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Selectivity of a Model Zeolite Ring over Hydrocarbons with Different Symmetry, Travelling with Different Orientations and Speeds

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We explore the selectivity of a model zeolite ring over representative hydrocarbons of crude oil. The model ring consists of 7 silicon tetrahedral units and one chemically active aluminum site through which hydrocarbons with symmetries varying from almost spherically symmetric to linear chains (1D), planar (2D), and pyramidal (3D) structures diffuse. The selectivity is further investigated when the hydrocarbons travel with different orientations and speeds. The semiclassical Born−Oppenheimer molecular dynamics approximation is used to characterize the chemical dynamics, as well as to determine the energetics and reaction products. The simulations reveal noticeable differences in energy profiles and charge populations. Our results are important to understand aspects of mass transport and some of the factors that control the catalytic activity in zeolites.

Introduction

When crude oil is extracted from the ground it contains a variety of hydrocarbons showing structures from straight chains up to complex branched molecules. However, the proper use of the petroleum demands the separation of its components. The separation of the hydrocarbons is commonly achieved by fractional distillation, a process based on the different boiling points of the components. But hydrocarbons with similar boiling points are difficult to separate by distillation. In this case, the zeolites are used as molecular sieves to discriminate among the hydrocarbons with similar vaporization temperatures. The zeolites are characterized as ordered arrays of SiO_4 units; i.e., they are crystal structures whose main components are tetrahedrally coordinated silicon with bridging oxygens. The zeolites usually have small contents of chemically active aluminum in the form $(AlO_4)^-$, which have randomly replaced some of the SiO_4 sites, together with cationic species, like H^+, neutralizing the local charge. The arrangements of the tetrahedrons form rings of different molecular dimensions, and the rings build channels with different topologies. It is due to the rings that zeolites work as molecular sieves for the separation of compounds. In addition, the aluminum sites impart acidic properties to the zeolites, making them useful as catalysts or ion exchangers. The main use of zeolites is given in the petrochemical industry for the separation and transformation of petroleum into a variety of compounds such as fuels, plastics, etc.

A first approach to characterize the selectivity of zeolites has been based on their channel molecular dimensions. For instance, small hydrocarbons are expected to easily penetrate the zeolite, whereas the large ones should be rejected. Recent investigations have put in evidence additional types of zeolite selectivity exerted over the shape, polar charge, and transition state of the hydrocarbons[1] (Figure 1). However, the separation of hydrocarbons by zeolites is a complex process that still demands investigation. Our goal in this work is to explore the selectivity of the zeolites toward the hydrocarbons from a dynamical perspective. A description of this nature should not only exhibit the types of selectivity already mentioned above but also show their possible modifications, or even point to new types of selectivity associated with the dynamical character that the separation process of the hydrocarbons involves.[2] In particular, we chose mordenite because it is a zeolite of common use. We extract one of its rings and use it as a model silicate ring to investigate the local interactions with hydrocarbons that have different shapes, travel in different orientations, and diffuse through the ring model with different speeds. The ring additionally includes a $(AlO_4)^-$ tetrahedron site and a cationic neighbor H^+. The Born−Oppenheimer semiclassical dynamics method is used for this purpose, where the electronic wave equation is solved with resort to density functional theory, and the nuclei (supposed to be immersed in the field created by the electrons) follow a dynamics described by the newtonian equations.[3] A technique like this has previously shown to be accurate enough to characterize the zeolites in their interaction with a variety of hydrocarbons.[4,5]

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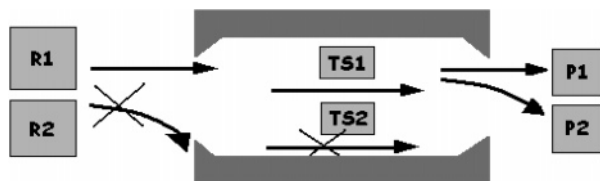
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Figure 1. Small hydrocarbons (R1) can diffuse through zeolitic channels, but others (R2) are too big to fit in. The zeolite confinement admits some transition states (TS1), forbidding others (TS2). The interaction of the zeolite with hydrocarbons also favors the formation of particular products (P1 and P2).

