

Strategies for modelling of catalysts

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INTRODUCTION

Modelling of catalysts and catalysis requires three distinct types of calculation. First is the modelling of the *substrate*, which may be for example a porous aluminosilicate or the surface of a metal or a metal oxide. Second is the simulation of the *substrate-sorbant interaction*, in particular the calculation of the sites occupied by the sorbed reacting molecule on the substrate. Third is the modelling of the reaction pathways of the sorbed molecule in order to understand the mechanism of the catalysed reaction. Using modern simulation and quantum mechanical techniques it is possible to perform realistic calculations in all three areas as discussed below.

SUBSTRATE MODELLING

The most effective strategy here for many applications is to use static lattice modelling techniques employing effective interatomic potentials coupled with efficient energy minimisation procedures. The techniques used in modelling methods for both perfect lattices and surfaces are well established [1–4] and good potentials are available for a wide range of materials including silicates and aluminosilicates. Illustrative results of recent applications to the latter are given in Tables 1 and 2. The former compares bond lengths and bond angles in the energy minimised structure for Na zeolite A – a system for which there is accurate crystallographic data – with experimental values. The agreement, although not perfect is good for such a complex structure. The results in Table 2 give the relative lattice energies of a number of purely siliceous zeolites. The differences, although small, are significant and show that, for example, silicalite has higher stability, when purely siliceous, than zeolite A – a significant result in view of the observation that the latter is difficult to prepare with a high Si/Al ratio, unlike the former which is invariably synthesised with a low Al content.

Greater details of the results on Na zeolite A are given in Ref. 5, and it is clear from these and other studies that these techniques have a major role to play in the study of complex catalyst materials.

TABLE 1
COMPARISON OF BOND LENGTHS (Å) AND BOND ANGLES (deg) IN THE ENERGY MINIMISED STRUCTURE FOR Na ZEOLITE A

Bond length or angle	Experiment	Model (a)	Model (b)	Model (c)	Model (d)	Model (e)
<i>A. Comparison of experimental and calculated Si-O bonds and O-Si-O angles</i>						
Si-O(1)	1.595	1.537	1.493	1.525	1.523	1.531
Si-O(2)	1.586	1.541	1.562	1.551	1.554	1.562
Si-O(3)	1.604	1.579	1.602	1.548	1.550	1.554
Mean	1.597	1.552	1.552	1.541	1.542	1.549
O(1)-Si-O(2)	108.8	109.5	110.4	107.7	106.3	106.2
O(1)-Si-O(3)	111.3	109.3	109.7	110.0	110.9	110.9
O(2)-Si-O(3)	107.2	109.2	108.3	108.7	107.9	107.7
<i>B. Comparison of experimental and calculated Na-O bonds and T-O-T angles</i>						
Na(1)-O(3)	2.3227	2.4707	2.3596	2.4768	2.3735	2.3776
Na(1)-O(2)	2.9146	2.8995	2.9407	2.9672	2.9911	2.9926
Na(2)-O(1)	2.557	2.6643	2.3832	2.7069	2.5131	2.5115
Na(2)-O(1)	2.673	2.8116	2.4332	2.8307	2.4043	2.3985
T-O(1)-T	142.2	142.4	152.1	137.1	141.3	142.2
T-O(2)-T	164.7	169.7	159.8	171.6	165.4	165.1
T-O(3)-T	144.8	153.3	148.3	151.0	147.5	144.6
<i>C. Comparison of experimental and calculated Al-O bonds and O-Al-O angles</i>						
Al-O(1)	1.723	1.731	1.734	1.740	1.747	1.718
Al-O(2)	1.717	1.718	1.721	1.761	1.761	1.747
Al-O(3)	1.741	1.736	1.739	1.777	1.784	1.806
Mean	1.731	1.728	1.731	1.759	1.764	1.757
O(1)-Al-O(2)	108.1	109.5	107.1	114.1	117.0	118.0
O(1)-Al-O(3)	112.3	108.8	109.9	108.4	108.2	108.4
O(2)-Al-O(3)	106.0	109.7	109.7	107.4	105.6	105.2

SUBSTRATE-SORBATE MODELLING

Again, the most effective techniques here are based on energy minimisation using effective potentials. Moreover, interface with graphics is essential. Several useful studies of this type have been reported by Cheetham and co-workers [6-8]. These calculations have used potential parameters derived by Kiselev et al. [9] to locate the energy minimum for molecules within zeolite cages. An important extension of the work has recently been reported by Yashonath et al. [10] who have coupled the calculation of sorption energy with Monte Carlo sampling techniques in order to study the distribution of sorbed molecules within the pores of zeolite Y, as a function of temperature.

