

Hydrogen Interaction with Platinum and Palladium Surfaces

by
Amanda Boechler

A THESIS

submitted to
Oregon State University
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degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

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Líney Árnadóttir

Platinum and palladium surfaces are utilized as catalytic surfaces in the chemical industry. Understanding how hydrogen atoms interact with the metal surfaces will allow for further advancement in this area. Specifically, the interaction of hydrogen on the surface and subsurface of these metals was investigated using density functional theory calculations through Python scripts and the VASP software. The tests concluded that the hydrogen adsorption is favorable on the surface of both metals, but only on the subsurface of palladium. In addition, when more than one atom of hydrogen was introduced to the metal, the two hydrogen atoms demonstrated repulsive effects on one another.

Key Words: Platinum, Palladium, catalytic surfaces, hydrogen atom
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I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

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Hydrogen Interaction with Platinum and Palladium Surfaces

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ABSTRACT

Platinum and palladium surfaces are utilized as catalytic surfaces in the chemical industry. Understanding how hydrogen atoms interact with the metal surfaces will allow for further advancement in this area. Specifically, the interaction of hydrogen on the surface and subsurface of these metals was investigated using density functional theory calculations through Python scripts and the VASP software. The tests concluded that the hydrogen adsorption is favorable on the surface of both metals, but only on the subsurface of palladium. In addition, when more than one atom of hydrogen was introduced to the metal, the two hydrogen atoms demonstrated repulsive effects on one another.

1. Introduction

Simulations can be used to study the effects surface and subsurface hydrogen atoms have on platinum and palladium surfaces. Hydrogenation, hydrogenolysis processes, and dehydrogenation all play a vital role in the chemical industry and are often performed on platinum and palladium catalytic surfaces. Understanding how hydrogen interacts with these surfaces can give a better understanding to the complex chemical processes that occur as well as allowing for further advancements in this area. Hydrogen atoms interact differently at different locations on the surface of both platinum and palladium. Investigating the energy of the interaction at different locations on the surface and under the surface will help to determine where hydrogen atoms tend to settle when interacting with these surfaces. This will grant a better understanding of where the reactions will occur on the catalytic site.

2. Background

Hydrogenation, dehydrogenation, and hydrogenolysis are all processes that are very important to the chemical industry. Many of these processes are performed on platinum and palladium surfaces. The adsorption of hydrogen on transition metals like platinum and palladium is important in understanding the chemical process occurring in both catalytic and surface chemistry. Even though the reactions that takes place on the catalytic surfaces is very complex, the behavior of hydrogen can have a large impact on the overall performance of the catalytic

surface. Therefore, it is vital to understand how hydrogen interacts with transition metals like platinum and palladium in order to understand and improve upon the processes currently used in the chemical industry [1-2].

A lot of studies have been conducted on the interaction of hydrogen on transition metals. Extensive studies have been specifically done on the interaction of hydrogen with palladium 111 [3-6], platinum 111 [7-10], iron 110 [11-12], ruthenium 0001 [13-15], tungsten 110 [16-18], and nickel 111 [19-21] as well as other transition metals. Through all the studies, the hydrogen atom binds strongly to the surface of transition metals with the exception of the noble metals [2]. The interaction of hydrogen on transition metal alloys has also been studied quite extensively. One of the most looked at cases is the hydrogen interaction with near surface alloys where the composition near the surface of the metal is different than the composition of the bulk of the metal [22-23].

The interaction of hydrogen on the surface of transition metals is very important for many scientific applications. There are also some important applications for utilizing subsurface hydrogen. Palladium could be used in the hydrogen separation and purification process [24-25]. Palladium hydride also has the potential to be utilized for hydrogen storage, cold fusion and electrochemistry. Many hydrogenation reactions, such as ammonia synthesis, suffer from low selectivity due to the fast hydrogen evolution reaction on many transition metals. In electrochemistry, one can use applied potential to control the amount of subsurface hydrogen in palladium, but the reactivity of subsurface hydrogen differs from surface hydrogen, changing the balance between hydrogenation and hydrogen evolution. So, it is important to investigate the interaction of hydrogen on the surface of transition metals as well as on the subsurface to better understand the technological and scientific uses of these surfaces.

3. Methods

Density functional theory calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [26-29]. The Kohn-Sham equations were solved with a plane-wave basis set and core electrons were described using the projector augmented wave (PAW) method [30]. Electron exchange and correlation were described within the PW91 (Perdew-Wang 91) generalized gradient approximation (GGA) [31-33]. Spin polarization was used for all calculations, and the cutoff energy for the plane wave basis set was 400 eV.

The Pd (111) and Pt (111) surfaces were represented by a six-atomic layer slab using a (2×2) unit cell, the layer was allowed to relax, and the remaining layers were kept fixed. Zero-point energy corrections (ZPE) were not included in the energies reported herein. The adsorption energies were converged for number of KPOINTS using a Monkhorst-Pack grid of 1×1×1, 2×2×1, 4×4×1, and 6×6×1 KPOINTS.

