

Ab-Initio Study of Hydrogen Adsorption and Evolution on Pt(100) Surface

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Abstract

Hydrogen evolution on catalytic surfaces of platinum is of paramount importance in the production and storage of hydrogen-fueled power systems. Here, the potential energy surface for hydrogen on Pt(100) is calculated using density functional theory. The bridge site is distinctly identified as the preferred site on Pt(100) surface. This is in contrast to the potential energy surface of hydrogen on Pt(111), which is almost flat and anharmonic. The hollow adsorbed hydrogen is found to be the least stable site. The interaction of an adsorbed hydrogen at a bridge site on Pt(100) surface with a second adsorbed hydrogen is also considered. Site-to-site interaction energetics of two adsorbed hydrogen atoms prefer two neighboring bridge sites. This suggests a certain pathway for the formation and evolution of molecular hydrogen from the Pt(100) surface.

Keywords: DFT calculations, catalysts, surface sites, hydrogen evolution, diffusion rates, adsorbate interaction

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I. INTRODUCTION

In recent years, hydrogen has emerged as a potential substitute for fossil fuels in transforming conventional energy systems to cleaner, more efficient, and cost-effective power sources. Assuming ideal conditions for the adoption of its technologies, hydrogen is estimated to be the major energy carrier, taking about 49 percent of the global energy consumption by the end of the 21st century [1]. Hydrogen can be produced from a variety of processes, such as gas steam reforming, coal and biomass gasification [2, 3], and solar thermal methods. It can be stored and transported as a fuel with high energy density using catalysts with improved selectivity [4]. Development of highly effective and selective catalysts is an active research area, for which understanding transition state chemistry is crucial [5].

Among the current catalysts for hydrogen evolution reaction (HER), platinum shows the greatest selectivity. The reason is that HER occurs mostly thermo-neutral on Pt surfaces at all coverage, unlike being largely either exothermic or endothermic on other transition metals [6]. Interestingly, different surface structures of Pt exhibit different catalytic activity depending on their atomic scale morphology [7–10]. Marković *et al.* [11] experimentally determined an activation energy of 12 kJ/mol for HER mechanism on Pt(100), which is 6 kJ/mol lower than on Pt(111), both in 0.05 M H₂SO₄ acidic environment. In 0.1 M KOH alkaline solution, an exchange current density of 0.5 mA/cm² is reported for HER on Pt(100), which is one order of magnitude larger than on Pt(111) [12]. In contrast, Barber *et al.* [13] reported a reversed order of activity based on EIS measurements. The disagreement between measured activities was later attributed to the strong effect of HER on the temperature of the electrolyte [14]. Zhang and Anderson [15] studied potential-dependent activation energies for the electron transfer steps of hydrogen evolution and oxidation reactions in base. However, the activation energies at the reversible potential are reportedly lower than the experimental values on Pt(111) and Pt(110) [14]. The difference is attributed to the complexities caused by the surface coverage of H_(ads).

To rationalize the differences in catalytic activity with crystal face, Marković *et al.* [10, 12] postulated that on Pt(100) surface, the atop sites are blocked by strongly adsorbed hydrogen, H_(upd). They suggest that H_(upd) has to move to a subsurface state to recombine with the weakly adsorbed hydrogen, H_(opd). Following this pathway, Skulason *et al.* [16] computed an activation energy of 0.55 eV for the Tafel step ($2\text{H}_{(\text{ads})} \rightarrow \text{H}_2$) with one adsorbed

hydrogen on atop site and the other on an fcc hollow site on Pt(111) surface. Although these site preferences are consistent with quantum calculations for hydrogen on Pt(111) surface, they have not been shown on Pt(100) surface. Computational efforts, thus far, have focused on studying the adsorption of hydrogen on Pt(111)[17, 18]. It was found that the potential energy surface (PES) of hydrogen on Pt(111) is flat and anharmonic with very minor differences between the various possible adsorption sites. Ab-initio calculations have been used to identify the energetics and site preference of hydrogen on Pt clusters [19] and on the single crystal surfaces of Pt(211) [20] and Pt(111) [21, 22]. However, no such detailed calculations have been reported for hydrogen on Pt(100) surface.

