



# Theoretical study of the adsorption of isobutane over H-mordenite zeolite by ab initio and DFT methods

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## Abstract

Values of relative interaction energy between an isobutane molecule and the surface of the H-mordenite zeolite were obtained. Sixteen tetrahedral sites were taken into account for the surface. Results showed that the adsorption energies were 4 and 8 kJ/mol, for ab initio restricted Hartree–Fock (RHF) method and density functional Becke–Lee–Yang Parr (B3-LYP) approaches, respectively, when C<sub>2</sub>–H<sub>2</sub> bond is located in front of H<sup>+</sup> atom of H-mordenite surface. The minimum value for the interaction in the adsorption was around 2.25 and 2.50 Å distance from the DFT and ab initio method, respectively. The interaction of isobutane by methyl groups side over the catalytic surface caused a repulsive interaction. Therefore, adsorption of isobutane is a selective process by the H<sub>2</sub> side of the molecule. Calculations were done by employing the 6-31G\*\* basis set. © 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** H-Mordenite; Isobutane; ab initio Calculations; DFT calculations; Interaction energy; Selective adsorption; Steric hindrance

## 1. Introduction

Zeolites are open-framework structures composed of tetrahedral SiO<sub>4</sub> and AlO<sub>4</sub>, which are widely used as solid acid/base catalysts [1]. Their network of cavities and channels allows them to accommodate even moderately large molecules. Zeolites have applications in bulk separation processes [2,3], gasoil refinement [4], and long-term storage of nuclear waste products [5,6]. A clear picture of the nature and location of adsorbed molecules is fundamental to the mechanistic understanding of catalytic processes. The adsorption of hydrocarbons in zeolites has been subject of research due to the important role that zeolites

play in the reactions involved in catalytic cracking. The adsorption energies of alkanes in zeolites have been studied experimentally for nearly 30 years [7]; it was observed that the adsorption energy depends on the pore diameter. Experimental studies such as NMR [8,9] can provide information on the location and diffusion of small sorbates. Webster et al. performed a multiple equilibrium analysis description of adsorption on Na- and H-mordenite for some compounds [10]. They reported the experimentally adsorption isotherms at various temperatures, process-designated enthalpies and entropies of adsorption for isobutane on Na-mordenite. A study on reaction kinetics was conducted of isobutane conversion over H-mordenite at 473 K, however, the presence of isobutylene caused an increment in the rate of isobutane isomerization and also increased the rates of side reactions such as oligomerization and β-scission [11]. Fogash et al.

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studied the catalytic properties of sulfated-zirconia and H-mordenite for isomerization of *n*-butane and isobutane at temperatures near 450 K [12]. Both catalysts showed rapid deactivation during isomerization of *n*-butane when olefins were present in the feed stream.

On the field of theoretical studies in the adsorption of organic molecules in zeolites, Rueda et al. reported a molecular approach in order to evaluate the adsorption and desorption energies of *n*-butene over alumina and sulfated alumina catalysts [13]. The adsorption of benzene in acid mordenite was studied employing DFT. Different adsorption modes of benzene were proposed for several acid sites [14]. Also, the interaction of benzene with HZSM-5 zeolite has been studied [15]. The ab initio calculations were performed to study the H/H exchange between light alkanes in protonated zeolites. The results of the H/H exchange indicated that the transition state resembles a pentacoordinated carbonium ion [16]. Additionally, studies on the H/D exchange have been carried out [17]. The mechanism of monomolecular cracking of *n*-butane over Brønsted acid sites of zeolite was studied by the DFT method, which showed that the reaction proceeds via a protolytic attack at the centre of the C–C bonds [18].

In this work, the main goal is to describe, from a theoretical point of view, the catalytic function of the acid site when an isobutane molecule is present on a representative zeolite cluster. Special attention was drawn to the acidity of H-mordenite because this property can reflect its catalytic behavior. Developed model has one acid site which was chosen in order to determine the effect of this site in the adsorption step. To model a proper environment for the adsorption process, values of relative interaction energy, point by point, considering several interatomic distances between isobutane and the surface of the H-mordenite were obtained. This model is supposed to account for the effect of the active sites and the effects of long border forces. It was found that the isobutane molecule must be approached by the H<sub>2</sub> side, as indicated by the potential energy curves as a function of the interaction distance between isobutane and the H-mordenite surface. Also, we analyzed the electronic and steric effects that govern the interactions between isobutane molecule and H-mordenite zeolite obtained by calculating the interaction energies. The interaction energies were obtained using single-point energy calculations. Restricted Hartree–Fock (RHF)

and Becke–Lee–Yang–Parr (B3-LYP) calculations with the 6-31G\*\* basis set were employed.

