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Application of modeling in zeolite science

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Abstract

Zeolites form an important class of inorganic materials with an enormous industrial interest which derives from their molecular sieving, ion-exchange and catalytic properties. The research in this field now takes advantage on advanced modeling programs which allow us to examine in details the structure of these complex materials and their interactions with adsorbed species both under static or dynamic conditions. The information obtained is often fundamental for better understanding of the mechanism of formation of these materials and their shape selective properties. In this paper, selected applications of modeling in zeolite science are presented and discussed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolites form a class of tectosilicates with a microporous framework built up by a three-dimensional network of corner-sharing [TO_4] (T=Si, Al) tetrahedra. The industrial importance of these materials derives from their molecular sieving, ion-exchange and catalytic properties arising from the acidity of the framework and from the ability to accommodate exchangeable metal cations and organic molecules within the porous system.

The use of zeolites as catalysts is probably the most exciting application of these materials. In fact, when the catalytic process takes place in a porous system with free dimensions in the range 3–12 Å, the reaction pathway is strongly influenced by the framework geometry and the steric constraints are fundamental for driving the reaction towards the desired products. For these *shape selective* properties, the zeolites are often preferred to other non-shape selective catalysts for either economical and environmental reasons.

One of the most significant developments in the study of zeolites concerns the application of structural modeling and computational chemistry methods, favored by the development of computing and high-resolution graphics technology. It is easy to image the advantages coming from the facile visualization and manipulation of the complex zeolite structure, the simulation and even the refinement of diffraction and spectroscopic data, the simulation of adsorption and diffusion processes of organic molecules, etc. Furthermore, the application of quantum-chemical methods gives information about the structure of the active site (usually difficult to assess experimentally) and even the reaction mechanism.

The actual tendency is to develop integrated modeling packages that contain all the functionalities

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necessary for the accurate study of inorganic materials. Some packages, such as Catalysis and Cerius^2 (Molecular Simulation, San Diego, CA), are available in the market and actually have a widespread diffusion. Since an exhaustive illustration of all these topics is impossible here, attention will be focused only on the interactions between the organic molecules (*guest*) and the zeolite framework (*host*). This topic will be illustrated with some practical examples. Interested readers who would like to have a deeper knowledge of zeolite modeling are invited to refer to a recent book published by Catlow [1].

2. Structure building and visualization

A deeper insight into the structure–properties relationship of zeolites is strongly connected with the ability to build and visualize their extremely complex structures at atomic level. The use of classic crystallographic programs for drawing the structure model of a material is clearly limited with respect to the easier and more flexible building tools offered by the modern computer graphics. Such an operation necessarily requires knowledge of the crystallographic data (unit cell parameters, space group symmetry, coordinates of atoms) which can be found in the appropriate structure library of the software or in the specialized scientific literature. In the case of a new microporous material, its crystal structure must be determined by using the classical crystallographic methods or by applying alternative procedures, such as the *simulated annealing* [2–5], which requires little structural and compositional information (unit cell dimension, space group symmetry, T-atom density). This procedure initially considers a random distribution of the required T-atoms within the unit cell; during the calculation, the symmetry-independent T-atoms are adjusted by simulated annealing to reach a number of possible structure solutions, which match the imposed geometrical constraints. Each of these solutions contains the approximate coordinates for the independent T atoms, which constitute the input for the distance least-squares (DLS) program [6,7] necessary for generating the structure model, including the oxygen atoms, optimized on the basis of geometrical constraints. The most probable solution is selected by comparing the experimental X-ray powder diffraction pattern with that simulated by using the DLS atomic coordinates and is finally refined by using *full-profile fitting methods* (Rietveld analysis [8]). Though the *simulated annealing* is a significant advance in the determination of zeolite structures [2–5], its application becomes troublesome in the case of complex structures (i.e. low symmetry/high T-atom density framework) because of the large number of possible solutions. In these cases, the probabilities of success are increased if the experimental X-ray diffraction profile is included in the calculation. Nevertheless, for relatively simple structures, it is a good alternative to the conventional crystallographic methods.

