



Theoretical Study of Hydrogen Adsorption Energy on Nano Metal Crystal

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ABSTRACT

In this study, we determined effects of changing nano metal crystal on the binding energy of hydrogen adsorption by hydrogen adsorption modeling and gas molecule adsorption on Cu, Ag and Au nano metals. The calculated of $DG_{(ads)}(H_2+metal)$ and how the adsorption may affect the entropy, adsorption energy and dipole moment of surface.

Key words: Adsorption, Hydrogen, Nano- Metal Crystal, Adsorption Energy.

INTRODUCTION

Nanoparticles and Nanometal crystals play a vital role in modern industries¹⁻³. Intermediate metals play a major role in catalytic processes and facilitate chemical reactions by absorbing substances on their surface. Diversity in the surficial absorption phenomena, high expenses and need to the repeatability of the process explain the reason of using calculative chemical approaches with less expenses, repeatability and high precision. Most metals have a close array in solid state; Cu, Ag and Au are from the cubic type with filled Centered faces (FCC). Diameter of metal particles Cu, Ag, Au is 0.256, 0.289 and 0.288 nm respectively⁴. Considering 4 atoms per each unit cell for gold, copper and silver nanoparticles, the surficial absorption in these metals has been assessed and their thermodynamic functions and

absorption power⁵ have been discussed. Based on what has been mentioned in the reference⁶⁻⁷, chemical absorption decreases along with the series of intermediate elements. At the beginning of the elements series, chemical absorption bonds are so strong that cannot be broken easily, and at the end of the series they are so weak that cannot be shaped adequately for the proper speed of the covered surface. Therefore the optimum state can be observed at the middle of the elements series. The absorption of Hydrogen on Nano crystal surface of copper, silver and gold is modeled in the two states of close and remote which are equal to tangent and free modes respectively, in order to compare them in columns. The Gibbs free energy of hydrogen molecule, isolated hydrogen, and isolated metal Nano crystals are calculated and following this the Gibbs free energy of Combined system which includes hydrogen metal and

molecules. Absorption energy changes in combined entropy and dipole moment of Hydrogen with copper is higher due to a stronger Van der Waals force.

Computational Methods

Frequency calculations in B3LYP level of density function theory (DFT) with the base series of metal LANL2Z and Hydrogen 6-31G were conducted by Gaussian 98 software. In order to analyze the Hydrogen absorption on Nano surface of metal crystals, two states have been taken into account:

- I) Close (Metal- H₂) which stands for absorbed Hydrogen on crystal surface of metal in tangent state,
- II) Remote (Metal- H₂) which stands for the system with Hydrogen in a distance 0.5 & farther than tangent state.

RESULTS AND DISCUSSION

Gibbs free energy of hydrogen and isolated

metal have been calculated and the absorption energy can be obtained through the following equation:

$$\Delta G_{\text{Ads}} = G_{(\text{combined})} - \Sigma G$$

Tables 1 exhibit that the physical absorption energy of H₂ on surfaces of Nano metal crystals reduces from copper to gold. The percentage of change is obtained through the following relationship:

$$\% \text{changing} = [(G_{\text{combined}} - \Sigma G) / G_{\text{combined}}] \times 100$$

Which indicates a decrease in absorption force in a group from the top to the bottom, so that for H₂ the strongest absorption is observed on copper surface and the weakest one is recorded on gold surface. ΣG is the sum of isolated H₂ and metal Nano crystal Gibbs free energies.

The adsorption energy is always regarded as a measure of the strength of adsorbate-substrate

Table 1: ΔG of calculated absorption in the system (metal+H₂)

Metal Crystal	Cu	Ag	Au
G isolated Metal (J/mol)	-2.058E+09	-1.529E+09	-1.421E+09
ΣG (J/mol)	-2.061E+09	-1.921E+09	-1.813E+09
G combined system (J/mol)	-2.061E+09	-1.924E+09	-1.815E+09
$\Delta G(\text{ads})$ (KJ/mol)	-73.783	-68.716	-40.424
%changing	0.003%	0.004%	0.005%

Table 2: Values of E_{ad} for the systems (metal+C₂H₂) and (metal+H₂)

Metal Crystal	Cu	Ag	Au
$E_{(\text{ads})} \text{H}_2$ (J/mol)	-5.476	-4.581	-3.988

Table 3: Values of dipole moment (metal+H₂)

Dipole Moment(Debye)	Cu	Ag	Au
μ metal	0.0000	0.0000	0.0000
$\mu(\text{metal+H}_2)\text{close } \frac{1}{4}$	1.4858	2.2201	1.4932
$\mu(\text{metal+H}_2)\text{remote}$	0.8202	1.0532	0.3394

Table 4: Entropy values of the system (metal+H₂)

Entropy(cal/mol.K)	Cu	Ag	Au
S isolated metal	79.859	86.024	91.646
S(metal+H ₂) close	88.632	95.236	101.454
S(metal+H ₂) remote	91.750	94.146	100.099

