Hydrogen atom absorption in hydrogen-covered Pd(110) (1×2) missing-row surface

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Abstract

The absorption of H atom in H-covered Pd(110) (1×2) missing-row surface is investigated using density functional theory based calculations. For 1.5 monolayer H coverage, interaction among the adsorbed H atoms is found to be negligible and was verified by analyzing the electronic structure of the system and by comparing the calculated binding energies with low H coverage case. Neither the monoatomic absorption of H nor the assistance from the initially adsorbed H atom explains the experimentally observed presence of subsurface H in Pd(110) at high H coverage. Instead, H absorption is realized through the assistance of incoming H atoms from vacuum. The absorption of H in the H-covered surface is non-activated while the dissociation of H₂ is the rate-limiting process. Dissociation on ridge site is energetically more preferred than on trough site and the difference in the activation barrier is elucidated by investigating the electronic structures of the system.

Keywords: Pd(110) (1×2) missing-row surface, Hydrogen absorption, Density functional theory, Hydrogen molecule dissociation

1. Introduction

The interaction of H with metal surfaces is a fundamental process in the field of surface science that is often used as standard to understand the catalytic reactivity of metals and to observe or establish relevant scientific concepts. Studies related to this system are continuously conducted due to the central role of hydrogen in the realization of clean and efficient energy source [1-4]. Specifically, the absorption of H atoms in subsurface and bulk regions is an important process in hydrogen storage, hydrogen purification and hydrogenation / dehydrogenation applications [5-9]. These phenomena are manifestations on the importance of elucidating the absorption of hydrogen to develop sustainable hydrogen-based economy.

Pd is among the popular metals for hydrogen-related applications because it is capable to absorb large volume of H [10]. Hydrogen absorption is the crucial process for the formation of Pd hydride due to the high activation barrier that accompanies the absorption of chemisorbed hydrogen atom to the subsurface region [11,12]. While the absorption of H (for low and high coverages) in (111) and (100) facets of Pd are already investigated theoretically [13-16], the (110) system receives less attention. It is interesting to note, nonetheless, that Pd(110) surface reconstructs when dosed by H atoms. At low temperature and for H coverage greater than 1 ML (monolayer), the repulsion of adsorbed H atoms leads to the formation of (1×2) pairing-row reconstructed surface [17-19]. Increasing either the temperature or the amount of H results to (1×2) missing-row structure and is attributed to the migration of Pd atoms to other surface sites [20]. In fact, even small amount of H exposed on Pd(110) at room temperature can induce missing-row reconstruction [21,22]. The pairing-row structure, therefore, is a metastable state [20,23] and during actual operating condition for certain application, the missing-row structure is dominant for H/Pd(110).

Previous theoretical works have focused on the geometric and electronic structures of adsorbed H atoms on Pd(110) [24-26]. Notably, it was experimentally reported that at low temperature, absorption of H in the subsurface region of Pd(110) only happens at high H coverage and when the surface is already reconstructed [18,19]. The (1×2) missing-row structure also represents the edge sites of the most stable (111) facet and could therefore provide useful information for the catalytic performance of Pd surface in general. Based on these, it is necessary to address theoretically the interaction of H in this surface to unravel its properties and to explain the underlying mechanism of the absorption.

By employing density functional theory investigation, this present study deals with the absorption of H atom in Pd(110) (1×2) missing-row surface with H coverage of 1.5 ML. Previous study demonstrated that at 1.5 ML coverage, the missing-row reconstructed surface is energetically more stable than the pairing-row reconstructed surface [26]. In this work, it was identified that adsorbed H atoms can either sit on ridge and trough sites of the missing-row surface. Neither the monoatomic absorption of H nor the assisted absorption of trough-H via the diffusion of ridge-H toward it is energetically favored. Absorption occurs through the assistance of other H atoms from vacuum that approach the initially adsorbed H atoms or through the direct absorption of H from dissociating H₂ molecule.

