

## Study of the Structure Effect on Water Adsorption by a Group of Nano Copper Clusters

M. Totonkoban<sup>1</sup>, M. Oftadeh<sup>1,\*</sup>, N. Farzi<sup>2</sup><sup>1</sup> Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. of IRAN<sup>2</sup> Chemistry Department, University of Isfahan, Isfahan, I. R. of IRAN

(Received 4 June 2012; published online 18 August 2012)

According to the previous studies, water adsorption energy on the metal surface like as Cu strongly dependent to the structure surface and the size. During the study of the mechanism of the interaction of water and Cu in water gas shift reaction (WGS) ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ), it has been determined Cu is active site of catalysis. These studies inspired the authors to consider theoretically the effect of the structure in the process of the water adsorption in order to select the suitable structures of the copper clusters,  $\text{Cu}_{10}$ , for  $\text{H}_2$  releasing in the fuel cells at B3LYP/6-31G level of theory. The results showed the distinct effect of the structure on the type of adsorption process (physical or chemical) through three structure of  $\text{Cu}_{10}$  (I, II, III structures, Fig. 1). The structures I and II showed physical surface adsorption in reaction with water and the structure III showed chemical adsorption with  $\text{H}_2$  releasing. The adsorption energies are 0.38, 1.15, -28.27 (kcal/mol) and  $\Delta G_{\text{ads}}$  are 11.14, 13.49, -20.12 (kcal/mol), respectively.

**Keywords:** Copper cluster, Water adsorption, Density functional theory, Surface interaction.

PACS numbers: 34.35.+a, 34.50.Lf

## 1. INTRODUCTION

Copper is an important transition metal with high electrical and thermal conductivity which is used in many industrial processes in the pure state as sheets, tubes, rods and wires but also as an alloy with other metals. In fact copper is an important material for structural, electrical, and electronics application [1, 2]. Studies show that copper clusters have three dimensional interconnected structures quite different from solid state materials. They are aggregates of nanoscale size that have strange physical, chemical, structural, electrical and thermodynamical properties. Due to broad application of metal clusters in biology, catalysis and nanotechnology, investigation about clusters is an important aspect of theoretical and experimental researches. In metal clusters, bridge and hollow positions are important adsorption sites [3]. Analysis of transition metals complexes is critical due to specific molecular properties for systems including high amount of electrons and also for study the role of ligand-metal interaction in catalytic processes [4]. The water gas shift reaction is wellknown reaction done by heterogeneous Cu-based catalysts that has important effect in  $\text{H}_2$  production for fuel cells. In this reaction Cu is active site of catalysis so comprehensive data about water adsorption on Cu surface is useful for understanding the WGS mechanism [5, 6]. Previous studies confirms that Cu(110) is the borderline between intact and dissociative water adsorption and this result could be potentially useful in  $\text{H}_2$  production and its application in fuel cells [7]. These studies also confirm that adsorption energy show strong dependence on the surface structure and the cluster size [8].

Water adsorption is outcome of transition of high amount of charge from water to metal. In fact molecule-metal interaction is arising from electron  $\sigma$  donation from the ligand to the metal and  $\pi$  back-donation of electrons the metal to the ligand that these interaction

are different for various ligands and weak interaction of  $\text{M}-\text{H}_2\text{O}$  is electrostatic interaction arising from the penetration of the water dipole into the metal atom charge cloud [4, 9]. In this paper only the process of monomer water adsorption is studied.

About the orientation of interaction generally it has been assumed that  $\text{H}_2\text{O}$  absorbs "up right" with the O end down and OH bonds pointing away from the surface, since this orientation maximizes the adsorbate dipole substrate image-dipole interactions [10].

DFT method is common quantum computation method that energy and other molecular properties in ground state are accessible by applying electron probability density in ground state uniquely. B3LYP method is the most common function including local and non-local terms. DFT analysis should not be done by basis sets lower than 6-31G. DFT methods for transition metals compounds like copper clusters are more reliable than HF analysis [11].

In this paper we present the results of quantum mechanical studies about water adsorption process on a group of decade copper clusters,  $\text{Cu}_{10}$ . This paper presents the results of  $\text{Cu}-\text{H}_2\text{O}$  interaction in three  $\text{Cu}_{10}$  cluster with different structures by density functional method. Special directionality and water adsorption interaction energy is studied too.