4. Testing and Results

The first step in looking at how platinum and palladium surfaces interact with hydrogen atoms was to determine the lattice constant. A lattice constant refers to the distance between two corner atoms in the unit cell of the crystal structure. Platinum and palladium are both face centered cubic metals. Face centered structures consist of an atom on each corner of the structure

as well as an atom in the center of each cubic face. The image below depicts the fcc, hcp, and bcc unit cell for comparison.

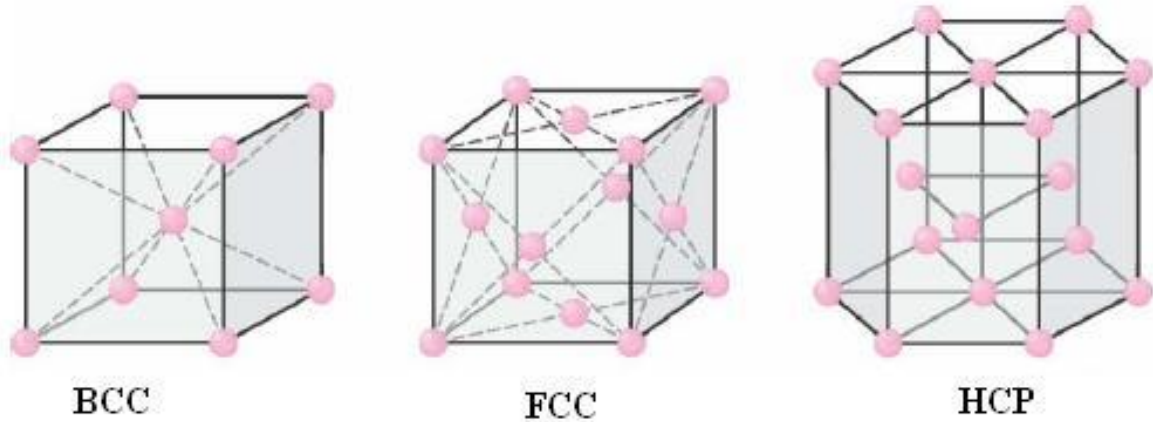


Figure 1: The image above depicts the bcc, fcc, and hcp surfaces from the top view for comparison [34].

The platinum (111) and palladium (111) surfaces used in the simulations herein are depicted in Figure 2.

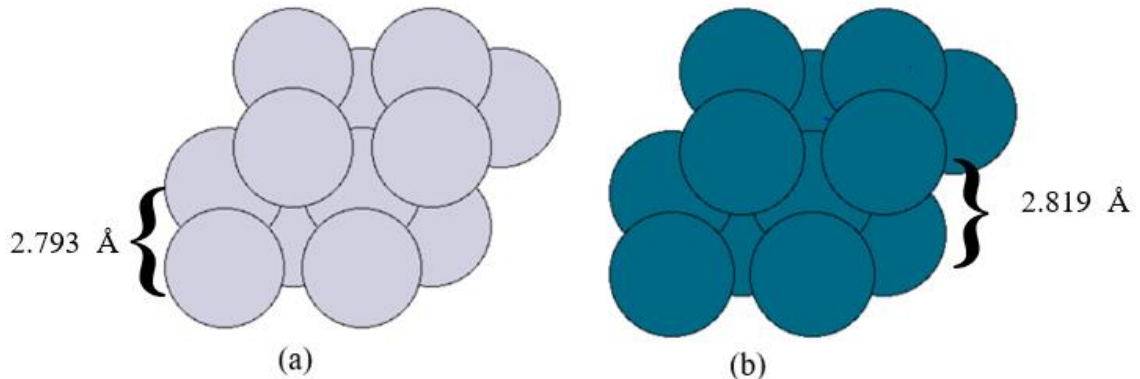


Figure 2: The above figure depicts the 2x2 simulation cells of platinum (a) and palladium (b)(111) surfaces. Since both metals are fcc the structure of the surface is the same, but the lattice constant differs by 0.04 Å.

The goal was to find the optimal distance between two corners on the face centered lattice structures, or the lattice constant, for both platinum and palladium surfaces. An estimated lattice constant was obtained for both metals based on experimental data [35-36]. In order to find the most accurate lattice constant, the estimated lattice constant was determined by calculating the energy of the bulk vs the distance between the atoms in the bulk. The goal was to determine at which lattice constant the metal bulk had the lowest energy. In practice, a scaling factor was used for the initial estimated lattice constant. Scaling factors ranges from 0.96 to 1.04 at intervals of 0.01. The obtained energies were then graphed verses the tested lattice constant. The graph

produced a parabola, and the vertex of the parabola was the lowest energy obtainable for a platinum surface. The data was fitted with second order parabolic trend and the minima determine by finding the zero point of the derivative of the fit. The surface with the lowest energy and its corresponding lattice constant was used in future trials. The same procedure was conducted for a palladium bulk. The lattice constant was determined to be 3.95 Å for palladium which agrees with the literature value of 3.951 Å [35]. The lattice constant for platinum was determined to be 3.99 Å which in good agreement with the literature value of 3.949 Å [36]. The results of the conducted trials are depicted in figure 3 below.