2. Computational Details

All the calculations were performed using Vienna Ab Initio Simulation Package (VASP) [27,28]. The exchange-correlation effects were treated within the generalized gradient approximation (GGA), in which the Perdew – Burke – Ernzerhof (PBE) exchange-correlation functional was employed [29]. The ionic cores were described by the projector augmented wave (PAW) method [30] and the Kohn-Sham one-electron valence states were expanded in a basis of plane waves with energy cutoff of 400 eV. The calculated equilibrium

lattice constant for bulk Pd is 3.94 Å which is in good agreement with previous computational and experimental studies [14,31].

The Pd(110) (1×2) missing-row surface was modeled by using six atomic layers, with four atoms in each layer except for the topmost layer. A vacuum layer of ~15 Å was introduced and the clean surface was initially optimized by allowing its three topmost layers to relax while keeping the remaining layers fixed in their bulk Pd parameters. Brillouin zone integration was performed on a grid of 4×6×1 Monkhorst – Pack k-points [32] and the accuracy is verified by doing energy convergence test. Similarly, the energetically stable structures of H-surface systems were identified by optimization process. The methods of Methfessel-Paxton [33] and tetrahedron with Blöchl corrections [34] were used as smearing methods for calculations that involved relaxations and for total energy calculations, respectively, with smearing width of 0.2 eV.

The transition states were determined by using climbing image – nudged elastic band (CI-NEB) method [35]. Four intermediate images were assigned to determine the transition state between the initial and final states of a particular reaction. Also, the three topmost layers and the H atoms were allowed to move during the CI-NEB calculations until the forces on the unconstrained atoms are less than 0.03 eV/Å. Vibrational frequency calculations were conducted to prove the true origin of the transition states and to justify the obtained energetically minimum structures.

3. Results and Discussion

The configuration for 1.5 ML of H on Pd(110) (1×2) missing-row surface is shown in Fig. 1. Different configurations were considered and the showed structure is the most stable for 1.5 ML of H case. On the surface, two distinct adsorption sites are recognized: the ridge site with four H atoms (dashed box) and the trough site with two adsorbed H (solid box). For

both cases, the stable positions of H correspond to the fcc threefold site of the (111) surface facet. With reference to total energies of H₂ in the gas phase and of the clean surface, the ridge- and trough- H atoms are energetically stable with binding energies of 0.55 eV and 0.44 eV, respectively. The calculated binding energies are in good agreement with results of previous experimental work [36]. A difference in reactivity between the adsorption sites can clearly be depicted based on these values. Pd atoms on ridge site have lower coordination than the Pd atoms on the trough site; thus, the less saturated ridge-Pd atoms can efficiently form chemical bond with adsorbate. Binding energies at low coverage system (0.25 ML) were also calculated to identify the variation of the adsorption characteristic of H in terms of the coverage. For this case, the binding energy of H on ridge site is 0.56 eV while it is 0.47 eV on trough site, which are comparable with the binding energies on the same sites at high coverage. It can be concluded that at this particular coverage, there is negligible H – H interaction in the missing-row surface and is attributed to the effective screening provided by the surface Pd atoms. These results are completely supported by the electronic structures of H/Pd(110) (1×2) missing-row system. The charge density difference distribution for 1.5 ML of H is shown in Fig. 2(a). Neither the removal of H atom in the ridge (Fig. 2(b)) nor trough (Fig. 2(c)) significantly changes the charge distribution. It confirms the negligible H-H interaction and effective screening of the Pd atoms leading to the comparable binding energies of H for low and high coverages.

Monoatomic absorption of H is initially studied and the reaction paths are shown in Fig. 3. For these cases, a H atom initially sitting on ridge or trough moves to the octahedral site of the next subsurface layer. The calculated activation energies for H absorption from ridge and trough sites are 0.54 and 0.37 eV, respectively. This implicates the necessity of high energy to compensate the strong interaction of H with the surface atoms. It should be noted that the barrier for the absorption of H atom (0.25 ML) from the surface to the next

subsurface layer of unreconstructed Pd(110) is $\sim 0.30 - 0.40$ eV [10,11] which is relatively lower than the measured value for the missing-row surface. This contradicts experimental findings that H atoms populate the subsurface region of Pd(110) only for coverage greater than 1 ML [18,19]. Based on these, it is conclusive that monoatomic H absorption is not the appropriate process to explain the presence of subsurface H in Pd(110) surface.