The Zeolite Model

The diffusion of hydrocarbons in zeolites has been investigated from the experimental and theoretical perspectives.[6] From the theoretical point of view, the computational simulations require representative models to yield accurate results. There are a number of representative models proposed by different authors[7,8,9,10] taking some of the main zeolite properties into account like, for example, the molecular dimensions of the confining cavities, the presence of chemically active centers, the effects of long-distance interactions due to the atoms located relatively far away from the catalytic centers, the symmetry of the crystal structure, etc. Unfortunately, the zeolite models containing most of these features turn out to be very large, intricate, and computationally demanding. A way to avoid such complications is by using model potentials to represent the interactions among atoms.[11] Assuming no hydrocarbon cracking and no molecular collisions, the molecular simulations using model potentials show periodic behavior in energy barriers due to the diffusion of the hydrocarbons in a crystal lattice. In mordenite, the spatial periodicity occurs in an interval of approximately 7 Å.[10] This indicates the possibility of reducing the size of the zeolite model when energetic profiles are to be investigated. Also, because we are to use a computationally demanding method, the zeolite model should be not only representative of the zeolite pores but also simple enough to explore the dynamics of hydrocarbons assuming quantum interaction potentials among all the atoms taking part in the model. These are the main reasons we extract one of the silicate rings that build a mordenite pore and propose it as the smallest model to study the selectivity phenomenon. In particular, the model zeolite ring consists of eight SiO_4 tetrahedral units (Figure 2) and represents one of the several ring types present in mordenite (whose differences mainly reside in the number of silicon tetrahedral units). In a real zeolite the four oxygen atoms of each silicon tetrahedral unit are linked to contiguous tetrahedrons. In our model, two oxygens of each SiO_4 unit maintain bonds with adjacent units, and the other two are treated as capping oxygens whose bonds are saturated with spatially fixed hydrogens. The purpose of introducing these last hydrogens is 2-fold: (i) avoid an unreal deformation of the ring due to the lack of the remaining crystal atoms that keep the ring away from crunching and (ii) contemplate (only to a limited extent) the large distance interactions produced precisely by the remaining atoms that conform the zeolite framework. In the zeolite model one silicon center is replaced by a negatively charged aluminum to produce a charge inhomogeneity. Still, the total charge of the system remains neutral due to the introduction of a cationic hydrogen in one of the bridging oxygens that links the aluminum atom. Because it has been shown that lattice vibrations of zeolites are several orders of magnitude longer than the translational motion of the hydrocarbons,[12,8] we suppose a partially rigid zeolite ring in the simulations by freezing all silicon tetrahedral units, except the

aluminum tetrahedron and cationic hydrogen, which are allowed to freely move. Note that we do not expect the large-distance interactions play a decisive role in the selectivity exerted by the zeolite ring for the following reasons: (i) the cluster model of this work shows an acceptable (large) size,[13] (ii) the electric field produced by the acid site plus the other atoms of the ring contributes more inside the ring than that produced by the zeolite lattice, (iii) most of the atomic interactions of the zeolitic crystal are symmetrically convergent onto the hydrocarbon, and (iv) the hydrocarbons under analysis are nonionic hydrocarbons. According to these points, the selectivity exerted by the ring should have a local character and our ring model includes some of the most important zeolite factors known to play an important role in the selectivity phenomenon.[9] It is important to emphasize that more sophisticated approximations like, for example, the *cluster embedded approach*, do not necessarily guarantee a more realistic description of the selectivity, because we are still required to propose a representation of the environmental electrostatic potential, which is usually a difficult task. Such an approach is presently under debate[14] but, when correctly applied, it certainly becomes an alternative to investigate the zeolite selectivity.

