

# Hydrogen Adsorption on Mg-DFT Zeolite Cluster: A Density Functional Theory Study

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## Abstract

Hydrogen molecule adsorption has been investigated on additional framework of Mg atom in DFT type zeolite by way of Density Functional Theory. The electronegativity, HOMO and LUMO energies chemical hardness, chemical potential, adsorption enthalpy and adsorption energy values have been calculated on a 16T zeolite cluster model and compared with those of Mg exchanged ERI and LTL zeolite structures. Hydrogen adsorption enthalpy value has been computed as -26.2 kJ/mol. This enthalpy value is meaningfully higher than the hydrogen molecule's liquefaction enthalpy value. This accordingly specifies that Mg-DFT zeolite structure appears to be an encouraging candidate cryoadsorbent for hydrogen storage.

*Keywords:* Hydrogen adsorption, DFT zeolite, Mg atom, DFT

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## 1. Introduction

The idea of consuming hydrogen as an energy carrier of the future was important over the past three decades due to limited hydrocarbon resources. Large-scale storage of hydrogen safely should be developed [1] in order to make it economically affordable. Cryogenically cooled, pressure and containers covering an appropriate adsorbent material are methods known as hydrogen storage. Among the adsorbents for the hydrogen adsorption; zeolites, activated carbon and metal alloys are the most important candidates. Several research groups studied the hydrogen adsorption on exchanged Mg atom site in zeolites such as zeolite X [2,3], zeolite Y [4-6], zeolite FAU [6], zeolite ERI [7] and zeolite LTL [8]. There are no studies neither in theoretical nor experimental literature, concerning adsorption of hydrogen on Mg metal atom exchanged DFT type zeolite in either theoretical or experimental open literature. The aim of this study is to examine the activity of Mg<sup>2+</sup> site in DFT type zeolite for the hydrogen molecule adsorption.

## 2. Material and Methods

The theoretical calculations employed were based on Density Functional Theory (DFT) [9] used in Gaussian 09 software [10] with the B3LYP-Hybrid formalism method in present work. It has been known that one of the DFT methods for high-quality procedure of theoretical calculations for organic chemistry is the B3LYP method. For all atoms 6-31G(d,p) basis set was utilized in calculations.

The lattice constants values of the DFT type zeolite are  $a = b = 7.075 \text{ \AA}$  and  $c = 9.023 \text{ \AA}$  and angles of  $\alpha = \beta = \gamma = 90^\circ$  with P4<sub>2</sub>/mmc space group. The zeolite DFT covers a main straight 8-membered ring channel (See Figure 1). In current study the cluster utilized for theoretical calculations has been cut from the channel of DFT type zeolite, which offers the feature of the existence of 8T pair rings (where T is called as SiO<sub>4</sub> tetrahedral structure). The model of 16T DFT zeolite cluster has 20 O and 16 Si atoms. Two Si atoms were replaced by two Al atoms in the 4T ring of 16T cluster model ([Si<sub>14</sub>Al<sub>2</sub>O<sub>20</sub>H<sub>24</sub>]<sup>2-</sup>). The part b of Figure 1 shows the final cluster model. The cluster's negative charge (2-) was saturated by the additional framework of [Mg]<sup>2+</sup>. Free bonds of the Si and Al atoms have been terminated by hydrogen (H) atoms in order to neutralize the charge of the cluster. In this work terminating hydrogen atoms are kept fixed and all other atoms were relaxed during all theoretical calculations. Additional hydrogen atoms were kept fixed in order to direct the next Si site in the tetrahedral direction in DFT type zeolite structure.

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Received 12 September 2017; Accepted 5 October 2017

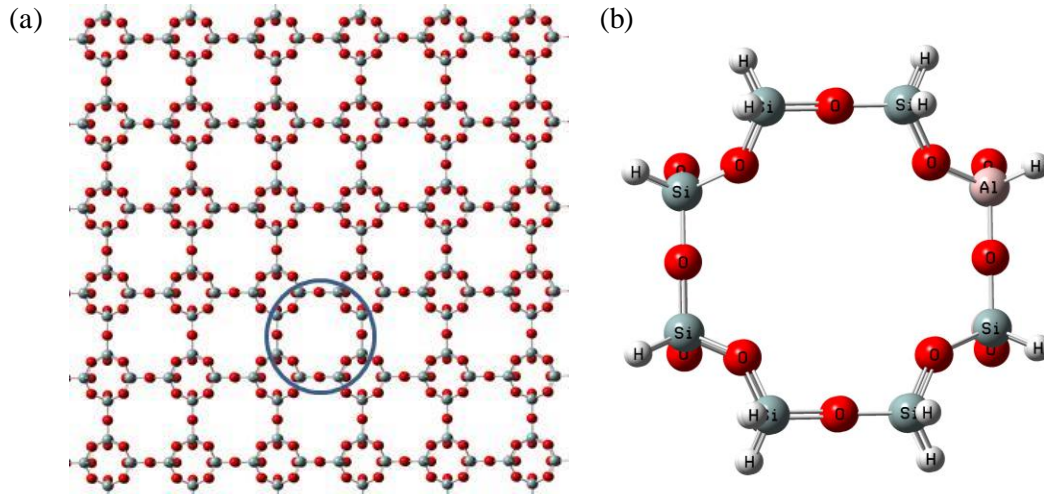


Figure 1. DFT type zeolite structure with crystallographic position of the cluster (a) and 16T DFT (b) cluster

