

Computer simulations in zeolite chemistry

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SUMMARY

Recent developments in molecular modelling techniques have provided us with a new and powerful tool for the simulation and better understanding of the complex chemistry of zeolites. The range of applications include cation distributions, acid strengths of catalytic sites, intergrowth phenomena, derivation of new structures, molecular adsorption and selective diffusion of organic molecules through zeolite frameworks. A perspective summary of a number of simulation methods and their specific areas of applicability is given in this article.

INTRODUCTION TO ZEOLITE CHEMISTRY

Zeolites can be described by a general formula, $[M_{x/n}(AlO_4)_x(SiO_4)_y]mH_2O$, where the cations M of valence n neutralise the charges on the aluminosilicate framework built up from the corner sharing SiO_4 and AlO_4 tetrahedra. Thus, we have a framework consisting entirely of Si, Al and oxygen atoms with neutralising non-framework cations like Na, K, Cs, Ca, Mg, La, etc. which can be easily ion-exchanged (Fig. 1). In fact, in the preparation of zeolite catalysts for hydrocarbon conversions, it is usual to calcine the NH_4^+ -exchanged form of the zeolite to yield a high concentration of Bronsted acid sites of various strengths which depends on the structure and the number of Al atoms present in the framework. Full or partial replacement of Al by other framework ions like B, P, Fe, Ga, etc. also alters the acid strengths and the catalytic properties of a given zeolite material.

In addition to such modifications, different topologies of frameworks also provide unique variants to their adsorption, ion-exchange and catalytic properties. There is, therefore, a constant demand to discover new structures and their relationships to the ones known already. Since most of the new zeolites are likely to be realized from very narrow crystallisation fields, there is also a need to design suitable organic molecules which could selectively act as template in the formation of frameworks of potential value.

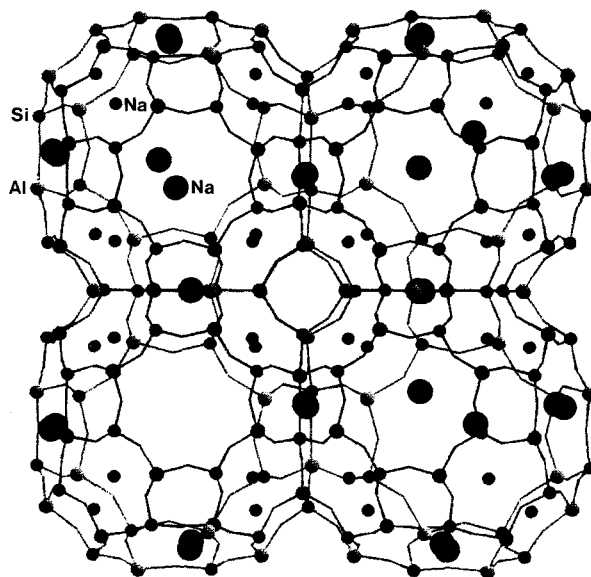


Fig. 1. Structure of the zeolite Na-A. Si and Al alternate in the tetrahedral framework of this zeolite. Na^+ ions are distributed in two types of locations, both of which can be exchanged by divalent cations like Ca^{2+} , leaving the 8-ring channels free for diffusion of small organic molecules like *n*-alkanes.

With this rather brief outline of the highly complex chemistry of zeolites [1], let us first examine the specific nature of the various computer simulations that require evaluation of energies of one kind or the other, to assess certain physicochemical properties of these materials.

SIMULATIONS BASED ON OPTIMISATION OF ENERGIES

When zeolites are fully dealuminated, the resulting framework can be approximated to another polymorph of quartz in view of the resulting three-dimensional network of corner sharing SiO_4 tetrahedra. The stabilities of various aluminium-free frameworks can be assessed by the computational procedures analogous to those developed by Sanders et al. [2]. They essentially use the classical Born model of an ionic solid with parametrised pair potentials supplemented by specific bending terms for the O–Si–O bonds. Though the transferability and validity of these model calculations have been well tested on the cohesive properties of various silica materials, similar comparisons have not yet been made on zeolites. In an alternative approach, MO calculations [3] (employing CNDO/2) on clusters of various silica polymorphs, have shown excellent correlations between Si–O–Si bond angles and Si–O bond lengths. Such correlations have already contributed [4,5] to the understanding and interpretation of Magic Angle Spinning NMR (MASNMR) spectra of these materials in the solid state. There have been several attempts [6] to determine the locations and distributions of Al atoms in the framework through successful interpretation of MASNMR spectra (X-ray diffraction studies do not give unambiguous results in view of the similar scattering powers of Si and Al atoms). These deductions give various starting models for rationalising the most likely distribution of non-framework cations associated with the various Al

sites. Using these models on Si, Al ordering Catlow and coworkers [7] have been able to extend the Born approximation and interatomic potentials to locate the non-framework cation sites by optimising the corresponding lattice energies.