The dynamical character of the selectivity is investigated with the diffusion of different hydrocarbons through the zeolite ring model. In this regard, we chose compounds like methane, ethylene, isobutene and isobutane because they appear in large quantities in crude oil and their geometries vary from almost spherically symmetric to linear chains (1D), planar (2D) and pyramidal (3D) structures, respectively (Figure 2). These hydrocarbons also present single and double bonds and they are representative molecules of major hydrocarbon families such as the paraffins, naphthenes, etc.

The Method

The simulation techniques that include the dynamical nature of the nuclear particles are important to gain a deeper understanding of the selectivity and catalytic processes performed by zeolites.[15,16] In particular, it is possible to simulate the diffusion of molecules through zeolite channel models with the Born−Oppenheimer (BO) semiclassical dynamics method. In this method the electronic wave function is obtained by assuming electrons immersed in a field of instantaneously fixed nuclei, whereas the nuclear particles are immersed in an average electronic field. The heavy masses and very short spatial extension of the nuclear particles compared with these of the electrons let us simplify the problem by considering the nuclei as classical particles. In this regard, each nucleus follows a newtonian trajectory due to the quantum forces derived from the electron potential plus the electrostatic forces exerted by the other nuclear particles. We refer to the total potential as the effective potential V_{eff}. The classical limit of the nuclear motion makes the BO semiclassical dynamics a relatively low computational-cost method. The formal details of the BO semiclassical dynamics approximation can be found in ref 3. On the other hand, we have recourse to density functional theory (DFT) to solve the Schroedinger equation corresponding to the electrons. Gradient corrections of the electron density are included in the exchange and correlation functionals because they give the proper energetics of weakly bonded systems.[17,18] We use effective core potentials of the type LANL2DZ for the first 10 electrons of each Si atom. The Si valence electrons are represented by LANL2DZ molecular orbitals, compatible with the LANL2DZ effective core potentials.[19] The molecular orbitals of all the other atoms (Al, O, H) that make up the zeolite model
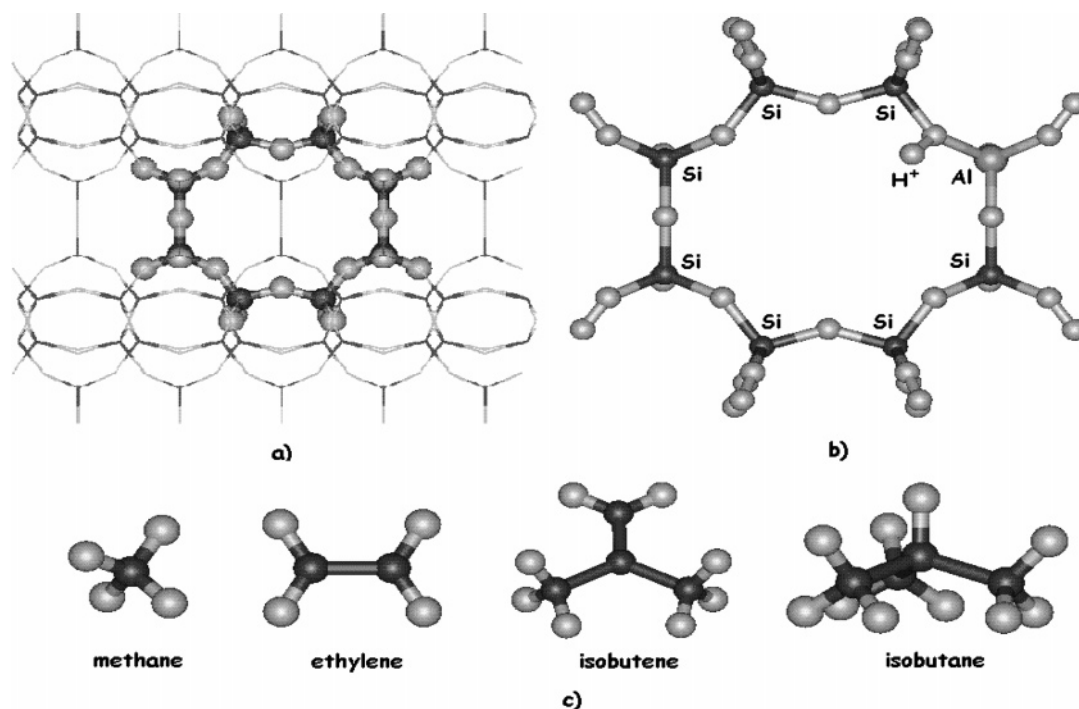
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Figure 2. (a) Structure of mordenite (with focus on one of its rings). (b) Silicate ring model with a $(AlO_4)^{-1}$ unit and a cationic neighbor H^+. (c) Hydrocarbons that diffuse through the ring model, which have different shapes and can travel in different orientations and with different speeds.

