied the interaction of CO with the surface of CeO_2. Simulations using an infinite two-dimensional periodic surface

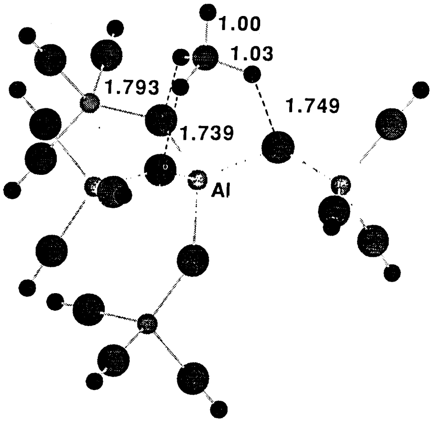

Figure 7. Protonated configuration of NH_3, above the face of an AlO_4 tetrahedron (as predicted by Gale (1992)). The protonated molecule binds to the tetrahedron via three hydrogen bonds.

(following the techniques developed by Tasker (1979) showed that both the (111) and (110) surfaces are stable with the former having the lower energy. Calculations of the energies to form surface vacancies were then performed using an adaptation due to Tasker (1979) of the general defect-simulation methodologies based on the procedure of Mott & Littleton (1938). The energies of formation of surface vacancies are found to be significantly, less in the case of the (110) surface. Moreover, using these calculated values (combined with standard electron affinity and bond energy data) we may estimate the energetics of the reaction:

$$O_s + CO \rightarrow V_s + CO_2,$$

where by O_s and V_s we indicate a surface oxygen atom and surface vacancy respectively. The values obtained are *ca.* 0.3 eV and -3.5 eV for the (111) and (110) surfaces respectively. The large negative value for the energy indicates that the surface could be highly active in promoting CO oxidation by release of oxygen from the solid in the classical sacrificial manner demonstrated recently for spinel catalysts in CO oxidation by Wright *et al.* (1992). Calculations of the barrier energies are in progress.

Our second example is provided by the recent study of Shluger *et al.* (1992) who investigated the dissociation of H_2 on the surface of MgO. Their work showed the efficacy of MgO molecules in effecting dissociation. Semi-empirical calculations on the interaction of H_2 with the MgO molecule 'adsorbed' on a large ($Mg_{25}O_{25}$) cluster indicated that the molecule dissociated to give an H–Mg–O–H species on the surface. A detailed examination using *ab initio* techniques of the dissociation mechanism for H_2 the reaction of H_2 with an isolated MgO molecule indicated a low barrier to dissociation of *ca.* 70 kJ mol^{-1}. The relevance of this type of efficient surface process in effecting catalytic dissociation is clearly demonstrated.

4. Conclusions

The recent results summarized in this paper illustrate how computational methods are able to guide the interpretation of experimental data in the field of catalytic studies; and moreover, that they are playing an increasingly predictive role in the field. With the availability of new techniques such as *ab initio* molecular dynamics and greatly enhanced computer power available in massively parallel architectures, predictive application in catalysis of theoretical and computational methodologies are certain to expand.

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Discussion

A. M. Stoneham (*Harwell Laboratory, Didcot, U.K.*): Is it diffusion or the reaction step that is rate limiting? Can you model the rate of the reaction step yet?

C. R. A. Catlow: It depends on the system as to whether diffusion or reaction is rate limiting. We can model diffusion rates well; modelling of reaction rates is still a major challenge.

M. Lal (*Unilever Research, Port Sunlight Laboratory, U.K.*): To obtain reliable information on the long-time diffusion coefficients of adsorbed molecules, it is essential that the molecular dynamics computation is continued for times sufficiently long that the molecule is able to diffuse through a distance at least an order of magnitude greater than its own dimension. Do the present-day computers offer us a realistic prospect of calculating the diffusion coefficients in situations where activation energies associated with the diffusive process are reasonably high, say, 20 kT or more?

C. R. A. Catlow: You are correct that long simulation times are needed to obtain good diffusion coefficients in studies. However, with parallel architecture systems very long simulations are increasingly practicable.