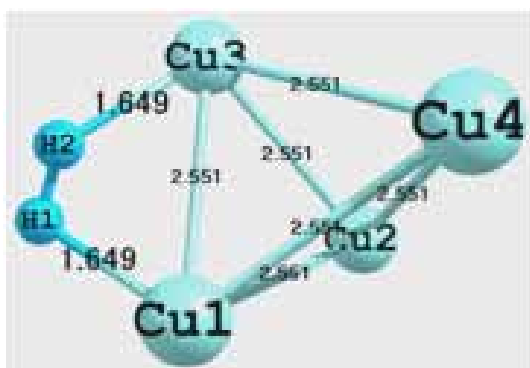


Fig 1. structure Cu & H₂(close)

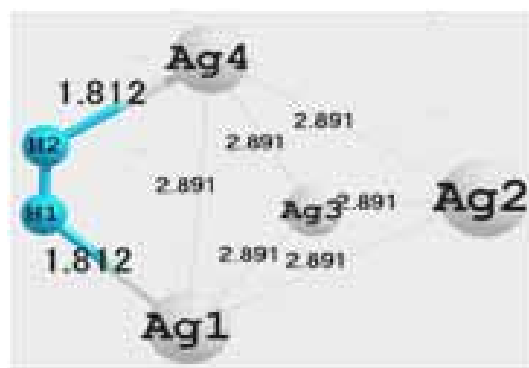


Fig 2. structure Ag & H₂(close)

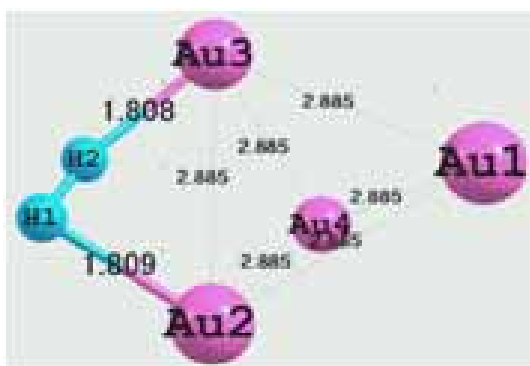


Fig 3. structure Au & H₂(close)

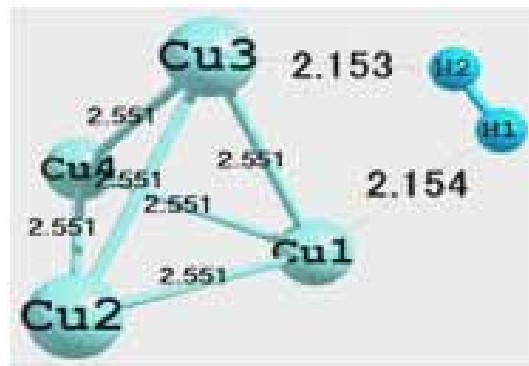


Fig 4. structure Cu & H₂(remote)

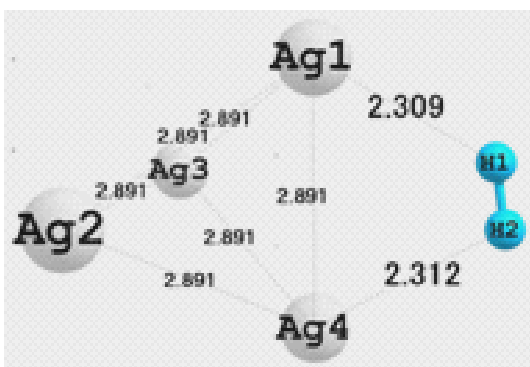


Fig 5. structure Ag & H₂(remote)



Fig 6. structure Au & H₂(remote)

adsorption. The adsorption energies E_{ads} are defined as: $E_{ads} = E_{sub} + E_{ads} - E_{ads/sub}$, where $E_{ads/sub}$ is the total energy of adsorbate–substrate system in the equilibrium state, E_{sub} and E_{ads} are the total energy of fixed substrate and free adsorbate alone, respectively (Table 2). Based on this definition, negative values indicate heat in process⁵.

Based on the obtained results from tables 1, 2 the absorption force of Hydrogen on the copper surface is apparently more than Ag and Au. These results are in accommodation with the information obtained from the resources⁸. In fact, the surficial absorption force decreases in a group from top to the bottom due to the increase in atomic diameter. Tables 3 indicate the difference between calculated dipole moment in forms of close and remote for hydrogen molecules respectively which shows asymmetry of molecular load distribution⁹⁻¹³.

Based on these results, the surficial absorption process of H_2 on these metal Nano

crystals is autonomous (negative values of Gibbs energy) and heat producing (negative values of E_{ads}). Magnitude of E_{ads} values indicates a stronger absorption between H_2 and metal's Nano crystal surface. Entropy results for adsorption of Hydrogen are calculated and shown in Tables 4.

Based on obtained results from Table 4, entropy of close forms for copper, silver and gold Nano-crystals in tangent condition is less effective than remote forms due to the decrease in electron distribution of system.

This entropy decline in close mode is due to the decrease of freedom levels at the time of surficial absorption; since in this mode the movement of molecules declines from 3 to 2 dimensions.

The structures of close and remote forms of metal and H_2 can be observed in Figs 1-6. The structure of metal crystals for Au, Cu and Ag is Fcc. The diameter of metal atoms in the crystal network is based on the angstrom unit.

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