Adsorption of Phenol on Fe (110) and Pd (111) from First Principles

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Abstract

The adsorption of phenol on the Fe (110) and Pd (111) surfaces was studied using density functional theory with the inclusion of van der Waals corrections. Model structures with the phenol adsorbing both via the aromatic ring (parallel) and via the oxygen functional group (perpendicular) were studied. The parallel adsorption sites were found to be significantly more favorable than the perpendicular sites on both surfaces, with the Pd (111) surface binding stronger with the adsorbate than the Fe (110) surface. The preference of the parallel sites over the perpendicular sites was found to be due to the increased amount of charge transfer between the surface and adsorbate in the parallel configuration through the aromatic ring. Comparing the differential charge density distributions for phenol's adsorption on the Fe (110) and Pd (111) surfaces shows that there is a small amount of electronic exchange that occurs between the oxygen atom and the Fe surface, while the Pd surface exchanges electrons with the hydroxyl group's hydrogen atom instead. Overall, our results show that the Fe (110) surface produces a

greater degree of distortion of the C-O bond while the Pd surface has a stronger surface-adsorbate interaction.

Keywords

Density Functional Theory; Phenol Adsorption; Fe (110); Pd (111); van der Waals Corrections

1. Introduction

Aromatic molecules form a large group of cyclic molecules characterized by a planar cloud of π electrons[1] and are used widely in industry as precursor chemicals. Because of their cloud of π electrons, these compounds are known to strongly interact with numerous surfaces, increasing the usefulness of such compounds by providing new ways to specifically target key bonds, thereby increasing selectivity, through heterogeneous catalysis or by changing the properties of surfaces for applications in semiconductors.[2] In order to better understand and characterize the aromatic compound to surface interactions, as well as interpret experimental results, first principle modeling techniques, like density functional theory (DFT), are used. To date, the majority of adsorption studies on aromatic compounds involve the adsorption of benzene on numerous pure metal[2], bimetallic[3, 4], and non-metal surfaces[5-7]. Few studies have examined the effects of substituted benzenes or other aromatic compounds on the surface-adsorbate interactions.[2, 8, 9] In this study, we examine phenol's adsorption on two metal surfaces as phenol is a common intermediate species in the hydrodeoxygenation of bio-oil phenolics[10]. The adsorption of phenol has been previously studied on Ni (111), (211), and (110)[11, 12]; Pt (111) and (211)[10]; Rh (111) and (211)[10]; Pd (111)[13]; graphite (0001)[14]; and alumina (0001)[14].

For the metal surfaces, both the parallel and perpendicular adsorption of phenol was examined on the Ni[11, 12], Pt[10], and Rh[10] surfaces while the Pd[13] surface study

examined only the parallel adsorption of phenol. On the flat (111) metal surfaces [10, 11, 13], the parallel adsorption of phenol occurs with the aromatic ring in the bridge 30° site. For the noble metals (Pt, Pd, and Rh), the hydroxyl group prefers to adsorb above a nearby bridge site, while the hydroxyl group above the (111) Ni surface prefers adsorption at a nearby top site. On each metal, the hydroxyl group is distorted away from the metal surface and the hydrogen in the functional group is tilted towards the metal surface. In addition to the flat surfaces, the adsorption of phenol was studied on the stepped (211) surface for the Pt, Rh and Ni metals and the kinked (110) surface for the Ni metal. On the (211) surface, the perpendicular adsorption of phenol had a stronger adsorption energy relative to the flat surface[12] while the parallel adsorption of phenol was weaker on the stepped surface than on the flat surface[10]. Only the perpendicular adsorption of phenol was studied on the (110) Ni surface and had a similar adsorption strength to the perpendicular adsorption on the stepped surface.

For the non-metal surfaces studied, the phenol configuration on graphite (0001) was found to have a parallel ring adsorption while the alumina (0001) surface interacts with phenol through the oxygen group in a perpendicular configuration.[14] On the graphite (0001) surface, phenol was found to have a weak adsorption energy, even though the ring was parallel to the surface. The application of van der Waals corrections to the system increased the overall adsorption energy and decreased the distance from adsorbate to surface, but the structure of phenol remains unaffected by the surface interaction. Moving to the alumina (0001) surface, there is a distinct increase in the adsorption energy of phenol relative to the graphite surface. Also, the adsorption configuration switches from parallel to the surface into a perpendicular configuration with the surface to adsorbate interactions occurring solely between the surface and

hydroxyl group. The addition of van der Waals corrections to the alumina system has a smaller effect on the adsorption energy than the graphite surface.

