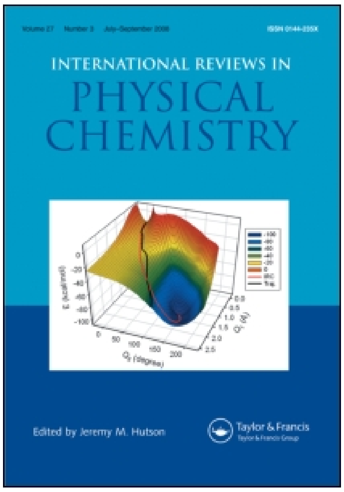

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Theoretical studies on zeolites

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Theoretical studies on zeolites

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Theoretical studies on zeolites are reviewed following four topics: quantum-mechanical studies, empirical energy calculations, statistical methods, and dynamic simulations. Problems and perspectives in these fields are also discussed.

Contents

1. Introduction

Zeolites are a variety of complex porous crystalline aluminosilicates, both natural (Gottardi and Galli 1985) and synthetic (Breck 1973), well known for their industrial applications as adsorbants, molecular sieves and catalysts.

Their structure consists of a three-dimensional aluminosilicate framework with regular cavities joined by channels, which usually contain metallic ions and water molecules. The ions can be exchanged even with non-metallic ones, and water molecules can easily be removed by heating or by inert gases, often in a completely reversible way. Partially or completely dehydrated zeolites can accommodate in their cavities (typically about 10 Å wide) small molecules which can diffuse and, under suitable conditions, give rise to chemical reactions.

The aluminosilicate framework is made up of tetrahedra connected by the vertices. The centre of each tetrahedron is usually occupied by Si or Al atoms, but chemically related atoms such as Ga, Ge, and P can be found in synthetic zeolites, while at the vertices oxygen atoms are present.

Substitution of Si with Al or other trivalent atoms yields a residual charge to the framework, which is balanced by positive ions localized in the cavities and channels of the structure or, sometimes, by H^+ ions chemically bonded with surface atoms to form hydroxyl groups.

It would seem that the complexity of zeolites hinders theoretical work on these fascinating substances, yet a surprisingly large number of studies has been attempted in this field. In the present paper, they are reviewed following four principal topics. In § 2 quantum-mechanical studies are described. They consist mainly of calculations on large molecular models that mimic interesting sites of zeolites and their interactions with adsorbed molecules, in order to explore a variety of structural and chemical problems. However, these systems are too small to represent the contents of even one crystallographic cell.

Empirical energy calculations, which are described in § 3, have been able to elucidate some properties, mainly structural, of zeolites, by including approximate energetic contributions, but extended to the whole crystal or to a significant portion of it.

The empirical potentials can be used not only for static calculations, but may also be the starting point for statistical models, including analytical and numerical (essentially Monte Carlo) methods. They are illustrated in § 4.

Moreover, with similar potentials, vibrational or more general dynamical calculations on zeolites have been performed, and they are reviewed in § 5.

In this article, emphasis is given to the recent advances in theoretical research on zeolites from the methodological viewpoint, by underlying the present problems and perspectives. The references were selected to provide an illustrative rather than a complete literature in this field.

2. Quantum-mechanical studies

The application of computational quantum chemistry to problems concerning zeolites requires a detailed understanding of their structure and reactivity, assuming that observable variables such as bond lengths, angles and strengths, charge density distributions and force constants are governed in large part by the local atomic arrangements.

The state of the art of applications of quantum chemistry to zeolites was described by Sauer and Zahradnik (1984) in a review covering the literature till 1983. It appears that quantum chemistry provides both the theoretical background for understanding bonding phenomena and predictions on the structure and properties of bulk and surface sites, which may not be accessible by experimental means.

However, there is a severe limitation for the use of *ab initio* quantum-mechanical methods, due to the huge computational effort involved (one crystallographic cell may contain several hundred atoms!). These calculations become feasible only for models of reduced size representing significant portions either of the bulk, or of surface sites, or of sorption complexes.

At present, even more powerful computer facilities allow us to increase the dimensions of the systems, so that more realistic models can be chosen and investigated, and the use of semiempirical and empirical quantum methods, whose reliability depends closely on the *ad hoc* parametrization adopted, could be drastically reduced.

On the other hand, the present need for reliable potentials for energy calculations and statistical methods like Monte Carlo and Molecular Dynamics, requires the application of quantum chemistry, in particular when experimental parameters are not available (see, e.g., Sauer *et al.* 1984).

A number of quantum-mechanical calculations, not reviewed by Sauer and Zahradnik (1984), have been performed recently. We first consider the work by Fripiat *et al.* (1983), using MO-SCF calculations to study the monomer and dimer clusters which have the geometrical structure of zeolites ZSM-5 and ZSM-11. These systems had been investigated by semiempirical methods (see, e.g., Hass *et al.* 1981 and 1982, and Sauer *et al.* 1980). It is found that the 12 tetrahedral sites of ZSM-5 are significantly different from each other, while the seven tetrahedral sites of ZMS-11 fall into two categories. Preferential locations of aluminium, present in small quantities in these zeolites, were proposed for both structures. Moreover, the instabilities of the ZSM-5 framework were identified and the validity of the Al avoidance principle and the acidic properties of these zeolites were discussed.