It is also presumable that absorption of H will proceed through the assistance of other adsorbed H atoms in the missing-row surface. From the geometric structure, ridge-H is in a higher position than the trough-H with reference to surface normal. In this regard, it is a possibility that the absorption of trough-H to the subsurface may result to lower activation energy when ridge-H simultaneously diffuses to the initial position of the former. The reaction path for this is also shown in Fig. 3. A larger activation barrier (0.65 eV), however, was obtained compared to the monoatomic absorption from trough site. The geometric structures further suggest that the ridge-H atom only diffuses to the trough site once the trough-H atom is already in the subsurface region (marked as B and C in Fig. 3). Additionally, the energetics and geometric structure of the transition state of the monoatomic absorption from trough is completely similar at some point in the reaction path (marked as B in Fig. 3) of the combined diffusion and absorption configuration. This behavior proposes that simultaneous diffusion of ridge-H and absorption of trough-H is not possible. It can be inferred that this process induces repulsion between the H atoms and therefore, sequential process is more preferred in order to minimize the energy path of the defined reaction. To further clarify this finding, the diffusion of ridge-H to an empty trough site (1.25 ML of H) was examined and the calculated barrier is 0.30 eV. The activation barriers exhibit additive property: the sum of activation barriers for ridge-H diffusion at 1.25 ML and monoatomic absorption of trough-H is comparable to the activation barrier of combined ridge-H diffusion and trough-H absorption configuration. The additive characteristic of the activation barriers

further supports the sequential process mentioned above; otherwise, a discrepancy in the energy value should be obtained from the sum if the ridge-H assists the absorption of trough-H.

Given these results, it was hypothesized that adsorbing H from vacuum may be involved in the absorption of initially adsorbed H atoms. In this regard, a model with an extra H atom from vacuum (1.75 ML of H) that approaches a ridge- or trough- H atom was studied where the latter moves to the subsurface site. Remarkably, both processes are found to be non-activated and thus, facile absorption of H occurs through the presence of adsorbing H atoms from vacuum. The investigation is followed by dissociation of H₂ on H-empty ridge and trough sites (corresponding to 1.75 ML of H) to resemble a more realistic scenario. It was previously reported that on a H-covered Pd surface, a single H-vacancy is sufficient to dissociate H₂ [37]. Figure 4 illustrates the reaction paths for the dissociation of H₂ and the subsequent absorption of one H (from the dissociated H₂) to the next subsurface layer. Notably, the transition states for both cases are observed to occur during the dissociation process and not during the absorption. This is in contrast with the case of low H coverage in which the absorption is the rate-limiting step and H₂ dissociation normally proceeds as a non-activated process [38,39]. Pre-adsorbed H atoms clearly modify the reactivity of the surface resulting to the occurrence of energetically different reactions for low and high H concentrations. H₂ dissociation on the ridge site exhibits a precursor state prior to dissociation and the reaction is only accompanied by 0.06 eV activation barrier. On the other hand, the reaction on the trough site experiences larger activation barrier, 0.28 eV. Once the H₂ is already dissociated, assisted absorption of H atom happens (as shown from the geometric configurations in Fig. 4) and the process occurs without any activation barrier. We therefore conclude that the absorption of H in the missing-row surface will only happen through the assistance of vacuum-H.