Overall, these results show that on metal surfaces the parallel adsorption of phenol is significantly stronger than the perpendicular configurations and that the stepped surfaces weaken the adsorption of parallel phenol while strengthening the adsorption of perpendicular phenol. In addition to these trends, phenol's parallel adsorption configuration is governed mostly by the symmetry of the surface and not the metal type, e.g. that the aromatic ring configuration will be on the bridge 30° site on the (111) surface. This is consistent with work performed by Norskov, et al.[15] which suggests that the adsorbate structure is nearly independent of the metal type for a given metal surface structure (e.g. flat versus stepped). The major difference in adsorption structure between the metal types is the placement of the hydroxyl group on the surface. In the noble metal surfaces (Pt, Pd, and Rh), the hydroxyl group prefers to adsorb above a bridge site which reduces the interaction between the surface and oxygen species.[10, 13] On the Ni base metal surface, the hydroxyl group preferentially adsorbs atop a surface Ni atom which maximizes the interaction between the surface and the oxygen species.[11] These results suggest a trend in the binding of the hydroxyl group in phenol to metal surfaces based on the type of metal examined, e.g. base versus noble metal, which could significantly affect the catalytic mechanisms promoted by each surface. However, the energetic, geometric, and electronic characterization of phenol on other transition metal surfaces is required before a significant trend in adsorption configuration based on metal type can be established.

In this work, we characterize the energetic, geometric, and electronic effect that the Fe (110) and Pd (111) have on the adsorption of phenol both parallel and perpendicular to the flat surfaces. Numerous configurations for the parallel and perpendicular adsorption of phenol were

examined on each surface and the most favorable of each structure type was then examined using van der Waals corrections. We show that the parallel adsorption of phenol is significantly stronger than the perpendicular adsorption of phenol on both surfaces which agrees with the adsorption results for phenol on the flat Ni[11], Pt[10], and Rh[10] surfaces. The differential charge density distribution, partial density of states, and partial charge density for each of the most favorable structures was also examined and showed that for the parallel adsorption of phenol, the oxygen in the hydroxyl group weakly binds to the nearest Fe top site on the Fe (110) surface while the hydrogen in the hydroxyl group weakly binds to the nearest Pd top site on the Pd (111) surface. The difference in the hydroxyl group's binding preference on the Fe (110) and Pd (111) surfaces agrees with the results for the flat Ni[11], Pt[10], and Rh[10] surfaces and supports the trend that base metals preferentially bind directly with the oxygen in the phenol adsorbate while noble metals reduce the oxygen to surface interactions.

2. Methods

The theoretical calculations presented in this work were performed using the Vienna *Ab Initio* Simulation (VASP) package[16, 17]. The core electrons were treated using VASP's projector augmented waves (PAW)[18, 19] in order to solve the Kohn-Sham equations. The initial density functional theory (DFT) calculations (without van der Waals corrections) were performed using the generalized gradient approximation (GGA) which was parameterized with the Perdew-Wang 91 (PW91)[20, 21] functional. After the most favorable configurations for the parallel and perpendicular adsorption of phenol on Fe (110) and Pd (111) were identified using the PW91 functional, these most favorable configurations were examined using the optB88-vdW[22, 23] exchange-correlation functional to account for van der Waals corrections which has shown to strongly affect the adsorption energies of both physisorbed and chemisorbed species

[24, 25]. When using the optB88-vdW, we switched to the Perdew, Burke, and Ernzerhof (PBE)[26, 27] functional to generate the PAW core potentials as we found that the adsorption energy results for the optB88-vdW functional with the PW91 generation of the PAW core potentials varied significantly with minor changes to the model's vacuum thickness.

The surfaces were modeled using p(4x4) supercells in order to minimize the lateral interactions between the repeating supercells due to VASP's implementation of periodic boundary conditions. The near surface structure was modeled using four metal layers, the bottom two of which were kept fixed during the optimization. This number of metal layers was found to be sufficient for comparing the adsorption energies in order to identify the most favorable sites. All other atoms, including the adsorbates atop the metal slab, were allowed to relax in order to find the optimum structural configuration. In addition to these parameters, the repeating supercells in the $\hat{z}$ direction were separated by either ~ 13 or $18 \text{ \AA}$ of vacuum when studying either the parallel or perpendicular adsorption of phenol, respectively. The bulk fcc Pd and bcc Fe unit cells were optimized and the calculated lattice constants were found to be 3.957 and $2.827 \text{ \AA}$, respectively. These results agree well with previous work[28-30] and were found to be relatively unaffected by the van der Waals corrections.