Afterwards, the predictions on the preferential siting of Al were confirmed by Derouane and Fripiat (1985), showing that the random siting of Al on such sites might lead to the formation of Al pairs, contrary to Lowenstein's rule (Lowenstein 1954). Moreover, the calculations suggested that pairing might be favoured when it occurs along the boundary of the channel parallel to the crystallographic axis **b**, but this prevision has not yet been confirmed or excluded by experiment.

The charge distribution analysis indicated the highly covalent nature of zeolite frameworks. Their anionic part behaves as a weak base, explaining the high acid strength and the strong affinity for large and polarizable cations of these zeolites.

The difference in properties of bridging and terminal silanol groups considered as models of some zeolitic sites, were investigated by Mortier *et al.* (1984) on the basis of non-empirical calculations using 3-21G SCF wavefunctions. The comparison with structural and chemical arguments indicates greater acidity and sensitivity towards adsorbed molecules for bridging hydroxyls.

Following the same philosophy and using the same *ab initio* Gaussian basis set, Datka *et al.* (1985 a, b) investigated the influence of zeolite composition on the interaction of surface hydroxyls with adsorbed molecules. The model compound $H_3Al–OH–SiH_3$, describing the main bridging interaction with a water molecule, was used. The average electronegativity of the framework was simulated by substitution of terminal hydrogen atoms with fluorines. It was suggested that several properties of the unperturbed OH, derived by IR spectroscopy, vary linearly with the average electronegativity. For hydrogen-bonded OH groups, the interaction strength increases with the average electronegativity of the framework. The OH bond properties are much more sensitive to composition changes. The model systems $(OH)_3Si$ OH $Si(OH)_3$ and $(OH)_3Si–OH–Al(OH)_3$ were adopted by Beran (1985) and Senchenya *et al.* (1986) for both non-empirical SCF and semiempirical CNDO/2 calculations performed to study the influence of zeolite geometry on the bridging OH groups. Equivalent qualitative predictions were given by both computational techniques, showing a decrease in the proton abstraction energy of these OH groups on increasing Si–O–Al angle and decreasing Si–O and Al–O bond distances. These calculations showed that the effect of Si/Al ratio on the acidity of OH groups is somewhat more pronounced than on the structural characteristics.

Mortier *et al.* (1985, 1986) showed, on quantum theoretical grounds, how the application of the electronegativity equalization concept (Sanderson 1960) to zeolites can provide a powerful tool for a qualitative as well as quantitative understanding. In fact, the effective electronegativity of an atom in a molecule depends on the local charge as well as on the external potential. The equalization yields accurate information on the charge density distribution and the average electronegativity. Its application to zeolites is very useful as atomic sites differ in their crystallographic positions, or because the neighbours carry different charges. For instance, the presence or absence of an exchangeable cation near a zeolitic site was shown to influence the ^{29}Si chemical shift in dehydrated CaY zeolites (Grobet *et al.* 1985).

3. Empirical energy calculations

In order to give an energetic approach to structural and chemical problems of zeolites without involving quantum-mechanical calculations, but by including the contribution of a large number of atoms or even of the whole crystal, empirical potential functions have been adopted. They are of use for studying crystals and molecules, and in statistical simulations of condensed-state systems. If empirical potential functions are well calibrated (sometimes they are derived from good quantum-mechanical calculations on small model systems) satisfactory results can be achieved.

In their more usual form, the total energy of a system is evaluated as the sum of atom–atom contributions, and, in general, pair additivity is postulated.

In the calculations performed on zeolites, the potential energy has been partitioned into a number of terms, so that it assumes the following general form:

$$E=\Phi_{\mathrm{e}}+\Phi_{\mathrm{p}}+\Phi_{\mathrm{d}}+\Phi_{\mathrm{r}}+\Phi_{\mathrm{ct}} \tag{1}$$

where the first term, Φ_e, is the electrostatic energy, Φ_p represents polarization energy, Φ_d is the dispersion energy, Φ_r is the repulsive term, and Φ_{ct} gives an approximation of the charge-transfer stabilization energy.

Electrostatic energy includes the contributions due to the charges and the permanent electric multipole moments (dipole and quadrupole moments), when considered. The electrostatic interactions are typically long-ranged, and special techniques may be required for their correct evaluation, in particular for the Coulomb (charge–charge) term. The analytical form of the electrostatic energy is given by:

$$\Phi_{\mathrm{e}}=\sum_j q_j\phi_j+\sum_k m_k\nabla\phi_k+\sum_l\sum_{\alpha\beta}Q^l_{\alpha\beta}\frac{\partial^2\phi_l}{\partial r_\alpha\partial r_\beta}+\ldots \tag{2}$$

where q_j are the point charges of the system, m_k are the dipole moments, $Q^l_{\alpha\beta}$ are the quadrupole moment components, and ϕ_i is the electrostatic potential experienced by each charge, dipole and quadrupole moment respectively.

