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Understanding the mechanism of H atom absorption in the Pd(110) surface

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A B S T R A C T

The underlying mechanism of H atom absorption in the Pd(110) (1 × 2) missing-row reconstructed surface is investigated by performing density functional theory based calculations. The stronger binding energy of H on ridge than on trough site of the missing-row surface is due to the more pronounced creation of derived bonding state as had been depicted from the electronic structure of the system. Hydrogen absorption takes place with the involvement of other incoming H atoms through an assisted absorption process that is facilitated by the repulsion between the incoming H and the absorbing H. The geometry of the missing-row surface enables the Pd atoms to accommodate the H atoms efficiently leading to H absorption as well as H_2 dissociation.

1. Introduction

The interaction of hydrogen with materials has been widely studied for years [1–5]. It finds importance in probing various surface processes and reactivity trends among catalysts leading to the creation of factors that functionalize materials for various applications. Moreover, studies related to this system are continuously conducted due to the central role of hydrogen in the realization of clean and efficient energy source [6,7]. Massive production of fuel cell systems however is still hindered by the expensive materials employed in power generation and of the crucial problem in storing hydrogen [8].

Hydrogen storage is principally governed by the absorption of hydrogen atoms from the surface to the bulk system. This process is likewise essential in hydrogen purification [9,10] and hydrogenation/dehydrogenation applications [11,12]. Metals are often utilized for this purpose due to their suitability in forming metal hydrides under moderate temperature and pressure conditions that give them safety advantage [13]. Pd and Pd-based metals on the other hand are among the most popular due to their capability of absorbing a large amount of H [14]. Aside from this, Pd exhibits good reactivity toward H. For instance, the dissociation of H_2 on Pd surfaces is accompanied by a negligible activation barrier [15,16] implying the convenience of introducing H_2 under ambient conditions.

Among the low surface indexed of Pd, the (110) being the least stable and having the most open structure has been observed to undergo reconstruction in the presence of adsorbate. When H is introduced on the surface, pairing-row and missing-row reconstructed structures have been identified to occur. It was clarified however that in the presence of H, the missing-row structure is energetically preferred and that the pairing-row structure is a metastable [17,18]. It is conclusive therefore, that the missing-row dominates the H–Pd(110) system. Furthermore, it is experimentally found that the absorption of H in the Pd(110) surface takes place when there is large coverage of H on the surface and when the surface has already reconstructed [19–21].

In our previous study, we concluded that the absorption of H in the H-covered missing-row surface involves the assistance of another H atom [22]. This present work, on the other hand, elucidates the mechanism to understand the absorption of H atom in the Pd(110) in the atomic scale by employing density functional theory based calculations. In particular, the electronic structures of adsorbed H atoms on the surface as well as of the assisted H absorption are analyzed. The density of states profiles provide explanation on the stability of the adsorbed H atoms on the missing-row Pd(110) surface. The charge density difference distribution is used to clarify that the assisted absorption is facilitated by the repulsion between an approaching H atom and of an initially adsorbed H atom. Further insights that can help in

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the understanding of the interaction of H with Pd(1 1 0) in general are also provided.

2. Computational details

Density functional theory based calculations are performed using the Vienna Ab Initio Simulation Package (VASP) [23,24]. Generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is used to treat the exchange–correlation effects [25]. The projector augmented wave (PAW) method [26] is utilized to describe the ionic cores and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with an energy cutoff of 400 eV. The obtained equilibrium lattice constant of bulk Pd system is 3.94 Å which is in good agreement with results from previous works [27,28].

The modeled Pd(1 1 0) surface consists of six atomic layers with four atoms in each layer. One column of Pd atom in the topmost layer is removed to create the (1 × 2) missing-row surface. A vacuum layer of ~15 Å is introduced perpendicular to the surface in order to avoid the interaction of the slabs when repeated periodically. Before introducing H atoms in the system, the clean surface is optimized to take into account the presence of vacuum. In this regard, three topmost layers of Pd atoms are allowed to relax while the bottom layers are kept fixed in their bulk parameter structure. Brillouin zone integration is performed on a grid of 4 × 6 × 1 Monkhorst–Pack *k*-points [29] and the accuracy is verified by doing energy convergence tests. The energetically stable structures of H–surface systems are also identified by optimization process. The methods of Methfessel and Paxton [30] and tetrahedron with Blöchl corrections [31] are used as smearing methods for calculations that involved relaxations and for total energy calculations, respectively, with a smearing width of 0.2 eV.

Climbing image – nudged elastic band (CI–NEB) method [32] is carried out to determine the transition states and activation barriers. Four intermediate images are 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 are allowed to move in CI–NEB calculations until the forces on the unconstrained atoms are less than 0.03 eV/Å. The obtained transition states are further verified to be the true transition states by performing vibrational frequency calculations.