## 2. Computational procedure

The ab initio and DFT calculations were done by using the Gaussian 98 program [19]. The RHF method employs a set of fixed, electron basis functions, in terms of which orbitals are expanded and many electron wave functions are expressed. The integrals are sometimes computed exactly by these systems, which give better results for energies of weakly bonded systems. RHF method has been successfully used to predict molecular structures, vibrational spectra and reaction energies. DFT calculations are employed with the B3-LYP exchange–correlation functional [20]. In both cases the 6-31G\*\* basis set [21] were used. The basis set is given as numerical values on an atom-centered set of grid points. The methods mentioned earlier described well the electronic properties in the interaction of the isobutane and zeolite surface. Origin-2000 SGI with R-12000 processors was used as the server. Molecular mechanic by Dreiding method [22] and semi-empirical AM1 calculations [23] are implemented in the Gaussian program.

## 3. Results and discussion

Natural mordenite has the composition formula Na<sub>8</sub>Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>·24H<sub>2</sub>O. In this solid grid, a monodimensional pore-system runs parallel to the *c*-axis, consisting of large 12- and small 8-membered rings (MR). The main 12 MR channel exhibits diameters between 6.7 and 7.9 Å. The main channels are interconnected via 8-ring side pockets, parallel to the *b*-direction and present diameters between 2.6 and 7.5 Å. The Si/Al ratio in mordenite is usually within the range of 5–12 as described Demuth [14]. Mordenite framework was obtained from the crystallographic structure [14]. For different positions of the active site as best substitution of Al<sup>3+</sup> by Si<sup>4+</sup> and an hydrogen atom was added in order to have a neutral charge in the unit cell. After that, values of energy for all position selected in the unit cell were calculated by molecular mechanic [22]. In this case, we considered only one acid site because this system is representative of the

interaction over this site. The calculations were done in both size rings, where acidic hydrogen has a preference localization to the mayor cavity, due to that, it was found the low energetic value. The position of low energetic value of the acid site was corroborated using single-point energy AM1 semi-empirical calculations [23]. However, 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. The area was chosen enough to avoid the border effect in the interaction of the isobutane molecule. This fragment has sixteen tetrahedral sites, which takes into account 94 atoms; the edge oxygen atoms were saturated with hydrogen atoms. The surface model employed in the calculation is shown in Fig. 1.

The adsorption of the isobutane over acid site should be by the side less crowded. Thus, the steric hindrance plays an important role in the adsorption step. In order to study the adsorption in function of steric hindrance, we decided to employ the same systems with several interatomic distances of the isobutane molecule over acid site, for obtaining the interaction energies. Isobutane and zeolite surface were labeled as shown in Fig. 2. The isobutane molecule was optimized by

HF method, it was considered that mordenite structure is stable, therefore, it was not optimized.

In position *a*, H<sub>2</sub> atom bonding to C<sub>2</sub> in the isobutane molecule is located in front of the acid hydrogen. The O<sub>1</sub>–H<sup>+</sup>–H<sub>2</sub> angle is 176°, while the interatomic distance was taken from H<sub>2</sub> of the isobutane molecule to H<sup>+</sup> as shown in Fig. 2a. In position *b* the methyl groups in the isobutane are located in front of the acid hydrogen. The O<sub>1</sub>–H<sup>+</sup>–C<sub>2</sub> angle is 174° and interatomic distance was taken from the tertiary carbon atom in the isobutane molecule to the H<sup>+</sup> of H-mordenite surface, as shown in Fig. 2b. Initial interatomic distances was 5.0 Å for *a* and *b* position.