In equation (2), the first term is the Coulomb energy, the second represents the charge–dipole interactions. and the third the charge–quadrupole energy. Other possible contributions, like dipole–dipole, dipole–quadrupole, etc. terms have not often been considered in studies on zeolites. Moreover, dipole and quadrupole moments have been considered only for interactions between the framework and small adsorbed molecules, mostly when they are approximated with spheres.

As mentioned above, the coulombic potential is long-ranged, and a direct summation over the charges contained in a crystal would require the inclusion of an enormous number of terms to give the correct result. However, the translational symmetry of the crystals can be exploited, and, by using Fourier transforms, the evaluation of the Coulomb energy becomes relatively simple. This technique was introduced firstly by Ewald (1921) and was extended by Bertaut (1952). Its application to zeolites was made by Dempsey (1969) using the original Ewald formulation and by Bonin and Legrand (1975).

The symmetry of the crystals can be used to evaluate the potential energy with direct summations over a carefully chosen set of charges, and a number of studies on zeolites have followed this approach.

The second term in equation (1) represents the interaction energy between the charges and the dipole moments induced by the electric field of the charges themselves, and is calculated from the following expression:

$$\Phi_p = -\frac{1}{2}\sum_j E_j^T \alpha_j E_j \tag{3}$$

where $E_j = \nabla\phi_j$ is the electric field experienced by the jth atom or molecule and α_j is its polarizability tensor.

To express the dispersion energy, Φ_d in equation (1), corresponding to induced dipole–induced dipole interaction several formulae have been proposed. The first term has the general form:

$$\Phi_d = -A/r^6 \tag{4}$$

where r is the separation, and A may be estimated either from (London 1930):

$$A = \tfrac{3}{2}\alpha_1\alpha_2 \frac{E_1E_2}{E_1+E_2} \tag{5}$$

or (Kirkwood 1932, Muller 1936):

$$A = -6mc^2 \frac{\alpha_1\alpha_2}{(\alpha_1/\chi_1)+(\alpha_2/\chi_2)} \tag{6}$$

In equations (5) and (6) the α, χ and E are respectively the polarizabilities, magnetic susceptibilities and characteristic energies (usually approximated by the ionization energies) of each interacting atom or molecule; m is the mass and c is the velocity of light. In many cases the parameter A has been evaluated directly from fitting experimental data or quantum-mechanical results.

Sometimes higher-order terms are added to dispersion energy. They have the form: $-C_{2n}r^{-2n}$ with $n > 3$.

The repulsive energy Φ_r, which prevents the interacting centres from collapsing when let free to move, may be represented by two formulae:

$$\Phi_r = Br^{-n} \tag{7}$$

or:

$$\Phi_r = B\exp(-\alpha r) \tag{8}$$

In equations (7) and (8) r is the centre distance, B and α are fitted to experimental data, and usually $n = 12$.

In some papers on zeolites a term representing the charge-transfer energy, Φ_{ct}, was considered, and was estimated from quantum-mechanical calculations at semi-empirical level.

The empirical energy expressed by equation (1), often with the exclusion of one or more terms, has been used to localize, by energy minimization, the most probable positions of cations and adsorbed molecules in zeolite cavities, to study the effect of the crystal field on the adsorbate and to estimate adsorption heats.

This estimate was included in a paper by Barrer and Gibbons (1963), who evaluated the adsorption energy of ammonia in Linde Sieve X, a synthetic near-faujasite zeolite, with various different cations. Electrostatic (without quadrupoles), polarization, dispersion (with the Kirkwood and Muller form), and repulsion (r^{-12}) terms were considered.

The alumino-silicate framework was represented by the wall oxygen atoms of one large cavity of the crystal, the cations were located in the experimental positions and one ammonia molecule (as a polarizable and dipole-bearing point) in the centre of this cavity. The charges of the oxygen atoms were assumed to neutralize the cations.

The calculated values of the adsorption energy verified the importance of the electrostatic terms and reproduced the observed sequence of the adsorption heats, but quantitative agreement was less satisfactory, the overall relative error being about 30–40%.

Bosáček and Dubskí (1975) extended the calculations of Barrer and Gibbons (1963) to the adsorption of Ar, Kr, Xe, and N_2 in Y-type zeolite with Na cations. In the electrostatic term, instead of charge–dipole energy, charge–quadrupole interactions were introduced, because the adsorbates had no dipole moment. Moreover, the coulombic term was evaluated by direct summation over the charges within a sphere with a radius of about 50 Å, and Si^{+4} and Al^{+3} were explicitly considered with their formal charges.

The variation of the adsorption energy with the charges on the cations (and oxygen atoms) and as a function of the position of the adsorbate in the cavity was studied. With $Na^{+0\cdot 7}$ and $O^{-0\cdot 75}$ the calculated values were reasonable and followed the experimental sequence $Ar < Kr < Xe$.

The problem of the localization of adsorbed molecules in channels and cavities and of the evaluation of the adsorption energy has been considered by several authors, but, as it often has been treated in connection with statistical or dynamical calculations, it is also discussed in §§4 and 5.