and the molecular orbitals of the atoms (C, H) that build the hydrocarbons are expanded in terms of double-ζ basis sets, with polarization functions in the valence electrons that minimize basis set superposition errors. A similar DFT approach has proven very useful in the investigation of molecular structures and reactions of zeolites with hydrocarbons.[5] The present DFT approach shows more detail of the important short-range atomic interactions than other schemes using model potentials. Nevertheless, we should be careful in the interpretation of our results, because the zeolite model proposed here is considerably smaller than those commonly used in approaches that have recourse to model potentials. The time evolution of the nuclear particles is carried in steps of 1 fs to avoid possible mathematical divergences when integrating the Newtonian equations of motion. More details of the DFT method and nuclear dynamics can be followed elsewhere.[4,7] The computations are carried out by making use of the NWChem software package[20] in a 16-node PC cluster and in a Silicon Graphics machine with 8 processors.

Validation of the Method

In the Born−Oppenheimer molecular dynamics the forces over the nuclei are calculated as the first derivatives of the V_{eff} potential with respect to the nuclear positions $\mathbf{R}_\alpha(t)$, $\alpha = 1, ...,$ N, that is, $\mathbf{F}_\alpha = -\nabla_\alpha V_{eff}(\mathbf{R}_1(t),\mathbf{R}_2(t),...,\mathbf{R}_N(t))$. Such forces determine the temporal evolution of the molecular system. From the experimental point of view, the task of establishing the trajectory of each nuclear particle is extremely difficult, and this complicates the comparison between theory and experiment. Then, if we want to establish the reliability of the forces over the nuclei, derived from the DFT level of theory already described, we must go one step further and compute the vibrational spectrum, because in this case it is possible to compare results such as vibrational frequencies and normal modes with experimental measurements. Taking note that the vibrational spectrum demands the calculation of second derivatives of the total potential with respect to the nuclear positions,[21]

TABLE 1: Vibrational Modes and Frequencies (in cm^{-1}) of Ethylene and Isobutene^a

ethylene			isobutene		
exp	calc	normal mode	exp	calc	normal mode
949	922	wagging CH$_2$	890	851	wagging CH$_2$
1023	1022	twisting CH$_2$	1381	1367	umbrella CH$_3$
1623	1635	C=C stretch	1458	1473	scissoring CH$_3$
2989	3063	sym CH$_2$ stretch	1661	1641	C=CH$_2$ stretch
3026	3077	sym CH$_2$ stretch	2945	3025	sym CH$_3$ stretch
3103	3141	asym CH$_2$ stretch	3086	3143	asym CH$_2$ stretch
3106	3169	asym CH$_2$ stretch			

^{a} Abbreviations: asym = antisymmetric, calc = calculated, exp = experiment, sym = symmetric.