In order to obtain the energy behavior for these systems, interaction energies were obtained by using single-point calculations; this assumption also allows observe the existence of the adsorption over H-mordenite surface. The interaction energies were calculated using Eq. (1):

$$E_{\text{interaction}} = E_{\text{complex}} - [E_{\text{mordenite}} + E_{\text{isobutane}}] \quad (1)$$

$E_{\text{mordenite}}$  and  $E_{\text{isobutane}}$  were obtained in gas phase.  $E_{\text{complex}}$  is the energy due to the system isobutane-zeolite. In this way,  $E_{\text{interaction}}$  was calculated as

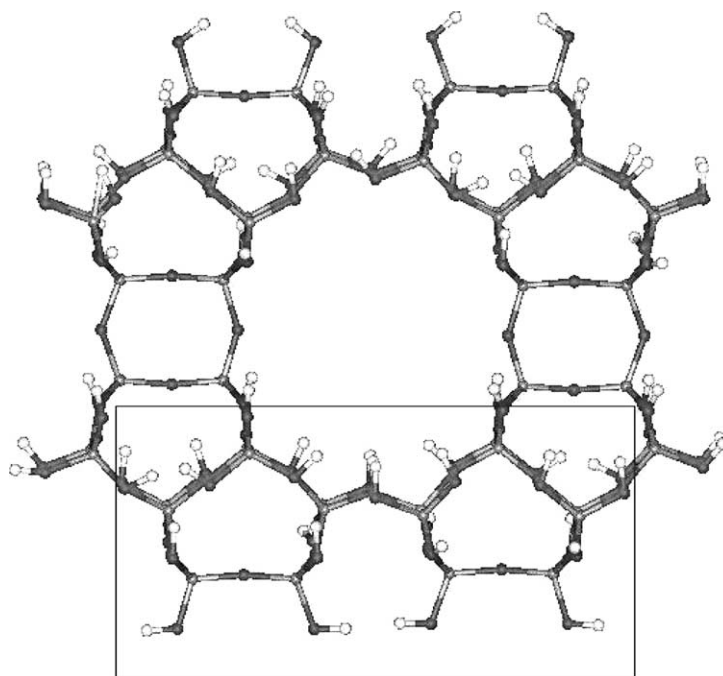


Fig. 1. The selection of surface of H-mordenite model.

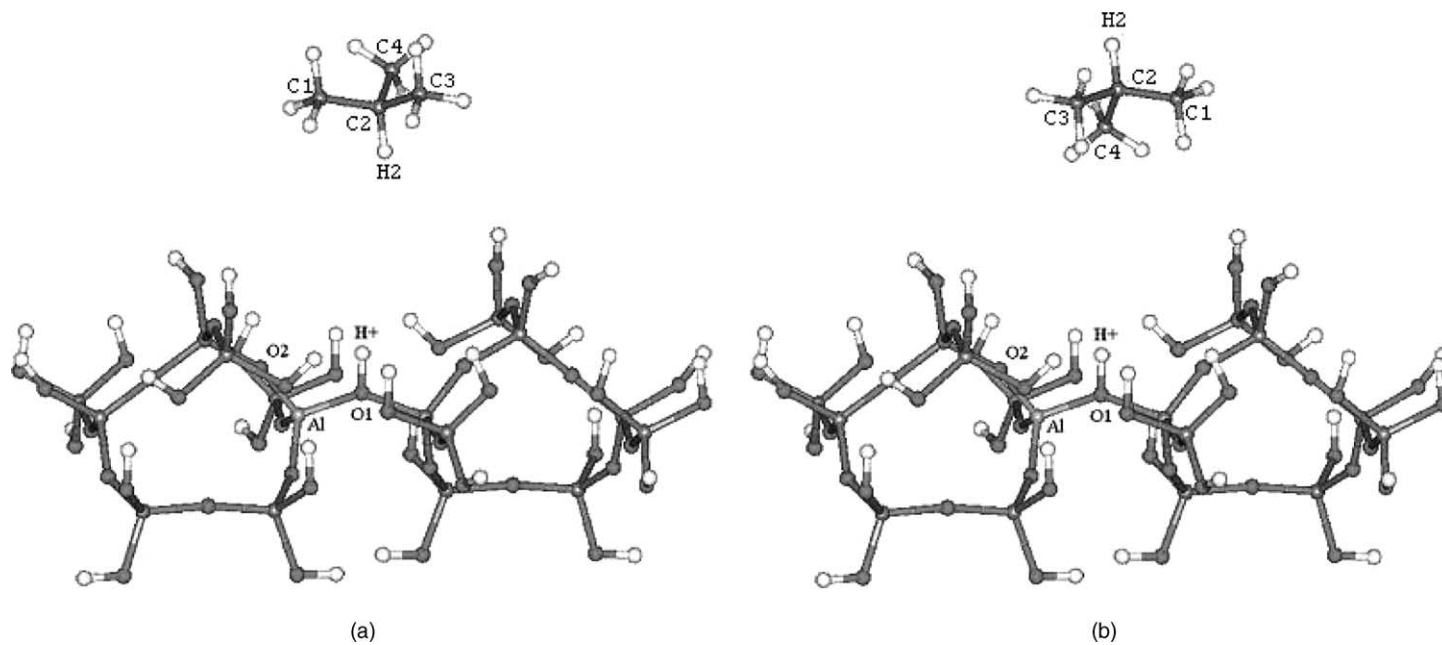


Fig. 2. (a) Position *a* when C<sub>2</sub>-H<sub>2</sub> bond of isobutane is located in front of acid site of H-mordenite surface at 5.0 Å. (b) Position *b* when methyl groups of isobutane are locate in front of acid site of H-mordenite surface at 5.0 Å.