In some cases the study was limited to the calculation of the electric field in a zeolitic cavity: see, e.g., the work by Cohen de Lara and Nguyen Tan (1976) where the electrostatic field in zeolites NaA and CaNaA (Zeolites of type A with Na cations and with the same cations partially substituted by Ca^{++}) was evaluated. For the framework charges the approach of Barrer and Gibbons (1963; see also above) was adopted and the direct summation was extended to 26 crystallographic cells surrounding a central one.

Ragaini *et al.* (1979) calculated the activation energy for diffusion of four molecules (*o*-, *m*-, *p*-xylene and ethylbenzene) in zeolite 13X as the results of repulsion and dispersion interactions with the oxygen atoms of the ring connecting two adjacent cavities. Three different atom–atom functions were considered, but the results did not explain the selectivity of the zeolite 13X for the diffusion of the four compounds, probably because the cations and possible residual water were not considered.

A recent paper by Anderson *et al.* (1986) has described the adsorption of xenon in dealuminated (and thus with no extra framework cation) zeolite Y. Atom–atom potentials with an exponential repulsion term, equation (8), and dispersion energy, equation (4), were used to indicate the preferred adsorption sites for xenon. For loadings higher than one atom per zeolitic cavity the formation of xenon clusters was predicted, in agreement with experiment.

Another structural problem often considered in zeolites is the determination of the preferred sites and bond energy of cations, in particular when partial occupancies or scarce experimental data occur. This problem was first considered by Dempsey (1969). Using the assumption of complete ionicity (also for Si^{+4}, Al^{+3}, and O^{-2}), Coulomb potentials have been calculated with the Ewald method for various cation sizes, valencies, and distributions of ions in zeolites X and Y. For monovalent cations the results agreed well with ionic distributions found from X-ray studies. For divalent cations the divergences between the results of the calculations and the experimental data were explained on the basis of residual water present in the samples used for X-ray diffraction work and ignored in the model.

A similar study was carried out by No *et al.* (1981) on the influence of the silicon to aluminium ratio on the acidity and site selectivity of cations (essentially K^+) in faujasite-type zeolite. The following energy contributions were considered: electrostatic, with charges derived from electronegativity equalization (Sanderson 1960) for framework atoms and direct summations extended to the atoms within 17 Å from the ion; polarization, equation (3), dispersion (with constants from equation (5)) and repulsion, equation (8). The distribution of cations was determined by calculating the binding energies for several possible cation arrangements. Generally, the cation binding energies decreased with decrease of aluminium content.

More recently, in the same laboratory and with a similar method, a study on the site selectivity of alkali-metal ions in the dehydrated and hydrated zeolite A was carried out (Koh and Jhon 1985). Energy minimization was used to obtain the coordinates of the hydrogen atoms of water, since only the positions of oxygen atoms were known from X-ray data. The calculated solvation heats of gaseous ions and the heats of sorption of water molecules agreed (within a few percent) with experimental data. The site symmetry and the cation size explained the site selectivity.

The problem of the site selectivity of exchangeable alkali and alkaline-earth metal cations in zeolite A was also studied by Ogawa, Nitta and Aomura (Ogawa *et al.* 1978 a, b, Nitta *et al.* 1980) with a slightly different technique. The total energy was computed as the mean between the energy of an ionic structure (with full ionicity assumed) and the energy of a covalent structure in which all atoms were considered as neutral, except Al^- and the cations.

The cation-framework interaction energies consisting of the electrostatic (direct summation), polarization, dispersion (including r^{-8} and r^{-10} terms), repulsion, and charge-transfer (only for the covalent structure) energies were calculated for different cation sites and ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+}). The results were in good agreement with experiment.

Energy-minimization calculations based on atom–atom electrostatic, repulsive, equation (8), and dispersion terms have been carried out by Sanders *et al.* (1984) for strontium ions in Zeolite A. The results agree partially with X-ray diffraction data, but the need to consider the effects of thermal energy and of perturbation from strict alternation of Si and Al atoms in the framework was suggested.

Empirical energy calculations have been used by mineralogists to elucidate some of the following problems, which cannot be solved by X-ray or neutron diffraction: the Si/Al distribution for structures which appear to be partially or fully disorderd, as in mazzite (Alberti and Vezzalini 1981) and in thomsonite (Alberti *et al.* 1981); the determination of sites occupied by the hydrogen atoms of water molecules in the channels (Alberti *et al.* 1981); the distribution of exchangeable cations in the sites found by diffractometry (Alberti and Vezzalini 1981, Alberti *et al.* 1981, Sanders and Catlow 1983, besides the studies mentioned above), and, lastly, the determination of the most probable coordination of the cations, when the sites of the cations and of the water are not fully occupied (Alberti and Vezzalini 1981). In these calculations the electrostatic term and sometimes the repulsive energy have been considered.

Empirical potential functions have been used for some computer-graphics applications where, e.g., the sorption or diffusion of an organic molecule can be driven through the channels and cages of a zeolite and the energetics involved in such a process can be estimated (Ramdas *et al.* 1984).