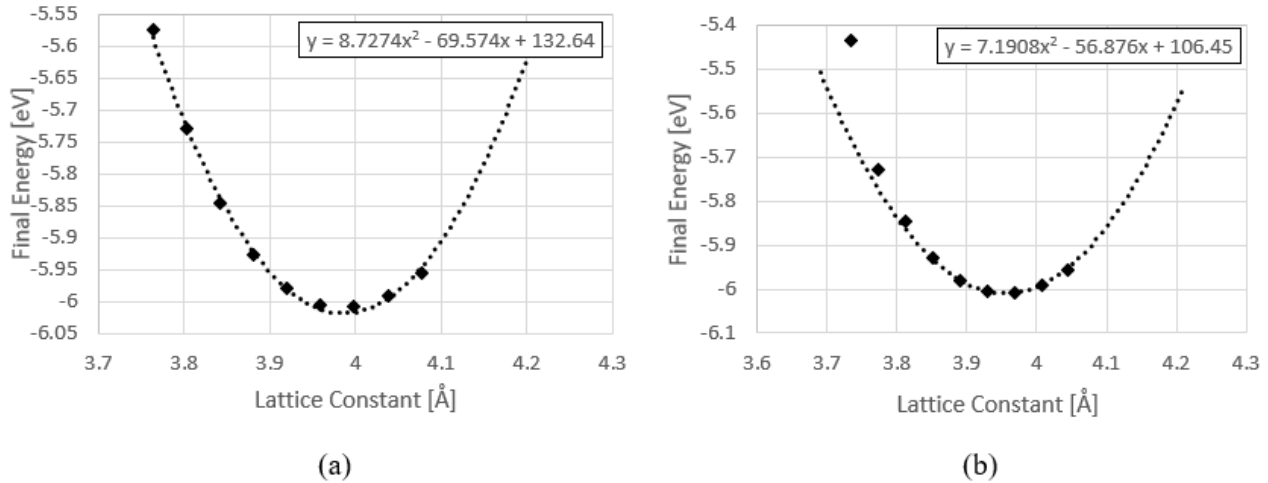


Figure 3: Graph (a) depicts the lattice constant results for platinum. The lowest energy point was found to be at a lattice constant of 3.99 Å. While, graph (b) depicts the lattice constant results for palladium. The lowest energy point was found to be at a lattice constant of 3.95 Å.

The 111, closed packed surface structure was selected because it is the most stable surface for palladium and platinum, and the most likely to be used as a catalytic surface. The platinum and palladium have two other closed packed surface structures, 100 and 110 surfaces. However, these surfaces are slightly less thermodynamically stable [37].

The structure of the 100 and 110 surfaces are shown in the figure 4 for contrast.

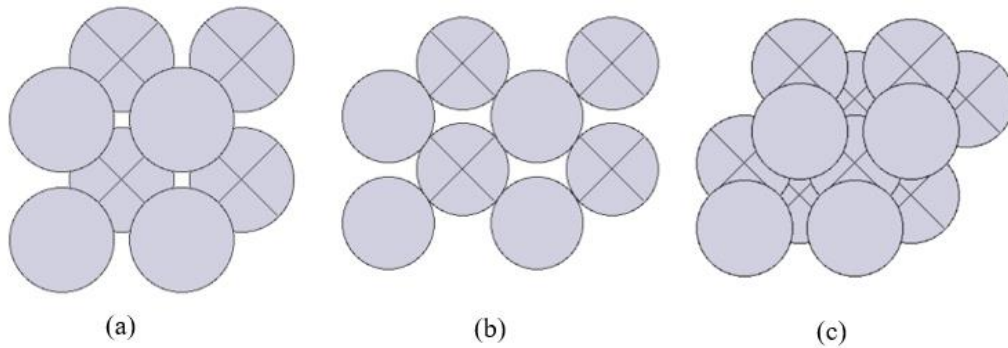


Figure 4: The above image depicts the surfaces 100 (a), 110 (b), and 111(c). The lower layers are depicted with an x through them, so the layers can be differentiated in a two-dimensional image.

Once the lattice constants were determined, a hydrogen atom was added to the system. The hydrogen atom was added at four different locations: fcc, hcp, top, and bridge sites. The locations where the hydrogen was placed are depicted in figure 5 below.