Visualization of the zeolite framework is a fundamental step in a modeling study because it allows the identification of the main structural features and facilitates modifications of the basic structure. To do that, several structure editing tools are available which allow iterative monitoring and modification of geometrical features, the addition, replacement or removal of atoms or groups (either maintaining symmetry constraints or not), the creation of sub- or supercells with the modification of the space group symmetry, the reproduction of structures characterized by stacking faults such as Beta zeolite [9] and MFI/MEL intergrowths [10].

To validate a new structural model, its consistency with the experimental physico-chemical data must be checked. For this purpose, several functionalities are available for the simulation of diffraction (X-ray, neutron, electron, both from powder and single crystal) and spectroscopic data (IR, Raman, ^{29}Si NMR, EXAFS). Furthermore, analytical data such as pore dimensions and volume, occupiable and accessible pore volume for a given sorbate, T-atom density, coordination sequences, statistical distributions of bond lengths and angles, can be easily computed and compared with the experimentally derived data. Finally, the structure model must be refined by, for instance, the full-profile fitting methods and the resulting crystallographic data included in the appropriate structure library for further future use.

3. Host/guest interactions

Steric effects play a fundamental role in two different fields of application to zeolites: separation and catalysis. For this reason, computational chemistry and modeling are useful for evaluating the interactions between a sorbate molecule (*guest*) and the framework (*host*). These interactions are also relevant for understanding how an organic molecule (*template*) favors the crystallization of a microporous structure in a selective way. Furthermore, host/guest interactions are fundamental for determining the diffusivity of a sorbate molecule in a porous structure, for instance by determining the energy barriers which hamper the diffusion of the guest through a porous host. All these calculations can be conveniently performed by using *molecular mechanics* methods. These methods take advantage of the so-called *force fields*, sets of functions (directly derived from classical mechanics) and terms necessary for their parametrization (force constants, equilibrium bond lengths and angles, etc.). These parameters are generally empirical, derived from the fit of experimental data (mainly crystal structures) but, in the absence of experimental data, they can be derived from ab initio quantum-mechanical calculations.

The interested readers can refer to a recent book edited by Comba and Hambley [11], which exhaustively treats this topic [11].

3.1. Application of molecular mechanics: the docking method

The first step concerns the determination of the preferential adsorption sites and the corresponding binding energies for a sorbate in a porous structure. To do that, Freeman et al. [12] proposed the procedure schematized in Fig. 1.

The docking procedure begins with a high temperature (e.g. 1000–1500 K) *molecular dynamics* (MD) simulation of the isolated sorbate molecule. This step is necessary only in the case of highly flexible molecules and is performed for exploring the conformational space of the sorbate. During the MD run, some of the conformations generated are randomly extracted from the dynamics trajectory and stored in an archive file to be successively used in Monte Carlo docking within the microporous structure. This

