Investigation of H(2H) - Pt(111) Interaction System: using Density Functional Methods

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Abstract:
In this study, interaction system of hydrogen (two hydrogen) with Pt(111) surface has been investigated theoretically by using density functional theory DFT method. With respect to the definitions of interactions of H-Pt(111) and 2H-Pt(111), the potential energy curves PECs belonging to these interactions have been calculated for four symmetric configurations and two configurations, respectively, which have been considered as top, bridge, fcc-hollow and hcp-hollow sites for H-Pt(111) system and collinear and quasicollinear set for 2H-Pt(111). For this purposes, DFT energy values of H atom (two H atoms) as a function of the height from the Pt(111) surface for all configurations have been calculated by using oniom method with the basis sets of B3LYP/6-311G and B3LYP/LANL2DZ. By taking these calculated energy values into consideration, for H and 2H atoms, adsorption, scattering, and penetration to the sub-surface sites of Pt(111) surface were assessed and analysed in detail. The potential energy surface PES has been also formed and analysed. By considering PES, around the top site and hollow sites have been found as repulsive and attractive behaviours, respectively. Moreover, it is found that hollow sites are suitable for adsorption and penetration to subsurface. Results also show that the potential energy values of hydrogen atom are almost same value under the subsurface for fcc-hollow site.

Key words: *Adsorption, DFT, hydrogen storage, oniom method, platinum surface, potential energy surface*

Introduction

Electronic structure and quasiclassical studies were comprehensively performed to analyze reactions between hydrogen atoms on Ni(100) [1]. In the study, electronic structure calculations based on spin-polarized gradient-corrected density functional theory were carried out to obtain PES for H atom reactions on Ni(100) by using VASP code. After that, PES parameters were fitted by using results of electronic structure calculations to perform the quasiclassical simulations [1]. In addition, by means of PES parameters, studies of kinetic model for reactions of H atoms on Ni(100) surface [2], the effects of lattice motion on reactions of H atoms on Ni(100) [3] and hydrogen recombination on a mixed adsorption layer on Ni(100) [4] were performed by using results of quasiclassical simulations.

To form PES for hydrogen atoms on Cu(111) surface, DFT-GGA energies of H atom (two H atom) interactions with Cu(111) surface were computed in a super cell geometry by using a plane-wave and pseudopotential code DACOPO [5,6]. Then, PES parameters were fitted by using results of DFT-GGA energies to perform quasiclassical simulations of H atoms on Cu(111) surface [5,6,7]. Moreover, new PES parameters were fitted by using the results of DFT-GGA energies [6] for the quasiclassical studies of H atoms reactions on Cu(111) [8]. Besides, molecular dynamics study of surface temperature effects was performed for H(D) → D(H) + Cu(111) collision system by using these parameters [9]. In addition, two PES parameter sets were developed for potential definition for interaction of H (2H) on Cu(111) surface [10]. According to results of these studies, both of hollow sites were found quite considerable for the H atom adsorption over the Cu(111) surface [5-10].

Interactions of atomic hydrogen with Cu(111), Pt(111) and Pd(111) surfaces were studied and total energies values of these interactions were computed in a super cell geometry by using a plane-wave and pseudopotential code DACOPO [11]. In this study, PECs for various configurations of H atoms on Cu(111), Pt(111) and Pd(111) surfaces were formed by using the DFT. One result of this study for Pt(111) surface is that the PEC exhibits strong dependence on the surface lateral position of the H atom at $z \approx 2$ Å and fcc-hollow and hcp-hollow sites were found energetically stable for the H atom adsorption over the surface. It was also seen that very high potential energy barriers of surface were found for the incident H atom around the top site at $z \approx 1$ Å and around the fcc-hollow and hcp-hollow sites $z \approx -1$ Å. Besides, quantum mechanical behavior for H atom on Cu(111) and Pt(111) showed [12] that a three-dimensional adiabatic PES of this interactions was constructed by using PECs calculated within the DFT method [11]. It was concluded that fcc-hollow and hcp-hollow sites were found energetically stable for the H atom adsorption over the surface.

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In addition, Ludwig and Vlachos used the DACAPO code for DFT calculations of energy values belonging to interaction system of H on three symmetric sites of Pt(111) surface [13]. Its result showed that binding energy of hydrogen over the hollow site was calculated as about 2.7 eV at z = 0.976 Å. Furthermore, interactions of atomic and molecular hydrogen with Pt(111) were studied by using DFT within the generalized gradient approximation GGA [14]. In this study, a three layer slab with a 2×2 surface unit cell was used in order to determine the adsorption energy, the adsorption height above the surface and frequency normal to the surface for H adsorbing at different surface sites of Pt(111). In another study, electronic properties of H atom adsorbed on the Pt(111) surface was performed within the DFT method by using the Vienna *ab-initio* Simulation Package VASP [15]. They showed that fcc-hollow site has a local minimum energy at equilibrium height.