The use of the differential geometry of periodic minimal surfaces to describe some features of zeolite structures (Andersson *et al.* 1984) and of structural transformations (Hyde and Andersson 1985) has been proposed. They are mentioned in this section only because they are concerned with static properties of zeolites.

At the end of this section, one may conclude that empirical energy calculations are useful guidelines for clarifying many structural problems of zeolites, though in some cases the calculated energies are unrealistic.

The problem of determining the most likely choice for the potential parameters is still unsolved. The values of the charges for the framework atoms are not definitively stated. Indeed, quantum calculations (see § 2) often yield unreliable results both because of the relatively small basis sets and the limited size of the models used. Electronegativity equalization (Sanderson 1960, Mortier *et al.* 1985) can provide useful information on the charge density distribution, but does not define uniquely the point charges for the atoms. Residual charges can be derived from very accurate X-ray diffraction experiments, and this method has been applied to orthopyroxenes and other silicates (Sasaki *et al.* 1980, Sasaki and Takeuchi 1982), but not to zeolites. The 'experimental' charge ranges are 1·8 to 2·8 for Si, $-0·84$ to $-1·51$ for O, and for Al a residual charge of about 2·4 *e* was obtained.

These ranges are reasonable and agree with quantum results; perhaps they include the most appropriate values, once electroneutrality and agreement with experimental binding energies (when available) are accounted for. It should be remarked, however, that the charges have little influence on the structural results.

The polarization energy, equation (3), is often small, and it is usually neglected, except for framework–adsorbate interactions when the polarizability of the adsorbed molecules is known (see e.g. Ruthven and Derrah 1972).

Dispersion energy parameters can be calculated from equations (5) or (6), which give similar results, and they can be adjusted to fit experimental data. A useful discussion is reported in the papers by Kiselev and coworkers (Bezus *et al.* 1978, Kiselev and Du 1981 a, b, which are reviewed in § 4), where repulsion energy parameters, that are usually chosen to obtain correct values for the minimum bond distances, are also treated.

Empirical potentials can always be adjusted to fit the experimental properties of sufficiently large classes of zeolites. On the other hand, if energy minimization procedures are used in these calculations, they become lengthy and some problems arise, like the presence of cavities or incomplete coordination, which do not allow full minimization of the energy of the whole structure with spherical atom–atom potential functions, unless special constraints are applied. Moreover, they cannot take into account any temperature dependence or dynamical effects.

In order to overcome these limitations, statistical and dynamical studies have been attempted. They are considered in the next two sections.

4. Statistical models

Once the energy of zeolitic systems has been calculated, statistical mechanics can be used to evaluate thermodynamic functions which are directly comparable with experimental results. Several attempts have been made in this field, mainly concerning the adsorption of various compounds in zeolite cavities, while just one computation related to framework properties was found.

The work on adsorption properties could be divided into three classes involving, respectively, semiempirical theories or explicit formulae derived from statistical mechanics, numerical evaluation of configuration integrals needed to estimate thermodynamic quantities, and Monte Carlo calculations both in canonical and in grand canonical ensembles. One of the earliest papers of the first class was published by Sargent and Whitford (1971), who calculated equilibrium sorption isotherms, heats of sorption, and diffusivities for CO_2 in Zeolite A, using an idealized model of the molecular potential field. This one was evaluated with empirical formulae including repulsion (r^{-12}), polarization, and spherically-averaged quadrupole terms for framework-CO_2 and CO_2–CO_2 interactions, thus considering carbon dioxide as a spherical molecule.

Thermodynamic functions were calculated with formulae derived from standard statistical mechanics and using some approximations. Good agreement with experimental data was obtained for heats of sorption, but results were poor for equilibrium isotherms, and the simple approximation used for diffusivity, neglecting even the rotations and the anisotropy of CO_2, appeared to be inadequate.

Better results were obtained by Ruthven and Derrah (1972), who developed a simple theory of zeolitic diffusion from the principles of transition state theory. General expressions for diffusivities were derived in terms of the lattice parameter and the partition function for the transition state which, for type A zeolites, was identified as a molecule in passage through the 8-membered oxygen window connecting two adjacent cavities.

Theoretical diffusivities calculated for CH_4 and for CF_4 in 5A zeolite agreed with experimental data and it was shown that the CF_4 molecule had a high degree of rotational freedom, whereas the rotation of the CH_4 molecule was severely restricted. This difference was attributed to the difference in moments of inertia.

Ruthven and Wong (1985) used an approximate form of the grand partition function, with semiempirically evaluated configuration integrals, to derive a simple generalized statistical thermodynamic representation of adsorption equilibrium isotherms which was used as a basis for the prediction of binary equilibrium isotherms.

The model was shown to provide a good representation of binary equilibrium isotherms for sorption of cyclohexane - *n*-heptane in 13X zeolite as well as other binary equilibrium data.

A statistical thermodynamic approach to the distribution of cations in silicate minerals was proposed by Mortier (1975). The ratio of the occupancy number of cation sites was related to the energy difference (with the assumption of the equilibrium in the site distribution) by:

$$\ln(n_i\omega_j/n_j\omega_i) = -(\varepsilon_i - \varepsilon_j)/kT \qquad (9)$$

where n_i, ω_i, and ε_i are the occupation numbers, the site degeneracies and the site energies respectively. If the l.h.s. of equation (9) is known from experimental data as a function of temperature, the energy differences can be evaluated. It was found that for potassium-exchanged X and Y zeolites the energy differences between the sites varied linearly with the Si/Al ratio.