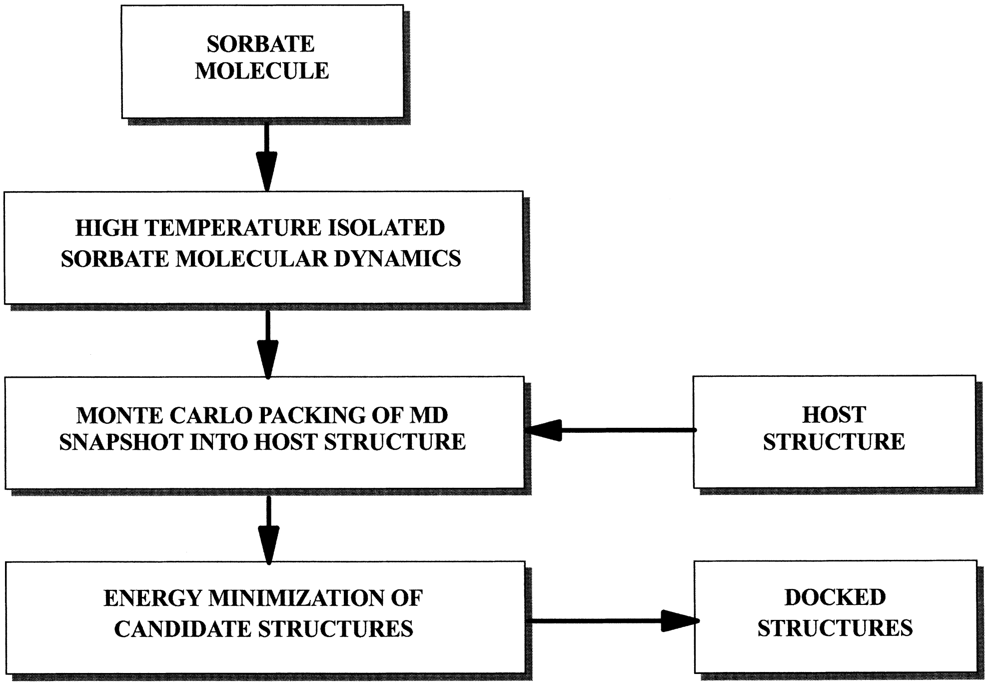

Fig. 1. The docking scheme [12].

procedure consists in a random selection of the position and orientation of each of the sorbate conformations stored in the archive file in the zeolite framework and in the evaluation of the non-bonding interaction energy. A threshold energy is chosen to avoid excessive steric overlaps between host and guest (e.g. 5000–6000 kJ mol^{-1}) provided that a conformation is accepted only if the interaction energy is below this value, otherwise the process is iteratively repeated until a favorable location is found.

Once the docking procedure is completed, the energy of each of the docked structures is minimized to allow the sorbate molecule to optimize its interactions with the zeolite framework. Practically, the molecule reaches the nearest low energy sorption site while its energy is minimized with respect to the internal degrees of freedom and to the short-range non-bonding interactions with the pore wall, described by a potential function of the Lennard-Jones form.

Some important approximations are often applied to reduce computational costs. Though the zeolite framework is known to be flexible, the influence of the guest molecule on the host is considered very small and framework relaxation phenomena are neglected during the energy minimization. Also, electrostatic interactions are neglected only in the case of sorbates with low polarity and purely siliceous framework, otherwise this approximation is not admissible.

3.1.1. *Examples*

3.1.1.1. Location and energetics of organic molecules in a porous system Freeman et al. [12] applied this procedure to obtain information about the location and energetics of different butene isomers within the ZSM-5 (MFI) porous system.

For each isomer, the MD trajectory was simulated at 1400 K during 10 ps and at every 0.1 ps the conformation was stored in an archive file. The results of the subsequent Monte Carlo docking, exemplified in Fig. 2 for isobutene, reveals a wide distribution of 100 conformations docked within the MFI structure, as a consequence of the high threshold of the interaction energy (ca. 6300 kJ mol^{-1}) chosen for the acceptance of the trial structures. This apparently unacceptable threshold value is a direct consequence of the Lennard-Jones potential function which implies

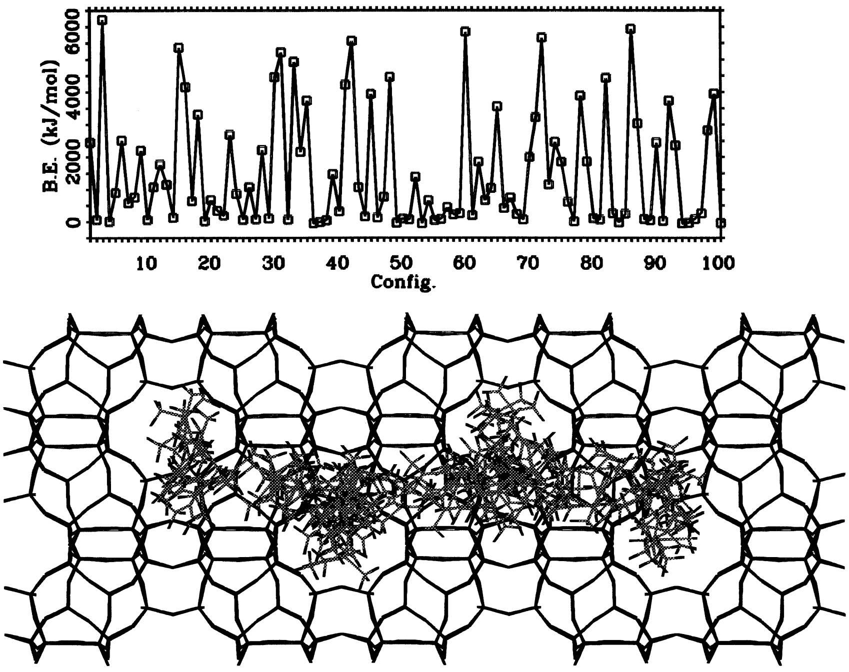

Fig. 2. The different conformations of isobutene in MFI before energy minimization.

