

Hydrogen Separation via Metallic Membranes

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Abstract

Density functional theory was used to study the effects of alloying Pd-Cu membranes on the binding energy of several hydrogen and sulfur containing molecules. The purpose of this study was to determine the benefits of alloying a Pd-Cu membrane for the purposes of hydrogen separation. It was found that the binding energy of most adsorbates decreased with the addition of copper to the membrane, regardless of the position of the copper layer. This results in a decrease in the total production of hydrogen in exchange for a cheaper, more resilient membrane.

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Introduction:

Hydrogen is a valuable resource once purified. It has many industrial applications, such as being a fuel source, hydrogenations in the chemical process industry, use as a coolant in power station generators, and hydrodesulfurization of fuels (Paglieri , pg. 4). It is the most abundant element on the planet and can be obtained from many sources, such as water, biomass, and natural gas. Pure hydrogen can be used to refine fossil fuels, in fuel cells, as well as metal and fertilizer production (Lu, pg. 2). The production of hydrogen is a major industry, with a global generation market value of \$138.2 billion expected by 2019 (Hydrogen Generation). Obtaining pure hydrogen requires separation from other gasses.

One technique for separating and purifying hydrogen is by using metallic membranes such as palladium or palladium alloys. This process involves passing a stream of gas containing hydrogen or hydrogen rich molecules over the surface of an extremely thin membrane of the metal chosen. The surface of the membrane has a lot of available energy for attracting atoms because the atoms on the surface of the metal are exposed on one side, leaving a site for bonding to occur. This surface energy attracts hydrogen enabling the bonds connecting hydrogen to its molecule to be broken, but it also can attract other molecules like sulfur, CO, and H₂S.

Palladium is specifically useful for separating hydrogen from a stream of other gasses because of its extremely high selectivity for hydrogen. Palladium is very permeable to hydrogen and doesn't allow most other gasses to pass through it, leading to an almost pure hydrogen product. How well the hydrogen can pass through the palladium membrane, or the permeability (P), is a function of diffusivity (D) and solubility (S):

$$P = D * S \text{ (Paglieri , pg. 9)}$$

When other metals are added to the membrane, such as an alloy with copper, will alter the diffusivity and solubility properties but may also provide other useful properties (Paglieri, pg. 9). This can lead to higher permeability and more resilient membranes.

Molecules other than hydrogen that adsorb to the surface of the membrane, such as sulfur, can remain on the surface. This is called poisoning of the membrane because the sulfur atoms that adsorb to the surface block useful sites that hydrogen could use to diffuse through the membrane. Thus, for every atom or molecule other than hydrogen on the surface of the membrane, the effectiveness of the membrane decreases.

One potential solution to this problem is to make the membrane out of a material that is resistant to poisoning, or one that sulfur will be less likely to be attracted to. For this reason many membranes are made of alloys instead of pure palladium, such as silver or copper-palladium alloys. These alloys can also affect selectivity, vulnerability to becoming brittle due to repeated thermal cycling, and solubility of hydrogen. In addition, copper reduces the cost of the membrane by replacing the more expensive palladium. Thus, the benefits of using a material that will prevent or deter sulfur poisoning must be weighed against potential negatives, such as decreased selectivity (Paglieri, pgs. 22-23).

Copper alloys and the benefits of alloying copper with palladium will be the focus of this project. Specifically, a surface with layers of copper in varying positions was used to determine how Cu-Pd membranes compare to a pure palladium surface. Thus, this project focused on alloys containing palladium and copper as a solution to sulfur poisoning.

Background:

Adsorption:

Adsorption is the bonding that occurs between molecules in the gas phase and a surface. The molecules bonding to the surface are known as the adsorbate and the surface they are bonding to is called the adsorbent. Desorption is the removal of these same molecules from the surface (Masel, pg. 108). This project focused mainly on small molecules, such as hydrogen, sulfur, and H_2S , bonding to a Pd or Cu-Pd layered surface. The driving force behind adsorption is surface energy generated by exposed atoms at the surface of the metal which have an inadequate number of bonds to satisfy their valence needs. These surface atoms attract molecules such as hydrogen, and the pull from multiple exposed Pd atoms can pull the hydrogen molecule apart into individual hydrogen atoms. This separation of the molecule due to surface forces is known as dissociation. In many cases, dissociation has a large activation barrier, so the molecule may simply desorb from the surface before it can be split. This energy barrier can be overcome by keeping the temperature and pressure high enough (Masel, pg. 118).

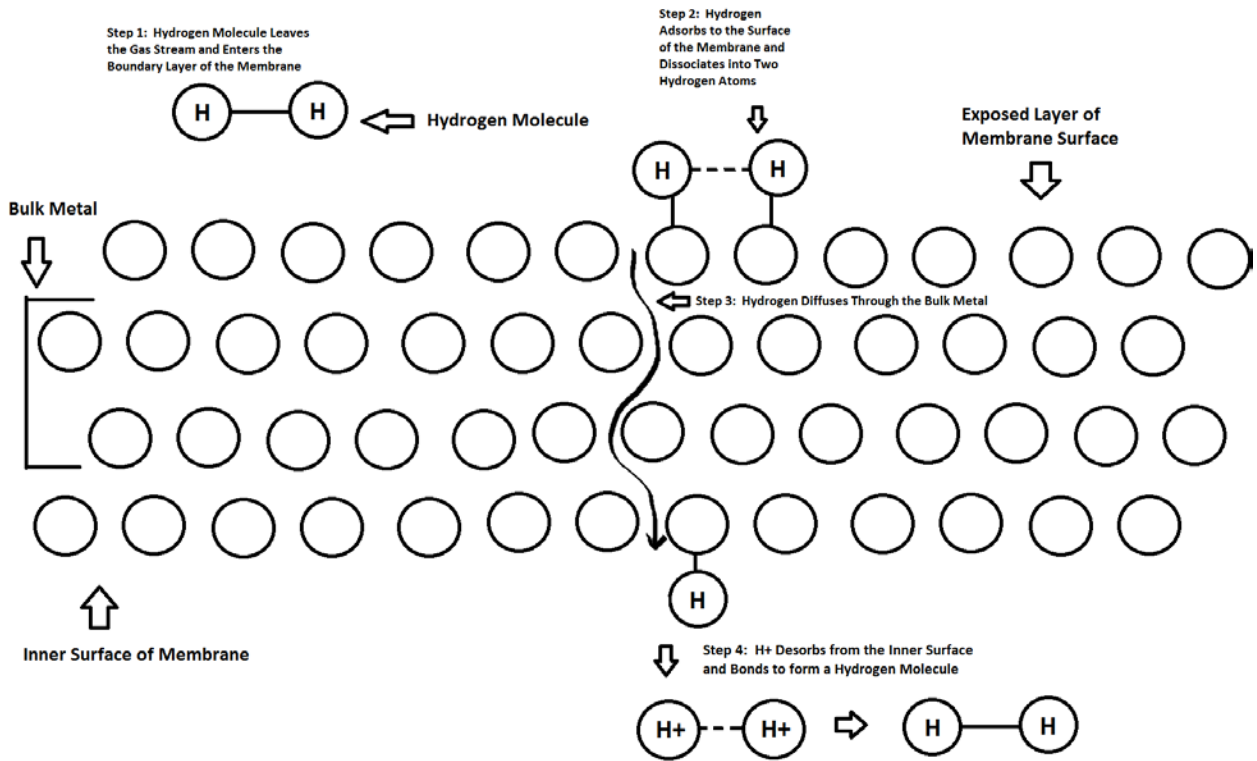
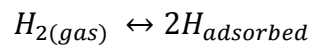