According to the Conference policy, the proceedings will be published instead of the abstract book. The conference proceedings will be published up to the conference sessions for the convenience of the participants and the best dissemination through the Web, since the proceedings paper will be freely available on-line. In order to speed up the availability of your paper online, the submitted manuscript must appear like ready for publication. So, the strict requirements to the manuscript preparation exist.

\* [M\\_oftadeh@pnu.ac.ir](mailto:M_oftadeh@pnu.ac.ir)

## 2. THEORETICAL METHODS AND MODELS

### 2.1 Methods

Different methods and basis set have been tested for  $\text{Cu} + (\text{H}_2\text{O})_n$  clusters, that results with MP2 and medium sized basis set were in a good agreement with higher level methods like CCSD(T) [2]. B3LYP method and split valence 6-31G and diffuse 6-31+G\* basis sets were selected for optimization copper clusters and  $\text{H}_2\text{O}$ . Duo to Cu is a heavy metal B3LYP/GEN was used for analyzing adsorption process. All of calculations were performed by Gaussian 09 Windows that is very powerful program thought the rate of analysis increased 4 times rather than Gaussian 03.

### 2.2 Models

The most studied cleavage planes for copper are (100) (111) (110). These planes have difficult properties atomic spacing and the adsorption energies will therefore be different. A surface atom on the (111) plane has nine coordinated atoms, six beside and three below, whereas a surface atom on the (100) plane has eight neighbors, four beside and four below. In fact (111) surface has a 3-fold hollow site, whereas the (100) surface has a 4-fold site [6].

Three structures of  $\text{Cu}_{10}$  (I, II, and III, Fig. 2) were selected and made interaction with water in which the structures I and II the oxygen took on-top site (upper of one copper atom), and in the structure III the oxygen located in bridge position, upper side of connection site of two Cu atoms. A template is a tool for enforcing a standard layout and look and feel across multiple pages or within content regions. It provides stricter standardization controls of the documents. In other words, a template is a form, or pattern used as a guide to making something. Due to it you do not need every time set the margins, spacing, page layout, fonts, format options, etc.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows water adsorption process on every  $\text{Cu}_{10}$  clusters. The results of the calculated electronic energy,  $E_{\text{HF}}$ , the interaction energy of water with three structures,  $E_{\text{int}}$ , the BSSE corrected interaction energy,  $E_{\text{int-BSSE}}$ , the Gibbs free adsorption energy,  $\Delta G_{\text{ads}}$ , at 298 K and 1 atm, the distance of the oxygen atom from Cu,  $d_{\text{Cu-O}}$ , and the HOH angle,  $\angle \text{HOH}$ , after adsorption have been listed in Table 1.

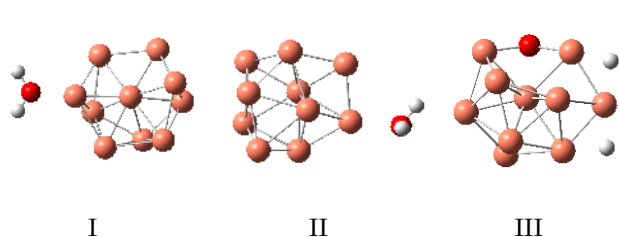
The results indicate that the water adsorption on the structures I and II are physical adsorption and the spontaneous and chemical adsorption process occur for the structure III. In this case, water located between two Cu atoms as a bridge with releasing two hydrogen atoms and this could be a suitable model to use in fuel cells. The energy scan diagram versus Cu-O distance for the structures I, II and III have been depicted in Fig. 3.

## 4. CONCLUSION

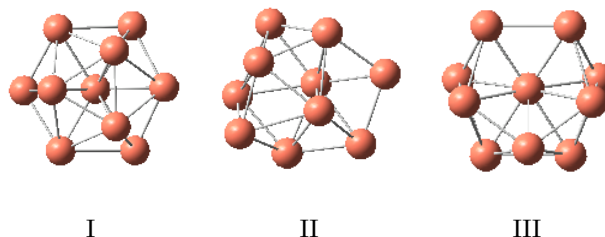
In this study B3LYP method and 6-31G basis set was used for optimization of every cluster. Also B3LYP method and 6-31+G\* Basis set is used for water optimization. The studies show that BSSE correction has strong effect on interaction energies. The structure type has direct effect on type of adsorption process. All of the structures achieved positive frequency after optimization. The results showed physical adsorption in water interaction for the structures I and II, and the other undergo spontaneous chemical adsorption associating  $\text{H}_2$  releasing. Water orientation and HOH angle change during adsorption process, and it is determined that  $\text{H}_2\text{O}$  molecule get close to clusters due to the oxygen atom. The equilibrium distance and energies are reported by single point test performance. The oxygen atom of water molecule located in bridge site between two Cu atoms of cluster and released two hydrogen atom in the cluster undergoing chemical adsorption.