3. Results and discussion

The H-covered Pd(1 1 0) surface is modeled with 1.5 ML of H on the Pd(1 1 0) (1 × 2) missing-row surface. Initially, the stability of adsorbed H atoms is examined given the possibility of having pairing-row and missing-row structures. For a H coverage of 1.5 ML, the missing-row reconstructed surface is energetically more stable (determined by getting the average H binding energy) than the pairing-row reconstructed surface by ~0.070 eV and is agreeing with the result of a previous work [18]. The configuration for 1.5 ML of H on the Pd(1 1 0) (1 × 2) missing-row surface is shown in Fig. 1(a) and this structural geometry is the most stable among the different possible configurations that are considered. On the surface, two distinct adsorption sites are recognized: the ridge site with four H atoms and the trough site with two H atoms. Take note that for both cases, the stable positions of H correspond to the fcc hollow site of the (1 1 1) microfacet which exists in the (1 1 0) missing-row surface.

With reference to the total energies of H_2 in gas phase and of the clean surface, the ridge- and trough-H atoms are energetically stable with binding energies of 0.55 and 0.44 eV, respectively, as had been reported earlier [22]. These values indicate the different reactivity of ridge and trough Pd atoms toward H adsorbates. It is evident that such characteristic is due to the lower coordination of ridge-Pd atoms than that of trough-Pd atoms which enables the former to efficiently form chemical bonds. This is further verified by analyzing the electronic structure of the system, in which, the local density of states (LDOS) projected on the *s* orbital of ridge-H and trough-H atoms are shown in Fig. 1(b). Charge density distributions (insets) projected on the bonding states of both cases indeed illustrate the more pronounced establishment of derived bonding orbital between ridge-H and Pd atoms than between trough-H and Pd atoms. This characteristic of the electronic structure confirms the stronger binding energy of H on ridge than on trough site.

The lesser saturated ridge-Pd atoms also justifies the calculated stronger binding energy in comparison to the pseudo-threefold site of unreconstructed Pd(1 1 0) and even with the reported binding energy of H on fcc site (~0.50 eV) of Pd(1 1 1) [27,33]. Notably, the adsorption site of H on the missing-row surface is the fcc hollow site which rationalizes the obtained configuration presented in Fig. 1(a). That is, in order to minimize the energy, the H atoms should first occupy the most stable fcc sites on the ridge before filling the fcc sites on the trough.

In our previous work [22], absorption is studied by looking on the possibility of direct H atom absorption (Fig. 2(a)) and by a combined process of ridge-H diffusion and trough-H absorption (Fig. 2(b)). The absorption of adsorbed H from ridge and trough sites, however, are accompanied by large activation barriers: 0.54 and 0.37 eV, respectively. The comparable values of barriers and of binding energies depict the necessity for the H atom to overcome the surface binding energy in order to move to the subsurface. Large activation barrier (0.65 eV) also accompanied the combined process (ridge-H diffusion and trough-H absorption) and is due to the preference of the H atoms to perform the process in a sequential manner than in a simultaneous way. Given these calculated large barriers, it was concluded that these absorption mechanisms are not appropriate to explain the presence of H in the subsurface. Otherwise, H will be able to move to subsurface even at a low coverage since the absorption barrier for 0.25 ML of H in unreconstructed Pd(1 1 0) is just about 0.30–0.40 eV [34,35]. Nonetheless, this was not observed in experiments [19,20].

The involvement of another H atom (Fig. 2(c)) was reported to be the appropriate explanation for the absorption mechanism [22]. Non-activated reaction paths were obtained for both ridge and trough cases. This means that there is this drop in the energetics for this process in which an incoming H atom takes the position of the initially adsorbed H while the latter absorbs in the subsurface site. This characteristic of reaction path is understood due to the energetically unstable incoming H atom that seeks stability when it reaches the surface. It is interesting to note however that in such case, the intermediate geometries show an assisted absorption mechanism (Fig. 3). The non-activated absorption that involves another H can likewise be interpreted in such a way that it exists through this assisted process.

To clearly establish the origin of the assisted absorption, the charge density difference distribution projected on the approaching H and absorbing H from either ridge or trough site is analyzed and is shown in Fig. 3. The structures correspond to the intermediate geometries for the reaction path. Yellow and blue regions signify electron-rich and electron-depleted regions in which the involved H atoms gain charge from Pd atoms. Since both of the H atoms gain charge from the surface atoms, it can be concluded that repulsion between them exists. Thus, it is inferred based on this that the assisted absorption as illustrated from the structural geometries is facilitated by the repulsion between the H atoms.

Fig. 3 also shows that the geometry of the missing-row surface enables the Pd atoms to accommodate the H atoms efficiently. The charge density profile illustrates that different Pd atoms interact