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INTERACTION OF HYDROGEN WITH PALLADIUM ATOMS AND CLUSTERS

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ABSTRACT

The interaction between hydrogen and palladium atoms leading to the formation of palladium hydrides has been studied theoretically. Ab initio calculations with Becke's Three Parameter Hybrid Functional using the LYP Correlation Functional (B3LYP) have been performed to establish the binding characteristics of palladium hydrides species. The interaction of hydrogen with four- and six- atom clusters (like tetra- and octahedral voids) has been compared. It has been proved that the binding of hydrogen with the tetrahedral void is stronger than in the second case.

INTRODUCTION

The interaction of hydrogen with isolated d-transition metals leads to the formation of both, mono- and dihydrides[1]. In case of palladium creation of palladium monohydrides have been noticed [2].

It has been established experimentally by measurements of surface potential and H_2 pressure [eg.3] that during the hydrogen adsorption process two kind of adspecies appear on the Pd surface: stable on the surface negatively polarized atomic adspecies referred to as β^- and arising with the increasing coverage positively polarized atomic adspecies referred to as β^+, which incorporate into the bulk quickly. The unique solubility of hydrogen in palladium bulk enables to use palladium as energy storage and for this reason hydrogen-palladium systems have been investigated by a wide variety of experimental ways: TDS [4-8], LEED [4-7], work function measurements [4-7], HREELS [8].

In the course of the field evaporation process of palladium in hydrogen atmosphere, spectrum consisting of Pd^+, PdH^+ and PdH_2^+ has been detected by using the magnetic sector atom-probe FIM [9]. On the other hand Stępień and Tsong have recorded the occurrence of Pd^+, PdH^+, PdH_2^+, PdH_3^+ and PdH_4^+[10] by using pulsed- laser time-of –flight atom-probe FIM . The observed ions seem to be formed after the processes of field desorption and ionization the respective molecules.

In the present study we are interested in: can PdH_x (x=1,2,3,4) species exist free in space? And what are their binding characteristics?

To shed some light on above problems the ab initio studies of the interaction of hydrogen with isolated Pd atom have been performed. In addition, the process of hydrogen diffusion from the surface into tetra- and octahedral voids has been considered. In our computation the effect of the high electric field is neglected.

METHODS

For numerical calculations the GAUSSIAN 98 program package [11] was employed. The self consistent field *ab initio* method with the Becke's hybrid functional [12] has been used.

In this functional the exchange functional is a linear combination of the Hartree-Fock exchange and the density- functional theory exchange- correlation and has the following form:

$$A * E_x^{Slater} + (1-A) * E_x^{HF} + B * \Delta E_x^{Becke} + E_c^{VWN} + C * \Delta E_c^{non-local};$$

where the non-local correlation is provided by the LYP expression [13], the VWN correlation functional has been described by Vosko, Wilk and Nusair in [14] and the constants A,B,C have been determined by Becke by fitting to the G1 molecule set. The basis set taken for a cobalt atom has been CEP-4G, since it is known to give- for palladium the best accuracy in the all- electron calculations.

RESULTS AND DISCUSSION

The first step of our investigations was to determine the binding characteristics of PdH_x (x=1,2,3,4).The geometry of the molecules in the equilibrium states has been found by the way of minimization of the total energy with respect to all their independent coordinates, i.e. bond length, valence angles and dihedral angles.

The theoretical results of the binding energy (per H atom), free-space total dipole moment and ionization energy for the palladium hydrides in the equilibrium states are listed in Table1. In addition, the geometry of the systems has been performed in Fig 1.

Table 1. The binding characteristics of palladium hydrides in the equilibrium states

Hydrides	Binding energy (eV)	Ionization potential (eV)	Dipole moment (Debye unit)
PdH	3.20	8.82	2.079
PdH_2	3.38	8.76	2.191
PdH_3	3.27	8.74	2.742
PdH_4	2.98	9.35	0.288

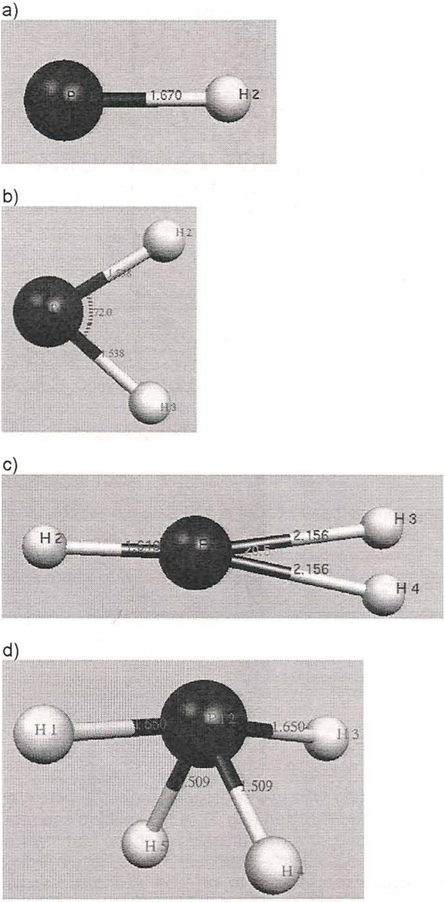

Figure 1. The equilibrium geometry of palladium hydrides a) PdH, b) PdH_2 c) PdH_3 d) PdH_4

The binding energy has been calculated according to the following equation:

$$E_b = \{E_{total}(PdH_x) - [E_{total}(Pd) + xE_{total}(H)]\}/x \qquad x = 1,2,3,4$$

where $E_{total}(PdH_x)$ is the total energy of the considered system, $E_{total}(Pd)$ and $E_{total}(H)$ are the total energies of an palladium atom and interacting hydrogen atom/atoms.