Figure 1: Example of Hydrogen Adsorbing and Diffusing Through a Palladium Membrane

Diffusion:

Diffusion is the process of something moving from an area of high concentration to an area of low concentration. In this case, hydrogen leaves the side of the membrane that is hydrogen rich for the side that is hydrogen poor. This involves diffusion through the boundary layer of the metal to the surface. Next, the molecule dissociates into two hydrogen atoms on the surface of membrane:



Once the attracted hydrogen is adsorbed to the surface of the metal it can pass through the interior of the membrane (known as the bulk metal) by diffusion, while other atoms such as sulfur will be stuck on the surface or picked up by other passing molecules because of the selectivity of the membrane for hydrogen. Once the hydrogen has diffused through the bulk metal and to the opposite surface of the membrane it will desorb, or detach, from the surface and bond with a free hydrogen to give a hydrogen molecule, H_2 (Paglieri, pgs. 9-10). Thus, in order for the hydrogen to continue diffusing through the membrane the levels of pure hydrogen must be kept lower than the levels of hydrogen in the exit stream from the process or else there will be no driving force for the separation.

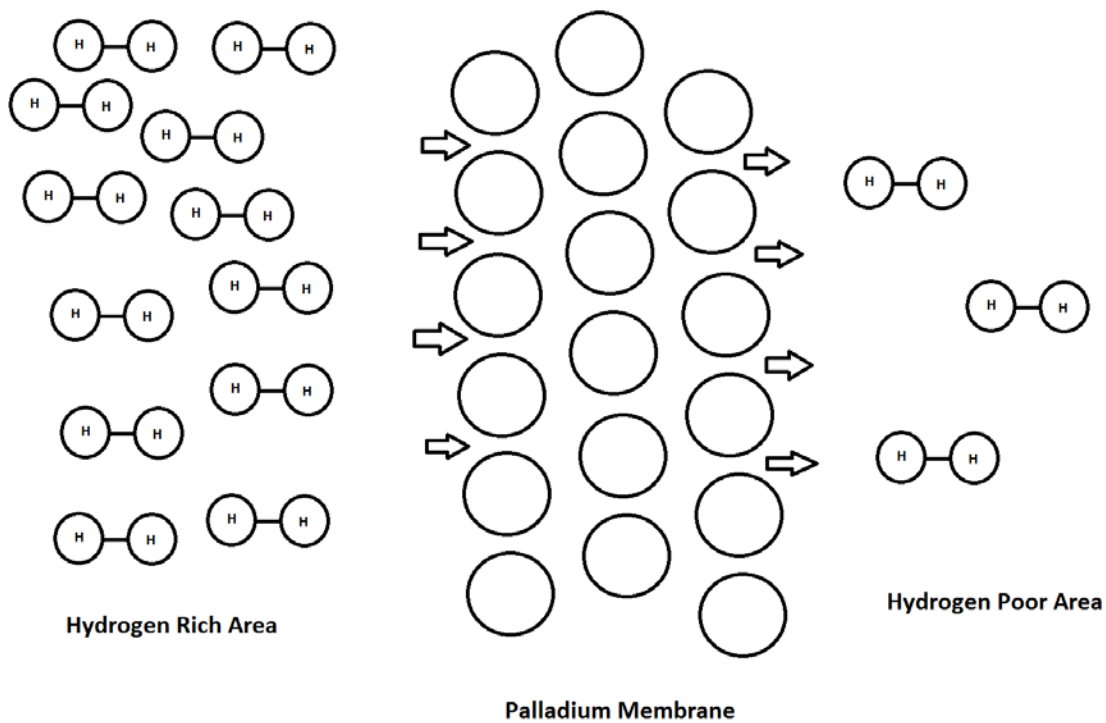


Figure 2: Example of Driving Force and Diffusion of Hydrogen Through a Palladium Membrane

Binding Sites:

Metals are comprised of many closely packed atoms all connected to one another. A metallic surface is a plane where the metal has been cut to provide a smooth surface. The surfaces studied in this project are face-centered cubic (FCC) and 111 surfaces. The arrangements of the atoms and how they are layered determines the structure, and both copper and palladium have an FCC structure, which means that their atoms are layered in an ABCABC packing sequence.

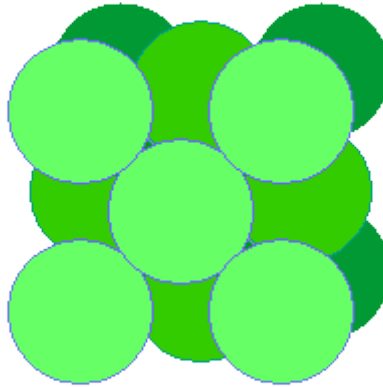


Figure 3: FCC Structure (An Introduction to Surface Chemistry)

A 111 surface is defined by the x, y, and z axes sharing the same value. This is simply the view of the surface. In this case, the 111 view of the surface gives a very closely packed layer.

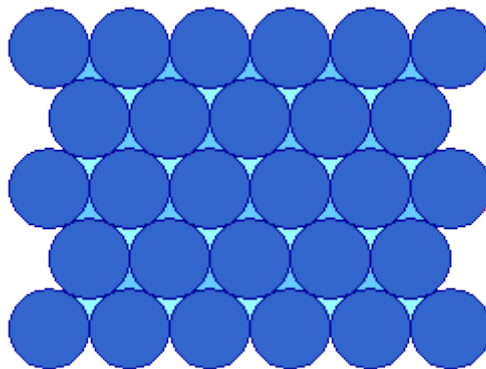


Figure 4: FCC (111) Surface Plane (An Introduction to Surface Chemistry)

This surface structure leads to four surface binding sites: top, bridge, HCP-hollow and FCC-hollow.