Numerical evaluation of configuration integrals (with a modification of the Monte Carlo procedure) was used by Stroud *et al.* (1976) for a thermodynamic study of zeolite 5A + methane. A statistical–mechanical theory for point particles sorbed in the cavities of this zeolite was examined for the case in which the sorbate–sorbate interactions and the interactions between each sorbate molecule and an element of the cavity wall are of the Lennard-Jones 12–6 type. The sorbate–wall interactions were further approximated by a potential derived from the Lennard-Jones and Devonshire cell model. Fairly good agreement with the results for CH_4 as sorbate was obtained for the isotherms and for the isosteric heats, but not for the heat capacities.

The modified Lennard-Jones and Devonshire cell model was adopted in a paper by Soto *et al.* (1981) to calculate the contribution due to the dispersion energy in a theory which took into account both dispersion and electrostatic energies (ion–dipole, ion–induced dipole, etc.), developed to calculate Henry's constant for the sorption of gases in molecular sieves. The energy due to electrostatic forces was calculated by a direct summation. Comparison of the theory with experimental data showed that the dispersion and electrostatic energies of non-polar adsorbate molecules are of the same order of magnitude.

Kiselev and coworkers (Bezus *et al.* 1978, Kiselev and Du 1981 a, b) wrote a series of papers on statistical calculations of thermodynamic adsorption characteristics of zeolites using the atom–atom approximation, taking into account all the oxygen atoms and the extra-framework cations of the crystal. Repulsion, dispersion and polarization (charge-dipole and -quadrupole) terms were considered, and the configuration integrals were calculated numerically. Henry's constants, changes in differential internal energy, isosteric heats of adsorption, and heat capacities of the adsorbed substance were evaluated for methane in Zeolite NaX (Bezus *et al.* 1978), Ar, Kr, Xe, O_2, N_2, CO, CO_2, NH_3 (Kiselev and Du 1981 a), and hydrocarbons, namely CH_4, C_2H_6, C_3H_8, *n*-pentane, neopentane, cyclopropane, cyclopentane, cyclohexane, ethylene and benzene (Kiselev and Du, 1981 b) in NaX, KX, and NaY zeolites. By making a reasonable choice of the molecular parameters the atom–atom approximation gave thermodynamic quantities which were in satisfactory agreement with the corresponding experimental values, except for cyclopropane. This discrepancy was attributed to the strained structure of this molecule.

The adsorption of *n*-alkanes (C_1 to C_{10}) in faujasite-type zeolites was studied by Fiedler and coworkers (von Kretschmer and Fiedler 1977, Fiedler *et al.* 1980) using the Monte Carlo method in the grand canonical ensemble to evaluate adsorption heats, entropies, and specific heats of the adsorbed molecules. For the zeolite-hydrocarbon interactions, repulsion, dispersion (including r^{-8} and r^{-10} terms), polarization, and charge–quadrupole energies were considered, assuming as interacting centres all the framework atoms and CH_2 (or CH_3) groups. Qualitative agreement with experimental data was obtained.

Another Monte Carlo study of adsorption in zeolites was performed by Soto and Myers (1981) who developed a model which took into account both dispersion (with the Lennard-Jones and Devonshire model) and electrostatic energies in zeolite cavities for the gas-solid interactions. Grand canonical ensemble Monte Carlo simulations were performed to evaluate adsorption isotherms, heats of adsorption, and radial distribution functions for hard-spheres and Lennard-Jones molecules in Zeolite 13X at various pressures. Though no direct comparison with experimental data was presented, the hard-sphere model was good for calculation of the heat of adsorption, but broke down for the adsorption isotherms. Another interesting result of this work was the establishment of a reference system which could be used to test models for adsorption in zeolites.

Kono and Takasaka (1986) performed a grand canonical Monte Carlo simulation of the N_2–Zeolite A system. The adsorption isotherm was calculated and the validity of the model potential, represented by an expansion in spherical harmonics, was tested by comparison with experiment. The role of the hindered molecular rotations was stressed as well as the importance of the adsorbate–adsorbate interactions.

In a study devoted to the framework composition of zeolites, the Monte Carlo method was used by Soukoulis (1984) to simulate the nearest-neighbour distributions of Si sites having 0 to 4 Al nearest neighbours. The atom–atom interactions were approximated by a model Hamiltonian imposing the Lowenstein rule (Lowenstein 1954) which states, on the basis of experimental evidence, that two Al atoms cannot occupy two adjacent tetrahedra in the framework. While Lowenstein's rule can explain the data qualitatively, to obtain quantitative agreement with experiment the introduction of the next-nearest neighbour Al–Al interactions was necessary. The numerical simulations predicted that the Al atom distribution is a function of the zeolite synthesis temperature, offering a unique way of controlling the atomic distributions in zeolites.