These model supercells were sampled using a (3x3x1) Monkhorst-Pack[31] mesh and the kinetic energy cutoff for the plane wave basis set was set at 400 eV . The Methfessel-Paxton[32] ($N=1$) smearing method was used with a smearing width of 0.1 eV to improve convergence, and the total energy was extrapolated to zero Kelvin. As both Fe and O are known to be ferromagnetic, spin polarization effects were accounted for in all calculations. Also, the effect of dipole interactions between the consecutive supercells was considered to be significant and dipole corrections were imposed in each calculation performed.[33] The total energy was

converged to at least 10^{-4} eV for all systems and the systems were considered to be fully optimized when the forces between atoms were less than 0.03 eV/Å. For the density of states calculations, the k-points grid was increased to (6x6x1) and (5x5x1) for the Fe (110) and Pd (111) surfaces, respectively, in order to increase the accuracy of the resulting density of states distributions.

All of the studied adsorption configurations of phenol on the surfaces were compared using the adsorption energy as defined by: $E_{ads} = E_{adsorbates + surface} - E_{surface} - E_{adsorbate}$, where $E_{adsorbates + surface}$, $E_{surface}$, and $E_{adsorbate}$ are the total energies of the adsorbed surface system, the clean surface, and the gas phase adsorbates for the given system. Each adsorption site was also evaluated using the distortion energy which is the energy the adsorbate molecule gains due to its geometric distortion from the interaction with the metal surface[34]. The distortion energy will be calculated according to: $E_{dist} = E_{Molecule}^{Distorted\ Geometry} - E_{Molecule}^{Free\ Gas\ Geometry}$, where $E_{Molecule}^{Distorted\ Geometry}$ and $E_{Molecule}^{Free\ Gas\ Geometry}$ are the energies of phenol in the gas phase with its optimized geometry and the distorted geometry caused by interaction with the surfaces studied here. This energy difference allows for a second evaluation of the strength of the interaction between the adsorbate and the surface.

The electronic exchange that occurred upon the adsorption of phenol on each surface was examined by calculating the differential charge density as defined by:

$$\Delta\rho = \rho_{adsorbate+surface} - \rho_{surface} - \rho_{adsorbate} \quad (1)$$

where $\rho_{adsorbate+surface}$, $\rho_{surface}$, and $\rho_{adsorbate}$ are the charge distributions for the optimized structure of the adsorbed system and the surface and gas phase adsorbate fixed in their adsorption geometries. In order to better quantify the electronic interactions observed between phenol and the Fe (110) and Pd (111) surfaces, we integrated the absolute value of the differential charge

density over the entire unit cell in order to obtain the total amount of charge transferred between the adsorbate and surface (Q) according to:[12]

$$Q=1/2\int d\vec{r}|\Delta\rho(\vec{r})| \quad (2)$$

where $\Delta\rho(\vec{r})$ is the differential charge density of the system. This analysis allows us to determine the mean absolute displacement of charge in the system with the addition of the factor of 1/2 which corrects for the double counting of charge due to the absolute value around $\Delta\rho(\vec{r})$ (e.g. a charge gain in one location is identical to charge loss in another and if both are counted, then the calculate amount of charge displaced upon adsorption is twice as large as the actual amount of charge displaced). Larger the value of Q , the more charge was exchanged between the surface and phenol. Finally, the change in the surface metal's electronic structure upon phenol's adsorption was evaluated using the d-band center and width according to:[4, 35]

$$\varepsilon_d = \int^{\varepsilon_{Fermi}} E\rho(E) dE / \int^{\varepsilon_{Fermi}} \rho(E) dE \quad (3)$$

$$w_d = \left(\int^{\varepsilon_{Fermi}} E^2 \rho(E) dE / \int^{\varepsilon_{Fermi}} \rho(E) dE \right)^{1/2} \quad (4)$$

where E is the given energy, $\rho(E)$ is the density of electronic states at the given energy, and ε_{Fermi} is the Fermi level.

3. Results and Discussion

3.1 Parallel Phenol Adsorption

The parallel adsorption of phenol on the Fe (110) surface can occur with the aromatic ring being centered on the 3-fold (3F), long bridge (LB), short bridge (SB), or top (T) sites with the ring oriented either in line with the perpendicular Fe rows (0°) or rotated by 30° , identical to the adsorption sites for benzene on this surface[4]. Each of these ring positions has several rotations with respect to the placement of the OH functional group and each site is labeled based

on the OH group's placement (LB, SB, 3F, and T). These adsorption sites are shown in Figure 1a and their corresponding adsorption energies (relative to gas phase phenol) are shown in Table 1.

Figure 1. Parallel adsorption sites for phenol on the (a) Fe (110) and (b) Pd (111).