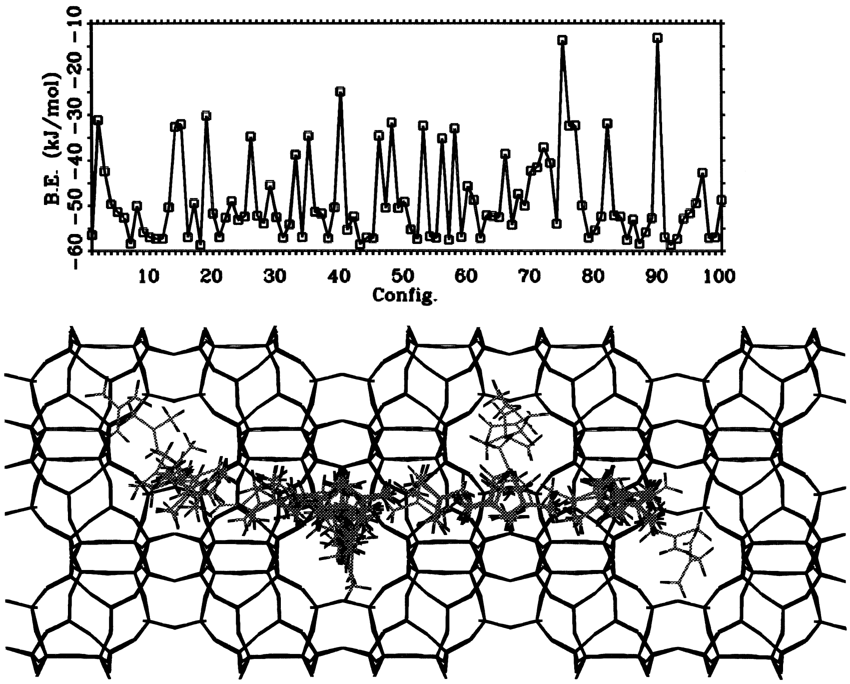

Fig. 3. The different conformations of isobutene in MFI after energy minimization.

a high value of the repulsion energy in the presence of even limited steric overlap between the host and the guest. Upon energy minimization, the situation becomes more regular, with similar low energy sorption sites reached by molecules docked in different points of the porous structure (Fig. 3).

After computing the binding energy for all the butene isomers in MFI, the authors observed that isobutene has the lowest binding energy and hence interacts least strongly with the MFI framework as a consequence of the unfavorable match between the host and the guest. On the contrary, the other butene isomers display a more favorable van der Waals contact with the host and are retained much more strongly by the framework. On the basis of these results, the authors concluded that MFI is a promising catalyst for skeletal isomerization of 1-butene.

3.1.1.2. Studies on the templating effect in zeolite synthesis Another interesting application of the docking procedure concerns the templating effect organic molecules have on zeolite synthesis. It is well known that the formation of a microporous solid generally requires the presence of a template molecule able to drive the crystallization towards a defined zeolite framework. Though only a few examples of true templates are known (i.e. organic molecules which selectively favor the crystallization of a zeolite), the presence of a structure directing agent is necessary for the formation of several microporous solids. In spite of the mass of data related to the synthesis of zeolites, the effective role of the organic molecule is often obscure particularly when considered in relation with the other synthesis parameters (e.g. gel composition, pH, temperature, etc.). For this reason, a deeper understanding of the role of the template is necessary to design the synthesis of new microporous frameworks through a rational selection of the structure directing agent. In this field, molecular modeling is useful for determining the location of template molecules within the pores, information experimentally achieved only in a few cases (e.g. tetrapropylammonium (TPA) cations in MFI [13], *N*-methyl-quinuclidinium in NU-3 (LEV) [14], crown-ether in EMT [15]).

