

DFT study of interaction between a hydrogen molecule and AgY-zeolite

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The cationic exchange of H by Ag in a HY-zeolite is carried out to study the adsorption of a hydrogen molecule in an AgY-zeolite, which is achieved by means of a BOMD simulation. The chosen zeolite model is representative of adsorbent materials when a cation Ag forms part of surface fragments, and they are considered in this interaction. This study provides a criterion to establish the electronic property of cation promoting a relevant characteristic that must have an adsorbent material. The energy values on this interaction are analyzed to determine an evaluation of the hydrogen adsorption using a AgY-zeolite ring and fragments of 3 tetrahedral sites. The AgY-zeolite ring represents a cavity that exhibits diffusivity after an adsorption process. This study was developed in the density functional theory level with DZVP function bases.

Keywords: Interaction energy; hydrogen storage; DFT; Born-Oppenheimer; dynamic interaction.

La simulación inicia con un intercambio catiónico de átomos de hidrogeno por plata, considerando a un modelo representativo de la HY-zeolita, se observa en los resultados una adsorción de una molécula de hidrogeno en la AgY-zeolita. El análisis de este modelo indica que la zeolita es un material representativo de adsorbedor de hidrogeno cuando se realiza un intercambio de catión (H por Ag). El estudio con base en el cálculo de la energía de interacción proporciona un criterio mediante las propiedades electrónicas acerca de la importancia del catión para que ocurra el fenómeno y se obtenga un material adsorbedor. El modelo usado es un anillo de AgY-zeolita además de un fragmento de 3 sitios tetrahedricos. El modelo del anillo de AgY-zeolita representado por una cavidad exhibe difusividad después del proceso de adsorción. Los cálculos de interacción dinámica utilizaron funcionales de intercambio y correlación en DFT con funciones base DZVP.

Descriptores: Energía de interacción, almacenamiento de hidrógeno, DFT, Born-Oppenheimer, interacción dinámica.

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1. Introduction

Nowadays, hydrogen adsorbent materials are subject of study due to hydrogen represents an alternative in the fuel for certain types of proton exchange membrane fuel cells. This energy transformation process will be an interesting technological development for hydrogen adsorption [1]. In the transformation process, hydrogen requires to be stored. Different methods of hydrogen storage are known as for example: high-pressure tanks for gaseous hydrogen, cryogenic vessels for liquid hydrogen and metal hydride storage systems [2]. These storage methods are dangerous during their handling. For this reason, there is experimental research [3] about storage using different materials as adsorbents, such as silica, alumina, activated carbon, and zeolite [4,5], in particular graphite oxide is a nano-porous material with a preferentially hydrogen adsorption in presence of oxygen traces. This

carbonaceous material has been studied since a theoretical point of view [6]. The zeolite use to be considered as hydrogen storage material [7]. Other materials have hydrogen adsorption preference due to their porous shape and chemical composition [8]. Ion-exchange process in zeolite has been studied as a promising adsorbent material for hydrogen storage by Callejas [9]. In the same way FAU zeolite in different models and methods has been studied at different temperatures and pressures showing hydrogen adsorption [10].

Zeolites have been used as catalyst materials due to their diffusion and adsorption properties. The adsorption property of zeolite is studied in some interactions with hydrocarbon [11]. The adsorption property of zeolites could be used in the process of hydrogen storage. The Hydrogen adsorption in organic ion-exchanged zeolite was previously studied by Bae [12]. Composed molecular structures for obtaining hydrogen storage materials must have physisorption proper-

ties over the molecular hydrogen in order to generate a cheap and safe method to recover hydrogen. The hydrogen adsorption process has previously shown reversibility [13,14]. The Electrochemical properties of zeolite will present a high storage capacity, due to its cavity.

The zeolites with different structural shapes conformed by tetrahedrons of alumina and silicon are being studied to determine the adequate properties of adsorption [15], and when they interact with a hydrogen molecule as in our case. In addition, potential barriers have been studied to understand the hydrogen interaction on metal surfaces as Au, Pd and Ag [16].