In a different approach, Baraeto and coworkers [8] have recently made use of the well known Del Re method [9] for calculating the net charges on all the framework atoms of a zeolite lattice and estimate the polarisation energy contributions to the total energy of the system. Their simulations represent an important development in that they are capable of taking ion-solvation also into account to predict equilibrium sites, their selectivity, free energies and energy barriers for jump between alternative sites.

The potential energy of interaction of rare gases and alkanes adsorbed on to zeolites has been calculated for a number of systems using the familiar 'atom-atom approximation'. The thermodynamic characteristics of adsorbed species can then be carried out through molecular statistics. Kiselev and his coworkers [10–12] have pioneered this approach to the study of adsorption energies and activation energies for self-diffusion of gaseous molecules within zeolite frameworks. They essentially use the Lennard–Jones type potentials with the constants for the attraction and repulsion terms given by Kirkwood–Muller relationships between polarisability, susceptibility and the electrostatic charges. Though a number of approximations are embedded in this approach, simulations of this kind [13–15] have yielded some valuable pointers to the various adsorption phenomena observed among zeolites. Such procedures for the prediction of adsorption sites have also led to an important extension [16,17], namely, to yield good starting models (Fig. 2) for the Rietveld profile analysis of neutron diffraction data on zeolite materials with adsorbed species.

Even though the three-dimensional network of a zeolite framework and its associated cations must be considered as a 'macromolecule', a number of quantum-chemical studies have been car-

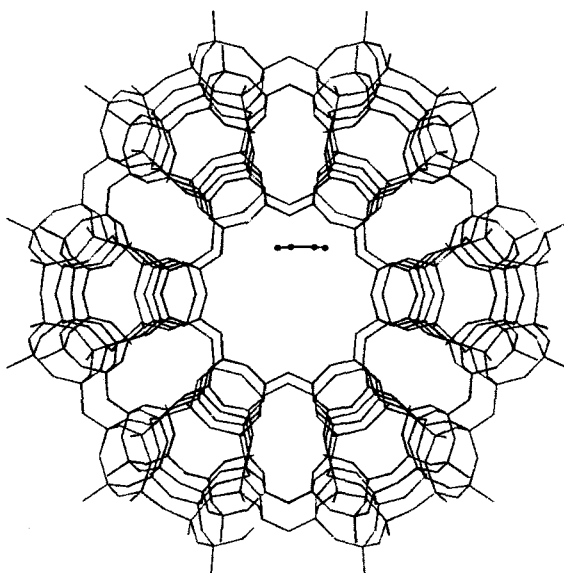


Fig. 2. Location of pyridine in zeolite L. Energy calculations predict optimum geometry which serves as a good starting model for the Rietveld profile analysis of neutron diffraction data (see Ref. [16]).

ried out on small clusters of atoms belonging to this 'macromolecule'. They have yielded valuable insight into the nature and strengths of acid sites common to zeolite catalysts. For example, Beran and coworkers [18,19] have used non-empirical SCF method with STO-3G basis set (other basis sets have also been tested by Mortier et al. [20]) and the CNDO/2 method to study the influence of the zeolite geometry characteristics on the properties of the bridging -OH groups in various model clusters. These simulations have yielded some valuable information concerning the acidity of these groups due to the influence of Si-O-Al angle and Si-O and Al-O bond lengths. Such studies can also be extended to systems with isomorphous substitution of Al by Fe, B, Ga and P atoms. Another area where *ab initio* molecular orbital calculations have been found to be of value is in the identification of preferential siting of Al ions [21] in the zeolite framework. Though there is no preparative control on the siting of these ions, theoretical studies may have a positive role to play in the characterisation of MASNMR spectra of dealuminated zeolites with high Si/Al ratios and with more than one crystallographic sites for Si or Al.