Bell et al. [16] were the first to study systematically the ability of four tetraalkylammonium ions ($(C_nH_{2n+1})_4N^+$, with n=1 (TMA), 2 (TEA), 3 (TPA)

Table 1
Non-bonded interaction energy of $(C_2H_{2n+1})_4N^+$ cations in various zeolite frameworks

MFI		MEL		BETA	
Tetraalkylammonium ion	E_{int} (KJ mol^{-1})	Tetraalkylammonium ion	E_{int} (kJ mol^{-1})	Tetraalkylammonium ion	E_{int} (kJ mol^{-1})
TMA	−51.7	TMA	−38.7	TMA	−43.1
TEA	−92.1	TEA	−73.0	**TEA***	−104.7
TPA*	−133.9	TPA	−119.9	TPA	−83.4
TBA	−165.5	**TBA***	−159.5	TBA	−56.7

Predicted templates are in bold; experimental template marked with an asterisk; data from [16].

and 4 (TBA)) to drive the formation of zeolite structures. By using the procedure described above, they computed the non-bonding interaction energies of these cations in three zeolite frameworks (MFI, MEL and *BEA (Polymorph A of the Beta zeolite structure [9], Table 1)). The results obtained are fully in agreement with the experimental observation both for MEL and *BEA zeolites but not for MFI, for which the TBA cations are predicted instead of the experimentally used TPA. The discrepancy was explained by the fact that the docking procedure was performed with a single template molecule; under this condition, the longer alkyl chains of TBA fit better than those of TPA and the MFI pores, increasing the stability of the system. When the calculations were performed by packing two template molecules (the first one located at the lowest energy position, the second at the next translationally equivalent site), the authors found the lowest non-bonded interaction energy for TPA, according to the experimental results, while the energy of the MFI/TBA system significantly increases because of the strong repulsion between the terminal –CH_3 groups of the two adjacent ions. More recently, Lewis et al. re-examined the data reported in [16] and extended the analysis to dicationic templates $[(CH_3)_3N–(CH_2)_n–N(CH_3)_3]^{2+}$ (n=3–8) used in the synthesis of EUO and MTT zeolites [17]. The simulations were carried out by packing two template molecules and the degree of interaction between them was computed by defining a packing energy (ΔE_{pack}) according to the equation

$$\Delta E_{pack} = (E_n/n) - E_1,$$

where E_n and E_1 are the interaction energies of n and 1 template molecules, respectively. The results of the calculations were fully consistent with the experiments and demonstrated the importance of the interaction among the template molecules in driving the formation of a zeolite framework.

3.2. *Application of molecular mechanics: diffusion of sorbates in zeolites*

A zeolite is defined as shape selective catalyst because the reaction generally occurs in the limited space allowed by pore structure. Csicsery [18] classified the shape selectivity properties of a zeolite catalyst with respect to the reagents, products and transition state. While determination of the transition state selectivity properties of a zeolite requires knowledge of the reaction mechanism and the modeling needs the use of quantum-chemical methods, information on both reagents and products selectivity properties can be easily obtained by using molecular mechanics. In fact, these types of shape selectivity are closely related to the diffusion behavior of the molecules within the zeolite. Since experimental determination of diffusion coefficients for organic molecules in microporous solids is not easily feasible, simulation remains the only way for evaluating these values. This topic has been exhaustively treated in [19], thus attention will be focused on another way to face the problem, namely the determination of the minimum energy pathway (MEP) for diffusion of a sorbate in a zeolite [20,21]. Practically, the MEP represents the variation of the energy of the system during the diffusion of a guest in a given host and can be accurately evaluated by simulating the forced diffusion process (Fig. 4).

Once the diffusion path is defined by a pair of points (A and B in Fig. 4) located on the channel axis, at the opposite ends of the pore section, the guest is forced to

