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Schematic potential energy for interaction between isobutene and zeolite mordenite

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Abstract

A schematic representation of the potential energy for the interaction between isobutene and H mordenite was presented by using eight different positions (P1–P8) of C_1 or C_2 atoms located in front of the acid hydrogen (H^+). In all cases a π complex was formed yielding different values of the adsorption energy. In some cases of the adsorption point in P1–P8 the frontier orbitals are shown. The P8 position exhibits the highest value obtained for the adsorption energy, where the C_1 atom is in front of the H^+. Calculations were of all electron type employing HF/6-31G**.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zeolites are microporous aluminosilicates, which are used widely in the chemical and petrochemical industries for hydrocarbon conversion processes [1]. Several transformations of hydrocarbons occur in the microporous region. Microporous materials such as zeolite act as Brønsted acids protonating hydrocarbon molecules such as olefins; therefore, the acid hydrogen is transferred to the olefin in order to form a protonated species [2–5]. This species interacts with an oxygen atom from the framework that acts as a nucleophilic centre in the formation of an alkoxide species. In this way, the protonation reaction for the propylene and isobutene molecules by means of the zeolite bridged hydroxyls ZOH was studied. The latter study was done using *ab initio* molecular-orbital calculations employing the basis set 3-21G. The study was extended to include the clusters with different compositions introducing B and Ga atom in the positions of HT_3 [2]. A molecular-orbital approach is the extended Hückel (EH) method, together with the dynamic molecular calculations. These methods were

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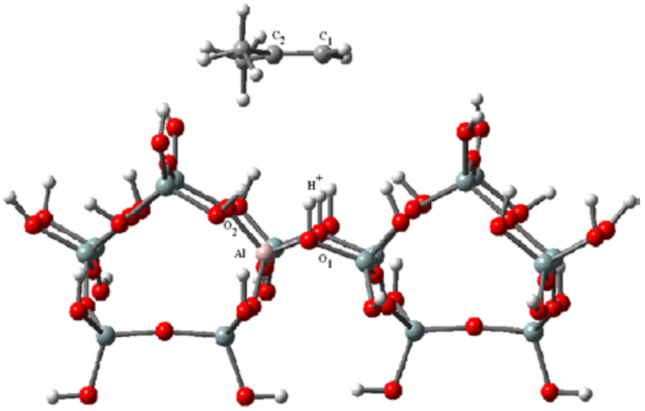


Figure 1. This model consists of an isobutene molecule and a mordenite having one acid site (AlO_3OH).

carried out to evaluate the adsorption and desorption energy for intermediary species in the isomerization reaction on the double bond of n-butene using alumina and sulfated alumina as catalysts [3]. Similar reports were studied in the protonation mechanism of ethylene over catalyst HZSM-5, by employing SCF-MO/STO-3G calculations. In another study, four models were proposed to carry out calculations of interactions for ethylene and zeolite [4]. Correa and Mota [5] presented a DFT study of the protonation of but-1-ene, (E)-but-2-ene and isobutene over a three-tetrahedron cluster which represents the zeolite acid site (HT_3). One method of formation of a π complex is to consider the initial point involved between the double bond and acidic proton showing a small dependence on the olefin structure. In experimental studies, the reaction of 1-butene over ferrierite has been studied by ^{13}C MAS NMR, where double-bond isomerization and the formation of dimers were observed [6]. NaH-ferrierites (FER) with different concentrations of Brønsted sites were employed to carry out the skeletal isomerization of n-butenes to isobutene [7]. In this work we carry out the study of the adsorption for isobutene over the acid site in H mordenite. At this point, eight different position were selected to obtain the π complex. These positions allow us to find the behaviour of the potential energy for interaction between isobutene and H mordenite in order to determine which is the best path for the adsorption process. This was done by calculating the interaction energy as a function of interatomic distance for all positions of the isobutene molecule in an acid site.