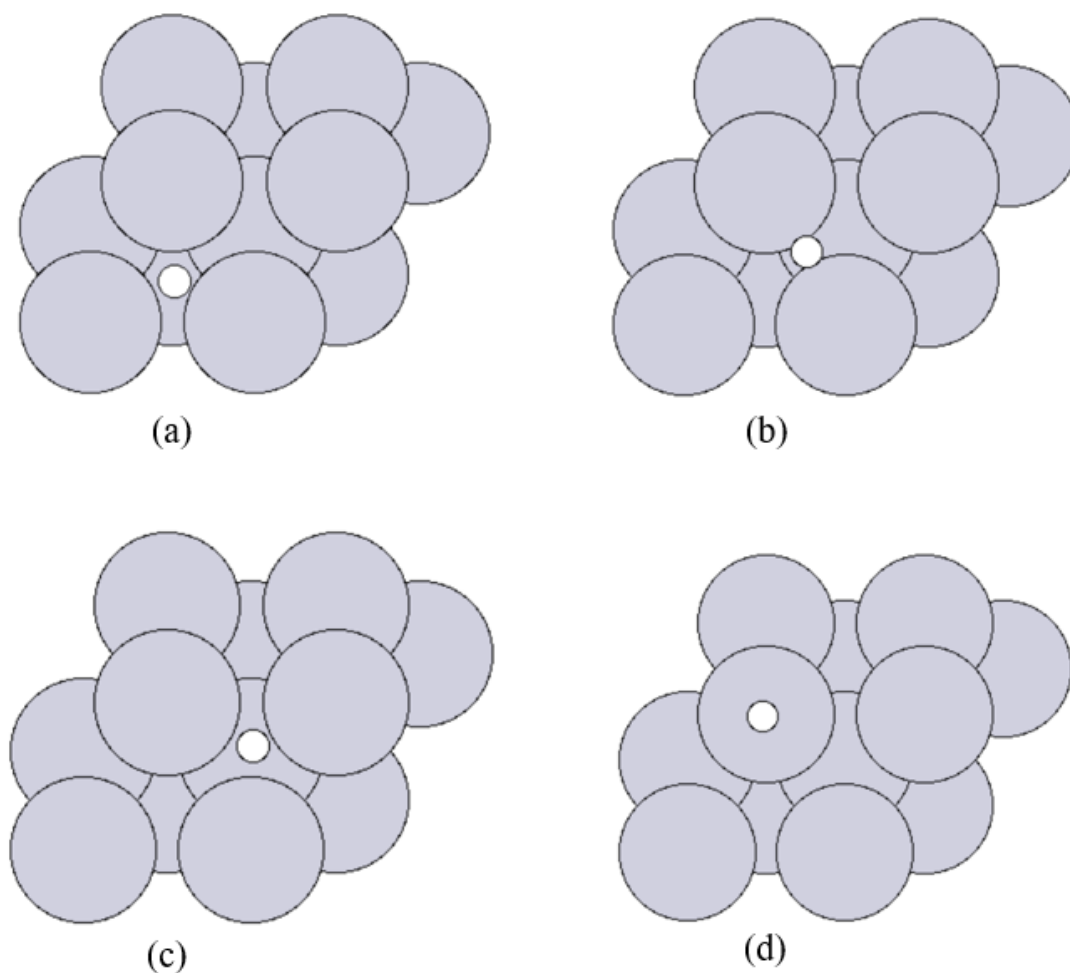


Figure 5: The above image depicts the different locations including fcc (a), bridge (b), hcp (c), and top (d) where the hydrogen atom was placed on the platinum and palladium surfaces.

Once the hydrogen was placed on the surface, an energy minimization calculation was performed to determine at which adsorption site hydrogen atom had the strongest hydrogen-metal interaction. For the initial calculations to determine the most favorable adsorption sites on the two different surfaces the calculations were run at 111 KPOINTS to save computational time. The calculations were run until the force on each atom was less than 0.03 eV/\AA to determine the lowest energy for the hydrogen-metal interaction. To determine the lowest energy site, four different initial sites were calculated. Once all hydrogen placement tests on platinum were completed, the same process was repeated for testing on the palladium surface. For both

platinum and palladium, placing the hydrogen in the fcc position produced the lowest energy which is depicted in the table 1 below.

Table 1: The below table contains: the obtained energy values for the different Hydrogen atom locations for both the platinum and palladium surfaces.

H -Location	Energy [eV]	
	Platinum	Palladium
hcp	-98.010	-98.200
fcc	-98.090	-98.260
top	-97.789	-97.971
bridge	-98.005	-98.193

The adsorption energy was defined as the energy difference between the adsorbed hydrogen, and metal surface and $1/2H_2$ in the gas phase.

$$E = E_{S-H} - \left(E_S + \frac{E_{H_2}}{2} \right) \quad (1)$$

Where E is the interaction energy, E_{S-H} is the total energy of the hydrogen and surface interaction, E_S is the energy of the platinum surface, and E_H is the energy of the hydrogen molecule.

In this density functional theory approach the core electrons are presented with a PAW potential so the energy calculated is not the exact total energy of the system, but the total energy of the valence electrons and the core electrons grouped together. So, although the total energy does not have a physical meaning the difference in energy does, as illustrated in figure 6.

For example, the total energy of H adsorbed on the Pt subtracting the energy of Pt leaves us with the bond between the Pt and the H as well as the energy of the H. When we then subtract the energy of $1/2 H_2$ we are left with the energy of the bond. We could also have subtracted a H atom, which often is done in the literature [38], but the total energy of H atom has larger error then molecular hydrogen so that is used instead.