**Table 1** – Results of the optimization of different structures of  $\text{Cu}_{10}$  and of water adsorption on different structures of  $\text{Cu}_{10}$

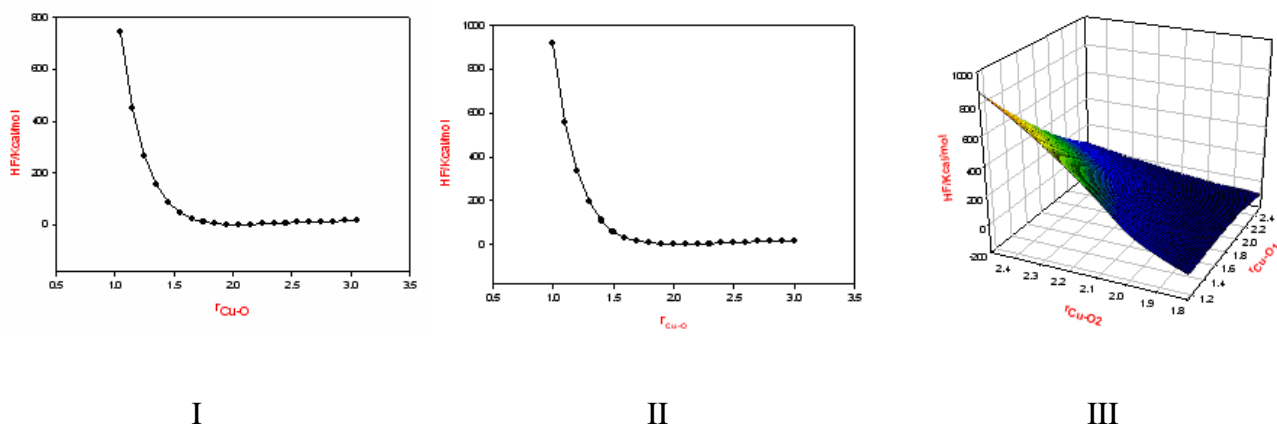
Structure	EHF Hartree	Eads kcal/mol	EHFBSSE kcal/mol	$\Delta G_{\text{ads}}$ kcal/mol	d Cu-O $\text{\AA}$	$\angle \text{HOH}$ After ad- sorption
I	-16402.9410	0.38	13.87	11.14	1.994	108.74
II	-16402.9501	1.15	15.91	13.49	2.049	104.91
III	-16402.9706	-28.27	30.10	-20.12	-	-



**Fig. 1** – Water adsorption on  $\text{Cu}_{10}$  clusters



**Fig. 2** – Selected structures of  $\text{Cu}_{10}$



**Fig. 3** – Energy scan diagram versus Cu-O distance for structure I and II, and versus Cu-O<sub>1</sub> and Cu-O<sub>2</sub> distances for the structure III

## REFERENCES

1. S. Wang, Y. Cao, P.A. Rikvold, *Phys. Rev. B* **70**, 205410 (2004)
2. H. Ruuska, T.A. Pakkanen, R.L. Rowley, *J. Phys. Chem.* **108**, 2614 (2004).
3. M. Büyükata, Janson C. Belchier, *J. Braz. Chem.* **19**, 884 (2008).
4. C. Adamo, F. Lelj, *J. Mol. Struct. (THEOCHEM)* **389**, 83 (1997).
5. N.A. Koryabkina, A. A. Phtak, W.F. Ruetthnger, R.J. Farrauto, F.H. Riberio, *J. Catal.* **217**, 233 (2003).
6. Q.L. Tang, Z.X. Chen, *Surf. Sci.* **600**, 954 (2007).
7. J. Ren, S. Meng, *Phys. Rev. B* **77**, 54110 (2008).
8. Z. Hu, R.J. Boyd, *J. Chem. Phys.* **112**, 9562 (2000).
9. A. Ignaczak, J. Gomes, *J. Electroanal. Chem.* **420**, 209 (1997).
10. A. Michaelides, V.A. Ranea, P.L. de Andres, D.A. King, *Phys. Rev. Lett.* **90**, 216102 (2003).
11. F. Jensen, *Introduction to computational chemistry, 2nd Edition*, (John Wiley & Sons Ltd, 2007).