2. Model and methods of calculations

Natural mordenite has the composition formula $Na_8Al_8Si_{40}O_{96}24H_2O$. In this solid grid, a monodimensional pore system runs parallel to the c-axis, consisting of large 12- and small eight-membered rings (MR). The main 12MR channel exhibits diameters between 6.7 and 7.9 Å. The main channels are interconnected via eight-ring side pockets, parallel to the b-direction, and present diameters between 2.6 and 7.5 Å. The mordenite framework was obtained from the crystallographic structure [8]. Due to the size of the unit cell, it was decided to employ only a fragment of the unit cell which included the acid site [9]. A sufficient area was chosen to avoid the border effect in the interaction of the isobutene molecule. This fragment has 16 tetrahedral sites, which takes into account 94 atoms; the edge oxygen atoms were saturated with hydrogen atoms as shown in figure 1. We considered only one acid site because this system is representative of the interaction over this site. The isobutene molecule was optimized in order to find the character of the atomic bonds in the molecular structure as a reference for this interaction. An Origin-2000 SGI with R-1200 processors was used as a server and the Gaussian 98 program [10] was employed for the calculations. Restricted Hartree–Fock (RHF) calculations were utilized [11]. The RHF method uses a set of fixed electron basis functions in terms of which orbitals are expanded, and many-electron wavefunctions are expressed. The integrals are sometimes computed exactly by these systems, which give better results for energies of weakly bonded systems. The RHF method has been successfully used to predict molecular structures, vibrational spectra and reaction energies. RHF is a method that allows us to calculate the potential energy of the system with a good accuracy. For all calculations the basis set 6-31G** was employed [12]. The interaction energy values are obtained employing equation (1). The curves obtained to plot interaction energy values versus intermolecular distance allowed us to observe whether there is an attractive or repulsive interaction.

$$E_{\mathrm{interaction}} = E_{\mathrm{complex}} - [E_{\mathrm{isobutene}} + E_{\mathrm{mordenite}}]. \tag{1}$$

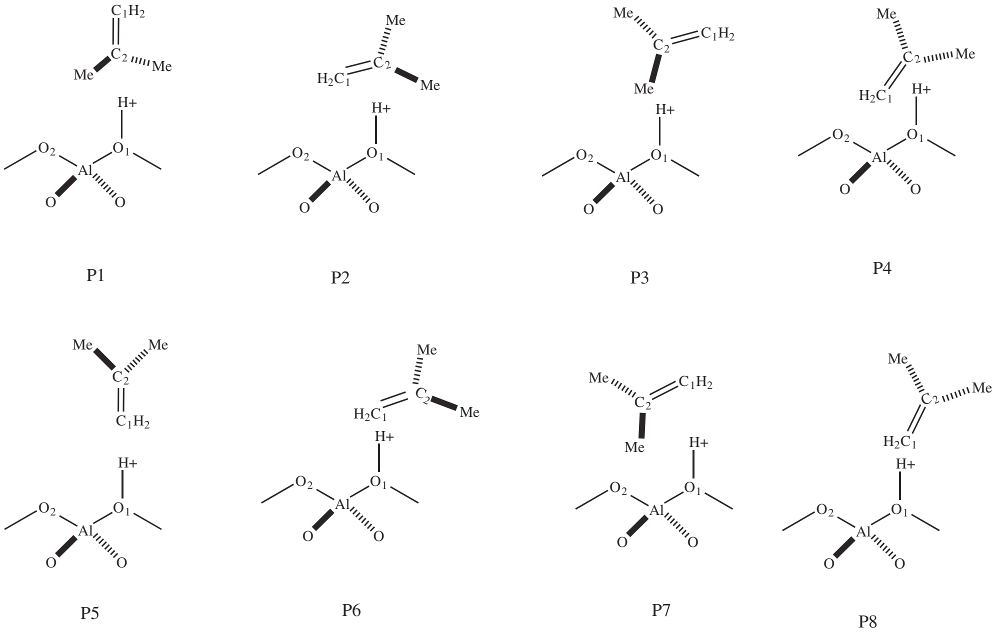
In order to determine whether the interaction among two molecules is attractive or repulsive, the values of the interaction energy were considered for an interval of distances. The attraction is when the interaction energy presents a well potential energy with a certain depth, which is associated with adsorption energy.

3. Results and discussion

In the mechanics of reaction when the interaction between the olefin and the surface of the zeolite is analysed, a first step is the formation of the π complex. Thus, we can obtain information on the electronic properties that are reflecting changes in the values of the energy due to the adsorption. For this reason, the adsorption of isobutene over the mordenite surface allows us to characterize the formation of the π complex. This adsorption procedure was studied by calculating the interaction energy for different positions of carbon atoms having a double bond, which are applied in the interaction among the isobutene and acid site. We selected four positions of the C_2 atom and another four of the C_1 atom, due to the reactivity of the double bond. The isobutene and H mordenite fragment model was labelled and collocated for eight positions of the double bond at different distances of the H^+–O_1–Al–O_2 fragment as shown in figure 2.