In this work the interaction between AgY-zeolite and a hydrogen molecule is studied in order to determine the structural and electronic properties that can be considered for hydrogen adsorption. The mechanism of the adsorption involved is studied by Born-Oppenheimer interaction energy calculation using dynamics aspect. The effects of confining and diffusion are present in the simulation and are represented by calculations of energy developed by means of interchange and correlation functional with double numerical basis sets of functions on Born-Oppenheimer approach with dynamics aspect. Furthermore, this first stage is corroborated with study of the interaction energies for adsorption of H_2 , in the zeolite by single point energy.

2. Models

Zeolite has catalytic properties such as hydrophilicity-phobicity by the relation Si/Al with different strength of acid site. Zeolite micropore having molecular diameters comparable to molecular dimension allows conferring small molecules as molecular hydrogen due to shape selectivity [17].

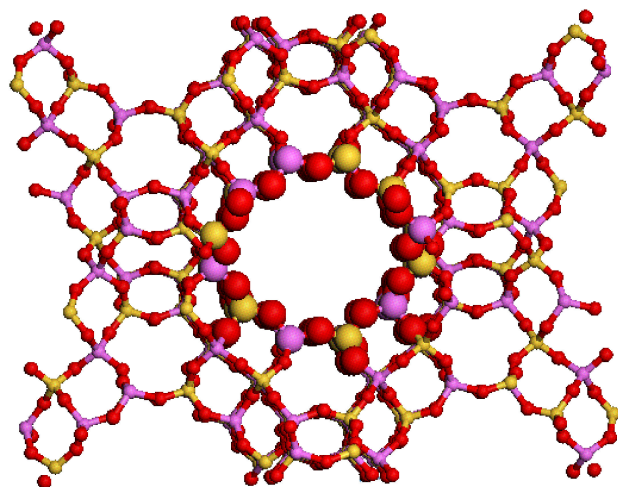


FIGURE 1. The molecular structure of Y-zeolite with Si/Al as ratio unit. Zeolite is structured by tetrahedral sites standing out the region of interest: a ring. The spheres in different colors represent red-oxygen, purple-aluminum, yellow-silicon.

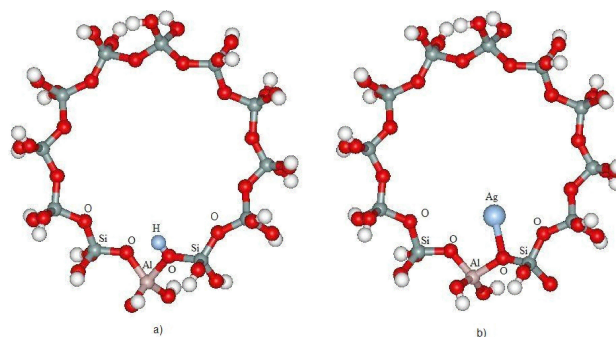


FIGURE 2. Molecular structure of twelve tetrahedral sites with an acid site located where a cationic interchange is implemented: a) region of the acid site of HY-zeolite ring, b) cationic substitution Ag atom on the region of the acid site to form AgYzeolite.

Taking into account Fig. 1, the model consists of 12 tetrahedral sites with one acid site selected as well as ring structural form [18]. In this picture, this model selects local effects to elucidate the participation and contribution of each atom in the catalytic effect. The molecular orbitals of Si and Al atoms do not participate independently in the zeolite catalytic pocket, but forming the zeolite framework. The atoms that do not participate in the zeolite catalytic pocket are assumed to play a less important role in the interaction between hydrogen molecules. The importance resides in the acid site of the HY-zeolite where the tetrahedron with central atoms Al presents a H^+ . This model was partially optimized in the region of the acid site only considering the neighborhood of tetrahedron ($SiO_3-H^+OAlO_3-SiO_3$) that initially presents a proton in the acid site as shown in Fig. 2a. In particular, special attention is paid to investigate about the cationic substitution. In order to simulate this substitution in the HY-zeolite we achieved calculations on the modified zeolite by means of the proton interchange with the silver atom Ag. We considered a Y-zeolite ring with a partial optimizing in the acid site on the structure of the partial place of the Y-zeolite obtained as a resulting AgY-zeolite ring model with ($SiO_3-AgOAlO_3-SiO_3$) as shown in the Fig. 2b.