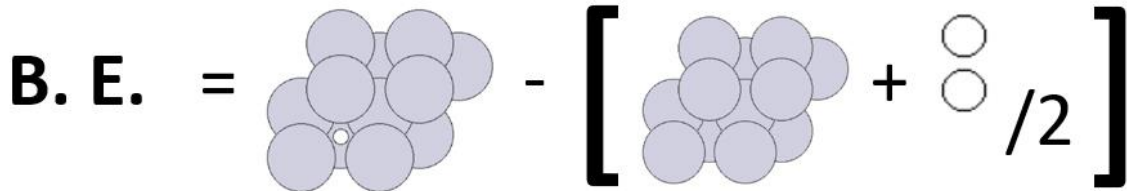


Figure 6: The above image shows the definition of absorption energy with relationship to the chemical compounds.

The difference in adsorption energy for hydrogen was very similar for all four locations. In fact, for both surfaces the variation was 0.05 %. These results show the hydrogen atom can settle

on any location on the surface of both platinum and palladium with a very slight preference for the fcc location based on the first and second laws of thermodynamics. This means that hydrogen has a very flat energy landscape and many local minima are also stable. The test results agree with the literature results in which the fcc location has a slightly lower adsorption energy for both platinum and palladium when compared with the hcp, bridge, and top locations [39].

The hydrogen atom was determined to be most stable in the fcc location so next we converged for number of KPOINTS. A grid of 221, 441, and 661 was included in the test. The testing began by changing the KPOINTS of the platinum surface to 221. The hydrogen atom was again placed in the fcc location. The calculations were run until the results converged on the lowest energy for that surface. Two additional calculations were also run to determine the energy of a 221-platinum surface by itself as well as a hydrogen molecule by itself to more accurately determine the adsorption energy. The total adsorption energy created by the interaction between the hydrogen atom with the platinum surface was calculated using equation (1).

The tests were run for the three different KPOINT grids, and the results are depicted in the table below.

Table 2: The table depicts the different adsorption energies found for the different KPOINTS on a platinum surface.

	KPOINTS			
	111	221	441	661
Pt-H [eV]	-98.01	-142.15	-143.89	-143.70
Pt surface [eV]	-93.89	-138.24	-140.03	-139.92
H ₂ [eV]	-6.78	-6.78	-6.78	-6.78
E [eV]	-0.73	-0.51	-0.47	-0.39

The tests were repeated for different kpoints on the palladium surface. The palladium interaction energies were also obtained for a 221, 441, and 661 surface. The results of the tests are depicted in the table below.

Table 3: The table depicts the different adsorption energies found for the different KPOINTS on a palladium surface.

	KPOINTS			
	111	221	441	661
Pd-H [eV]	-98.26	-123.62	-124.68	-124.62
Pd surface [eV]	-94.48	-119.63	-120.71	-120.66
H ₂ [eV]	-6.78	-6.78	-6.78	-6.78
E [eV]	-0.39	-0.60	-0.58	-0.56

Based on the results obtained for both platinum and palladium surfaces, the ideal KPOINTS for each surface is the 221. The graphs depicted in figure 7 below show the adsorption energy for each of the KPOINTS. The graph begins to level out at 221 with very little variation between the results for 221, 441, and 661. So, the ideal KPOINTS are 221 since it reaches the asymptotic energy and is the lowest KPOINT that achieves this. This result agrees with tests done by M. Johansson on palladium surfaces [40].

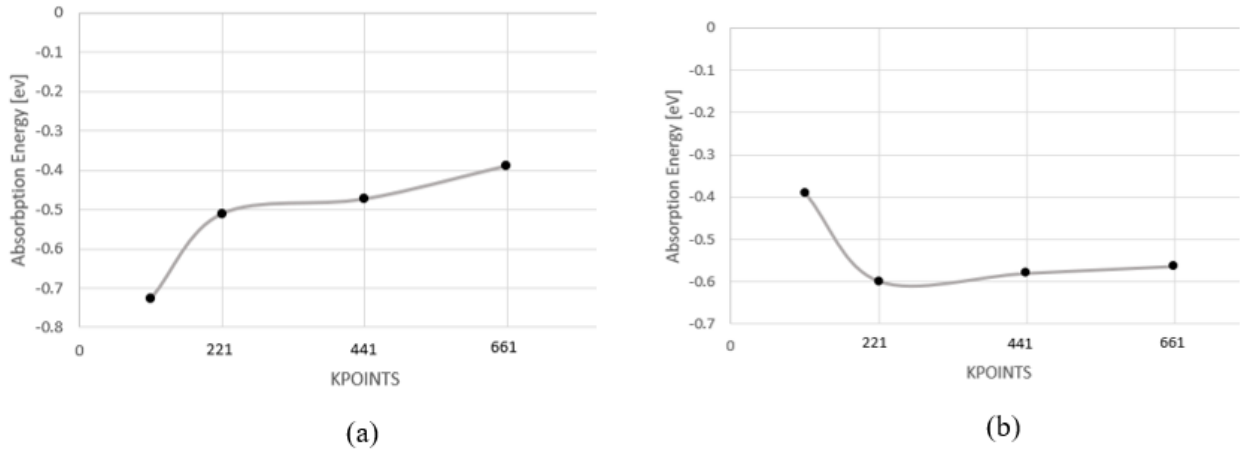


Figure 7: The above graphs depict the relationship between adsorption energy and KPOINTS for platinum (a) and palladium (b).