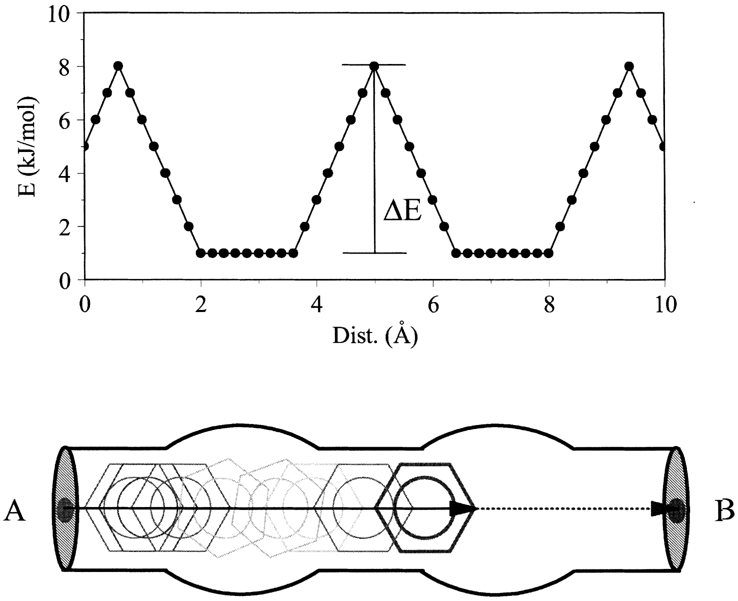

Fig. 4. The forced diffusion scheme [21].

move stepwise along this path. At each step of the trajectory (usually 0.1–0.5 Å long) the molecule is constrained to lie at a fixed distance from the origin while the energy of the system is minimized with respect to its internal degrees of freedom (bond lengths, valence and torsion angle variation, deformation from planarity in the case of aromatics) and to the non-bonded interactions with the host described with a potential function of the Lennard-Jones form. Optionally, electrostatic interactions can also be included in the calculations, but they can be neglected in the systems involving non-polar sorbate molecules and pure siliceous zeolite models.

In order to reduce computational costs, the simulations can be performed with the framework having a fixed crystallographically determined geometry, i.e. by neglecting the framework flexibility. Simulations of the framework dynamics for a number of zeolites performed by Deem et al. [22] revealed a non-negligible motion of the framework atoms from their equilibrium (crystallographic) positions. This implies a dynamic fluctuation of the pore apertures (*pore-mouth breathing motion*), which at relatively high temperature (550 K) can be of the order of 0.2–0.3 Å. In principle, such a fluctuation may significantly influence the non-bonded interaction energy since the repulsive component strongly varies with a small variation in the distances. However, since the timescale of the breathing motion is some orders of magnitude shorter than that for diffusion of a relatively large molecule it is possible to conclude that the crystallographically determined pore dimensions really represent the average configuration during the diffusion of the sorbate. Furthermore, in the case of bulky sorbates relaxation of the framework is expected to reduce the repulsive host/guest interactions. However, owing to the small degree of flexibility of the zeolite framework, the magnitude of this effect is considered negligible, leading to the conclusion that the rigid framework approximation gives a reasonable estimation of the MEP.

The results of the forced diffusion simulation is a plot in which the energy of the system is related to the position of the sorbate (Fig. 4). From this plot, it is possible to evaluate the entity of the energy barriers (in turn related to the activation energy of the diffusion process) that hinder the diffusion of the molecule and by comparing the same plot with the snapshot of the simulation it is easy to identify the steric situations responsible for these barriers (see later).

3.2.1. Examples of application

3.2.1.1. Screening of zeolite catalysts for the selective isopropylation of naphthalene Horsley et al. [21] were the first to apply this procedure in a screening of the possible zeolite catalysts for the synthesis of 2,6-diisopropylnaphthalene (2,6-DIPN) via alkylation of naphthalene with propylene. The authors tried to select a priori the zeolite structures potentially able to enhance the yield of 2,6-isomer with respect to the useless 2,7-isomer. Note that with non-selective acid catalysts the two isomers are produced in equal amounts and their separation is difficult and expensive.

Two candidate structures (MOR and LTL) were selected first in a simple visual way, by comparing the dimensions and the shape of the DIPN isomers with the porous system of some *large pore* zeolites. Successively, the MEP was computed by applying the forced diffusion procedure. The results obtained showed that the 2,6-DIPN diffuses practically unhindered in MOR (energy barriers of ca. 15 kJ mol^{-1}), while the 2,7-isomer encounters higher energy barriers (ca. 45 kJ mol^{-1}). On the contrary, both isomers are expected to diffuse practically unhindered in LTL, leading to the conclusion that MOR should display a higher selectivity with respect to LTL. Indeed, this hypothesis was confirmed by catalytic tests, as shown in Table 2.