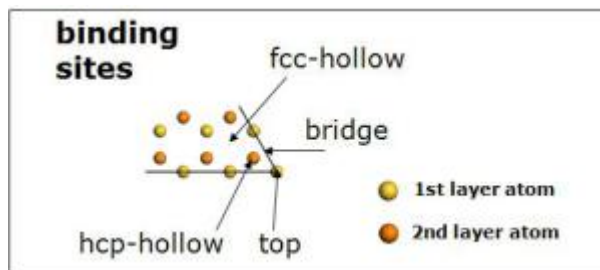


Figure 5: Binding Sites (Buonocore)

These sites are where atoms or molecules will be attracted to the surface and adsorb. As shown in Figure 5, the binding sites are located as follows: top is directly above a top layer atom; bridge is between two top layer atoms (not directly above a 2nd layer atom); HCP-hollow is in the hollow between three top layer atoms and directly above a 2nd layer atom; and FCC-hollow is in the hollow between three top layer atoms and not directly above a 2nd layer atom. Each of these locations will have a unique binding energy with a given adsorbate.

The site that requires the least energy to form a bond will be preferred by molecules. This energetic preference of molecules to bind in specific sites was a primary focus of this project, as the properties of various surface configurations was observed in part by how molecules preferred certain binding sites. The preference for a particular molecule to bind in different surface sites allowed for a point of comparison between pure palladium surfaces and Pd-Cu surfaces (An Introduction to Surface Chemistry).

Density Functional Theory:

Density functional theory (DFT) is a method of quantum mechanical simulation (Harrison, pg. 1). This allows for a computational method of solving for the interaction between a molecule and the surface it is adsorbed to. This is achieved by comparing the energy of the ground state for the molecule and surface to their energy profile once they have interacted. This ground state energy can be calculated from the Schrödinger equation

$$\hat{H}\psi(r_1, r_2, \dots, r_n) = E\psi(r_1, r_2, \dots, r_n)$$

where H is the Hamiltonian operator (the sum of kinetic energy, interaction with external potential, and electron-electron interaction), E is energy, r is the coordinate of an electron, and ψ is the wavefunction (in this case representing the probability that an electron will be in a given location at any given time) (Harrison, pgs. 1-2).

The ground state wavefunction is found by searching all possible wavefunctions and finding the one with the lowest possible energy (Harrison, pg. 3). The three terms that make up the Hamiltonian operator are also known as the energy functional and can be expressed as

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho]$$

where E is energy, ρ is electron density, T is kinetic energy, V_{ext} is interaction with external potential, and V_{ee} is electron-electron interaction (Harrison, pg. 7).

For this project DFT was used over the more simplified Hartree-Fock method. Hartree-Fock or self-consistent field method (SCF) is an approximation of the Schrödinger equation in which electrons do not interact with each other and are under a mean field potential that is made up of the classical Coulomb potential and a non-local exchange potential (Harrison, pg. 4). This saves a great deal of computational power by not calculating the interactions between every electron as well as a different field potential at every point. This can lead to deviations from

experimental results, as it only provides a ground state for the energy calculation. Hartree-Fock is an ab initio method, meaning it is derived from first principles (Harrison, pg. 10). Therefore, despite the much longer calculation times needed, DFT was chosen in this case for increased accuracy due to the inclusion of electron-electron interaction.

Status of the Field:

Many other reports on palladium and palladium-copper alloys being used for hydrogen separation already exist. This information was used as a resource to determine what experimentation would be useful and provide additional insight into the topic. For instance, surface contamination decreases the effectiveness of the membrane because it inhibits hydrogen dissociation and recombination reactions. This shows the importance of reducing sulfur poisoning, as sulfur compounds are common in hydrocarbon waste streams. As binding sites are taken up by sulfur compounds and rendered inactive, permeability decreases and the energy barrier between adsorbed and subsurface hydrogen states can increase (Paglieri, pg.15).

Copper alloyed with palladium shows a slight decrease in reactivity with sulfur due to the d-band center of surface atoms (Alfonso 2003, pg. 1). A Pd/Cu/Pd alloy membrane was shown to improve upon the permeability of a Pd/Cu membrane. This improvement was from 50-60% of a pure Pd foil's permeability up to 93%. This minimized the disadvantage of permeability loss with a copper alloy, allowing for less of a drawback in exchange for superior sulfur resistance (Pomerantz, pg. 11).

A sharp spike in permeability of hydrogen has been displayed for copper alloyed with palladium at 40% by weight. This is due to the ordered beta phase in the Pd-Cu system at that

point (Knapton, pg. 3). That much reduction in the weight of palladium required could make hydrogen purification much more practical and hydrogen a more affordable resource.

Sulfur poisoning increases as exposure time increases and temperature decreases. Pd-Cu membranes can regenerate from sulfur poisoning by flushing the membrane with pure hydrogen at high temperatures (Ma, pg. 9). This means that by using some of the product obtained via the membrane, the lifespan of that membrane can be dramatically improved. However, this also means that there is downtime in the process as the membrane is cleared of unwanted surface sulfides.

Methodology:

Reaction Energies:

The primary objectives of this project were to verify the methods used to do surface calculations by comparing calculated values to those from literature and to generate new values with different surface configurations of Pd and Cu. This was accomplished by performing surface energy calculations in CP2K along with energy values for all of the molecules and atoms used as adsorbates. Binding energies were then calculated by

$$E_{bind} = E_{surface+attachment} - E_{surface} - E_{attachment}$$

and could then be compared to literature values in order to determine the accuracy of the calculation. The greater the value of the binding energy (E_{bind}) the more likely that bond is to occur (note: in general the most negative binding energy is the “greatest value” as it is the most exothermic). This was used to evaluate which binding sites were preferred energetically as well as to compare different surfaces and how strongly molecules could bond with them.

In order to perform this calculation for all of the molecules and atoms used, first each adsorbate had to be run through CP2K in order to find its energy. This involved specifying coordinates for the molecule (or a single coordinate for an atom), ensuring that a basis set for the atoms that made up the molecule were included and using CP2K to run the energy optimization for the adsorbate. This value was then compared to values from the Computational Chemistry Comparison and Benchmark Database (CCCBDB) by creating example reactions. This meant calculating the energy of each molecule in the reaction via CP2K and finding values for the same molecules on the CCCBDB. Then, each reaction energy was calculated via

$$E_{rxn} = E_{products} - E_{reactants}$$

and the E_{rxn} values were compared to determine accuracy.