The molecule of isobutene has four different positions over a fixed C_2 atom, which are representative movements, and besides it is able to obtain its values of the adsorption energy for each position. The C_2 atom from P1 to P4 is located in front of the O_1–H^+ bond. Moreover, O_1–Al–O_2 is over the yz-plane in Cartesian coordinates; the O_1–H^+ bond is described over the z-axis. For the P1 position, the double bond is parallel to the O_1–H^+ bond, and the methyl groups are over the xz-plane. In the P2 position, the double bond is parallel to the O_1–Al bond forming an angle of 0°. In the P3 position, C_1–C_2 double bond is parallel and forms an angle of 180° with respect to the O_1–Al bond. For the P4 position, the double bond is over the xy-plane and is perpendicular to the O_1–Al bond.

Furthermore, the positions P5–P8 of the molecule of isobutene, which is representative of a feigned movement, will be described. For P5–P8 the C_1 atom is located in front of the O_1–H^+ bond. In these cases, the double bond for P5 is parallel to the O_1–H^+ bond. In this position the methyl group is over the xz-plane. In the P6 position the double bond is perpendicular to the O_1–Al bond. In P7 the double bond is parallel to the O_1–Al bond, and finally the P8 position has the double bond over the xy-plane, perpendicular to O_1–Al. The interaction energy calculation for each point to different interatomic distances among C_1 or C_2 atoms with the acid site allows us to describe the variation of nonbonding interaction. In all cases the



P1 P2 P3 P4

P5 P6 P7 P8

Figure 2. The eight positions used for different interactions among the mordenite model and the isobutene molecule.

interatomic distance was taken from H^+ to C_1 or C_2 atoms. The initial separation distance was taken as 2.0 Å, while the maximum separation was considered at 7.0 Å.

4. Interaction among acid site and C_1 or C_2 atoms of isobutene

The C_2 atom is considered in the first stage for the four positions. The C_2 atom is mainly positioned in front of OH^+; to do this we have two perpendicular positions to the double bond. In this interaction the C_2 atom with the acid site of H mordenite was observed for an attractive interaction from P1 to P4. In table 1 the values of the adsorption energy and the distances (C_2–H^+) are shown in a local minimum for P1–P4. In particular, P1 shows the highest adsorption energy of these four positions. The importance of the interaction among the acid site and the atom C_2 exhibits three similar adsorption energies and one different due to nonbonding interaction. The adsorption energy difference between P2 and P4 is of 2 kJ mol^{-1} and the interatomic distance of the adsorption difference is 0.75 Å. These differences are attributed to steric hindrance due to interaction between methyl groups and neighbour acid site atoms.

In P8 the double bond is over the xy-plane and it forms one angle of 90° with the O_1–Al bond. Adsorption curves show that P8 has the deeper hole, which is reflected in the adsorption value (as shown in figure 2). Compared with P4, in P8 the isobutene molecule is shifted by 1.33 Å which is double bond length over the xy-plane out of the surface in order to obtain the C_1 atom, which is in front of the H^+–O_1 bond. This shift of the molecule could cause less nonbonding interaction (less steric hindrance) of methyl groups with the OH terminals. For P4, because the molecule is inside the zeolitic surface by 1.33 Å groups; OH are nearest to the methyl groups, which provokes more steric hindrance and moreover a high repulsive interaction and less adsorption energy value. Complementarily, our values of adsorption energy for P5–P8

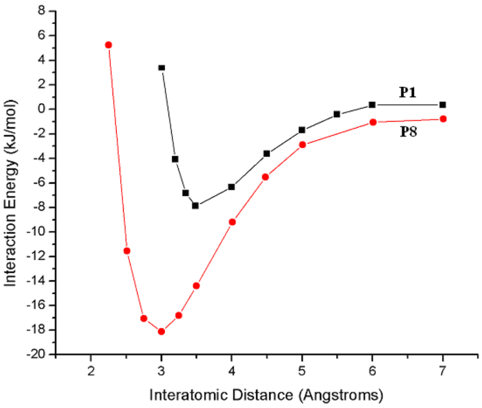


Figure 3. Relative interaction energy values for P1 and P8 show the adsorption at different separation distances.

Table 1. The values of the adsorption energy and the interatomic distances between 2 and 7 Å in a local minimum.