Once the surface with the ideal KPOINTS was determined, the next step was to determine the favorability of a subsurface hydrogen by placing the hydrogen under the surface of the metal and comparing its energy to the gas phase. The hydrogen atom was moved below the first level of the metal in the fcc location as depicted in the image below.

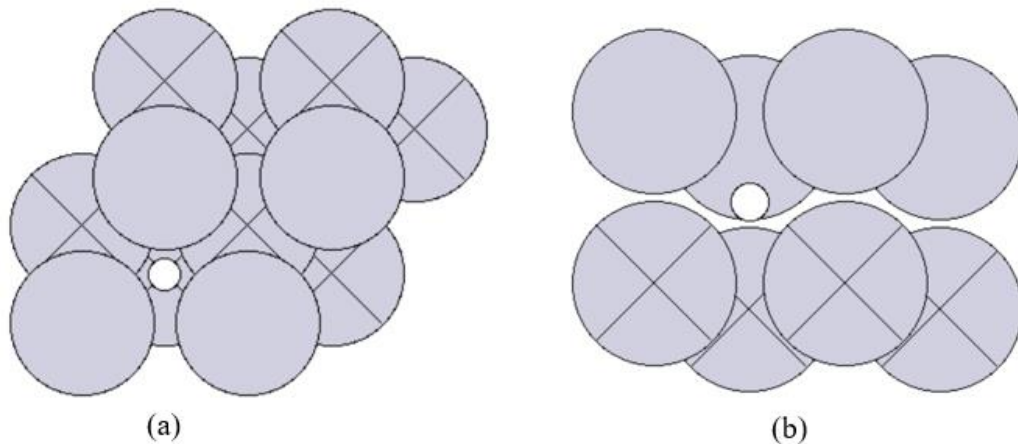


Figure 8: The above image depicts the top view (a) and side view (b) of the hydrogen atom in the subsurface of the metal surface.

Once the hydrogen was moved, the test was run to determine the energy of the interaction between the hydrogen atom and the surface. The process was tested for platinum and palladium surfaces at KPOINTS of 111, 221, 441, and 661. The results of the tests are depicted in the table below.

Table 4: The table depicts the different energies found for the different platinum and palladium surfaces for subsurface hydrogen.

KPOINTS/[eV]	Palladium				Platinum			
	111	221	441	661	111	221	441	661
Surface-H	-97.76	-123.27	-124.31	-124.26	-97.15	-141.25	-143.14	-142.87
Surface	-94.48	-119.63	-120.71	-120.66	-93.89	-138.24	-140.03	-139.92
H ₂	-6.78	-6.78	-6.78	-6.78	-6.78	-6.78	-6.78	-6.78
E	0.11	-0.25	-0.21	-0.20	0.13	0.38	0.28	0.44

The results show that the platinum surface is not ideal for subsurface hydrogens. The energy generated in each case is positive which means this is unfavorable and is unlikely to occur based on the first and second laws of thermodynamics. The results from the palladium, on the other hand, were negative except for the 111 which means it is possible for a hydrogen atom to be below the surface of palladium, and that is it more stable below the surface than in the gas phase. The difference between the interaction's hydrogen experiences between platinum and palladium is noteworthy since these two surfaces are very similar and the elements are neighbors in the periodic table. This is interesting since the lattice constant for the two metals is very similar but Pd-H interactions on the surface are stronger than Pt-H interactions. The palladium surface has a lower lattice constant compared to the platinum surface by only 0.04 Å so the difference is unlikely to be due to lattice structure alone. Palladium is well known to form a stable hydride and has even been used as a reference electrode in electrochemistry, Ni will also form a hydride or hydroxide while Pt readily forms neither. The adsorption energies obtained are supported by a study conducted by Jeff Greeley and Manos Mavrikakis where they found that placing a hydrogen atom on the subsurface of platinum and other alloys was an endothermic process with the exception of palladium [41].

In many catalytic reactions more than one hydrogen is adsorbed at a time on the surface, so the next step was to study the interaction between two adsorbed hydrogen atoms on the surface as well as between adsorbed hydrogen and a subsurface hydrogen. Two hydrogen atoms were added to the platinum and palladium surface using KPOINTS of 221 for all calculations. Three different tests were conducted. In the first test, both hydrogen atoms were placed in fcc locations on the surface of the metal. In the second test, one hydrogen remained in the fcc location on the surface of the metal while the other hydrogen was moved to the fcc location in the subsurface of the metal. The third and final test had both hydrogen atoms in the fcc locations in the subsurface of the metal. The surfaces tested are depicted in the figure below.