It is worthy to note that, in spite of the relatively small difference of the energy barriers computed in MOR, an effective enrichment of the 2,6-isomer was achieved (Table 2).

3.2.1.2. Screening of zeolite catalysts for skeletal isomerization of 1-butene Recently, we faced the problem of selecting zeolite catalysts for the synthesis of isobutene through the skeletal isomerization (SI) of 1-butene [23]. It is well known that the apparently simple SI reaction is accompanied by several side reactions which limit the yield of isobutene [24]. Among them, the most important are the dimer formations and their cracking. For this reason, the screening of the candidates was performed by computing the MEP not only for 1-butene and isobutene, but also for 3-methyl-3-heptene (MHEP), 2,4-dimethyl-3-hexene (DMH) and 2,4,4-trimethyl-2-pentene (TMP), chosen as representatives of the different branched dimers which can be produced during the reaction. Candidates were selected among the small pore (ERI, LEV), medium pore (FER, ZSM-48, EUO, MFI, MTT, TON) and large pore (BEA, MTW, MOR) zeolites.

The results of the calculations are exemplified in Fig. 5 and 6, where the snapshots of the migration of isobutene in LEV and ZSM-48 are reported together with the corresponding energy profiles. These results can be interpreted as follows: during the diffusion through the pores of LEV and ZSM-48, isobutene encounters energy barriers of ca. 210 and 13 kJ mol^{-1}, respectively. In the case of LEV, the highest energy is reached when isobutene is passing through the 8-membered ring windows connecting the cages. Clearly, the pore openings are too small for allowing isobutene to diffuse and the repulsive non-bonded interactions between the guest and the host prevail. On the contrary, the diffusion of isobutene in 10-membered ring channels of ZSM-48 is expected to be much easier. From these results, we can conclude that the small energy barriers computed for isobutene in ZSM-48 do not hamper the diffusion of this molecule, particularly at the high temperature at which the reaction is performed (>350°C). The same is

Table 2
Selectivity of catalysts in the alkylation of naphthalene with propylene (reaction performed in autoclave at 275°C, data from [21])

Catalyst	Naphthalene conversion	Isopropylnaphthalene selectivities (mol%)			2,6-/2,7-isomer ratio	Energy barriers (kJ mol^{-1})	
		Mono-	Di-	Poly-		2,6-DIPN	2,7-DIPN
MOR	54.4	73.9	25.7	0.4	2.51	12–17	40–50
LTL	69.0	77.8	20.6	1.6	0.82	17–25	12–17
SiO_2–Al_2O_3[a]	23.5	91.9	8.1	0.0	1.00	—	—
SiO_2–Al_2O_3[a]	94.2	31.1	51.5	17.4	1.03	—	—

[a] Grace, $SiO_2/Al_2O_3=2.98$.

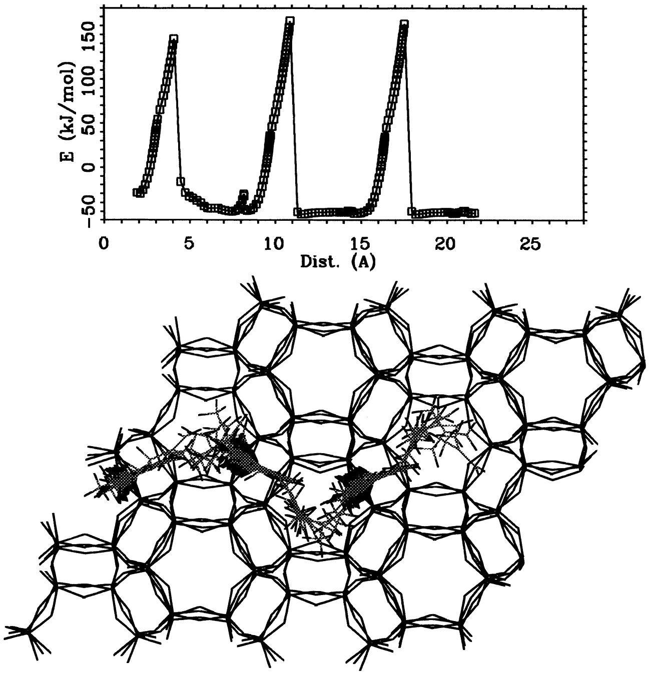

Fig. 5. MEP for diffusion of isobutene in LEV.