$\nabla_\alpha\nabla_\beta V_{eff}(\mathbf{R}_1(t),\mathbf{R}_2(t),...)$, a close agreement with the experimental results may be indicative of the accuracy of the first derivatives (or forces) used in the molecular dynamics simulations. In particular, we calculate the vibrational spectra of ethylene and isobutene, as such compounds are relatively small, their calculations are not computationally demanding, and their experimental measurements are available.[22]

The computations have been started from the optimized structures of ethylene and isobutene. The most representative vibrational fingerprints of ethylene in the gas phase appear in Table 1. The calculated frequencies and vibrational modes are similar to the experimental measurements. On the other hand, isobutene shows more complexity due to the different types of bonds present in the structure, which may be the reason we obtain two imaginary frequencies. Despite that, the calculated vibrational markers of vapor isobutene closely resemble their experimental counterparts (refer to Table 1). In a previous study,[4] a similar level of approximation has shown that the vibrations associated with the cationic hydrogen, a member of the aluminum tetrahedral unit, compare well with the experimental observations. Therefore, the level of density functional theory used here predicts spectroscopic variables in reasonable agreement with the experiment. It is to some extent assumed that a similar degree of accuracy is achieved in the computation
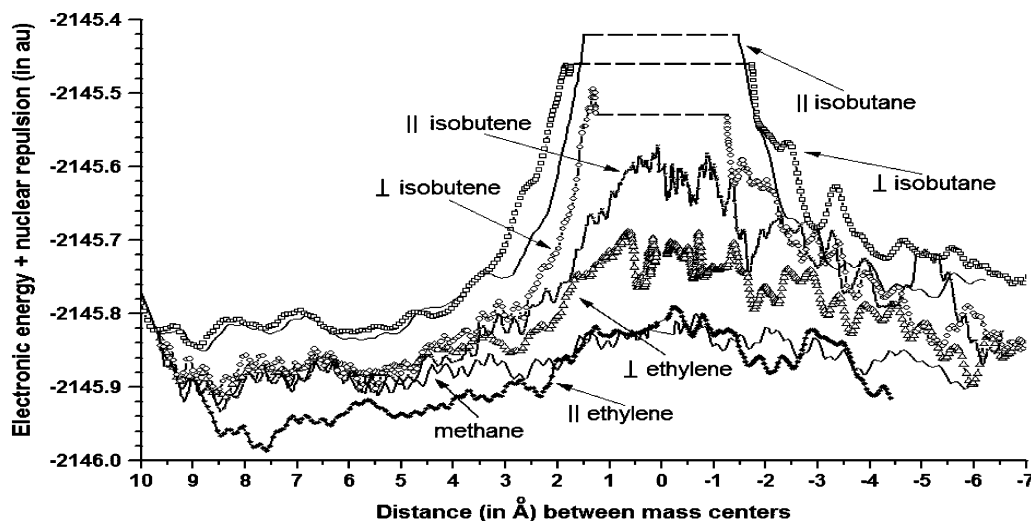
Figure 3. Variation of the electronic energy plus the nuclear repulsion with the distance between the center of mass of the hydrocarbon and that of the zeolite ring. The curves with dashed sections indicate the inability of the hydrocarbon to penetrate the zeolite ring. In such cases, the parts of the curves in the positive region represent the forward direction and in the negative region the backward direction. The symbols || and ⊥ identify the parallel and perpendicular orientations of the hydrocarbons.

of the atomic forces, which are the entities ruling the molecular dynamics.

Results

The small zeolite ring exerts a strong repulsive interaction and prohibits hydrocarbons such as methane (CH_4) to be relaxed inside the ring. Therefore, we have performed a series of simulations to determine the threshold speed required by methane to get through the ring. The methane molecule, initially located 10 Å away from the ring center, starts to travel practically with constant speed. As it gets closer to the ring, long-range repulsion interactions build up, reducing its velocity. For low initial speeds, the methane molecule is unable to penetrate the potential barrier imposed by the ring, but for initial speeds equal or higher than 0.063 Å/fs, the molecule surmounts the potential barrier and gets through (Figure 3). The particular velocity of 0.063 Å/fs is indicative of a dynamical-type selectivity exerted by the mordenite ring on methane. Due to its nature, this type of selectivity is not in evidence in optimization or transition-state calculations dealing with static atoms. Also, the speed selectivity should change according to the ring diameter: the larger the diameter, the smaller the threshold speed is expected to be. Under the consideration that methane is an almost spherically symmetric molecule,[23] we take 0.063 Å/fs as a reference speed to investigate the effects of molecular shape and orientation of other hydrocarbons in the selectivity exerted by the zeolitic ring. In the following simulations we impose similar initial conditions in the positions of the hydrocarbons as for methane, by locating the hydrocarbon mass centers approximately 10 Å away from the ring mass center. At such a distance the interaction between any of the selected hydrocarbons and the ring is negligible.