Once the binding energies of various adsorbates with the pure palladium surface were calculated, the same procedure was followed for two additional surface configurations: a top layer of copper atoms with 3 layers of palladium and a second layer of copper atoms with a top and two bottom layers of palladium. These calculations were used to compare the preferred binding sites of the adsorbates in order to determine the effect of layering copper into the membrane.

CP2K Setup:

CP2K was used for the energy calculations in this project. CP2K is a program that applies DFT using a mixed Gaussian and plane waves (GPW) approach. This method is implemented within CP2K via Quickstep, which combines Gaussian-type functions and plane waves in order to obtain the positive aspects of both. This means improved accuracy and faster computation time than either method used separately. The plane waves method is independent of atomic positions and efficiently calculates the Hartree potential term, but require a lot of additional terms near the nuclei. The Gaussian-type functions have a more compact description of atomic charge densities and thus deal with the calculations around the nuclei more efficiently, but the Hartree term can be much more complicated to calculate using this method. The combined method is expressed as follows:

$$E[n] = E^T[n] + E^V[n] + E^H[n] + E^{XC}[n] + E^{II}$$

$$\begin{aligned}
&= \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_\mu(r) | -\frac{1}{2} \nabla^2 | \varphi_\nu(r) \rangle + \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_\mu(r) | V_{loc}^{PP}(r) | \varphi_\nu(r) \rangle \\
&\quad + \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_\mu(r) | V_{nl}^{PP}(r, r') | \varphi_\nu(r') \rangle + 2\pi\Omega \sum_G \frac{\tilde{n}^*(G)\tilde{n}(G)}{G^2} + \int \bar{n}(r) \epsilon_{XC}[\bar{n}] dr \\
&\quad + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}
\end{aligned}$$

where $E^T[n]$ is kinetic energy, $E^V[n]$ is electronic interaction with the ionic cores, $E^H[n]$ is the Hartree energy, $E^{XC}[n]$ is the exchange correlation energy, and E^{II} denotes the interaction between the ionic core energies Z_I and positions R_I . Electronic interaction with the ionic cores is described using norm-conserving pseudo potentials with a potential split V_{loc}^{PP} and V_{nl}^{PP} representing the local and non-local parts, respectively. The electronic density is expressed by

$$\begin{aligned}
n(r) &= \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(r) \varphi_\nu(r) \\
\varphi_\mu(r) &= \sum_i d_{i\mu} g_i(r)
\end{aligned}$$

where $P_{\mu\nu}$ is a density matrix element, $g_i(r)$ is a primitive Gaussian function, and $d_{i\mu}$ is the corresponding contraction coefficient (Grotendorst, pgs. 42-43).

The GPW uses pseudo potentials like the plane waves method would because the Gaussian method is impractical with large exponents. These pseudo potentials are represented with the V_{loc}^{PP} and V_{nl}^{PP} terms mentioned earlier for the local and non-local parts. The basis sets for CP2K are Gaussian functions which have been optimized for the local and non-local pseudo potentials. Finally, the wavefunction was optimized with a self-consistent field (SCF) procedure, which minimizes the total ground state energy of a system (Grotendorst, pgs. 43-47). This means that the configuration of the molecule and the surface it is attached to is repeatedly iterated until

a minimum energy level is reached or the program exceeds the allotted number of maximum iterations.

Therefore, the inputs required for each CP2K trial included a basis set for the atoms involved, a pseudo potential set, a cutoff point for iterations, dimensions for the model, and coordinates for the atoms. With these inputs, CP2K can iterate the possible electron configurations and interactions in order to converge at a minimum energy value for the wavefunction. The geometry of the system is then optimized and iterated until convergence with SCF again. Finally, the optimized geometry is iterated with SCF to check that it is correct, and the energy calculation is complete.

Results and Discussion:

Verification of Methodology:

In order to justify my results, first the methodology discussed had to be verified. This was accomplished by finding established values for the substrate-surface bonding energies from other studies, creating CP2K input files for those same configurations, and obtaining bonding energy values. The comparison of these values provided no new information about Pd(111) membranes, but it served as a demonstration that this methodology could produce reliable results. As shown in Table 1, there was a general agreement between my results and the obtained literature values. H_2S in the HCP-hollow and top binding sites were outliers, leading to a disagreement between the preferred binding site for H_2S on Pd(111) in my results and the literature value.

Table 1: Pd(111) Binding Energies

	Literature Value (eV)	Calculated Value (eV)	% Error
S	4.77 (Alfonso, D 2003)	5.37	12.57
S @ FCC	4.85 (Alfonso, D 2003)	5.41	11.44
H ₂ S @ FCC	0.4 (Hyman)	0.44	9.62
H ₂ S @ HCP	0.51 (Hyman)	0.82	60.45
H ₂ S @ Top	0.52 (Alfonso, D 2005)	0.36	30.05
CO @ HCP	2.02 (Sakong)	2.05	1.67
CO @ FCC	2.04 (Sakong)	2.42	18.81
SH @ Bridge	3.02 (Alfonso, D 2005)	3.04	0.77
H @ FCC	0.6 (Hyman)	0.70	16.25
H ₂ O @ Top	-0.22 (Sakong)	-0.24	8.95

Preferred Binding Site:

The site with the lowest (most negative) energy value for a given adsorbate is the preferred binding site, as the molecule will adsorb in that site more readily than the others. Each adsorbate agreed with the literature findings except for H_2S , which had a large % error. The top layer being copper didn't change the preferred binding site in most cases except for with SH.

Table 2: Preferred Binding Site

(Note: preferred site from literature in parentheses)

	Pure Pd(111)	Top layer Cu
H ₂ S	HCP (Top)	Top
SH	Bridge (Bridge)	FCC
S	FCC (FCC)	FCC
H	FCC (FCC)	FCC

(H₂S top, SH bridge: Alfonso, D 2005; S FCC: Alfonso, D 2003, H FCC: Hyman)

Energy of Adsorption:

Figure 6 shows the step ladder-like graph that results from an adsorbate going through the process of binding with a metal surface. The energy level of the arrangement remains constant in each step until the energy barrier for continuing the process is reached. At this time, energy is released and another plateau is reached. This occurs as the adsorbate adsorbs to the surface and as each atom is pulled off of the molecule by the surface. This result is as expected, as the reaction would not take place if it were not energetically favored. That being said, if the energy barrier for any given step is not met, the process can stop or reverse, such as the adsorbed molecule desorbing before any disassociation can occur. This is discouraged by maintaining favorable temperature, pressure, and concentration conditions in order to maintain the driving force for the separation.