Statistical calculations are an improvement over mere energy calculations, but they cannot take into account dynamical phenomena like vibrations and diffusion, that are considered in the next section.

5. Vibrations and dynamical simulations

Many interesting phenomena occurring in zeolites have a dynamical nature: diffusion, cation exchange, and chemical reactions are among the most apparent. Moreover, the vibrational spectra of zeolites are a very important tool for elucidating structural and chemical problems of zeolitic systems.

Preparing a theoretical description of the dynamics of a zeolite is a formidable task, as there are at least a thousand degrees of freedom for the atoms contained in one crystallographic cell, and it is not easy to 'freeze' a significant number of them, because the bonds between atoms are approximately of the same strength in the whole structure. Nevertheless, a number of studies, devoted to vibrations as well as to more general dynamic phenomena, have been attempted.

For stable and (at least locally) ordered solids, the harmonic approximation can be applied. It assumes that atoms are held in equilibrium positions by elastic forces equal to the second derivatives of the potential experienced by each atom, with respect to the atomic coordinates. These derivatives can be substituted by empirical constants (force constants). Equations of motion are easily derived and can be solved by matrix diagonalization (see, e.g., Turrell 1972). Eigenvalues give vibrational frequencies, while from inspection of the eigenvectors the symmetry of the modes can be deduced. For crystals, the motion of atoms in adjacent crystallographic cells is correlated, and it is represented by plane waves (phonons) propagating through the lattice.

Pioneering work on the vibration frequencies of silicates, including zeolites, was published by Saksena (1961). The frequencies of some idealized silicate structures, like small chains or rings of SiO_4 tetrahedra, were calculated with the help of only three force constants. The results presented a reasonable interpretation of some silicate frequencies.

An investigation of vibrational properties of zeolite frameworks was carried out by Blackwell (1979 a, b). Normal coordinate calculations of two different structural subunits (D4R and D6R), characteristic of Zeolite A and faujasite-type zeolites respectively, were performed using a force field with only three independent constants. The former model subunit contained 28 atoms (4 Al, 4 Si, and 20 O), while the latter, $Al_6Si_6O_{18}$, was composed of 30 atoms. Results from using several force fields were presented.

The final force-field of choice, applied to model systems that mimicked the geometry changes with varying silicon-to-aluminium ratio, satisfactorily predicted the observed changes in frequencies for both subunits. The overall distribution of vibrational modes agreed well, for the former subunit, with the observed spectrum of Zeolite A, while the predicted spectrum of the latter subunit compared less well with that of Zeolite X. This fact should not be considered a drawback, particularly in view of the simplicity of the models and force field used.

A similar procedure was adopted by Baker *et al.* (1985) to calculate vibration frequencies of several metal cations present in Faujasite-type zeolites. Model systems consisting in several fixed-framework atoms and one cation, and representing different cation sites, were investigated in order to assign far-IR-active vibrational modes. The calculated frequencies could satisfactorily explain the observed frequency ordering of the various sites, and the method was proposed as an auxiliary tool for clarifying some structural problems of zeolites.

Miecznikowski and Hanuza (1985) proposed an approach to vibrational problems in X and Y zeolites on the basis of monodimensional lattice dynamics. The framework structure was represented by infinitely-long planar zig-zag chains with two atoms (one Si and one O) or four atoms (1 Si, 1 Al, and 2 O) in the unit cell. The range of frequency of some characteristic vibration modes of zeolites could be located, and vibrational spectra could be discussed in some detail.

No *et al.* (1986) performed a vibrational calculation on Zeolite A with the pseudolattice method. In this method, lattice dynamics is applied to pseudo unit cells (smaller than the real ones) which are chosen to provide interesting subunits with almost the same force field as in a real zeolite framework. The calculated vibrational frequencies and modes were used to interpret experimental spectra, and to reproduce the variation of some frequencies with changes in Al/Si ratio. Most calculated values were in good agreement with the observed spectra.

The problem of the influence of the framework and cations on the vibrational frequencies of the adsorbed molecules has been considered by Cohen de Lara and coworkers. In the first paper (Cohen de Lara and Vincent-Geisse 1976), the potential energy of the N_2O-molecule in the Zeolite NaA was calculated from its electrostatic, dispersion, and repulsion components for different positions and orientations of the molecule. The potential barriers to translation and rotation are high, and the molecule performs librational and translational oscillations, the frequencies of which were calculated. The calculated spectra may account for the observed far-IR spectra. The lifetime of the adsorption and the time of residence of the molecule in the potential well were also evaluated.

The relations between the integrated intensity of infrared forbidden bands and the field that induces those bands were investigated by Cohen de Lara and Delaval (1978) and the resulting theory applied to the spectrum of N_2 adsorbed in NaA zeolite. The field obtained through the band intensity agreed reasonably with theoretical values.

Finally, in order to interpret infrared spectra of methane adsorbed in NaA zeolite at low temperature, Kahn *et al.* (1985) calculated the frequencies of CH_4 and CD_4 perturbed by an electric field.