Contrary to methane, ethylene (C_2H_4) has cylindrical shape (1D) and two possible orientations are considered in the trajectory toward the zeolite ring. Ethylene may travel with the CC bond parallel or perpendicular to the ring axis. In both cases we observe it gets through the ring and no bond is broken. In Figure 3, the electronic energy plus the nuclear repulsion are plotted against the distance between the center of mass of the hydrocarbon and that of the zeolite ring. The energy profiles have been shifted upward or downward to match the initial

energy point of methane. The energy barrier widths of ethylene look very similar, but the barrier heights are substantially different. Perpendicular ethylene takes more energy to cross the ring, whereas parallel ethylene takes about the same energy as that of methane. The time spent by ethylene travelling in a perpendicular position is considerably longer than in the parallel position. The outcome of the two dynamics is ethylene with some rotational moment imparted by the ring.

The isobutene molecule is a planar structure (2D) with four carbons lying in a plane. We have performed simulations with the isobutene double bond in a parallel and a perpendicular orientation to the aluminosilicate ring axis. Isobutene is capable of getting through the ring in a parallel orientation, but not in the perpendicular one. This is due to the different volumes taken by isobutene inside the ring. The perpendicular orientation takes more volume, leading to stronger repulsive forces among the hydrocarbon atoms and zeolite atoms. Then, a higher initial speed is required for isobutene in its perpendicular form to cross the ring. We have also explored total Mulliken charges of isobutene travelling in a parallel and a perpendicular orientation (Figure 4). The zeolite ring takes electronic charge from isobutene in both orientations. The charge transfer effect starts when the hydrocarbon mass center is approximately 3 Å away from the ring mass center. In the perpendicular situation the transfer of charge is higher than in the parallel case, with a sudden drop in the hydrocarbon charge at the bouncing moment. Clearly, the charge-transfer effect is dependent on the molecular orientation. However, a common factor in the two orientations is that isobutene loses the planar structure when it gets closer to the ring center. The internal charge redistributions of the hydrocarbon atoms promote the unfolding from a 2D conformation to a 3D deformation.