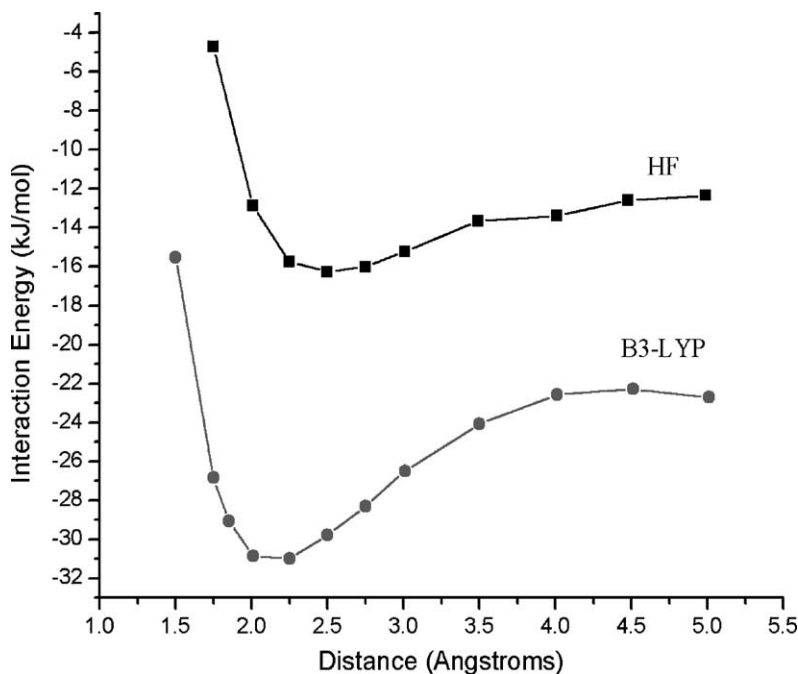


Fig. 3. Relative interaction energy values obtained by ab initio and DFT calculations for the position *a*.

function of the interatomic distance isobutane-H-mordenite. The adsorption energy was obtained from the differences between the initial energetic value and the minimum energetic value, as shown in the graphic of potentials (Fig. 3).

The ab initio calculations for position *a*, as it was pointed out earlier, indicated that the hydrogen atom  $H_2$  of the isobutane molecule was located in front of acid site on H-mordenite. The distance ranged from 1.75 to 5.00 Å. The interaction energies ( $E_{\text{interaction}}$ ) versus the distance are shown in Fig. 3. As it can be seen, the HF curve describes the behavior of minimum energy due to the interaction between the isobutane molecule and acid site of H-mordenite surface, when they are separated about 2.50 Å. The calculated adsorption energy is 4 kJ/mol. This adsorption of isobutane could increase in the presence of isobutylene molecule [11]. It was found that in the point of adsorption distances of  $C_2-O_1$  and  $C_2-O_2$  were 4.66 and 4.55 Å, respectively.

The Mulliken population analysis of isobutane and  $H^+-O_1-Al-O_2$  fragment for position *a* to all distances are listed in the Table 1. The atomic charge in the  $C_2$  atom of the isobutane molecule was  $-0.156$ ,  $-0.158$

and  $-0.163$  in 2.00, 2.50 and 5.00 Å, respectively. The acid hydrogen ( $H^+$ ) showed a decrease of the charge from 0.551 to 0.541 at 2.50 and 5.00 Å, respectively. For  $H_2$  atom the atomic charge is 0.099, in the adsorption step.

In position *b*, the methyl groups of the isobutane molecule are located in front of the acid site, at distances from 2.00 to 5.00 Å. Fig. 4 shows the values of the interaction energies. Approaches were started began at 2.00 Å because at 1.75 Å there is high interaction energy value. As it can be seen in this graphic, a repulsive interaction exist, this is due to the steric hindrance of methyl groups. In this form, the isobutane must be approached to H-mordenite surface only by  $H_2$  side, thus, this procedure is selective and only the system *a* can be considered as representative of the adsorption phenomenon.