In this paper, we will first describe the results from the calculations for the PES of hydrogen on Pt(100) surface using DFT within GGA approximation. The adsorption energetics demonstrate a distinct site preference. Furthermore, the interaction of two adsorbed hydrogen atoms is also studied to understand hydrogen-recombination and dissociation reactions. The site-to-site diffusion rates are calculated and used in discussing the suggested pathway for HER on Pt(100) surface.

II. COMPUTATIONAL METHOD

All calculations were performed using DFT within the generalized gradient approximation (GGA) [23] as implemented in the Vienna ab initio simulation package (VASP) [24–26]. The pseudopotentials were of the PAW type [27] with the sampling k-points generated by the Monkhorst and Pack scheme [28]. A bulk lattice constant of 3.983 Å was used to determine the initial position of Pt atoms. This value of the lattice constant is larger than the experimental value of 3.92 Å [29], but less than, or very close to, the corresponding value obtained by other theoretical methods such as HF(4.04 Å), BLYP(4.06 Å) and PBW91(3.99 Å) [30]. The Kohn-Sham equations were solved using a plane-wave basis set with a cutoff energy of 230.3 eV and 10 valence electrons for Pt atoms.

The effect of the number of platinum layers on the computational results was investigated by calculating energies of several Pt slabs having 1, 3, 5, 7, and 9 layers. In each case, the middle layer was fixed, while the other layers were allowed to relax during geometry optimization. The surface energy of the slab defined by [31]

$$E_{\text{surf}} = \frac{E_{\text{slab}}^n - nE_{\text{bulk}}}{2A}, \tag{1}$$

was used as the convergence criterion to determine the required number of Pt-layers. In equation (1), E_{slab}^n is the total energy of the n layer surface slab with area A , and E_{bulk} is the bulk energy. The maximum inward calculated relaxation distance was less than 3 % of the bulk planar spacing, which has also been predicted by semi-empirical calculations using the Equivalent-Crystal Theory (ECT) [32], and the Embedded-Atom method [33]. Using ECT, Rodriguez *et al.* [32] calculated the Pt(111) surface energy to be 0.107 eV, whereas the surface energies for (100), (110), and most high-index surfaces range from 0.124, which is close to the corresponding value found in this study, to 0.168 eV [30]. In our calculations, E_{surf} for $n \geq 5$ varied by less than 0.001 eV, that is less than 1 %. Hence, we used a 5-layer slab for all calculations on Pt(100) surface. For the calculation of the potential energy surface of hydrogen on Pt(100), a 2×2 unit cell is used. The structure of the Pt(100) surface was represented by a slab, with the vacuum region being six layers thick, thereby reducing the interaction of a supercell with its upper and lower images. Each layer consists of four Pt atoms with the supercell containing a single H as the adatom. This configuration corresponds to a surface coverage of 0.25. The k-point sampling was performed on a $6 \times 6 \times 1$ grid with a cutoff energy of 450 eV. For the interaction of two hydrogen atoms, the surface of the unit cell was composed of nine Pt atoms arranged as a 3×3 array.

III. RESULTS

A. Potential Energy Surface of $\mathbf{H}_{(\text{ads})}$

Fifteen single point energy calculations were performed to set up the potential energy surface (PES) of hydrogen on Pt(100). The results are shown in Figure 1, where the x and y coordinates are distances normalized with the Pt-Pt distance. Figure 2 demonstrates how the energy of the system in the ground state changes as the hydrogen atom moves along the path from hollow to bridge, atop, and back to hollow. The first and the last points on the curve are at the same position. Points $d = 1$ and $d = 2$ represent the bridge and atop positions, respectively. The horizontal axis has been normalized to the hollow-bridge distance. The adsorption energies for the atop and bridge sites are 40.5 and 59.8 kJ/mol, respectively, in good agreement with the microcalorimetric experimental value of 45 kJ/mol for hydrogen adsorption on Pt powders [34]. These values show that the bridge position is

more favorable than the atop and hollow positions. The adsorption on an atop site is more stable than a four-fold coordinated hollow site. These results and the corresponding bond length and H-surface distances are summarized in Table I.