In the same way, to obtain forces due to interaction with cationic atoms, the model fragment consisting of 3 tetrahedral sites (3T) contains one acid site, with a H^+ atom substituted by an Ag cation properly specified.

3. Computational Methods

The models are optimized considering atoms of the acid site; in particular the cationic Ag atom is the principal focus on electronic modifications affecting the molecular orbitals around both Si and Al atoms. These atoms have an important role in the interaction with the hydrogen molecule.

The density functional theory (DFT) was applied to investigate the interaction between a Hydrogen molecule and a zeolite ring because it is proper for determining structural and electronic property changes of compounds with relatively high accuracy. This level of theory applies a method that requires the proposal of an exchange-correlation energy func-

tional, as well as the molecular orbital basis sets. In this regard, the expressions of Becke for exchange [19] and Lee-Yang-Parr for correlation [20] are used to build the exchange-correlation energy functional. The procedure introduces generalized gradient approximations and is classified within the nonlocal approximations of DFT. When the nonlocal version of DFT is compared with the local approximation of DFT, it is found that the nonlocal approach gives an improved prediction of the electronic properties and interaction energies of molecules, due to its higher capacity to explain the anisotropy of the charge distribution. These indicated that the nonlocal DFT results are found in agreement with experimental measurements. With respect to the molecular orbitals, in the calculation we used atomic basis sets for their description, as the double-zeta valence polarization (DZVP) basis sets which exhibit a small basis set with superposition errors. The calculations were accomplished on the basis of the software.

An electric charge of zero is for the whole system considered. In this case the spin multiplicity is 1 (the reactivity is not biased by such a charge, as we shall see later). The scheme used in the optimization tasks is a quasi-Newton algorithm with line searches and approximate energy accomplished by Hessian updates, as implemented in the NWChem package [21]. A maximum Cartesian step of 0.0015 Bohr and a convergence of 0.0015 Hartree/Bohr in the energy gradients are conveniently chosen. All the Si and Al atoms of the zeolite fraction stay facing the hydrogen molecule; including their respective oxygen and hydrogen atoms were allowed to freely move in the optimization process. The remaining atoms were frozen since, under the consideration that the catalysis usually exhibits a local character, they are located far away of the catalytic pocket and can be considered static or hold by a larger framework. In all calculations, this condition was equivalent.

The dynamical aspects of the interaction are simulated with Born-Oppenheimer (BO) approach. In this approach, the electron wave function is (instantaneously) computed for static nuclei, while the nuclear particles are considered classical entities immersed in an average field created by the electrons. The time step in the dynamics aspect is 1 fs. The self-consistent approach is considered finished when a default convergence in the energy and density are obtained. The atoms allowed to move freely in the simulation are the same as these in the optimization process.

Earlier studies by Zaragoza *et al.* [22] showing the interaction energy between zeolite and hydrocarbons reveal good results when energy calculations are obtained, also those calculations of dynamics which use a LANL2DZ pseudopotential for Ag [23]. The interaction considers the criterion of minimum energy to accomplish the Born-Oppenheimer calculations. The computations are performed in a PC-cluster.

4. Results and Discussion

The molecular hydrogen storage is studied through methods of quantum mechanics at different stages, starting by choos-

ing the model that simulates the material which exhibits adequate specific structural characteristics to promote the hydrogen adsorption.

4.1. Energy calculations by dynamic interaction

The last model considers the study of the electronic properties in the interaction instants between the *AgY-zeolite* and the hydrogen molecule. The interaction was determined by means of energy interaction calculations between the zeolite and the hydrogen molecule for different separation distances.