Also, we carried out DFT calculations to be compared with those of the HF method. In this case, the range of distance was from 1.75 to 5.00 Å. Fig. 3 shows the behavior of the  $E_{\text{interaction}}$  as function of the distance. The minimum energy was found at a distance of 2.25 Å, which is 0.25 Å lower than in the case of the ab initio calculations. The calculated adsorption energy is

Table 1

Mulliken population charges for different distances on position *a* by ab initio calculations<sup>a</sup>

Atom	Distance (Å)										
	1.75	2.00	2.25	2.50	2.75	3.00	3.50	4.00	4.50	5.00	
O <sub>1</sub>	-1.290	-1.270	-1.257	-1.247	-1.241	-1.238	-1.236	-1.236	-1.236	-1.236	-1.236
Al	2.006	2.009	2.011	2.012	2.012	2.011	2.011	2.010	2.011	2.011	
O <sub>2</sub>	-1.357	-1.351	-1.347	-1.344	-1.343	-1.342	-1.342	-1.342	-1.342	-1.342	
H <sup>+</sup>	0.609	0.582	0.564	0.551	0.545	0.542	0.541	0.542	0.542	0.541	
H <sub>2</sub>	0.051	0.076	0.090	0.099	0.107	0.114	0.123	0.127	0.134	0.140	
C <sub>1</sub>	-0.447	-0.442	-0.439	-0.436	-0.434	-0.433	-0.433	-0.440	-0.436	-0.439	
C <sub>2</sub>	-0.150	-0.156	-0.158	-0.158	-0.158	-0.159	-0.160	-0.162	-0.162	-0.163	
C <sub>3</sub>	-0.456	-0.451	-0.447	-0.444	-0.442	-0.440	-0.439	-0.440	-0.439	-0.440	
C <sub>4</sub>	-0.450	-0.450	-0.450	-0.451	-0.451	-0.451	-0.454	-0.457	-0.456	-0.457	

<sup>a</sup> The distances refer to the conformation where H<sub>2</sub> of isobutene is in front of acid proton of H-mordenite surface.

8 kJ/mol, which is twice than that found in the ab initio calculations. This difference can be explained due to the functional employed (B3-LYP), which includes a HF part. This functional also takes into account the interchange and correlation energies exchange and correlation energies, which are not present in HF calculations.

The Mulliken population analysis on position *a*, for the isobutane molecule and H<sup>+</sup>-O<sub>1</sub>-Al-O<sub>2</sub> fragment

is shown in the Table 2. For all the atoms, the atomic charge is lower than the one obtained respectively by ab initio calculations. The atomic charge in C<sub>2</sub> was -0.085, -0.083 and -0.075 in 2.00, 2.25 and 5.00 Å, respectively, which are different to that observed in the ab initio calculations. Atomic charge in the acid hydrogen (H<sup>+</sup>) is 0.511, 0.498 and 0.484 at 2.00, 2.25 and 5.00 Å, respectively. The atomic charge for H<sub>2</sub> atom is 0.075 at 2.25 Å. Mota found that in the transition state

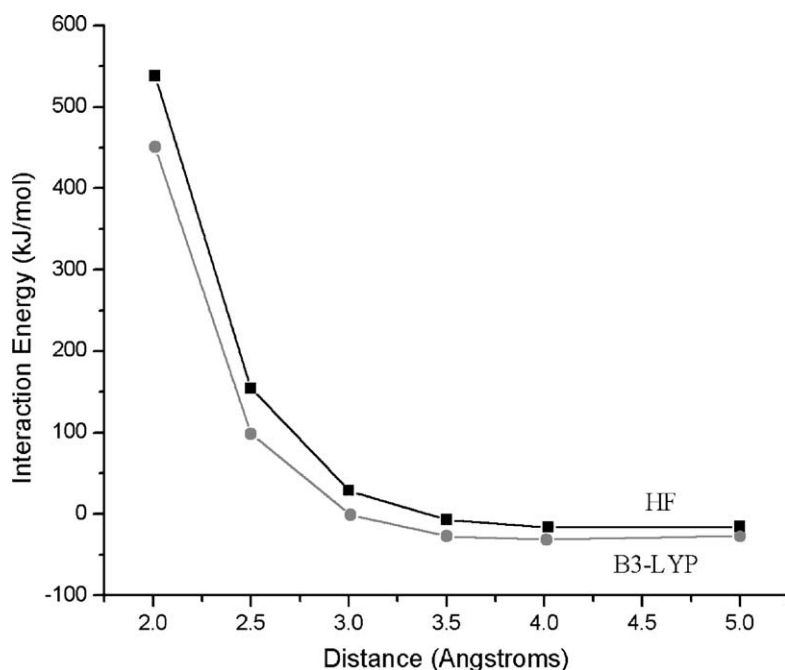


Fig. 4. Relative interaction energy values obtained by ab initio and DFT calculations for the position *b*.