Our last molecule under analysis is isobutane. It is a pyramidal structure where the methyl groups appear in the vertexes of a triangular base (Figure 2). The parallel/perpendicular orientation of the hydrocarbon corresponds to the parallel/perpendicular orientation of the C_3 molecular axis with respect to the zeolite ring axis. With an initial velocity of 0.063 Å/fs, isobutane in the two orientations is incapable of penetrating the barrier imposed by the ring atoms, because the electrostatic field of the ring is repulsive and, on the other hand, we are reaching
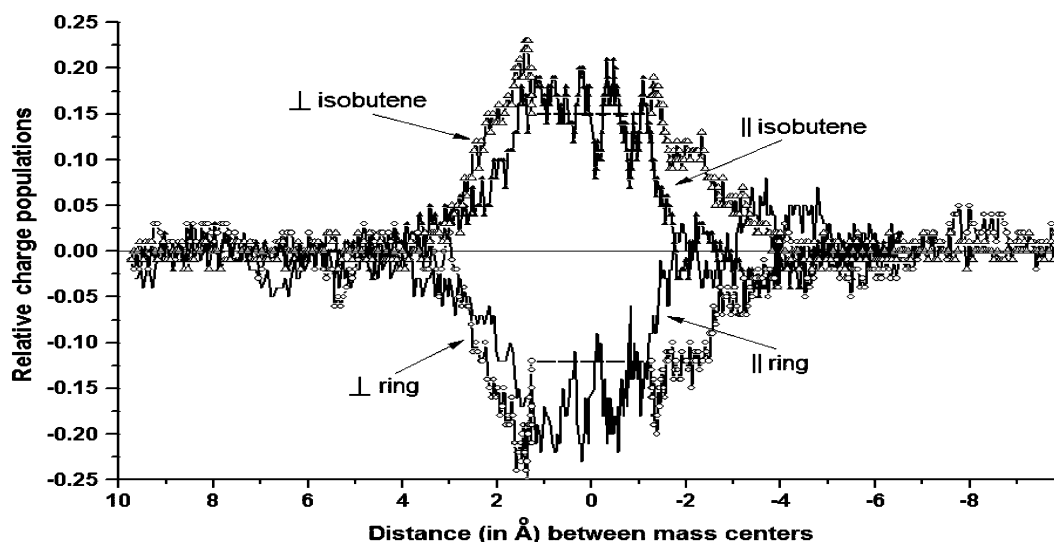
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Figure 4. Variation of the total charge populations of the zeolite ring and isobutene with the distance between their molecular mass centers. Two sets of curves are given for the situations in which isobutene travels in parallel (∥) or perpendicular (⊥) orientation with respect to the zeolite ring axis. The curves with dashed sections have the same meaning as those of Figure 3.
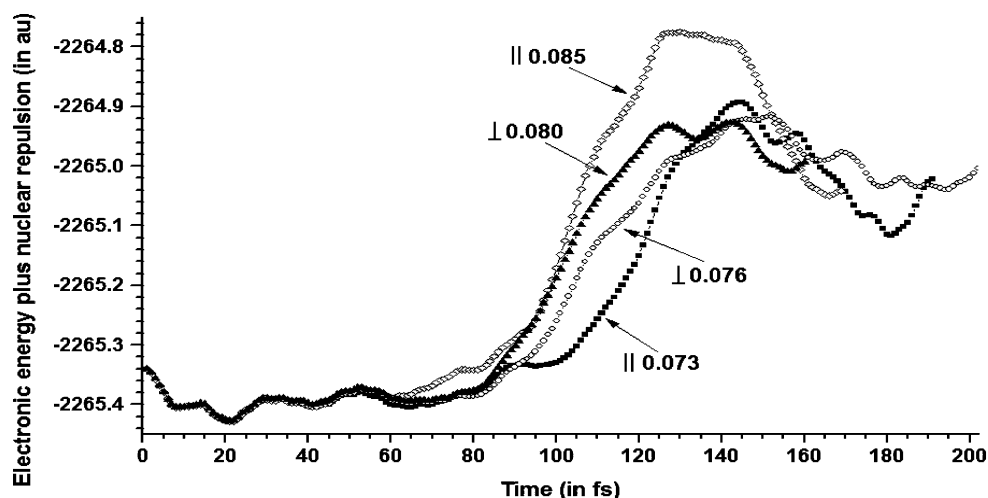

Figure 5. Variation of the electronic energy plus the nuclear repulsion of isobutane with time. The profiles correspond to the previous moments of isobutane cracking. The parallel (∥) and perpendicular (⊥) orientations, as well as the initial speeds (in Å/fs), of isobutane in its way to the zeolite ring are indicated.

the size limit of the hydrocarbons that fit in the ring. Apparently, isobutane requires a higher initial momentum to cross the barrier imposed by the ring atoms. The energy curves of isobutane follow the same pattern as the energy curves of the previous hydrocarbons; namely, before the penetration or a close approach between the hydrocarbon and the ring, the energy profile of parallel isobutane appears lower than the energy profile of perpendicular isobutane (Figure 3). In more general terms, the zeolite ring facilitates the diffusion of the hydrocarbons studied here in their parallel orientations rather than in their perpendicular ones. A growth of potential energy barriers heights is also observed as we consider hydrocarbons bigger in size. By increasing the initial speed to 0.073 and 0.085 Å/fs, parallel isobutane is cracked into two fragments, an isopropyl compound $(CH_3-CH-CH_3)$ and a methyl (CH_3) group. The difference in the two results shows that in the 0.085 speed case the products of the reaction get through the ring, and in the 0.73 speed case they are repelled and unable to cross the barrier. Isobutane in the perpendicular orientation shows different behavior at slightly different speeds. For instance, at 0.076 Å/fs the methyl group is able to cross, but not the isopropyl compound. In contrast, at 0.080 Å/fs both products have enough momentum to cross the
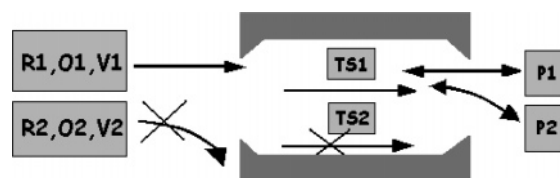