In the last picture on Fig. 2 the system constituted by atoms on zeolite ring is used to determine the confined effect generated over a hydrogen molecule by all steps of dynamic interaction. Nevertheless, when different atoms on the ring feel an atom neighbor the charge and bond properties are represented by changes in the total energy, where there are atomic bonding changes that allow showing possible types of reaction. These results are obtained by dynamics interaction calculations.

In order to search indicatives over adsorption process in the hydrogen molecule, we take a relevant model for hydrogen diffusion in a ring of the zeolite model study. To show also its present confined effect due to 12 tetrahedral sites: 11 with SiO_4 and one acid site AgOAlO_3 . The interaction energy was calculated at different separation distances between *AgY-zeolite* ring and H_2 . Starting at 10 Å of separation with respect to the central point of the ring, the hydrogen molecule goes to it with a constant small speed, as shown in Fig. 3.

Due to the Born Oppenheimer dynamic interaction simulation, the resultant energy changes are explained by a rela-

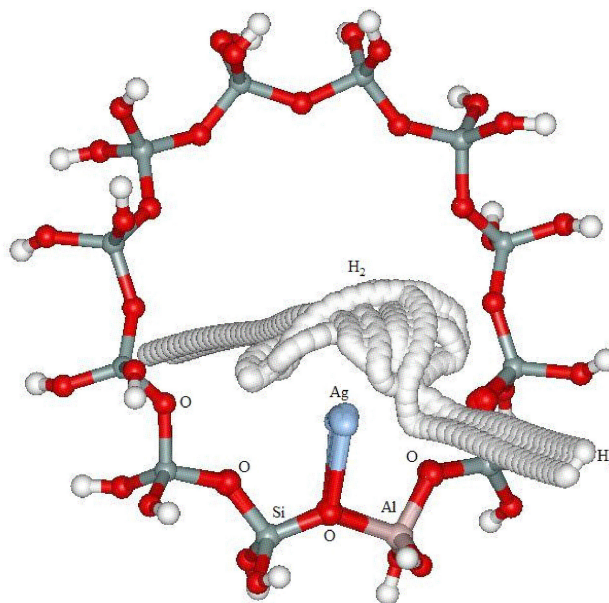


FIGURE 3. The cartoon shows the dynamic interaction simulation of hydrogen molecule and *AgY-zeolite* with an initial speed of hydrogen molecule with each step following a diffusion path showing attractive effect for a hydrogen molecule by an *AgY-zeolite* cation.

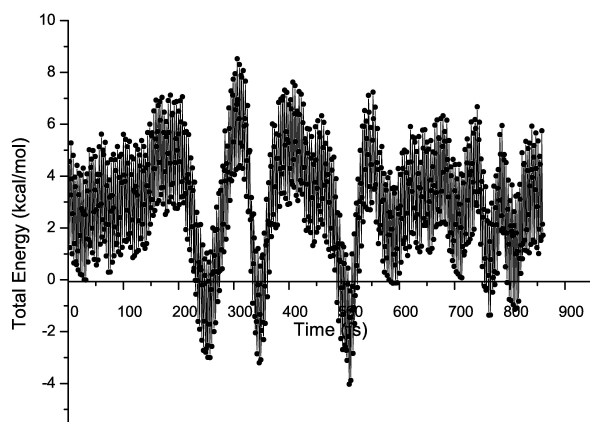


FIGURE 4. The interaction energy exhibits an attractive effect for the hydrogen molecule by the zeolite with an Ag cation system.

relationship between total energy and time. The energy changes at different regions of time indicate that for the first 100 steps of the dynamic obtained in the interaction, there is a small increase of the energy. These results indicate that a repulsive effect due to the electronic density of the ring is present when the hydrogen molecule arrives with a specific velocity. In this energy result of the interaction we see variation for all values. This type of changes in the energy values indicates that exists variation around 3 to 4 kcal/mol and corresponds to bonding oscillation in the H-H interaction, which generated a vibrational effect. Taking into account the Fig. 4, in the range 0 - 200 fs of simulation there is an average increase in the interaction energy. After that, the energy values corresponding to 200-600 fs show a variation point which exhibits 3 important minima related to a hydrogen molecule staying near to an Ag cation acid site.