A poster presented at the 7th International Zeolite Conference (Tokyo, Japan) by Foerster and coworkers (Foerster 1986) was devoted to the influence of the zeolite field on the IR spectra of CO adsorbed in NaA and NaCaA zeolites. The potential was calculated including electrostatic, polarization, dispersion, and anisotropic exponential repulsion terms, but considering CO as a point particle. Energies of adsorption, symmetry of IR bands and IR frequency shifts were calculated, and satisfactory agreement with experiment was obtained.

Molecular dynamics (MD) has been applied to zeolites in our laboratory. This technique was created for numerical studies on the statistical mechanics of fluids and was used also for the solid state (for a recent review see Klein 1985). It consists of numerical integration of the classical equation of motion for a system of point or rigid particles, free to move under the action of a given potential. MD can be applied both to ordered and disordered systems, and can be used for studying phenomena like diffusion or phase transitions. In its most usual form, the microcanonical ensemble is adopted, but recently extensions to other ensembles have been proposed. To avoid surface effects, periodic boundary conditions are commonly applied. The average kinetic energy provides a measure of the temperature. Moreover, for stable systems, mean coordinate values (along with their distribution functions) and anisotropic temperature factors are easily evaluated and can be compared to experimental data.

For crystals, the coordinate distribution functions (which give the density of probability for a given value of each coordinate of an atom) are usually referred by symmetry-group transformations to the asymmetric unit, and their more or less gaussian-like shape is a check of a correct simulation of the crystal symmetry, when no symmetry constraint is applied to the system.

The autocorrelation function

$$C(t)=\frac{\langle f(0)f(t)\rangle}{\langle f(0)^2\rangle} \tag{10}$$

where $f(t)$ is a time-dependent quantity and the angle brackets denote time averaging, can be used to study dynamical properties of the system. In particular, the Fourier transform of velocity, dipole moment, and polarizability autocorrelation functions provide the vibrational, infrared, and Raman spectra, respectively.

When diffusion is present, the diffusion coefficient can be derived by means of Einstein's formula

$$D=\lim_{\tau\to\infty}\frac{\langle \Delta r(\tau)^2\rangle}{6\tau} \tag{11}$$

where $\langle \Delta r(\tau)^2\rangle$ is the averaged squared displacement of the particles and τ is time.

Molecular dynamics appears to be especially suitable for studying zeolites, where some solid state and fluid-like characteristics are often jointly present.

The first attempt to apply this technique in the field of zeolites was made by Demontis *et al.* (1986). A study of water in the cavities of Natrolite, a natural zeolite, was performed using an atom–atom potential. The framework and the cations were held fixed. The positions of the water molecules were reproduced correctly, but the HOH angle was too small and the simulated frequencies of the stretching and bending bands were higher than the experimental ones. These shortcomings were attributed to deficiencies of the internal potential for water. Convergence properties of equation (11) were tested, and it was determined that, when the diffusion coefficient is close to zero, very long (>100 ps) simulations are necessary.

The model adopted in this work may be subject to some criticism, because the mass of the water molecules is only one order of magnitude smaller than the mass of the framework, so that the impulse is not conserved within acceptable error bounds.

A model potential was proposed (Demontis *et al.* 1987 a) for MD simulations of the framework. It relies on force constants but an extended form, using an anharmonic potential with terms up to the fifth power of the displacement, was also derived. The two forms of this model (harmonic and anharmonic) were applied to the calculation of structural and vibrational properties of anhydrous Natrolite. The disordered structure of this zeolite could be interpreted as resulting from the superposition of four ordered structures with different statistical weights. In spite of their simplicity, both models succeeded in representing the main features of the anhydrous Natrolite structure and of the infrared spectrum.

A similar study was performed on the anhydrous Zeolite A (Demontis *et al.* 1987 b), using the same model potentials. The structure, for the $Fm\bar{3}c$ symmetry group, was correctly reproduced (with coordinates close by 0·01–0·02 Å to experimental ones) and, starting from the $Pm\bar{3}m$ space group structure, the face-centred symmetry was recovered. Reasonable anisotropic temperature factors were calculated and the simulated spectra were satisfactory.

Finally, preliminary calculations for a complete (including cations, framework, and water) MD simulation of Natrolite have been presented (Demontis *et al.* 1987 c). Though the framework and cation properties were correctly reproduced, the agreement for the structural and dynamical properties of the water molecules was not significantly improved, in spite of using a modified potential.

The problem of a satisfactory potential for water in zeolites is being considered in our laboratory. Meanwhile, MD simulations of ZSM-5 zeolite, including also the diffusion of methane, are in progress.

6. Concluding remarks

Theoretical investigations on zeolites, as shown in this review, have been attempted with various methods. Structural problems and some important properties like adsorption can be studied, and, with a careful choice of the models, satisfactory agreement with experimental data can be achieved and predictions made. On the other hand, the reproduction of some other important phenomena, like the diffusion of molecules in the zeolite channels or the vibrational spectra, requires further investigation.

The major challenge in this field is a reliable interpretation of the catalytic reactions that occur in zeolites. Quantum chemistry (to provide potentials), statistical studies (for chemical equilibria), and dynamical simulations (to elucidate in detail reaction mechanisms) can be used together.

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