Position	Interatomic distances of adsorption (Å)	Adsorption energy (kJ mol^{-1})
P1	3.50	8.22
P2	3.50	7.35
P3	3.50	8.12
P4	4.25	5.34
P5	2.75	4.79
P6	5.00	2.89
P7	4.50	3.22
P8	3.00	17.33

are listed in table 1. The lower adsorption energy for P5–P7 could be explained because these positions present a higher steric hindrance because the OH and methyl groups are nearest. This nearness was achieved by moving the isobutene molecule by 1.33 Å. P1 and P8 show the higher adsorption energy when the interaction is between C_2 and C_1, respectively. After the adsorption process, the migration of the hydrogen of the acid site to C_1 or C_2 was followed. However, the migration will occur only to the C_1 atom, because it will form a tertiary carbocation, while in C_2 a primary carbocation will be formed.This is because the tertiary carbocation is more stable than the primary carbocation. Other authors obtained adsorption energy values of 23, 28.45 and 34.31 kJ mol^{-1} [2, 5] (considering an absolute value); these values are higher than for P8. This can be explained because they considered a cluster with only three tetrahedral sites and in our case the zeolitic surface has 16, therefore in our system more nonbonding interactions (steric effects) are taken into account than when only three tetrahedral sites are employed.

All values of the interaction energy were plotted for eight positions. All of them present an attractive potential behaviour. We only show two graphs (P1 and P8) in figure 3. In this case, P8 shows the highest adsorption energy, which is represented graphically in figure 3. Therefore, P8 is the principal way to form the π-complex. Electronic distributions obtained by frontier orbitals show for P8 a higher interaction between the double bond and the acid site than in P1, where interacting with this distribution is hindrance by methyl groups, which is observed in lower adsorption energy.

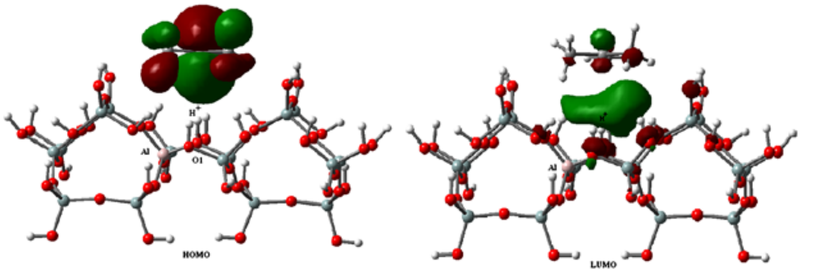


Figure 4. Distribution of frontier orbitals. The HOMO is located on the double bond carbons and the LUMO is located on the acidic hydrogen for the P8 position.

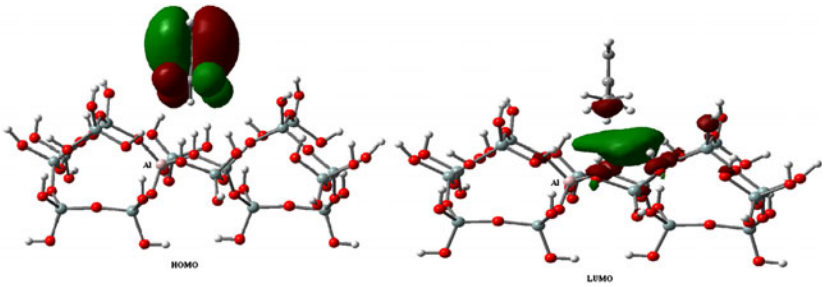


Figure 5. Distribution of frontier orbitals. The HOMO is located on the methyls and the LUMO is located on the acidic hydrogen for the P1 position.

5. Frontier orbital distribution

The distribution of HOMO and LUMO orbitals for P8 and P1 at the adsorption point are shown in figures 4 and 5, respectively. The HOMO orbital represents the higher electronic distribution which is located over the double bond of isobutene, while in the LUMO orbital it is localized over the acidic hydrogen in both positions. However, only in the LUMO orbital of P8 was the distribution over the C_1 atom observed. The principal reason for use of the frontier orbital is the associated reactivity. In this distribution the results can be attributed to the direction of electronic transfer between the methyl groups and the neighbourhood acid site OH group. This kind of description is according to the interaction energy result. By comparing P1 and P8, we observed a higher adsorption energy in the C_1 atom; therefore, P8 is the more reactive system.

6. Conclusions

In P1–P8 a π complex was formed by interaction of isobutene over the acid site of the H mordenite surface. All adsorption energy values were different. P8 presented the highest adsorption value. This can be explained because in P8 there exist lower nonbonding interactions (steric effects) between methyl groups and OH terminals, which mean that this position also has the lowest interaction energy values. Thus, lower adsorption energy values are due to high interaction between methyl groups and OH terminals; therefore, it gave a more repulsive attraction. Our system described in good form the nonbonding interaction between isobutene and the zeolitic surface. The frontier orbital distribution confirms that P8 is relevant to the reactivity, because the distribution suggests that P8 is the most reactive position.

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