In another study, it used Yet Another Extended Huckel Molecular Orbital Package "YAeHMOP" package to carry out quantum calculation of hydrogen adsorption and diffusion on Pt(111) cluster [16]. Moreover, density functional theory calculations of interaction of hydrogen with the {111} surfaces of Pt, Pd and Ni were performed to show an almost uniform adsorption energy by using VASP code [17]. Top, fcc-hollow, hcp-hollow and bridge sites were considered as adsorption sites over the surfaces for these calculations that adsorption energies of hydrogen over Pt(111) surface were almost similar in value with each other at all adsorption sites.

As seen, investigations of interaction hydrogen atom with various metal surfaces, such as Ni [1-4], Cu [5-10] and Pt [11-19], have been performed theoretically in order to describe particular reaction mechanism of hydrogen over the metal surface. Results of these studies have led to technologically important processes, such as catalysis, corrosion effects on metal surfaces and hydrogen storage etc. Density functional theory approach has been extensively used with increasing capacity of computational efforts for performing these interactions at least 20 years. Its results have also played important role on quasiclassical molecular dynamic studies [1-8, 19].

In this study, by using DFT methods, the adsorption, the penetration and scattering sites of H over the Pt(111) surface were determined. Since the binding energy values of H (and 2H) over the fcc-hollow, hcp-hollow and bridge site at 0 Å were calculated as negative energy, these sites could be considered to be directly penetration zones for H on Pt(111). Here PES was also formed to analyze this interaction in detail. Furthermore, our energy calculation model is one of the most accurate models with all valance electrons of the system are considered in the calculation. In the next section, the theoretical model is epitomized, and then the results of the energy calculation are submitted. In the final section, we conclude with a short summary.

Experimental

In this study, potential energy values, calculated for interaction of H on Pt(111) surface for four symmetric sites of surface, were calculated with the density functional theory method using oniom method with basis sets B3LYP/6-311g and B3LYP/LANL2DZ for H atom and Pt(111) surface, respectively. For this purpose, Gaussian 09 Package was used [20]. ONIOM method [21] means "Our own N-layered Integrated molecular Orbital and molecular Mechanics". Thanks to this method, interaction of the Pt(111) surface atoms formed three layers within the bulk and H atom can be computationally performed by using different levels of accuracy basis sets together which are molecular orbital method MO and molecular orbital method MO, namely MO:MO. In addition, potential energy values of interaction of two hydrogen with Pt(111) surface was carried out by using DFT method, mentioned above.

For calculation of potential energy values of interaction system, Pt(111) surface, face- centered-cubic structure fcc(111), consisting of 13 Pt atom was taken as 3 layers fixed in their positions that each layers had 7, 3 and 3 Pt atoms for first, second and third slabs, respectively. Lattice constant was taken as 3.92 Å [22]. The spacing length between two successive layers is 2.263 Å. Spin directions of uncoupled valance electrons of Pt atom were considered as the same direction with each other. Thus, spin multiplicities of H and Pt surface was 2 and 3 because of 1s1 and 5d9 6s1 valance electrons, respectively. Then, spin multiplicity real system was taken as 2. Spin multiplicity is 2S+1 where S is total spins of system or atom.

Results and Discussion

The potential energy curves PECs belonging to these interactions were calculated for four symmetric configurations and two configurations for H atom and two H atoms on Pt(111), respectively, which were considered as top, bridge, fcc-hollow and hcp-hollow sites for H-Pt(111) system and collinear and quasicollinear set for 2H-Pt(111) as shown in Figure 1 (a-c), respectively. For collinear configuration, one of the H atoms was placed and fixed on fcc-hollow binding site over the surface at equilibrium height of about 0.9 Å, while the second H atom, called incident atom, was located over the fcc-hollow site at initial height 7 Å. Incident atom location at initial height of 7 Å was over the bridge site where it was close to the location of the adsorbate atom which was on the same fixed location as collinear for quasicollinear configuration. Afterwards, potential energy values of H atom (two H atoms) as a function of the height from the Pt(111) surface for all configurations were calculated by using oniom method with the basis sets of B3LYP/6-311G and B3LYP/LANL2DZ.