B. Surface diffusion of $\text{H}_{(\text{ads})}$

Based on the presented PES, the transition states for surface diffusion are calculated next. By studying the PES, three different paths are identified for the diffusion process:

- bridge-to-atop: from a bridge site to an atop site
- atop-to-bridge: from an atop site to a bridge site
- bridge-to-bridge: from a bridge site to the nearest bridge site, from (0,0) to (0.5,0.5)

Although a complete quantum mechanical treatment is generally necessary for the diffusion of small adsorbates to obtain accurate rate parameters [35, 36], here we only apply quantum energies to compute the diffusion rates using classical rate theories. The energy barrier ΔE_{diff} is obtained by subtracting the total energy of the system at the initial state from the energy value at the transition state. The pre-exponential factors are computed using the curvature of the total energy of the system at the reactant state. Table II gives the computed rate parameters for the diffusion of hydrogen on Pt(100). Zhdanov and Kasemo [37] estimate the energy barrier of hydrogen diffusion to be about 250 meV or less, which agrees well with the values computed here. The pre-exponential factors are also comparable to the values used by Försth [38]. The results show that the slowest diffusion step is from bridge to bridge. The diffusion from bridge to atop is about ten times faster than bridge-to-bridge, and about three orders of magnitude slower than the reverse step atop-to-bridge. It can also be obtained from Table II that the differences between the diffusion rates mainly stem from the differences in activation barriers rather than from the pre-exponential factors.

C. Interaction of Two $\text{H}_{(\text{ads})}$

In the previous section, the bridge position was identified as the most stable site. Therefore, one hydrogen is now fixed at a bridge site, and the position of a second hydrogen atom

on the surface is used as a parameter. As Figure 3 shows, 11 positions are considered: 2 hollow, 5 bridge, and 4 atop sites.

The change in the total energy of the system, shown in Table III, determines how the two hydrogen atoms interact with each other. To better understand the implications of the numerical values, the energy differences are graphically shown in Figure 4. The height of the bars represents the energy difference of the system for each case with respect to the minimum observed energy, which is -271.46 eV for the second hydrogen on the next neighboring bridge site at (0,1). The fixed hydrogen atom is at (0,0), while the position of the second hydrogen atom has two degrees of freedom.

The hollow positions (0.5,0) and (0.5,1), with $\Delta E = 1.54$ and 0.74 eV, respectively, represent the least favorable positions. The four atop positions (0,0.5), (0,1.5), (1,0), and (1,1.5), also have high energies: ΔE is between 0.37 and 0.73 eV with respect to the lowest value. The nearest diagonal bridge site at (0.5,0.5) exhibits an energy difference of 0.11 eV, which is more stable than the nearest atop and hollow neighbors.

IV. DISCUSSION

A. Adsorption of Hydrogen

Unlike the relatively flat and anharmonic PES of hydrogen on Pt(111) [17, 39, 40], the PES for hydrogen adsorption on Pt(100) surface, calculated here, shows distinct maxima and minima indicating distinguished surface sites. Therefore, H-adsorption on Pt(100) surface is a highly site-selective process. The bridge site is most preferred among the high symmetry sites considered by about 0.2-0.4 eV from energetic point of view. The Pt-H bond length at atop 1.68 Å is shorter than Pt-H bond at bridge with 1.76 Å, and thus the atop bond is slightly stronger than a single bridge bond. However, the overall binding energy on a bridge site is substantially higher than atop, because at the bridge site a hydrogen atom is coordinated by two platinum atoms. In other words, the coordination number of two at a bridge outperforms the slightly stronger single bond on atop.

At a hollow site, the coordination number of hydrogen is highest, but there the Pt-H bond length 2.06 Å is much longer than on atop or at bridge. Thus the hydrogen in the hollow site moves toward the surface trying to bind to the second layer of Pt atoms. A hydrogen atom

fixed at hollow, as shown in Table I, is stabilized at about 0.57 Å above the Pt-surface, which is around 0.4-1.0 Å lower than on the other sites. From these considerations it follows that the hollow site is unfavorable for hydrogen adsorption on Pt(100) surface. The Pt-H bond length at hollow is also longer than the corresponding bond length 1.875 Å on Pt(111) [41]. This difference could justify why the fcc and hcp hollow sites have been reported as the preferred sites on Pt(111) [18, 42]. The knowledge about the bridge preference is used in the next section to elucidate the hydrogen evolution on Pt(100).