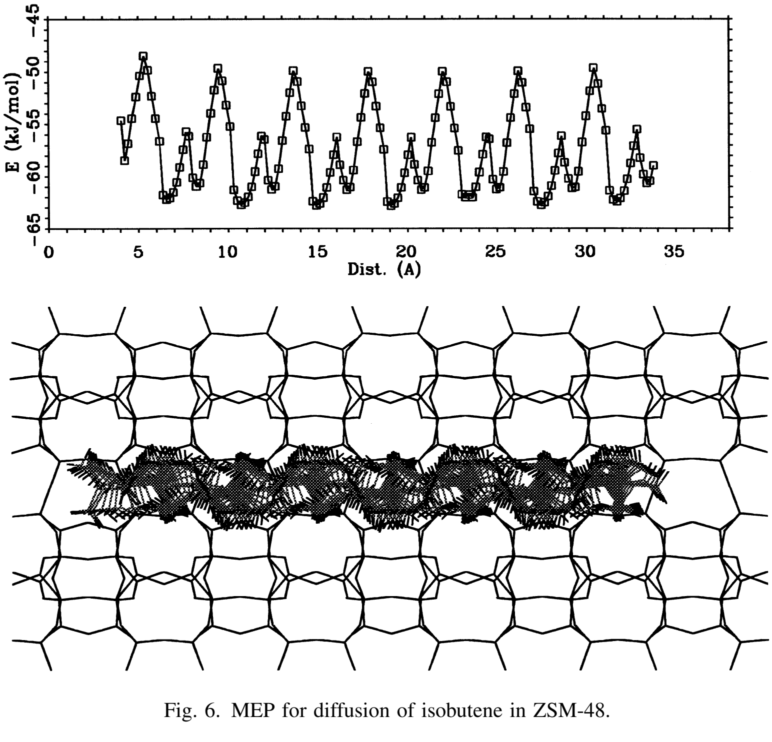

Fig. 6. MEP for diffusion of isobutene in ZSM-48.

not true for isobutene in LEV. This molecule cannot migrate through the 8-membered ring openings, and hence it is expected to remain trapped in the zeolite cages.

When we extended the molecular mechanics calculations to all the zeolite frameworks considered here, the following evidences were achieved:

- The small pore zeolites (ERI, LEV) are unsuitable catalysts for the SI reaction due to high energy barriers (>200 kJ mol^{-1}) hampering the diffusion of isobutene.
- The large pore zeolites are expected to be completely non-selective since the bulkiest TMP molecule easily diffuses within them.
- More favorable are the medium pore zeolites in which the diffusion of isobutene is significantly less hindered than that of the branched C_8 isomers.

Therefore, we concluded that a suitable catalyst for SI reaction has to belong to the class of the medium pore zeolites. These results were confirmed by the catalytic tests, which indicated FER and ZSM-48 as the most active zeolites for SI reaction.

4. Conclusive remarks

The studies mentioned here represent only a limited picture of the real potential of molecular modeling in zeolite science. Nevertheless, the examples reported clearly show how the use of these methods gives important information for better understanding of the complex phenomena occurring in this class of materials.

In spite of the high level reached in the development of the molecular modeling tools, several opportunities are still open. One of them concerns the development of potential functions for extending the molecular mechanics calculations to other interesting systems such as the porous alumino-phosphates (ALPO) or to study the host/guest interaction on microporous solids in which aluminum and/or part of silicon is isomorphously substituted with other tri- and tetravalent elements.

Another very exciting challenge concerns the application of quantum-chemistry methods. The actual hardware development strongly limits the possibility to apply these methods on extended structure, the calculations being usually performed over a few tens of atoms. Under these conditions, most of the structural information is lost and the results may be considered only indicative of the real situation. There are, indeed, several efforts for circumventing this limitation: the most significant concerns the use of embedding calculations in which a portion of the structure treated quantum-mechanically is embedded in a cluster treated with molecular mechanics methods. The main molecular modeling software packages already provide this capability, even if several problems still exist.

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