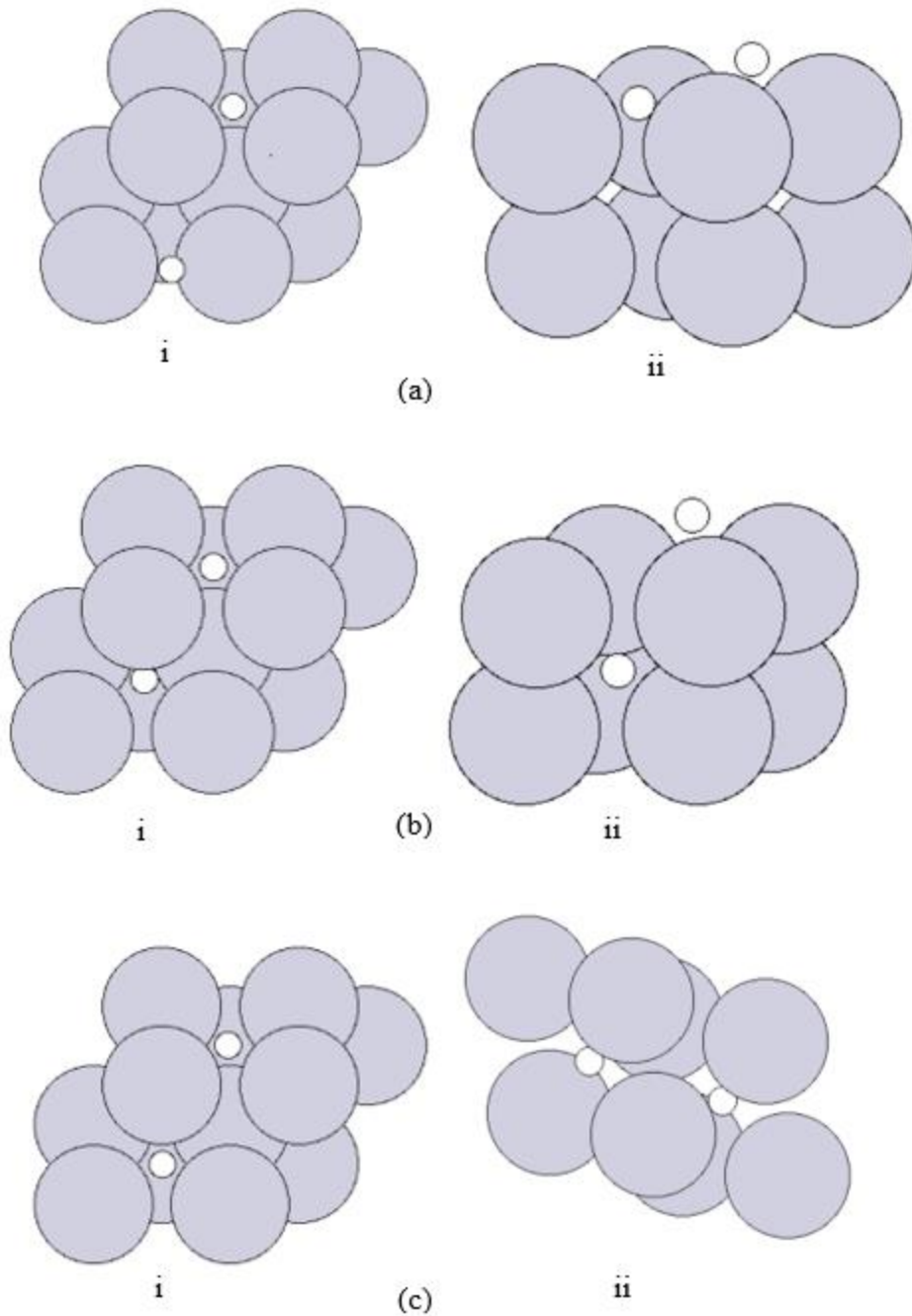


Figure 9: The above image depicts the surfaces from a top view (i) and side view (ii) for the tests run with two hydrogens on the surface (a), one on the surface and one on the subsurface (b), and two on the subsurface (c).

The tests were conducted to determine the affect a multiple hydrogen atoms will have on the surface and the interactions between them. The results from these tests are depicted in the table below.

Table 5: The below table depicts the energies produced by placing two hydrogen atoms on the platinum and palladium surfaces.

	molecules		surface-H [eV]	surface [eV]	H ₂ [eV]	E [eV]
	subsurface	surface				
Palladium	0	2	-127.56	-119.63	-6.78	-1.15
	1	1	-127.01	-119.63	-6.78	-0.60
	2	0	-126.73	-119.63	-6.78	-0.32
Platinum	0	2	-146.05	-138.24	-6.78	-1.02
	1	1	-145.20	-138.24	-6.78	-0.17
	2	0	-144.35	-138.24	-6.78	0.68

Starting with the palladium, the adsorption energy of a single H on palladium is -0.60 eV so if there were no interactions between the two hydrogens we would expect an adsorption energy of -1.2 eV, but the total energy is -1.15 eV suggestion only slight repulsive interactions between the adsorbates of 0.05 eV.