B. Interaction and Evolution of Two $H_{(ads)}$ Species

From Figure 4, it can be seen that the lateral interaction of the (0.5,0.5) bridge site is more favorable than the (0,0.5) atop site and the (0.5,0) hollow site, although both these sites are closer to the first hydrogen. The two hydrogen on neighboring bridge sites above the Pt surface are almost at the same height leading to maximum possible overlap of orbitals and stronger H-H bonding. In comparison, the second adsorbed hydrogen on a hollow site is 0.75 Å below, and the second adsorbed hydrogen on atop site is 0.70 Å above the height of the adsorbed hydrogen on the bridge site. None of these cases can lead to an H-H bonding as effectively as for a bridge-bridge combination. As a result, it can be concluded that the Tafel step in the hydrogen evolution is site-selective with the hydrogen species evolving from neighboring bridge sites in a Langmuir-Hinshelwood sense.

To relate the bridge-bridge pathway to hydrogen evolution, consider the surface reactions that start from the dissociation of hydrogen molecules on the surface. Even though the dissociation of hydrogen molecule on Pt clusters was reported to prefer atop sites [20], the diffusion rate to a bridge site from atop was shown here to be much faster than from a bridge site to atop (Table II), leading to the settlement of most hydrogen atoms at bridge sites. In other words, the surface diffusion of $H_{(ads)}$ aids the suggested bridge-to-bridge pathway for the Tafel step on Pt(100).

Now examine the energetics of hydrogen evolution through the bridge-bridge pathway. When a second hydrogen is adsorbed on the neighboring bridge site, the two bridge hydrogen exhibit a slight repulsive interaction of 0.11 eV, which is much less than 0.73 and 1.5 eV repulsion for bridge-atop and bridge-hollow combinations, respectively. The adsorbed hydrogen on the nearest bridge site is weaker than the hydrogen adsorbed on the next neigh-

boring bridge site by 0.11 eV (Figure 4). Energetically, this creates a situation where both the platinum-hydrogen bonds may be weakened for two closest H atoms adsorbed on two bridge sites such that they form a bond and eventually desorb from the surface.

It has to be mentioned that the bridge-bridge pathway above for HER is in contrast to the previous picture of hydrogen evolution from neighboring atop-hollow sites as presented in [12, 14]. Apparently, in the previous works bridge sites were not considered as potential sites for adsorption, the sites which were shown in this work to be the preferred sites at least on Pt(100). The energetic analysis of sites clearly identifies the hollow site being much more unstable than atop or bridge. In addition, H atoms adsorbed on atop sites easily move to bridge sites due to the fast one way diffusion rate from atop to bridge. The presence of one H atom at a bridge, while another sitting at a hollow site, is energetically forbidden and unlikely to happen for low coverage. When two H atoms are close to each other, they prefer to occupy not atop-hollow or atop-bridge combinations but two bridge sites, where their repulsion energy is lowest.

V. CONCLUSIONS

A comprehensive ab-initio study of hydrogen on Pt(100) surface was presented. The potential energy surface indicates distinct site preferences with the bridge site being the most preferred one. Even though the atop site is a local minimum, the high diffusion rate from atop to bridge results in a site change towards the bridge site. The hollow site is the least stable one. The interaction of one hydrogen on the bridge site with a second hydrogen in all possible nearest configurations was studied. The neighboring bridge-bridge interaction was identified as the most stable configuration, which potentially facilitates the formation and desorption of molecular hydrogen, suggesting this as the preferred pathway for the Tafel step.