Another recent theoretical development (due to Mortier and coworkers [22,23]) relevant to zeolite chemistry is in the application of electronegativity equalisation concepts based on density functional theory. The effective electronegativity of an atom in a molecule depends on the local charge and on the external potential. Its equalisation provides accurate information on the charge distribution and on the average electronegativity. The latter was found to correlate extremely well with the framework density of a number of silica polymorphs. The procedure has been extended to explicitly relate the structure type and composition of a zeolite to the electronic and therefore other physicochemical properties as well.

Though the actual simulations described so far are usually beyond the scope of many of the general purpose molecular modelling software (e.g., 'CHEMX' [24]), in recent years interface facilities are made available to illustrate graphically the results of some of the calculations mentioned above. These facilities also allow one to modify and manipulate zeolite frameworks to provide the necessary starting geometry for all the cluster type calculations mentioned above.

There are, however, some specific problems in the structural chemistry of zeolites that can be tackled effectively by computer graphics techniques that need not require evaluation of energies; application areas of this type are described below.

SIMULATIONS BASED ON GEOMETRICAL CONSTRAINTS

Computer modelling and graphics play an important role in not only providing a visual understanding of the structural chemistry, but also let us examine a number of structural peculiarities that may arise due to manipulation of frameworks [25,26]. For example, the ease with which zeolite frameworks could be modified to simulate intergrowths, twinning and other planar defects normally encountered in these materials, has actually helped in the characterisation and interpretation of High Resolution Electron Micrographs (HREM). In addition, interactive assembly of new and known basic building units of frameworks has helped to identify a number of new zeolite structures capable of some interesting variations in properties. Zeolites having closely related crystal structures often exhibit intergrowths along certain planes, the resulting solid still possessing continuous but defective framework. Since HREM can probe the structural defects from an area as little as $100 \times 100 \text{ \AA}^2$, it is often necessary to be able to calculate the HREM images of the suspected crystal structures at the appropriate settings of the electron microscope, the zone axis

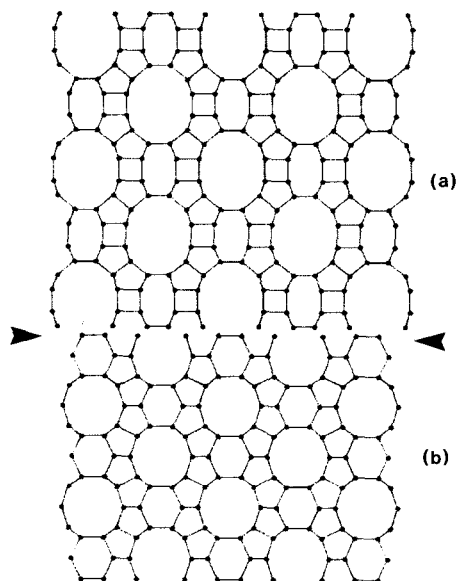


Fig. 3. The possibilities of intergrowths between (a) mordenite and (b) ferrierite frameworks. One can see how continuous topology arises from slight rearrangements of framework atoms at the intergrowth plane.

and the thickness of the sample. This task is an integral part of the usual characterisation procedure. In the case of materials with suspected intergrowths (Fig. 3) this becomes difficult and in recent years computer graphics techniques have been successfully used to overcome some of these difficulties [27,28].

The principle lies in identifying the symmetry elements that distinguish the two crystal structures constituting the intergrowths. By interactively arranging the common building units of the

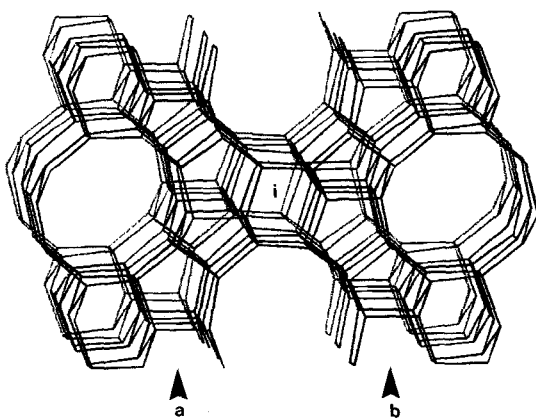


Fig. 4. The framework of ZSM-5. Here the adjacent chains (a) and (b) are related by centres of inversion. This zeolite has a straight channel and, perpendicular to it, a sinusoidal 10-ring channel. When (a) and (b) are related by mirror symmetry, as in ZSM-11, both the channels are straight. Such minor variations in the structure can be identified by high resolution electron microscopy.