Table 2

Mulliken population charges for different distances on position *a* by DFT calculations<sup>a</sup>

Atom	Distance (Å)									
	1.75	2.00	2.25	2.50	2.75	3.00	3.50	4.00	4.50	5.00
O <sub>1</sub>	-1.029	-1.013	-1.001	-0.992	-0.988	-0.985	-0.983	-0.983	-0.983	-0.983
Al	1.483	1.486	1.487	1.488	1.488	1.488	1.487	1.487	1.486	1.484
O <sub>2</sub>	-1.059	-1.054	-1.050	-1.048	-1.047	-1.046	-1.046	-1.046	-1.046	1.045
H <sup>+</sup>	0.528	0.511	0.498	0.490	0.485	0.483	0.484	0.484	0.484	0.484
H <sub>2</sub>	0.058	0.069	0.075	0.080	0.084	0.088	0.095	0.099	0.102	0.104
C <sub>1</sub>	-0.395	-0.393	-0.391	-0.390	-0.389	-0.389	-0.389	-0.391	-0.392	-0.393
C <sub>2</sub>	-0.086	-0.085	-0.083	-0.079	-0.076	-0.074	-0.074	-0.074	-0.075	-0.075
C <sub>3</sub>	-0.412	-0.407	-0.403	-0.401	-0.398	-0.397	-0.396	-0.396	-0.396	-0.396
C <sub>4</sub>	-0.408	-0.408	-0.408	-0.408	-0.409	-0.409	-0.410	-0.411	-0.412	-0.412

<sup>a</sup> The distances refer to the conformation where H<sub>2</sub> of isobutene is in front of acid proton of H-mordenite surface.

(TS) with a T3-cluster model (SiO<sub>4</sub>–AlO<sub>4</sub>H<sup>+</sup>–SiO<sub>4</sub>) [16], the H<sub>2</sub> atom has a charge value of 0.047. Therefore, our results obtained by DFT method represents better the next step possible, which is the TS. Furthermore, the distances in the point of minimum energy of C<sub>2</sub>–O<sub>1</sub> and C<sub>2</sub>–O<sub>2</sub> were 4.24 and 4.07 Å, respectively; these distances are shorter than the one found by the ab initio method.

As well as in the results for ab initio calculations, a repulsive interaction between the isobutane molecule and H-mordenite surface was observed at position *b* by DFT calculations. The range of distances employed was equal than ab initio method. Fig. 4 shows the curve obtained for the interaction energies by DFT calculations. Comparing the interaction energies point by point in ab initio and DFT methods for this system, it is observed that the values obtained by DFT calculations are lower than ab initio calculations. This is consequence, as it was pointed out earlier, of the functional employed.

Finally, the energy when two acidic hydrogen atoms were presented in the surface fragment was obtained by employing a B3-LYP functional. In this case, two different distances were observed with respect the principal acidic hydrogen: 1.94 and 5.72 Å. However, only the system with distance of 5.72 Å exhibit stability, therefore, the other was not considered. In this case, the adsorption of isobutane molecule has the same behavior than one acid site.

Adsorption is observed in a catalytic process when there is a selective interaction of isobutane-zeolitic fragment, therefore, all possible reaction involving the isobutane molecule will show a preferential way.

#### 4. Conclusions

The interaction energies were calculated in order to determine the adsorption process of the isobutane molecule over H-mordenite surface. Distance in the adsorption step was lower by DFT calculations than ab initio calculations for 0.25 Å. This difference is due to the functional employed in the DFT method, which correlated in better form with the adsorption process than ab initio method. The adsorption energy in DFT was twice than in the ab initio method. The adsorption is only carried out by the hydrogen side (H<sub>2</sub>) of the isobutane molecule. We can say that the approach is selective by this side of the molecule due to the steric hindrance.

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