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Figures

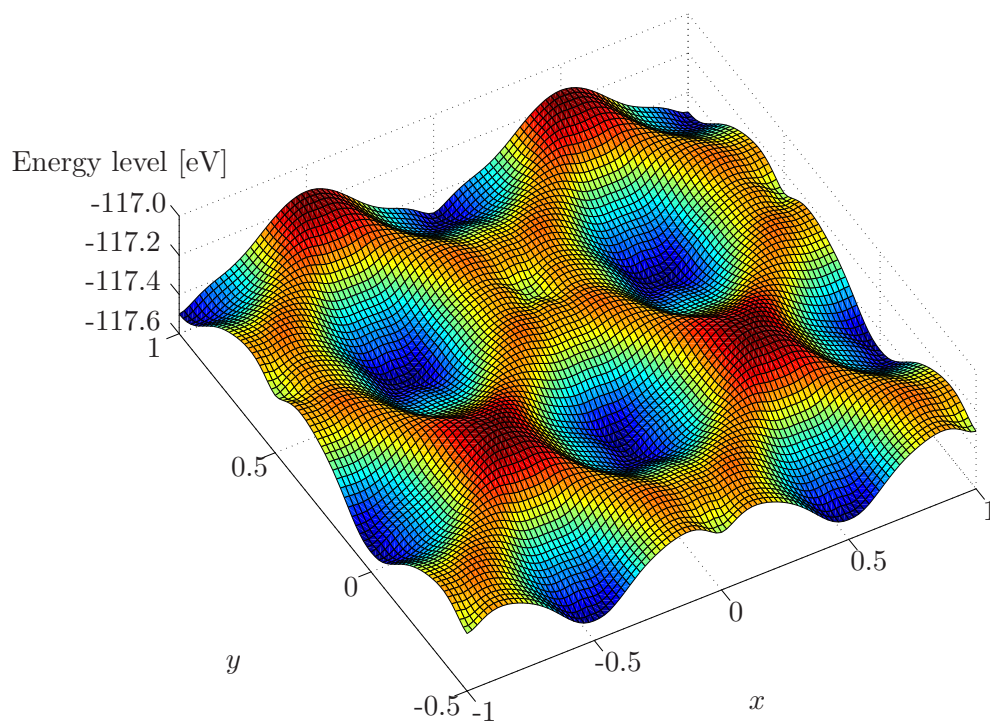


FIG. 1: Potential energy surface of H/Pt(100). The origin of the xy plane is at a bridge site, and the coordinates x and y are normalized distances with the Pt-Pt distance.

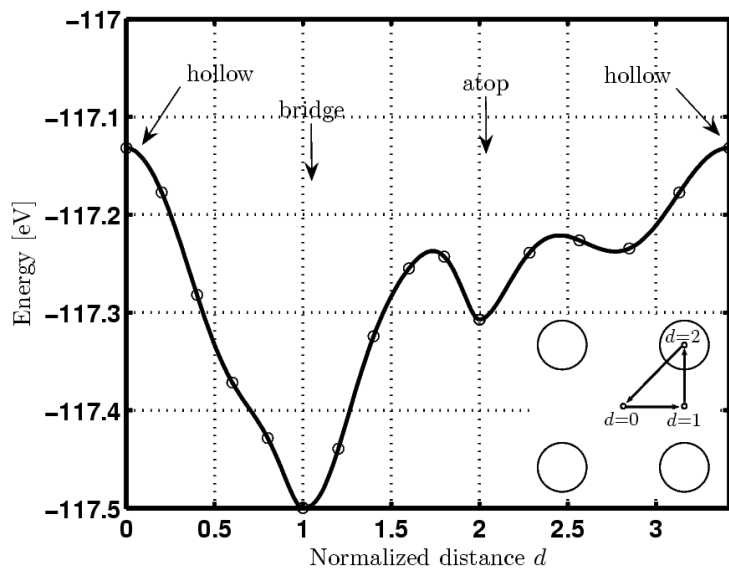


FIG. 2: Energy curve of the slab plus a hydrogen atom as H moves along the path from hollow to bridge, atop, and back to hollow

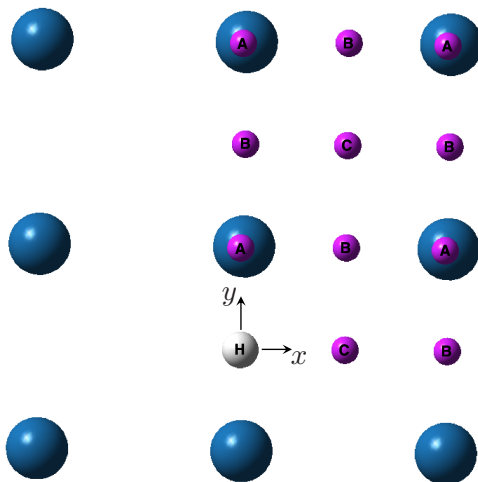


FIG. 3: Fixing one H (white) at a bridge site, there are 11 positions considered for the next H atom (marked as A-atop, B-bridge and C-hollow)