Even though, there is no big difference among adsorption energies of H atom on Pt(111) surface for four symmetric sites at their equilibrium heights, the symmetric sites have an effective role on potential energies of H atom under the surface according to PEC curves as shown in the Figure 2. Besides, the H atom can be adsorbed on the surface with energy range from –2.4 eV to –2.8 eV at equilibrium heights for any lateral position of H atom.

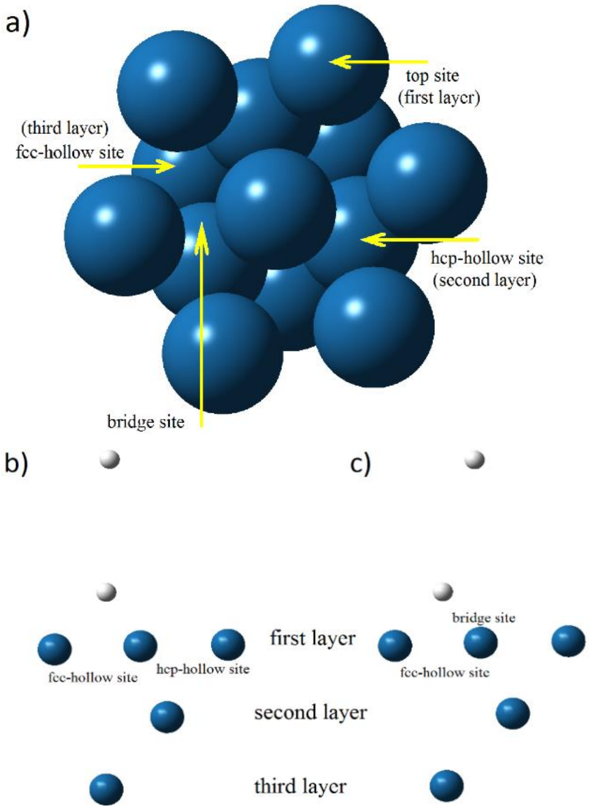

Figure 1. Presentation of a) bird's-eye view of four symmetric sites; top, bridge, fcc and hcp hollow sites on the Pt(111) surface and lateral cross-section of b) collinear and c) quasicollinear configuration of 2H – Pt(111) interaction system.

Even though it is an interesting result that absolute value of binding energy of H over the top site at equilibrium height, calculated as 1.53 Å, was found a little bigger than the others however it can be said that horizontal position dependence is hardly seen at the equilibrium heights as shown in Figure 2. This result is almost compatible with reference 11 and 13.

In addition, reaction mechanisms, such as hot-atom dynamics, penetration to subsurface, adsorption and scattering [8,9], can be forecasted by analyzing in detail the PECs for four symmetric sites. Because of the high potential energy barrier for an incident H atom over top site at about 1.2 Å, penetration to subsurface is not possible from a top site whereas probability of scattering can be high. The potential energy barriers exact over the surface of fcc- and hcp- hollow sites are –1.58 eV and –1.58 eV, respectively, given in Table 1.

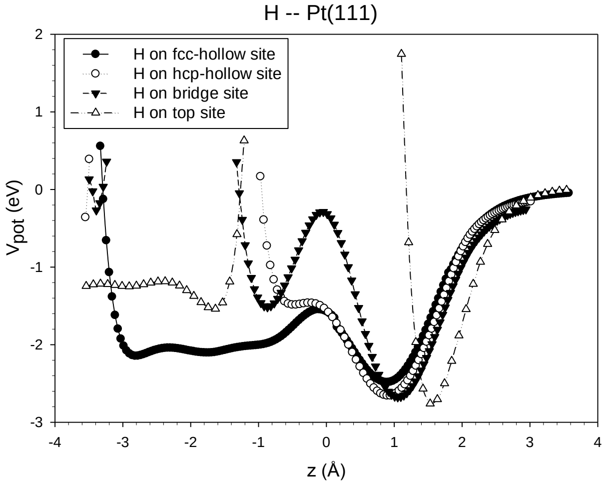

Figure 2. Potential energy curves of H atom on Pt(111) surface for four symmetric sites, which potential energy values were calculated by using DFT method.