The difference in the activation barriers for ridge and trough sites is elucidated from the different environments that H₂ encounters as it approaches the surface. Although H atoms are initially present on the ridge site, the H-vacant three-fold site is still capable to accommodate the incoming molecule. The initially adsorbed H atoms are completely screened by the Pd atoms and do not affect the approaching H₂. Dissociation on ridge site in a perpendicular orientation (relative to the surface plane) is hence more preferred rather than the parallel orientation which is favored for clean and low coverage Pd surfaces [39,40]. To explain the difference in the activation energies obtained for the dissociation of H₂ on ridge and trough sites, the local density of states (LDOS) of the σ orbital of H₂ and the d orbital of the closest Pd atom at transition state are analyzed and is illustrated in Fig. 5. The interaction of H₂ with the substrate is characterized by the overlap of the states of H₂ and metal atoms and by the formation of derived states. For both cases, the derived anti-bonding state when H₂ interacts with the surface are traced and marked by arrows. The anti-bonding characteristic was verified by plotting the charge density distribution projected on the states (as shown in the insets) defined by the arrows. The position of this derived state with respect to the Fermi level can explain the difference in the H₂ dissociation barrier [41,42]. The σ orbital experiences repulsion with respect to the derived states in the metal as H₂ approaches the substrate. The filled anti-bonding state (below the Fermi level) at the transition state for the case of H₂ on trough site leads to higher dissociation barrier due to the induced repulsion by the electrons with the surface. On the other hand, the anti-bonding state of H₂ on ridge site is located above the Fermi level yielding a very low dissociation barrier.

The findings of this study open the challenge to experimentally confirm the two possible dissociation/ absorption channels through the ridge and trough sites of the missing-row surface. Consequently, the catalytic performance of the missing-row surface can be anticipated to vary depending on the involved surface site and the different behaviors of

adsorbed H atoms can be further exploited for the purpose of selective catalytic reactions (for instance, hydrogenation or dehydrogenation reactions).

4. Conclusion

By implementing density functional theory investigation, the absorption of H atom in H-covered Pd(110) (1×2) missing-row surface was studied. The absorption of initially adsorbed H atoms is entirely assisted by the dissociated H₂ molecule from the vacuum region. Monoatomic H absorption or absorption through the assistance of initially adsorbed H atoms is not energetically favored. H₂ dissociation is preferred to occur on H-vacant ridge site than on trough site where the dissociation is only slightly activated (0.06 eV). The difference in the dissociation barrier is clarified by tracing the position of the derived anti-bonding state of the H₂-surface system in the transition states. Nonetheless, for both cases, the dissociation process is the rate-limiting step and H absorption is a non-activated process.

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Figure Captions

Fig. 1. (a) Top view and (b) side view of Pd(110) (1×2) missing-row surface with 1.5 ML of H. Adsorbed H atoms on ridge (trough) site are enclosed by dashed (solid) box. Pd and H atoms are represented by large and small spheres, respectively.

Fig. 2. Charge density difference distribution of (a) 1.5 ML of H – Pd(110) (1×2) missing-row surface. Removing H atom in (b) ridge or (c) trough site does not significantly modify the charge distribution indicating the negligible H-H interaction on the missing-row surface. Blue and red regions signify gain and loss of charge, respectively. Hydrogen atoms on ridge (trough) site are enclosed by dashed (solid) box. Pd and H atoms are represented by large and small spheres, respectively. Isosurface levels were set at $0.006 a_0^{-3}$.

Fig. 3. Reaction path of monoatomic hydrogen absorption from ridge (◆), from trough (■) and through a combined process where trough-H absorbs to the subsurface while ridge-H diffuses to the initial position of the former (▲). Monoatomic absorption is accompanied by large activation barrier while in the combined process; ridge-H will only diffuse once the trough-H is already absorbed in the subsurface. Pd and H atoms are represented by large and small spheres, respectively.

Fig. 4. Reaction path of H₂ dissociation on H-vacant ridge (◆) and trough (■) sites with subsequent absorption of H from the dissociated molecule. The transition states occur during the dissociation process for both cases. The absorption of H atom happens through the assistance of other H atom. Dissociation on ridge site has lower activation barrier and hence, is energetically preferred.

Fig. 5. The local density of states (LDOS) of the σ orbital (dotted line) of H₂ and d orbital (solid line) of its closest Pd atom. The LDOS profiles correspond to the configuration at transition state for H₂ dissociating on (a) ridge and (b) trough sites. The arrows mark the derived anti-bonding states that explain the difference in the H₂ dissociation barrier. The insets correspond to the charge density distributions projected on the energy states marked by arrows indicating the anti-bonding characteristic of the state.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5