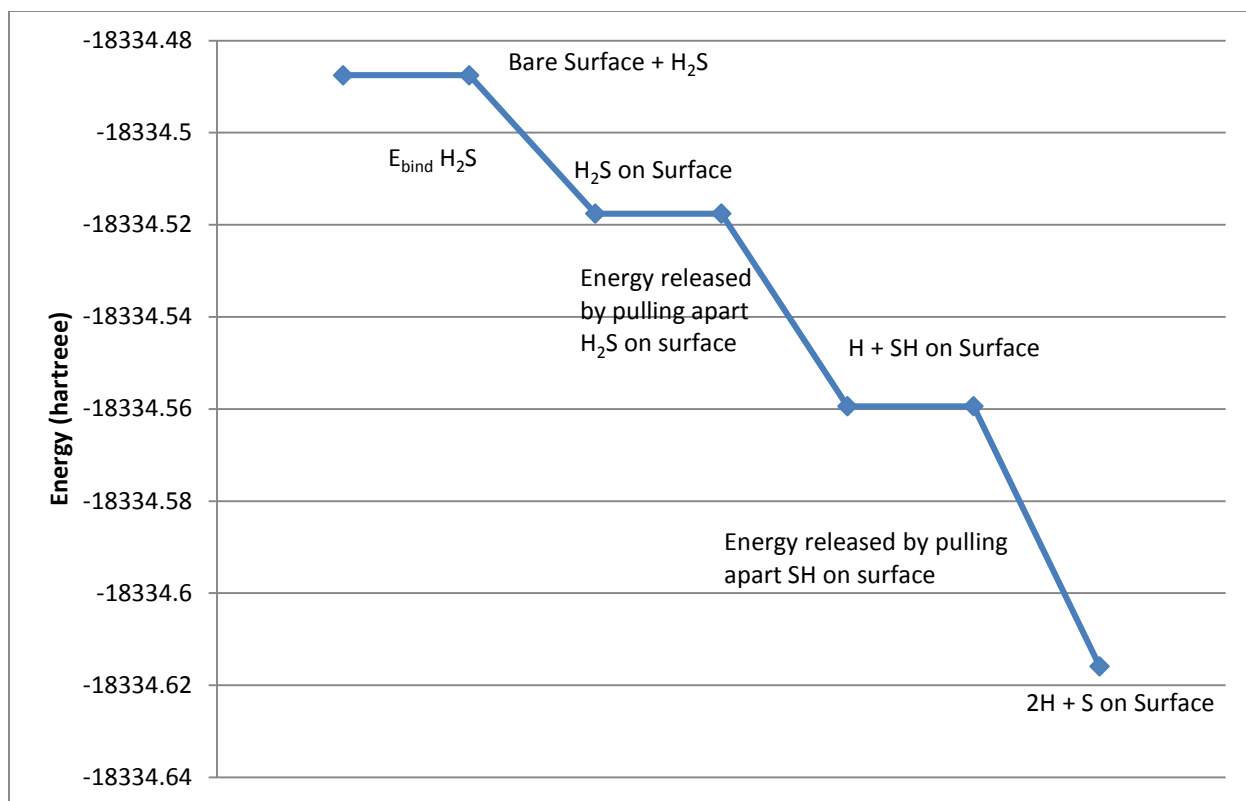


Figure 6: Energy of Adsorption for various H₂S species

Binding energy calculation:

$$E_{\text{bind}} = E_{\text{surface+molecule}} - E_{\text{surface}} - E_{\text{molecule}}$$

The energy of binding for various adsorbates was found and compared to literature values when available. The calculated binding energies matched up well with those found in the literature except for one case, H_2S in the HCP binding site. This is possibly an outlier, as the agreement with the rest of the figures is within a reasonable margin. The top layer being copper instead of palladium in general led to a slight decrease in binding energy, as was expected. Other reports consistently found that copper can add favorable physical traits, such as mechanical strength and resistance to sulfur poisoning, but it comes at the cost of permeability. The same is generally true in the case of the second layer down being copper atoms; the binding energy is less favorable in most cases because pure palladium is more hydrogen selective.

Table 3: Binding Energies of Pd(111). All Energies in Hartree, Except Molecule and Binding Energies (in eV).

Name	Surface+Molecule @ 2E-6	Bare Surface	Molecule	Ebind	Literature Ebind
Pd(111)Shcp	-18333.3973	-18323.09543	-10.10453753	-5.369825394	-4.77
Pd(111)Sfcc	-18333.3986	-18323.09543	-10.10453753	-5.405092639	-4.85
Pd(111)H2Sfcc	-18334.50363	-18323.09543	-11.39208489	-0.43850572	-0.4
Pd(111)H2Shcp	-18334.51759	-18323.09543	-11.39208489	-0.818303754	-0.51
Pd(111)H2Stop	-18334.50088	-18323.09543	-11.39208489	-0.36376468	-0.52
Pd(111)COhcp	-18344.84887	-18323.09543	-21.67796423	-2.053701218	-2.02
Pd(111)COfcc	-18344.86246	-18323.09543	-21.67796423	-2.423626985	-2.04
Pd(111)SHbridge	-18333.95076	-18323.09543	-10.74350247	-3.042970782	-3.02
Pd(111)Hfcc	-18323.70409	-18323.09543	-0.583025693	-0.697499318	-0.6
Pd(111)H2Otop	-18340.30889	-18323.09543	-17.22226535	-0.239682721	-0.22

(H_2S top, SH bridge: Alfonso, D 2005; S HCP, S FCC: Alfonso, D 2003; H_2S FCC, H_2S HCP, H FCC: Hyman; H_2O Top, CO HCP, CO FCC: Sakong)

Table 4: Binding Energies of Copper Top Layer. All Energies in Hartree, Except Molecule and Binding Energies (in eV).