The energy of a subsurface H on Pd is -0.25 eV so non-interactive adsorbate and a subsurface H would be -0.85 eV. Therefore, the interactions between the adsorbate and a subsurface H is repulsive by 0.25 eV. The two subsurface H are also repulsive but slightly less so then for an adsorbate and subsurface H by 0.18 eV.

Similarly, for the platinum, the adsorption energy of a single H is -0.51 eV and of a subsurface H is 0.38 eV, the subsurface adsorption energy is positive which means it is thermodynamically unfavorable. Two co-adsorbed H on platinum have very weak interactions if any, this difference between the interactions between adsorbate H on Pt and Pd is partly due to the slightly larger lattice of Pt leading to longer distance between the adsorbed hydrogens. For an adsorbed H and subsurface H infinitely far apart, the total adsorption energy is -0.13 eV while when co-existing the energy is -0.17 eV suggesting a slight stabilization of the subsurface H by the adsorption. Similar when two H atoms are interacting subsurface the interactions are favorable by 0.08eV.

It is worth noting that since these the calculations are periodic the simulations cell is infinitely large in all directions. To run calculations of surfaces with an extended periodic boundary we add a vacuum layer in z-direction (10Å) to prevent the interactions between the adsorbated and the bottom of the periodic image above. If the simulation cells were closer together then the adsorbates could interface with both surfaces like a pore, to model bulk no vacuum layer is added. The extended period boundary can be seen in Figure 10 below.

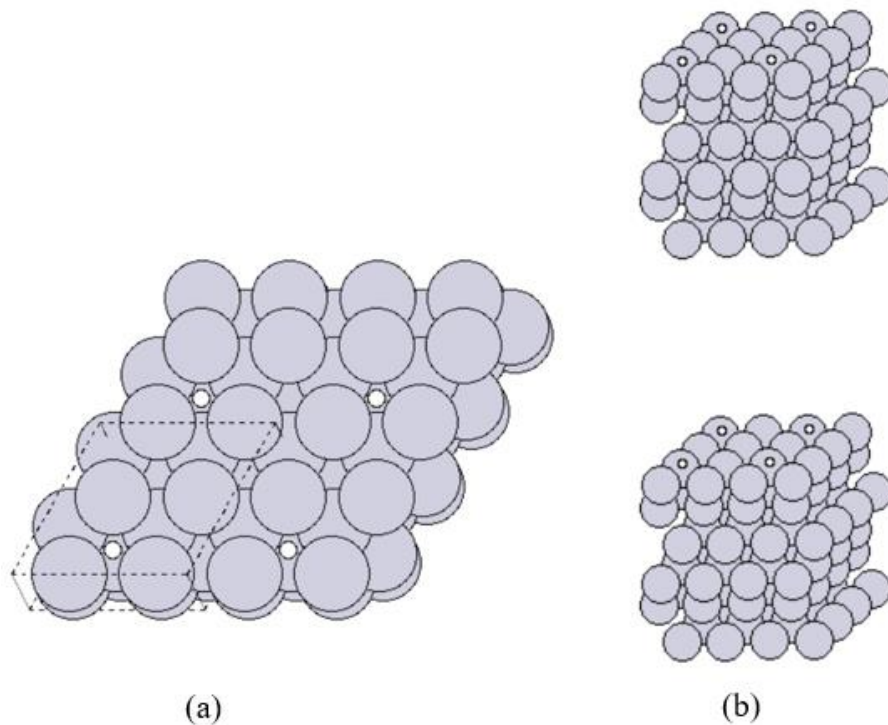


Figure 10: The above image depicts the extended period boundary from a top view (a) and side view (b).

Based on the obtained results, it can be concluded that the hydrogen atoms adsorbed on Pd(111) repulse one another while on Pt(111) the interactions are very weak. The energy produced between the interaction of one hydrogen atom on the palladium surface is -0.60 eV. So, ideally two hydrogen atoms on the surface of palladium would produce an energy of -1.20 eV. However, the two molecule on the surface of palladium produced and energy of -1.15 eV due to the repulsive interactions between the adsorbates. This value is slightly lower than the ideal value implying the hydrogen atoms having a repulse effect on one another.

5. Conclusion

Hydrogen atoms produce favorable adsorption energies on the surface of both platinum and palladium. However, hydrogen atoms only produce a favorable adsorption energy on the subsurface of palladium, but not on platinum. When more than one hydrogen atom interacts with the metal surface simultaneously, they will have a repulsive effects on one another causing the adsorption energy to be slightly lower on Pd while the interactions are very small on Pt. The repulsive interactions between adsorbed H and subsurface H on Pd were larger then between two subsurface hydrogens, this may suggest that once you have subsurface hydrogen adding more subsurface hydrogen becomes more favorable with adsorption, but more calculations are required to confirm.

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