Geometries have been optimized by Equilibrium Geometry (EG) calculations. In this study, values of energy difference consist of the zero-point energy (ZPE) corrections which have been calculated by using vibrational frequency calculations through Single Point Energy (SPE) calculations. Additionally, the thermal energy and thermal enthalpy were computed by frequency calculations at 298 K, because neither theoretical nor experimental literature has no thermochemistry data for hydrogen adsorption on Mg-DFT zeolite. These energy values have been computed as follows [11].

$$E = E_{\text{electronic}} + ZPE + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \quad (1)$$

$$H = E + RT \quad (2)$$

The chemical potential, electronegativity and chemical hardness values were computed by using the equations demonstrated below. Energy of the highest occupied molecular orbital ( $\epsilon_{\text{HOMO}}$ ) and energy of the lowest unoccupied molecular orbital ( $\epsilon_{\text{LUMO}}$ ) have been utilized in order to create these equations as based on the approximation of Koopmans [12-14].

$$\text{Chemical Hardness } (\eta) \cong \frac{I-A}{2} \quad (3)$$

$$\text{Chemical Potential } (\mu) \cong -\frac{I+A}{2} \quad (4)$$

$$\text{Electronegativity } (\chi) \cong -\text{Chemical Potential } (\mu) \quad (5)$$

where  $I \cong -\epsilon_{\text{HOMO}}$  and  $A \cong -\epsilon_{\text{LUMO}}$

The theoretical method in this study is the same with the methods of our previous studies [7,8]. In this study, the relative energy values for theoretical calculations have been obtained by the following equation.

$$\Delta(E/H) = (E/H)_{\text{system}} - (E/H)_{\text{Adsorbive}} - (E/H)_{\text{cluster}} \quad (6)$$

Here,  $(E/H)_{\text{system}}$  is the energy/enthalpy for the optimized adsorbing molecule-cluster system,  $(E/H)_{\text{Adsorbive}}$  is the energy/enthalpy for the adsorbing molecule, and  $(E/H)_{\text{cluster}}$  is the energy/enthalpy for the cluster.

### 3. Results and Discussion

Firstly Mg-DFT cluster was optimized by EG calculation with neutral charge and the singlet SM. Furthermore singlet SM was established for the cluster-hydrogen molecule system. EG of 16T Mg-DFT cluster is shown in Figure 2a. Charge and SM, determined for the calculation of obtaining EG of adsorbing molecule as hydrogen molecule, was neutral charge and singlet state. After the optimization of adsorbing molecule (H<sub>2</sub>) and cluster, hydrogen molecule adsorption was examined on Mg-DFT cluster by EG calculation. Optimized geometry of the hydrogen, adsorbed 16T Mg-DFT cluster structure, is represented in Figure 2b.

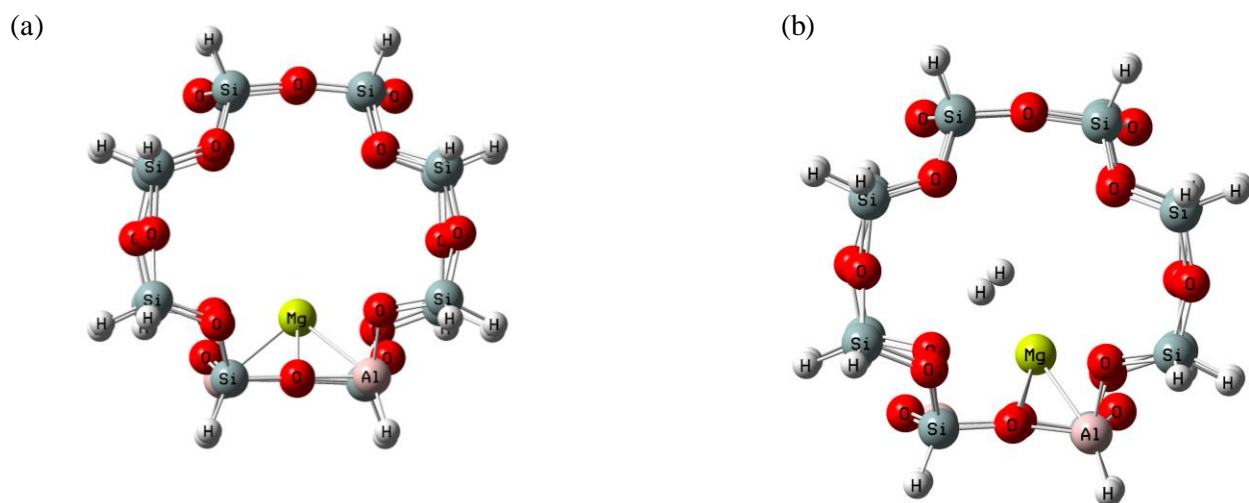


Figure 2. a) Optimized Mg-DFT zeolite cluster, b) Optimized hydrogen adsorbed 16T Mg-DFT cluster