Name	Suface+Molecule @ 2E-6	Bare Surface	Molecule	Ebind
CulayerH2Sfcc	-15486.10618	-15474.69763	-11.39208489	-0.447841261
CulayerH2Shcp	-15486.10147	-15474.69763	-11.39208489	-0.319701614
CulayerH2Sstop	-15486.10668	-15474.69763	-11.39208489	-0.461504684
CulayerH2Sbridge	-15486.10299	-15474.69763	-11.39208489	-0.361115259
CulayerSHbridge	-15485.5511	-15474.69763	-10.74350247	-2.992223835
CulayerSHfcc	-15485.55443	-15474.69763	-10.74350247	-3.082783437
CulayerSHhcp	-15485.55053	-15474.69763	-10.74350247	-2.976760161
CulayerSHtop	-15485.54515	-15474.69763	-10.74350247	-2.83025914
CulayerSfcc	-15484.97557	-15474.69763	-10.10453753	-4.718508458
CulayerShcp	-15484.96961	-15474.69763	-10.10453753	-4.556205561
CulayerSstop	-15484.97291	-15474.69763	-10.10453753	-4.646026575
CulayerSbridge	-15484.97487	-15474.69763	-10.10453753	-4.699425669
CulayerHfcc	-15475.29586	-15474.69763	-0.49913191	-2.696425223
CulayerHbridge	-15475.29056	-15474.69763	-0.49913191	-2.552170083
CulayerHhcp	-15475.29571	-15474.69763	-0.49913191	-2.692312216
CulayerHtop	-15475.27071	-15474.69763	-0.49913191	-2.012207659

Table 5: Binding Energies of Copper Second Layer. All Energies in Hartree, Except Molecule and Binding Energies (in eV).

Name	Suface+Molecule @ 2E-6	Bare Surface	Molecule	Ebind
Culayer2H2Otop	-15492.03975	-15474.81084	-17.22226535	-0.180652686
Culayer2Hfcc	-15475.42131	-15474.81084	-0.49913191	-3.029506646
Culayer2SHbridge	-15485.65905	-15474.81084	-10.74350247	-2.849104577
Culayer2COfcc	-15496.5761	-15474.81084	-21.67796423	-2.375317708
Culayer2H2Sstop	-15486.22748	-15474.81084	-11.39208489	-0.668093032
Culayer2Sfcc	-15485.10185	-15474.81084	-10.10453753	-5.074102382

Conclusions and Recommendations:

The effects of copper alloys with a palladium membrane were investigated using DFT. The preferred binding sites, binding energies, and energies of adsorption were determined. The addition of copper to a pure palladium membrane has both positive and negative impacts on the performance of the membrane for hydrogen separation. On the top layer, copper provides resistance to sulfur poisoning and physical resilience, but reduces the binding energy for adsorbates by 2-40% (with most values between 15-20%). The effects of copper as a second layer in the membrane were also studied and found to be similar to those of the top layer copper experiments. The bonding energy of most adsorbates diminished, and this layer does not provide the additional benefit of sulfur poisoning resistance on the surface. Thus, a second layer of copper is not ideal, as it reduces the overall yield of hydrogen with only some of the physical benefits copper can bring to the top layer. If the only objective is to yield as much hydrogen from a process as possible, alloying a palladium membrane with copper is suboptimal. However, if cost and durability of the membrane are also factors, a Pd-Cu alloy can produce cheaper, longer lasting membranes.

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Appendices

CP2K Input Sample:

```
&FORCE_EVAL
METHOD Quickstep
&DFT
UKS
#MULTIPLICITY 1
BASIS_SET_FILE_NAME ./GTH_BASIS_SETS_5-12-10
POTENTIAL_FILE_NAME ./GTH_POTENTIALS_5-12-10
WFN_RESTART_FILE_NAME x.wfn
&MGRID
CUTOFF 300
NGRIDS 5
&END MGRID
&QS
WF_INTERPOLATION ASPC
# WF_INTERPOLATION PS
EXTRAPOLATION_ORDER 3
&END QS
&SCF
EPS_SCF 1.E-6
SCF_GUESS RESTART
MAX_SCF 500
&OT T
PRECONDITIONER FULL_SINGLE_INVERSE
```

```
#MINIMIZER CG
MINIMIZER DIIS
LINESEARCH 3PNT
&END OT
&END SCF
&XC
  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
&END XC
&PRINT
&END PRINT
&END DFT
&SUBSYS
  &CELL
    ABC 25.0 25.0 25.0
  &END CELL
#####
# CHANGE COORDINATES HERE
#####
  &COORD
C 0.0000 0.0000 0.0000
H 0.6312 0.6312 0.6312
H -0.6312 -0.6312 0.6312
H -0.6312 0.6312 -0.6312
H 0.6312 -0.6312 -0.6312
  &END COORD
#####
```

```

&KIND C
  BASIS_SET TZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q4
&END KIND

&KIND H
  BASIS_SET TZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q1
&END KIND

&KIND O
  BASIS_SET TZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q6
&END KIND

&KIND N
  BASIS_SET TZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q5
&END KIND

&END SUBSYS

&END FORCE_EVAL

&GLOBAL
#####
# CHANGE PROJECT NAME HERE
#####
PROJECT ch4
#####
RUN_TYPE GEO_OPT
# RUN_TYPE ENERGY
PRINT_LEVEL LOW

```

&END GLOBAL

&MOTION

&GEO_OPT

MAX_ITER 500

MAX_FORCE 0.0009725

OPTIMIZER BFGS

&END GEO_OPT

&END MOTION

Examples of Surface Views:

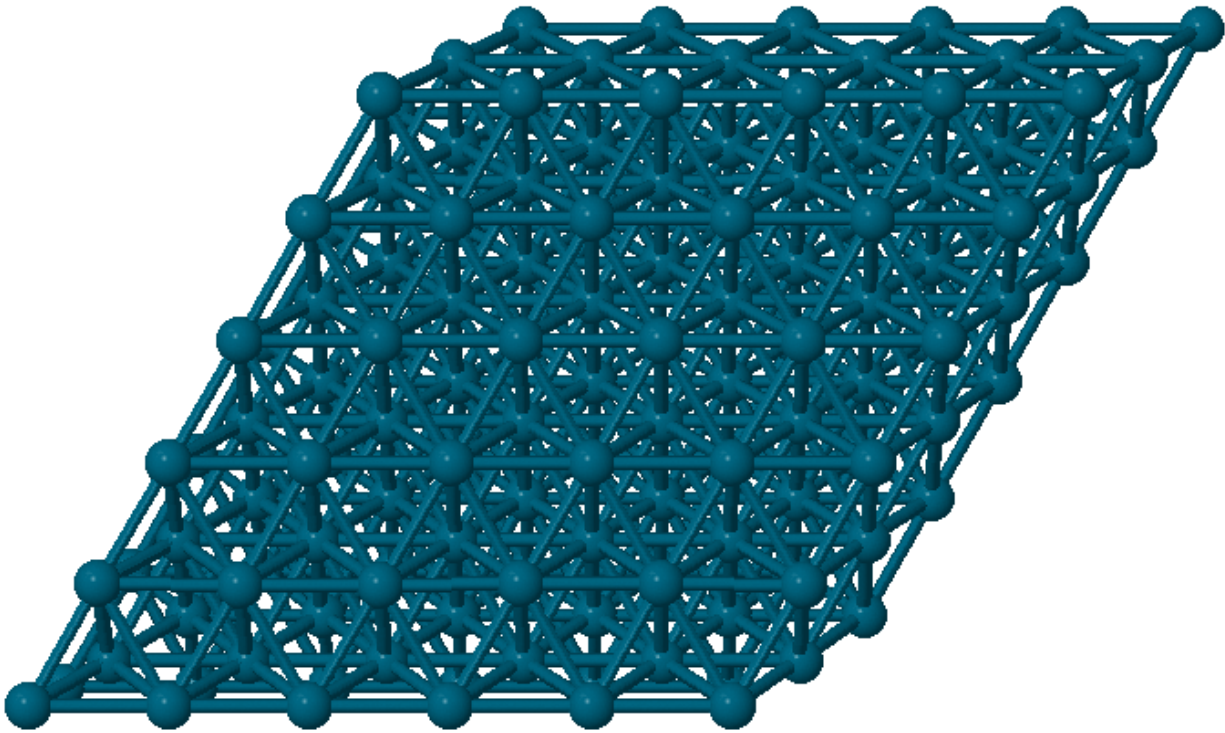


Figure 7: Pd(111) Surface (Top View)

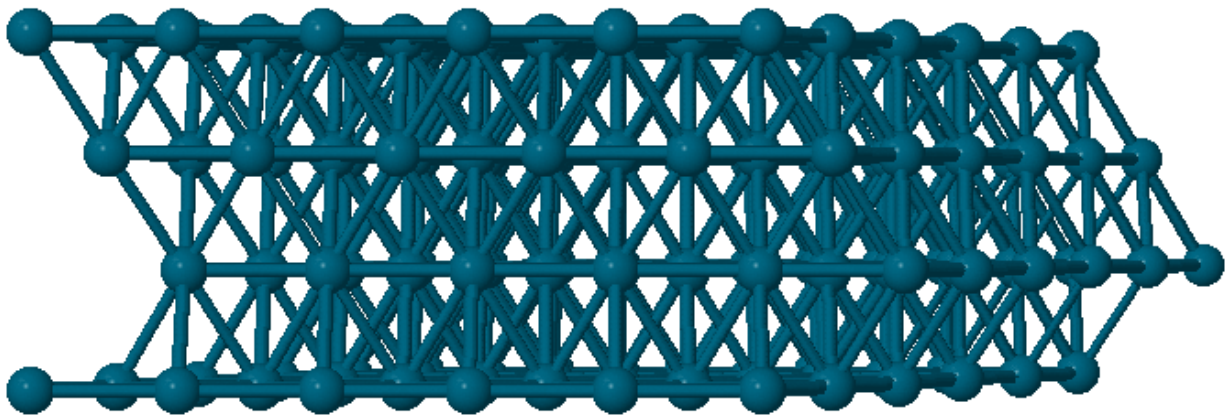


Figure 8: Pd(111) Surface (Side View)

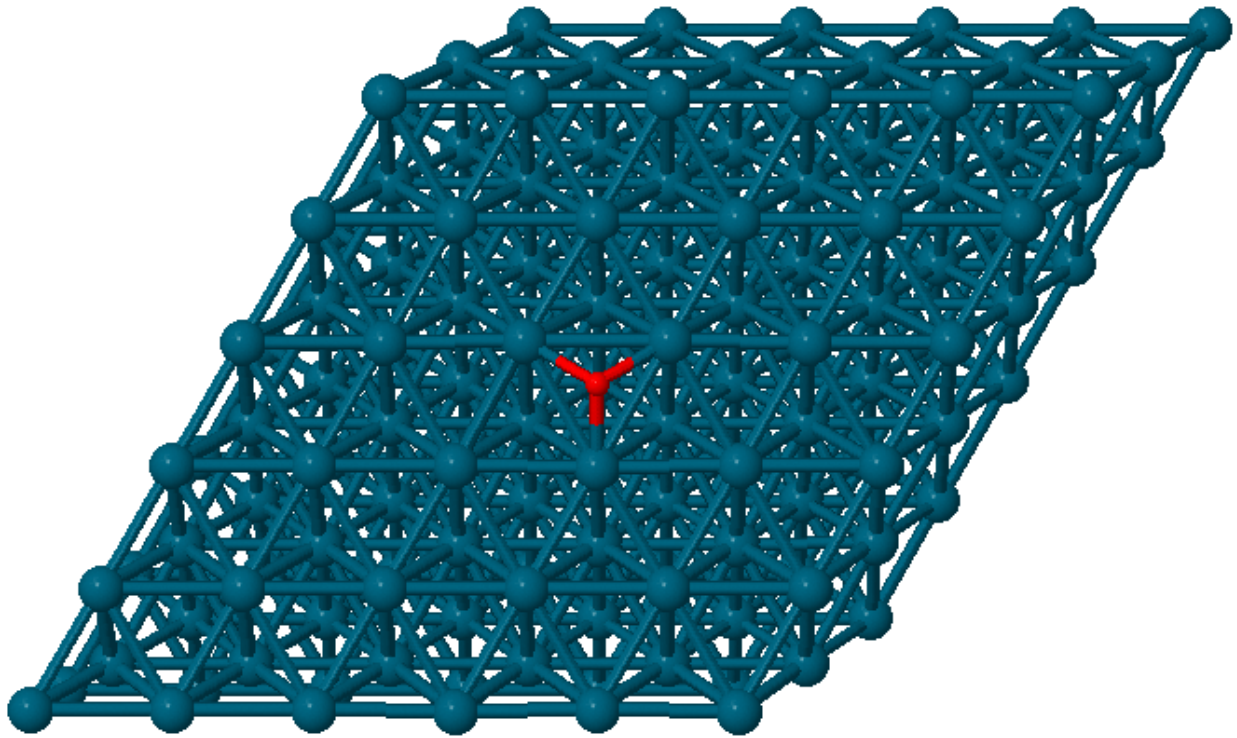


Figure 9: Pd(111) with CO in the FCC Site (Top View)