Table 1. Some DFT results of interaction of H-Pt(111) system. Binding energies $E_{binding}$ of H atom at equilibrium height Z_{eq} from the surface, Z_{eq} and potential energy values V_{pot} at z = 0 Å for four symmetric sites. ($V_H = E_{H+Pt(111)} - (E_{Pt(111)} - E_H)$)

Site	Z_{eq} (Å)	$E_{binding}$ (eV)	V_H (eV) at Z=0 Å
Fcc-hollow	0.91	–2.49	–1.58
Hcp-hollow	0.90	–2.66	–1.58
Bridge	1.05	–2.68	–0.32
Top	1.53	–2.76	----

This means that H atom can easily penetrate to subsurface from these sites. Thus, a hot atom mechanism or adsorption mechanism can be observed because of the missing kinetic energy of H atom over these sites. It resulted from Figure 2 that bridge site is also convenient of penetration and a hot atom mechanism. But both hollow sites are more appropriate than bridge site for penetration to subsurface, because potential energy values of H atom on bridge, fcc-hollow and hcp-hollow sites are –0.316 eV, –1.58 eV and –1.58 eV at z = 0 Å, respectively. Potential energy barriers of surface depend on the positions of the surface atoms that cause corrugation of the potential energy surface. These results are consistent virtually with [11]. Results of studies of H – Pt(111) interaction [11-17] showed that hollow sites are more suitable to adsorption of H atom over the surface and penetration of H atom to subsurface than others.

Under the subsurface at near the – 1 Å for all symmetric sites exception of fcc-hollow site, H atom encounters with potential energy barriers which comes from Pt atom of second slab. This may affect the scattering back of H atom. Our results show that since H atom can directly penetrate from fcc-hollow sites over the surface to third layer without any obstacle, the curve of potential energy of H atom under the subsurface between heights of –1 Å and –3 Å is almost in a linear behavior and potential energy values were calculated as near the 2 eV as seen in Figure 2. This result also shows that chemisorption of H atom is possible under the surface.

Table 2. DFT results of equilibrium situations of interaction of 2H-Pt(111) system for quasicollinear and collinear configurations.

	Z_1 (Å)*	Z_2 (Å)*	r_{eq} (Å)*	$V_H(r)$ (eV)*
Quasicollinear	0.90	1.39	0.94	–3.48
Collinear 1	0.90	1.81	0.91	–3.05
Collinear 2	1.05	1.92	0.87	–3.35
Collinear 3	2.5	3.30	0.80	–4.76
Collinear 4	3.5	4.25	0.75	–4.81

* Z_1, Z_2 and r_{eq} are heights of H atoms from the surface and equilibrium distance between H atoms, respectively. $V_H(r)$ are hydrogen bonding energy over the surface for two hydrogen at heights of Z_1 and Z_2. ($V_H(r)=E_{2H+Pt(111)} - (E_{Pt(111)} - 2E_H)$)

According to Table II, incident H atom can strongly affect other H atom and then can adsorb over the surface or scatter from the surface as H_2 molecule for quasicollinear configuration due to collinear where one of the H atoms is fixed over the fcc-hollow site at 0.9 Å for both conformations. Incident H atom can approach more closely to the surface for quasicollinear than for collinear, as seen clearly in Figure 3. Moreover, PECs were calculated for different collinear configurations as shown in Figure 4. For this calculation, one of the H atoms was placed and fixed on fcc-hollow binding site over the surface at different heights which are 0.9 Å, 1 Å, 2.5 Å and 3.5 Å when the second H atom, called incident atom, was located over the fcc-hollow site at initial height 7 Å. It is also shown in Figure 4 that minimum binding energy of H atoms over the surface was found stable from height of Z1 = 2.5 Å to up over the surface. These minimum binding energies of 2H are almost compatible with energy of H2 molecule which is calculated as –4.69 eV at 0.75 Å bond lengths by using Gaussian program with the basis set of B3LYP/6–311.

To form a potential energy surface of the interaction system, 135 positions were considered for H atom over the surface at 0.91 Å and single point energy calculations were performed for each positions of H atom. Potential energy surface of H atom on Pt(111) surface can clearly clarify that surface atoms apply attractive potential energy to H atom at a height of 0.91 Å around the hollow sites as shown in Figure 5. At this height, H atom also encounters big potential energy barrier near the locations of Pt atoms as seen in Figure 5. Moreover, it was shown in Figure 2 and Figure 5 that potential energy values of H atom, located on everywhere over the surface exception of around the top site, were calculated as approximately –2.5 eV at 0.91 Å. Corrugation of the PES was clearly seen in Figure 5 that H atom is possible to be trapped over the surface around the hollow sites over the surface.