In many applications it is desirable to include the possibility of framework relaxation around the sorbed molecule. This can be achieved simply and effectively using the general defect model-

TABLE 2
LATTICE ENERGIES (per SiO₂ unit) FOR PURELY SILICEOUS ZEOLITES

Zeolite	Lattice energy (eV)
Faujasite	-123.48
Zeolite A	-123.66
Mordenite	-123.78
Silicalite	-123.89
(α -Quartz)	-123.90)

ling code CASCADE developed by Leslie [11]. This will relax a region or the host lattice surrounding the sorbed molecule until equilibrium is attained. Recent calculations by Vetrivel on CH₃OH in the zeolite ZSM-5 (which converts methanol to gasoline) have shown the importance of including framework relaxation. Figure 1 gives the predicted configuration for this sorbed molecule.

A deficiency of any energy minimisation method is the omission of dynamics, and there is no doubt that future studies will require the inclusion of dynamical effects via the use of the molecular dynamics method, although the less computationally demanding minimisation procedures will combine to play an important role.

MODELLING OF REACTION PATHWAYS

For such studies quantum mechanical (QM) methods are needed, and indeed there is a large literature on the application of such methods to problems in catalysis. The most effective procedure is to locate the sorbed molecule by the methods described above and then to perform the QM calculations on a fragment of the substrate together with the sorbed molecule. Such studies were undertaken by Vetrivel [12] on the configuration shown in Fig. 1. Two Si, one Al and ten oxygen atoms are included in the QM cluster representing the zeolite; this cluster is in turn embedded in an array of point charges which simulate the remainder of the crystal. The calculations suggested that the methanol molecule would decompose by dissociation of a hydrogen atom from the methyl group. The work of Vetrivel was undertaken using *ab initio* methods (using the GAMESS program). There is clearly a role for semiempirical QM techniques such as CNDO and MINDO. Here we wish to stress basic features of the approach, i.e. the use of QM techniques on the configurations yielded by the energy minimisation studies.

SUMMARY AND CONCLUSIONS

The strategy summarised above in which modelling calculations are combined with QM cluster calculations is a viable procedure for the study of catalysis. Our discussion has emphasised studies of zeolite catalysts but the same approach could be used in modelling reactions catalysed on metal and metal oxide surfaces. Moreover, the techniques and potentials are available for these methods to have a wide range of applications.

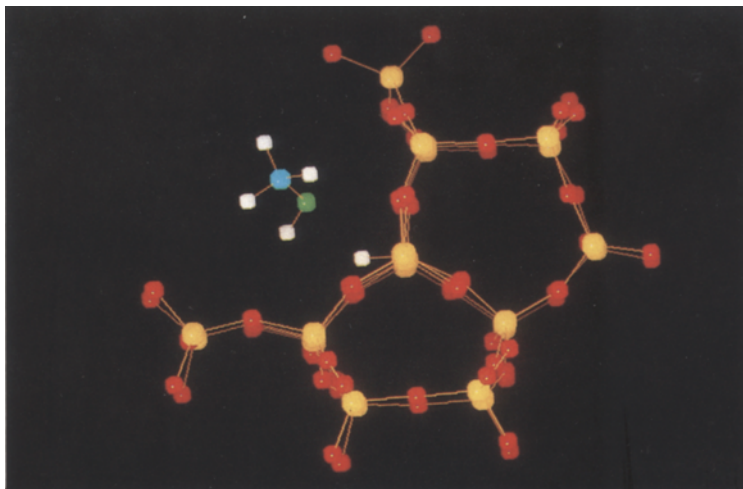


Fig. 1. The final adsorption configuration of the methanol molecule in ZSM-5 zeolite.

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