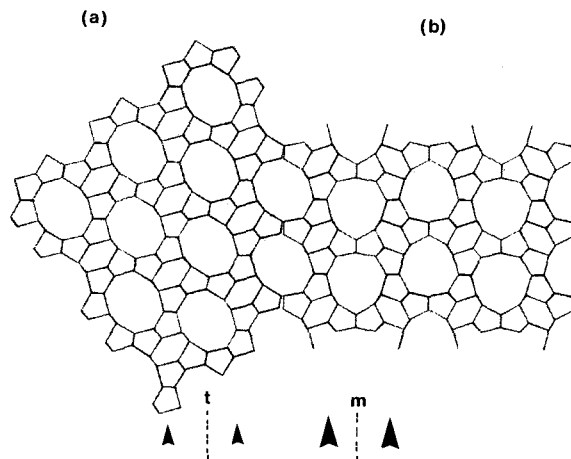


Fig. 5. Structural relationship between zeolites (a) Theta-1 and (b) ZSM-23. Adjacent chains are related by translations in (a) and by mirror in (b). Modelling techniques allow one to manipulate the atomic coordinates of asymmetric units of one zeolite to derive the frameworks of new zeolites.

two structures at different symmetry combinations, various models of intergrowths can be formulated. In each model the locations of the framework atoms are graphically recorded in a given projection and the optical diffraction of this object is compared with the electron diffraction pattern of the material. The intergrowths of important zeolites, such as ZSM-5 and ZSM-11 (Fig. 4) as well as Theta-1 and ZSM-23 (Fig. 5), have been successfully characterised by the use of such techniques. Another useful variation is to record the optically defocussed images of the displayed framework topologies (of the computer-generated intergrowth models). These simulations, under certain favourable condition, give the near equivalent of the HREM images expected for the assumed intergrowth sequence.

Characterisation of isolated defects of certain kinds have also been possible by novel use of the available graphical tools. One kind of planar fault, formed when one part of the crystal is rotated with respect to another in a well-defined plane, has been identified by HREM in the case of the zeolite L [29]. Modelling studies have shown the possibilities of two such boundaries, one of which interpreted the observed HREM image unambiguously.

There are over 40 different framework arrangements known for zeolites and some of which are adopted by the aluminophosphate molecular sieves as well. Among these known frameworks, a number of them have identical basic structural units, differing only in their inter-connectivities, in the three-dimensional space. Some of the observed structural features immediately point to the possibility of deriving new hypothetical frameworks from the known and modified basic units, in a computer graphic system.

Computer modelling techniques have, therefore, been developed [30] to incorporate: (a) interactive specifications of symmetry operations (e.g., translations, mirror, inversion and rotations) in any desired combination; (b) distance scanning, with appropriate warnings to test the feasibility of the model at every stage of the build up; (c) retain or erase (if unacceptable) a given portion of the framework; and (d) rotate the entire framework for visual verification of the three-dimensional topology. Such computer simulations of hypothetical frameworks can be further verified or

refined, using the Distance Least Square (DLS) programs [31] and to provide, ultimately the expected theoretical X-ray patterns; an atlas of such patterns could certainly quicken the experimental characterisation of new materials.

CONCLUDING REMARKS

It is now recognised that the two distinct computational approaches can, in fact, be complementary. Due to recent software developments for interfacing energy calculations to molecular graphics, we might get more revealing insight into the chemistry of zeolites in the coming years. Clearly, there is scope for development in deriving reliable and transferable interatomic potentials particularly for the framework atoms. This may bring about realistic molecular dynamical simulations for the adsorption and diffusion of molecules at the operating conditions of the actual industrial processes. Further, these improvements could enable us to tackle one of the least understood phenomena, namely, the role of organic template molecules in the crystallisation of zeolites. An appropriate simulation procedure for identifying the most optimum cluster geometry of aluminosilicate precursors around a template molecule could simply be a combination of various calculations mentioned above.

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