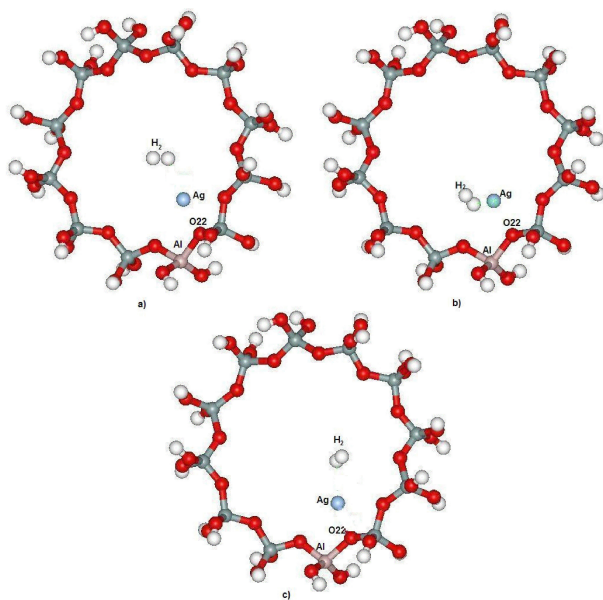


FIGURE 5. This figure shows rings corresponding to the molecular structures associated with a minimum energy value at the separation between Ag and H₂ of the: a) first minimum; b) second minimum; c) third minimum at least.

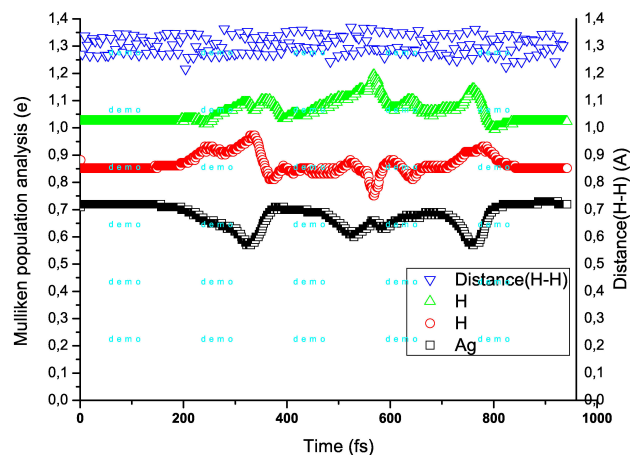


FIGURE 6. The calculation of the atomic charge distribution by means of Mulliken population analysis takes into account the Born Oppenheimer dynamic interaction simulation for molecular hydrogen diffusion throughout the ring interactively with the cation. The axes right is a graphics showing the changes of the H-H distance during time of simulation.

The time spent that remains in the cavity surmount the time that the hydrogen took to move since 10 Å to arrive to the AgY-zeolite ring. In the range of the first minimum 200-600 fs: i) there was a variation around 7 to -3 kcal/mol among 200-250 fs, ii) the next minimum in 250-350 fs increase from -3 to a maximum around 8 kcal/mol then decrease to around -4 kcal/mol, iii) in the third minimum the hydrogen molecule took 3 times more than the first minimum indicating that the adsorption process occurred for the hydrogen molecule with a difference among maximum and minimum of 5 kcal/mol of the Born Oppenheimer dynamics interaction. In the whole time there was not occurred a reaction modification in the system shown in Fig. 5.

The relative total Mulliken population values were plot taking into account the interaction between a hydrogen molecule and an AgY-zeolite ring during the simulation. The variation of the charge transference was obtained for the time interval 0-200 fs in which there were not changes in this molecular simulation. But during 200-800 fs the Ag cation exhibits charge transference on the hydrogen atoms. In the last range there are three important minima for Ag cation and three maxima for one hydrogen atom, however the other hydrogen present only two maxima and one minimum. In 450-600 fs there is charge transference in the molecular hydrogen. The opposite sign with a possible dipole formation is shown in the Fig. 6. In general the two hydrogen atoms allow transferring charge of equivalent values.