To study the process of binding a hydrogen atom to a palladium atom on the surface of emitter tip the scan of the total energy of (Pd- H) system as a function of a separation distance has been performed (Fig.2). The curve reveals a minimum for the distance of 0.17 nm.

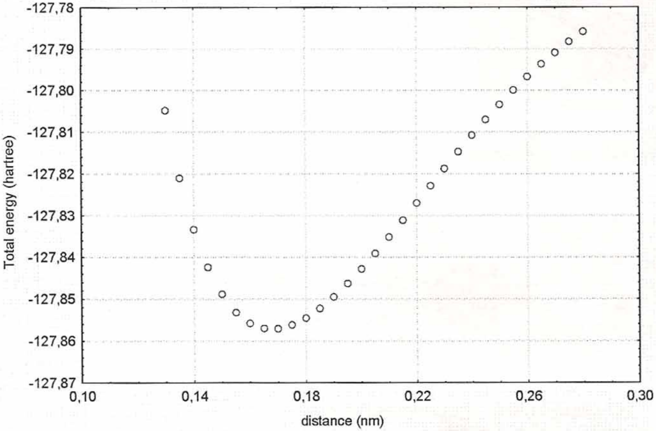

Figure 2. Calculated total energy changes in dependence on the distance between hydrogen atom and single palladium atom.

For a single palladium atom interacting with two hydrogen atoms the potential energy surfaces (PES) have been reconstructed (Fig 3). A minimum is seen for the following values: R=1.25 Å and d=0.90 Å.(the meaning of these parameters has been shown in the figure). The palladium –hydrogen bond length in PdH_2 calculated on the basis of above results seems to be 1.54 Å and the angle between palladium –hydrogen bonds is equal to 71.5 °.

From presented diagrams (Fig 2 and Fig. 3) we can state that palladium hydrides are stable in free space without external electric field.

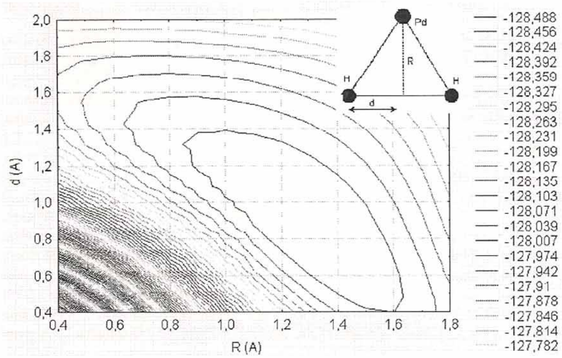

Figure 3. Contour plot of the potential energy surface (PES) of PdH_2

On the other hand it is known that metal hydrides are defined as interstitial compounds in which hydrogen atoms occupy the position inside of the tetra- or octahedral voids.

In this paper our attention is also focused on the description of the interaction of hydrogen atom with the clusters consisting of four- or six palladium atoms that imitate the model of the tetra- and octahedral voids. In both cases 3- fold hollow sites together with a subsurface interstitial position have been considered.

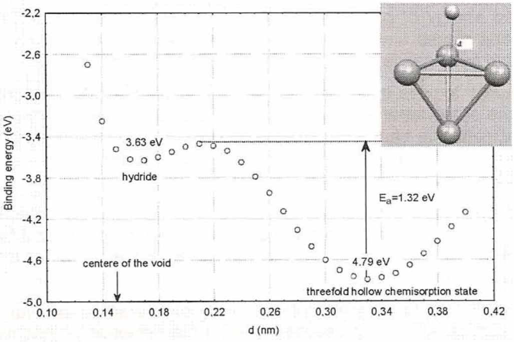

Figure 4. Hydrogen inside of the tetrahedral void

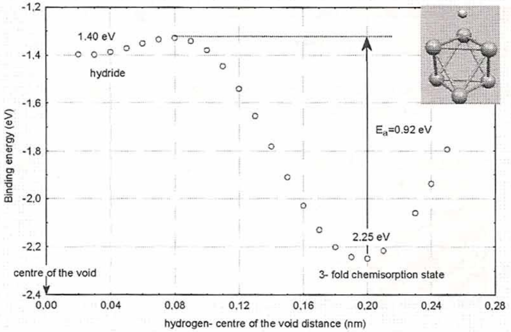

Figure 5. Hydrogen inside of the octahedral void

It is shown in Fig.4 and Fig.5 that the binding energy of hydrogen in threefold hollow site is equal to 4.79 eV in case of the tetrahedral void and 2.25 eV in the second void case. In view of the experimental value of 2.77 eV [6] our results do not seem to be credible. It can be due to a small number of palladium atoms taken into account. Hence, our results should be interpreted only qualitatively.

The diffusion from the surface into the void seems to be an activated process and requires energy of 1.32 eV and 0.92 eV, respectively.

However, the inverse process needs activation energy of 0.16 eV and 0.07 eV.

The binding energy of palladium hydride in the surface between the first and second metal planes amounts to 3.63 eV and 1.40 eV, respectively. It results from this that hydrogen is bound stronger in the tetrahedral void.

It is interesting to note that hydrogen atom is located above the center of the void. In case of the tetrahedral void it is shifted 0.02 nm towards the surface, in the second case the shift is equal to 0.03 nm. This fact can be explained by creating stronger palladium- hydrogen bonds due to existing of unsaturated bonds of the surface layer [15].

In view of theoretical results we can state, that PdH_x^+ ions, detected in the process of field evaporation seem to be the products of field ionization of PdH_x species which are formed in the subsurface sites. However, other explanation can be also probable.

Next we would like to complement our study of interaction of hydrogen with palladium surface with computations including the influence of external electric fields.

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