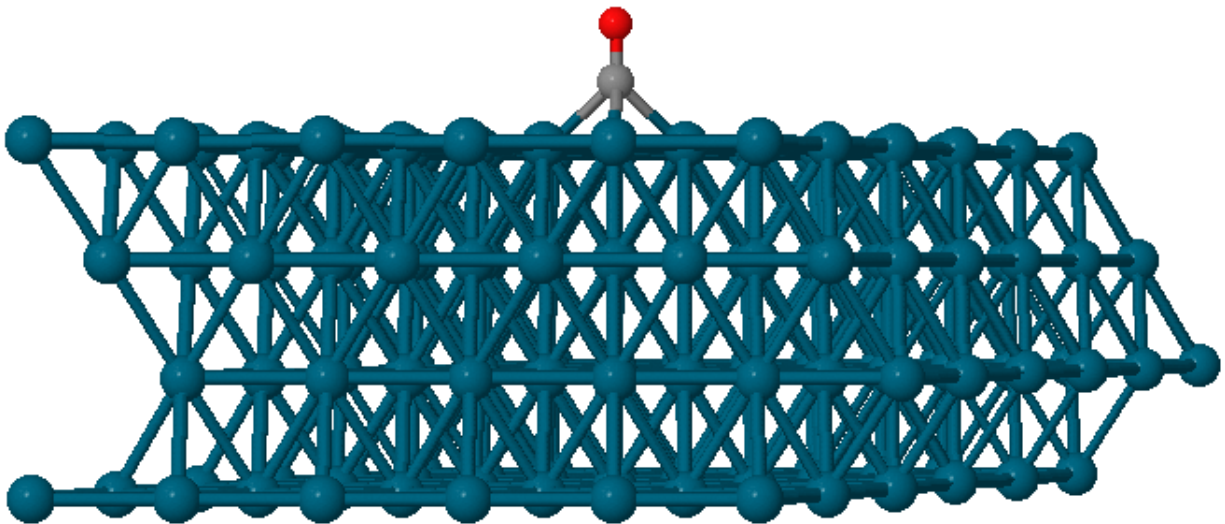


Figure 10: Pd(111) with CO in the FCC Site (Side View)

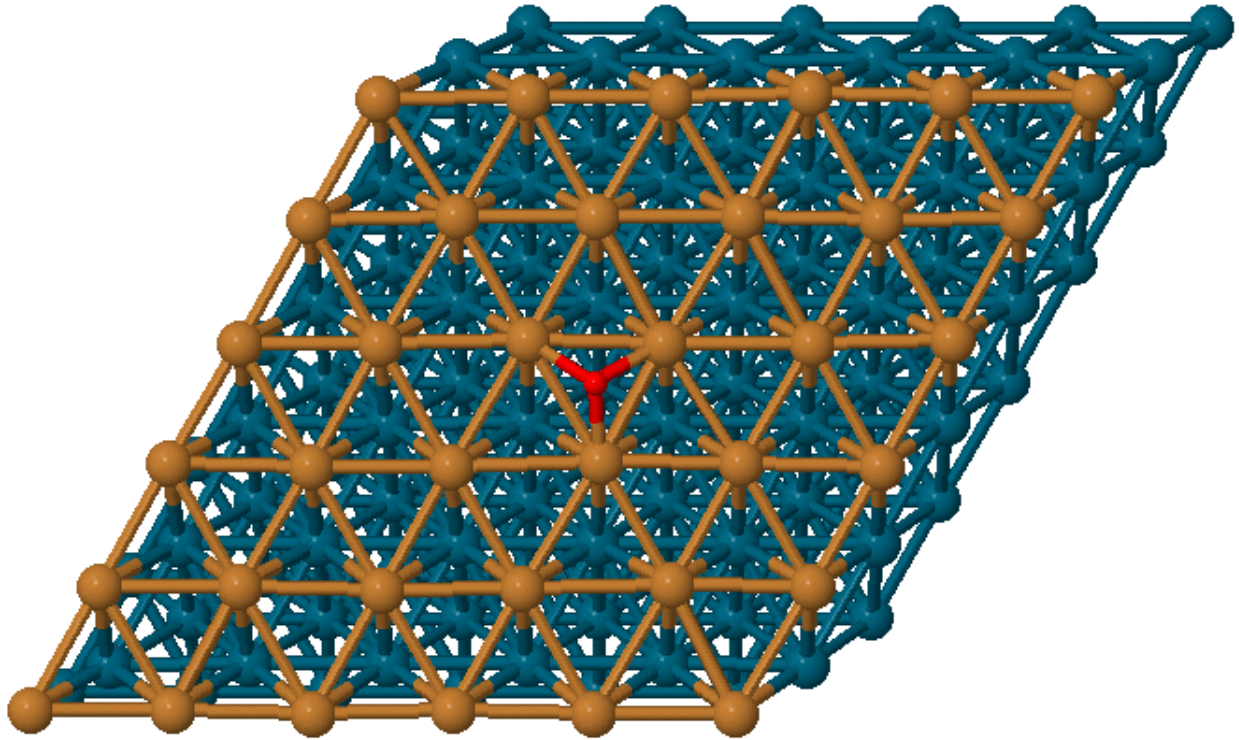


Figure 11: Cu layer on Pd(111) with H in the FCC Site (Top View)

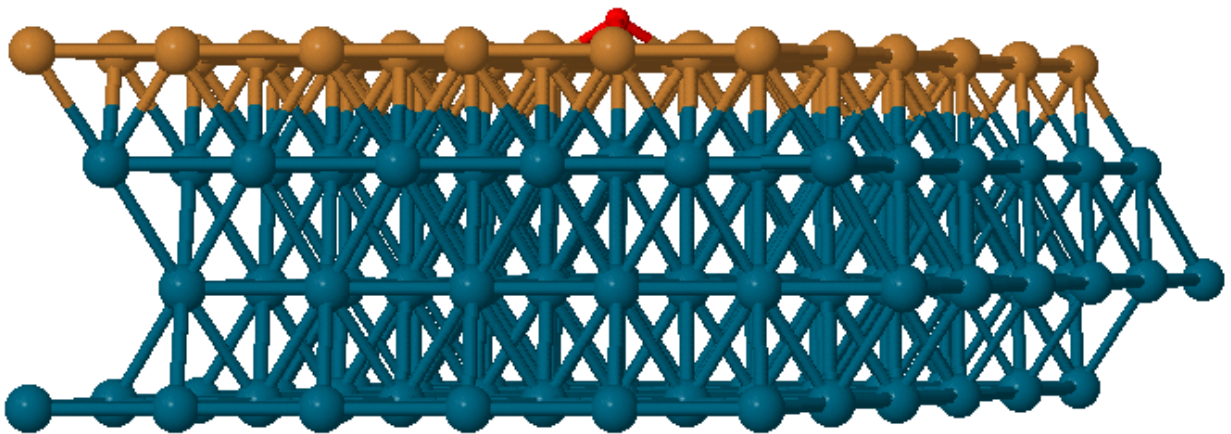


Figure 12: Cu layer on Pd(111) with H in the FCC Site (Side View)