4.2. Interaction energy calculations

In the same way, we also take only a fragment of the model constituted by 3 tetrahedral sites as Si-Al-Si central atoms, which corresponds to an acid site with cation (H⁺, Ag). This is used to explain the type of interaction forces (repulsive or

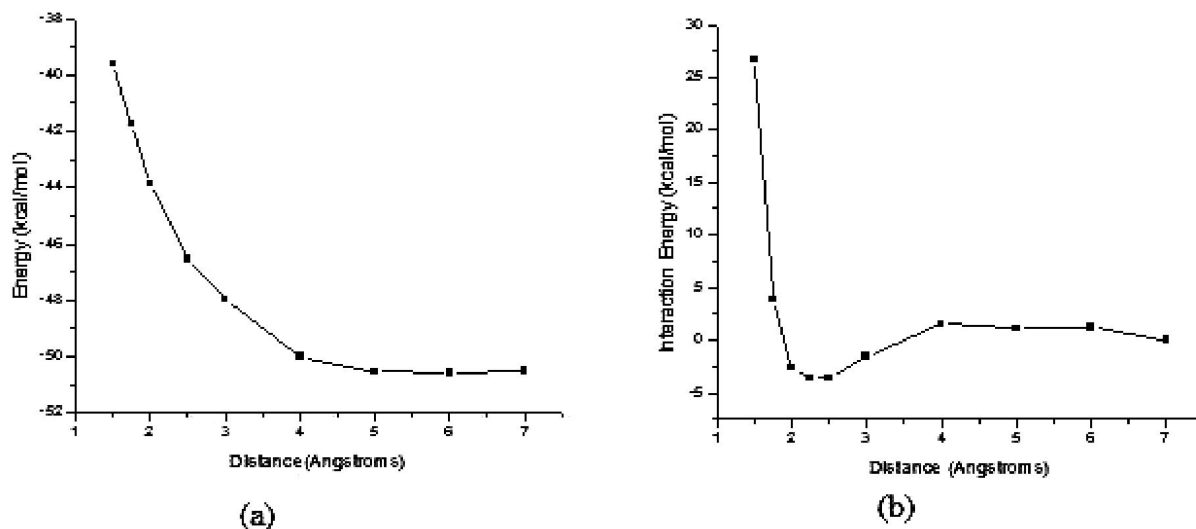


FIGURE 7. (a) This interaction corresponds to a repulsive effect between the H^+ zeolite and the hydrogen molecule, where the reactants stay unaffected. (b) The interaction exhibits both repulsive and attractive effects among the reactants, which cause adsorption and the formation of a new product $H_2AgY-Zeolite$ as a consequence.

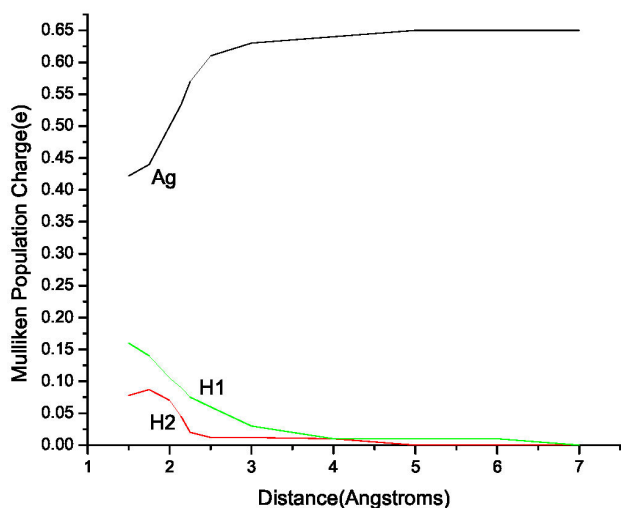


FIGURE 8. Calculation of the atomic charge distribution by means of Mulliken population analysis for every atom of the hydrogen molecule at different separation distances of the cation.