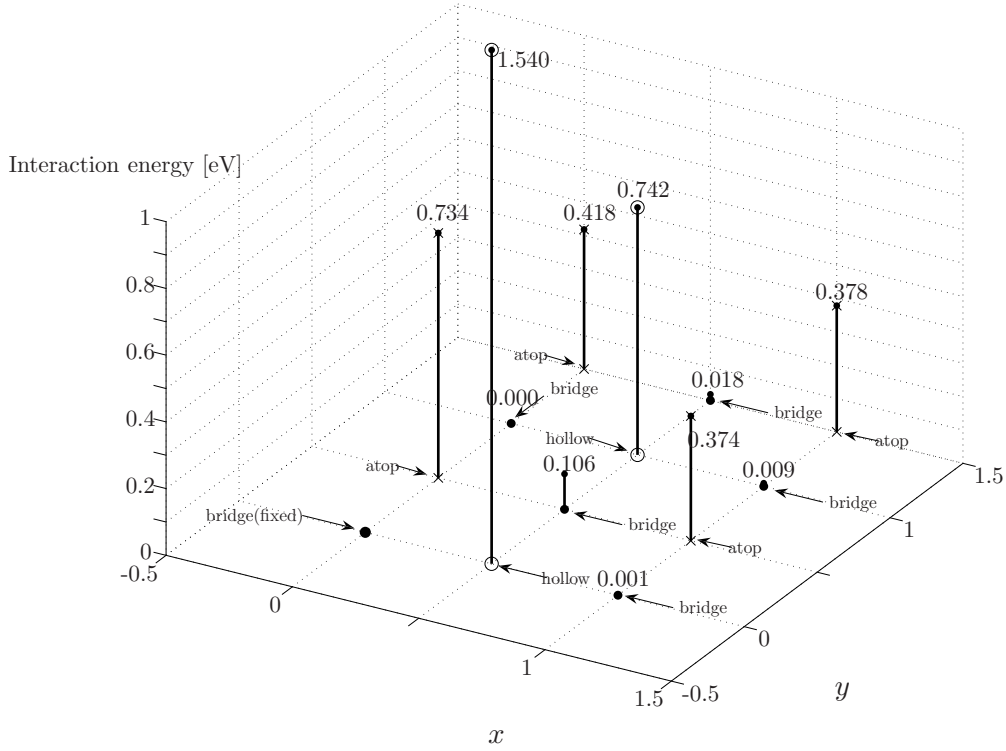


FIG. 4: Interaction energy of 2H/Pt(100) in eV, when one H atom is fixed at a bridge site, here the origin of the normalized coordinate system, and the other H is present at neighboring positions.

Tables

TABLE I: Energies, bond lengths Pt-H, and height of the hydrogen atom, z_{H} , above the plane defined by the centers of Pt atoms in the top layer.

	atop	bridge	hollow
E_{ads} (kJ/mol)	40.8	59.4	23.9
Pt-H (\AA)	1.6793	1.7574	2.0566
z_{H} (\AA)	1.6793	1.039	0.5691

TABLE II: Rate parameters of diffusion of hydrogen on Pt(100)

Path	A [s ⁻¹]	ΔE [meV]	k [s ⁻¹] _{@T=300°K}
bridge-to-atop	47×10^{12}	201.3	19.4×10^9
atop-to-bridge	26×10^{12}	8.9	18.7×10^{12}
bridge-to-bridge	35×10^{12}	247.1	2.5×10^9

TABLE III: Energetics of 2H/Pt(100), in units of eV, when one H is fixed at the (0,0) bridge site.

	$x=0$	$x=0.5$	$x=1$
$y=1.5$	-271.0491	-271.4490	-271.0889
$y=1$	-271.4673	-270.7256	-271.4579
$y=0.5$	-270.7333	-271.3613	-271.0933
$y=0$	-	-269.9274	-271.4658