Figure 6. Dynamical character of the zeolite selectivity modifies Figure 1, because the zeolite selectivity is also exerted over the orientations and penetrating velocities of the reactants. For instance, a reactant like R1 may be able to get through the zeolite ring in the O1 orientation, with velocity V1, but not in the O2 orientation or with the velocity V2. The orientations and speeds of reactants play an important role to determine the diffusion and counterdiffusion of the products.

potential barrier. In most of the simulations the methyl group is released from isobutane in the form of a sudden blow with a whip. The small size of the methyl group also makes it more favorable than isopropyl to cross the ring barrier. Figure 5 shows plots of the electronic energy plus nuclear repulsion versus time. The curves correspond to the different initial conditions of speed and orientations of isobutane before the cracking. All curves exhibit the same behavior in the interval 0–55 fs, indicating a negligible interaction between isobutane and the zeolite ring

when they are far (initially 10 Å) away from each other. At $t =$ 55 fs, the separation between the hydrocarbon and zeolite ring mass centers is approximately 3 Å. This is the distance at which the electrostatic field of the zeolite ring becomes influential over isobutane because the interactions start to evolve differently. From an energy point of view, the curve of isobutane in the perpendicular orientation and with an initial speed of 0.080 Å/fs indicates the most favorable way to crack isobutane into an isopropyl compound and a methyl group, without having a counterdiffusion of any of these last species. Unfortunately, we cannot make a conclusion on the charge populations of the isopropyl and methyl products because the populations are constantly changing according to the distance between products and to the ring atoms.

Conclusions

One of the important factors of the zeolite activity is the selectivity. In this work we have characterized from a dynamical perspective the selectivity of a model zeolite ring over representative hydrocarbons of crude oil like methane, ethylene, isobutene, and isobutane. The zeolite selectivity is strongly dependent on geometrical shapes, molecular orientations, and diffusion speeds. It was found that methane has a threshold speed of 0.063 Å/fs to overcome the zeolite ring barrier. Ethylene exhibits a similar energy profile to methane when it travels with the CC molecular axis parallel to the zeolite ring axis, but bigger when travelling in the perpendicular orientation. Isobutene may get through or be repelled by the zeolite ring depending on the initial orientation adopted by the molecule. The diffusion and cracking of isobutane depends on the penetrating speed and, in the case of cracking, the products may also get through or be repelled by the ring potential barrier. We have quantified such aspects and highlighted the importance of the shape, orientation, and speed of hydrocarbons in the selectivity phenomenon exerted by small zeolite rings (Figure 6). The model ring used in this work is considerably smaller compared to other models and, for this reason, the long-range interactions can be taken into consideration only to a limited extent. But, despite the poor description of the long-range forces, the high local character of the interactions between the zeolite ring and the hydrocarbons should give the dominant behavior. In general, the crossing of the hydrocarbons through the ring hole is facilitated when they travel in their parallel orientations (as defined in the text), because the hydrocarbons take less volume inside the ring hole. It is also important to mention that the selectivity of zeolites is intimately associated with the diffusion of the hydrocarbons within the zeolitic channels, and therefore, our observations should be of help in understanding mass transport, in analyzing the factors that control the catalytic activity in zeolites, and for the parametrization of model potentials.

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