attractive) due to the cation in the interaction between a fragment of zeolite and a hydrogen molecule. The calculations of interaction are of single point energy type. This calculation allow to understand the adsorption processes in the system in study through calculations of point to point of the interaction energy, and to be capable of establishing a criterion as indicator of adsorbent material. By this reason, the importance of the behavior of the total energy is described for the type of changes in the total energy [24]. This type of calculation describes different changes in the atomic and electronic properties represented as energy changes. The modification of the energy corresponds to atomic bonding and electronic density changes of the fragment.

The fragment of zeolite ring (3T) is used in order to carry out the interaction energy calculation with a cationic interchange (H^+ , Ag) simulated around the acid site. The interchange of H^+ by Ag gives the effect only associated to one acid site. Interaction energy calculations at different separation distances between 1.5 Å and 7 Å taking small increments of distance for determining the possible existence of either physisorption or repulsion were carried out.

The values obtained for the interaction energies are reported in Fig. 7. The first curve (a) represents the interaction of the zeolite (H^+ cation) with the hydrogen molecule. These values of total energy indicate existence of a repulsive behavior between the HY-zeolite fragment and the hydrogen. The values of total energy in the interaction of the zeolite (Ag cation) with the H_2 correspond to attractive forces.

These results demonstrate a behavior associated to a repulsion that exists between the zeolite with proton and the hydrogen molecule. The zeolite with an Ag cation provides a slight attractive force due to interaction energy when the hydrogen molecule is located at different separation distances of the AgY-zeolite.

This result shows a potential well associated to the attractive effect of the cation on the hydrogen revealing a minimum energy value located around 2.5 Å, and 5 kcal/mol of the well-depth representing the adsorption energy. Such fact allows us to establish the existence of physisorption as shown in the Fig. 6b. The results can be compared when both a proton and an Ag cation are used, where the adsorption is due to the Ag cation. The adsorption energy as can be seen in Fig. 7 is about -5 kcal/mol (-0.022 eV), a physisorption bond, which is within the suggest range for hydrogen, between 0.2-0.6 eV [25]. The adsorption energy within this range makes it possible the loading / unloading process at room temperature and reasonable rates. Lower adsorption energy, belong

0.1 eV, require lower temperature (no rooms one) to allow secure storage, and so, results expensive. The Ag cation also exhibits charge transference on the hydrogen molecule in the range 1.5-3.0 Å of separation distances, where the two hydrogen atoms allow charge transference of equivalent shape of an Ag cation. The charge transference between Zeolite (Ag) and H₂ is very important because describes which of the atoms is important for charge interchange and is a property for adsorption. To estimate a value of hydrogen storage capacity for this type of zeolite, we are doing a simulation employing GCMC method [26]. The values of the transference are plotted in a graphic as shown in Fig. 8.

5. Conclusions

The model consisting on the AgY-zeolite ring was used to analyze the adsorption by considering the diffusion and the confining effect between the zeolite and the acid site. Thus it can be concluded that the interaction is completely related to the motion towards the acid site in the Ag.

In this interaction the effect of the Ag of stopping the Hydrogen molecule appears as an attraction force. However,

when silver atom stops one hydrogen atom for large time in the dynamics the effect causes a force freedom of the hydrogen molecule.

The interaction of the AgY-zeolite with hydrogen using a fragment model shows an important variation of energy values for the interaction energy, describing a repulsive and an attractive effect, with a potential well associated with the H and Ag respectively. This result of interaction energy by single point energy calculation reveals the existence of a weak attractive interaction interpreted as adsorption.

The general conclusion is that the zeolite with Ag cations can be considered as a hydrogen adsorbent material. The result did not show reaction modification in the AgY-zeolite and hydrogen molecule. We conclude for this reason that there was a physisorption.

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