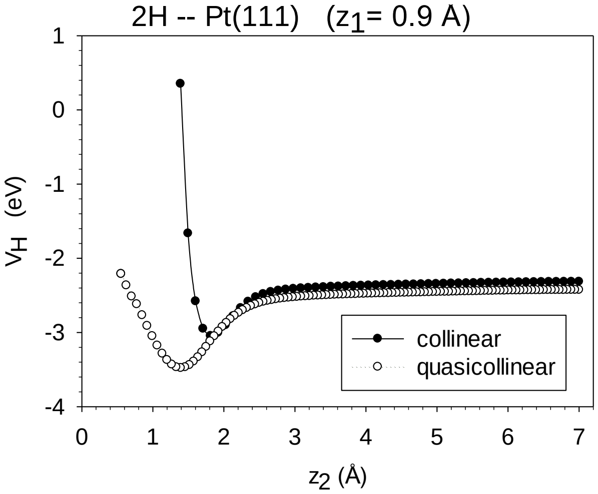

Figure 3. Potential energy curves PECs of collinear and quasicollinear configurations of 2H–Pt(111) interaction system.

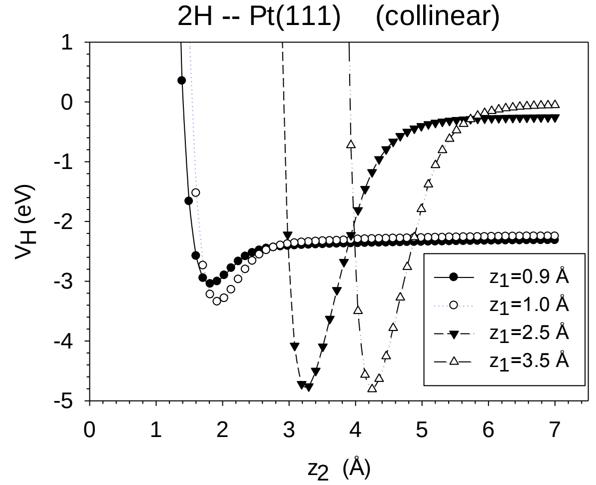

Figure 4. PECs of different collinear configuration of 2H–Pt(111) interaction system for Z1 = 0.9 Å, 1 Å, 2.5 Å and 3.5 Å.

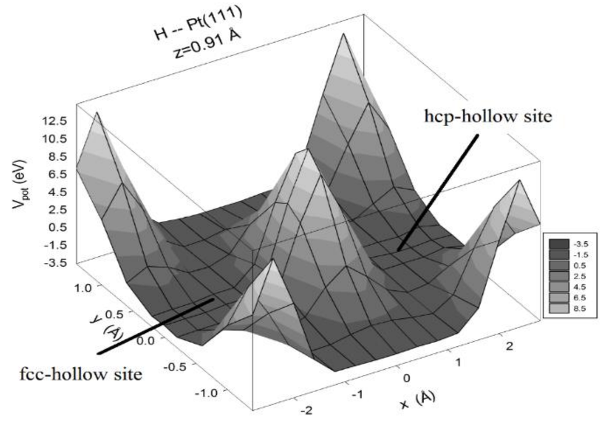

Figure 5. Counter graph of potential energy surface of H on Pt(111) surface at z = 0.91 Å. For this counter graph, 135 energy values were calculated by using DFT method mentioned above.

Conclusions

In accordance with PECs, both hollow sites can be suitable for penetration to subsurface, becoming hot atom, trapping and adsorption over the surface for H atom. Binding energies of H atom are nearly same with each other on Pt(111) surface for four symmetric sites at their equilibrium heights. Hence, the H atom can be adsorbed with approximately same energy on four symmetric sites of lateral positions at their equilibrium heights. Namely, this result shows that lateral position dependence of H atom over the surface is hardly seen for adsorption energy. In addition, the potential energy curves of H atom on the Pt(111) surface have almost the same behavior from height of $z = 1$ Å to up for all symmetric sites with exception of the top site.

Moreover, penetration event cannot be possible from a top site which has the high potential energy barrier at about 1.2 Å, whereas probability of scattering can be high from this site. H atom can easily penetrate to subsurface from hollow sites. Thus, a hot atom or adsorbate atom can be formed because of the loosing kinetic energy of H atom over these sites, appreciation to the existence of attractive potential of these sites. The bridge site is also convenient of penetration and a hot atom occurring.

In keeping with PES for H atom on the surface at 0.91 Å, Pt(111) surface has attractive and reflective behaviors around the hollow sites and top sites, respectively. Channels of penetration to subsurface and adsorption on the surface can be possible at the attractive region of surface whereas scattering channel can occur at reflective region of the surface.

To sum up, bridge, fcc- and hcp- hollow sites are convenient to penetrate to subsurface for H atom as well as adsorption on the surface. Since potential energy values of H atom are nearly the same at all equilibrium heights on the surface, lateral positions of H atom are not important for the adsorption energy at these heights. Moreover, H2 molecule is possible to be formed from the height of $Z1 \approx 2.5$ Å up to the surface after interaction of H with H covered Pt(111) surface.

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