The HOMO and LUMO energy values, chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and electronegativity ( $\chi$ ) values and the energy change values ( $\Delta E$  and  $\Delta H$ ) for hydrogen adsorption on Mg-DFT, Mg-ERI and Mg-LTL clusters have been presented in Table 1. Based on the LUMO energies, the LUMO energy changes to more negative values when Lewis acidity increases for Mg-DFT zeolite, Mg-LTL zeolite and Mg-ERI zeolite respectively. Correspondingly, this is parallel with decreasing of adsorption strength [7,8].

Table 1. Comparison of energy values for hydrogen adsorption (Values are in units of kJ/mol)

	Zeolite DFT		Zeolite LTL <sup>a</sup>		Zeolite ERI <sup>b</sup>	
	Cluster	Cluster with adsorbed H <sub>2</sub>	Cluster	Cluster with adsorbed H <sub>2</sub>	Cluster	Cluster with adsorbed H <sub>2</sub>
HOMO Energy	-737.9	-727.9	-715.1	-716.8	-733.0	-731.4
LUMO Energy	-266.6	-195.2	-131.4	-70.1	-103.6	-71.6
Chemical	235.6	266.3	291.8	323.4	314.7	329.9
Chemical Potential	-502.3	-461.5	-423.3	-393.5	-418.3	-401.5
Electronegativity	502.3	461.5	423.3	393.5	418.3	401.5
$\Delta E$		-23.8		-13.0		-1.2
$\Delta H$		-26.2		-14.7		-3.6

<sup>a</sup> Reference [8]

<sup>b</sup> Reference [7]

Chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and electronegativity ( $\chi$ ) values were calculated by using both the HOMO/LUMO values based on the values of free H<sub>2</sub> molecule and model cluster, and the HOMO/LUMO values based on the values of cluster with the optimized adsorbed H<sub>2</sub> molecule [12,14]. The chemical hardness values decreases in the order of Mg-ERI > Mg-LTL > Mg-DFT. It should be noted that the chemical potential values are strongly related with the energy issue of adsorption during a reaction. Lower chemical potential values indicate that, during the hydrogen adsorption on cluster, the adsorption energies on these clusters should be much lower with respect to the other Mg exchanged zeolite clusters [14]. According to Table 1, chemical potential values, electronegativity values and adsorption energy values are in the order of Mg-DFT > Mg-LTL > Mg-ERI. Besides, lower chemical hardness value of Mg-DFT cluster designates that this cluster is softer than other clusters for hydrogen adsorption.

Adsorption enthalpy values on Mg exchange zeolites were described in the range of -13 to -18 kJ/mol experimentally (zeolite X [3] and zeolite Y [5,6]) and in the range of -3.6(-12.9) kJ/mol theoretically (zeolite X [2], zeolite CHA[10], zeolite ERI [7] and zeolite LTL[8]) in literature. In this study, adsorption enthalpy of hydrogen has been computed as -26.2 kJ/mol Mg-DFT zeolite cluster model. In order to be able to claim that a material can be a possible candidate for cryoadsorbent material for storage of hydrogen the enthalpy value for hydrogen adsorption on that material should be larger than the liquefaction enthalpy of hydrogen molecule. In view of that, if adsorption enthalpy value for hydrogen on Mg-DFT cluster is compared to the hydrogen molecule's liquefaction enthalpy (0.9 kJ/mol [15]) and to the available literature data, it can be observed that the enthalpy values of hydrogen adsorption involved for Mg-DFT structure is substantially larger than the liquefaction enthalpy of hydrogen and the literature values. Consequently, based on these data, Mg-DFT zeolite structure seems to be strong candidate for cryoadsorbent material for hydrogen storage.

#### 4. Conclusions

For the adsorption of hydrogen molecule DFT calculations with B3LYP method have been utilized on Mg-DFT type zeolite cluster. Adsorption enthalpy value for hydrogen adsorption was computed as -26.2 kJ/mol, which is particularly greater than the hydrogen molecule's liquefaction enthalpy value. This shows that Mg-DFT zeolite structure looks to be a talented candidate cryoadsorbent for storage of hydrogen molecule.

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