Table 1. Adsorption energies for phenol (parallel) on the Fe (110) and Pd (111).^a The adsorption energies are shown in the order in which the structures appear in Figure 1. The *U* symbol marks an adsorption site as unstable.

Fe (110)		Pd (111)	
Site	E _{ads} (eV)	Site	E _{ads} (eV)
3-fold 0°	-1.06/ <i>U</i> / <i>U</i>	bridge 0°	<i>U</i> / <i>U</i> / <i>U</i>
3-fold 30°	-1.12/-1.12/-1.13	bridge 30°	-1.16/-1.28/-1.30
long bridge 0°	-1.04/-1.02/-1.05	fcc 0°	-1.07
long bridge 30°	-1.15/-1.07/ <i>U</i>	fcc 30°	<i>U</i> / <i>U</i>
short bridge 0°	-0.97/-1.00/-0.90	hcp 0°	-1.13
short bridge 30°	<i>U</i> / <i>U</i> / <i>U</i>	hcp 30°	<i>U</i> / <i>U</i>
top 0°	<i>U</i> / <i>U</i> / <i>U</i>	top 0°	-0.20
top 30°	<i>U</i> / <i>U</i> / <i>U</i>	top 30°	-0.18

^a adsorption energy, E_{ads}.

From these results, it is clear that the most stable adsorption site for phenol on the Fe (110) surface is the LB 30° site with the OH group in the T position. For this site, the average length for the C-C bonds in the adsorbate is 1.45 Å with the C-O bond distance increasing by ~0.03 Å from gas phase phenol to 1.40 Å. Also, the average metal-adsorbate distance is 2.05 Å for this site. Compared to the adsorption of benzene on the Fe (110) surface[4], phenol has a slightly weaker adsorption by ~0.06 eV and the favored ring adsorption site switches from the 3F 30° site to the LB 30° site.

The parallel adsorption of phenol on the Pd (111) surface can occur with the aromatic ring being centered on the bridge (B), fcc (F), hcp (H), or top (T) sites with the ring oriented either in line with the perpendicular Pd rows (0°) or rotated by 30°, identical to the adsorption sites for benzene on this surface[13]. Each of these ring positions can have several rotations with respect to the placement of the OH functional group and each site is labeled based on the OH group's placement (B, F, H, or T). These adsorption sites are shown in Figure 1b and their corresponding adsorption energies (relative to gas phase phenol) are shown in Table 1. These

results show that the most stable adsorption site for phenol on the Pd (111) surface is the B 30° site with the OH group in the B2 position. For this site, the average lengths for the C-C bonds in the adsorbate are 1.44 Å with a C-O bond distance of 1.37 Å. Also, the average metal-adsorbate distance is 2.15 Å for this site. Compared to the adsorption of benzene on the Pd (111) surface, phenol has a slightly weaker adsorption by ~0.13 eV and the favored ring adsorption site remains identical to that for benzene.

3.2 Perpendicular Phenol Adsorption

The perpendicular adsorption of phenol on the Fe (110) surface occurs via the oxygen functional group as the C-H bonds are known to be repelled by Fe surfaces.[4, 36] This adsorption can occur through the oxygen bonding with the 3F, LB, SB, or T sites. In addition to these sites for the oxygen adsorption, the H (labeled H_s) in the C-H bond that is adjacent to both the C-OH bond and the surface can also interact with the 3F, LB, SB, and T sites. These configurations are shown in Figure 2a and the resulting adsorption energies (relative to gas phase phenol) are found in Table 2.

Table 2. Adsorption energies for phenol (perpendicular) on the Fe (110) and Pd (111) surfaces.^a The adsorption energies are shown in the order in which the structures appear in Figure 2. The *U* symbol marks an adsorption site as unstable.

Fe (110)		Pd (111)	
Site	E _{ads} (eV)	Site	E _{ads} (eV)
3-fold	<i>U/U/U/U</i>	bridge	<i>U/U/U/-0.104</i>
long bridge	<i>U/U/U/U</i>	fcc	-0.089/-0.086/-0.102
short bridge	-0.095/ <i>U/U</i>	hcp	-0.080/-0.086/-0.097
top	-0.168/-0.187/-0.171/-0.158/-0.189	top	-0.157/-0.152

^a adsorption energy, E_{ads}.

Figure 2. Perpendicular adsorption sites for phenol on the (a) Fe (110) and (b) Pd (111). The sphere coloring is identical to that presented in Figure 1.

From the resulting adsorption energies, it is clear that the most stable adsorption site for perpendicular phenol on the Fe (110) surface is the T site with H_s in the SB position. However, for this system, there is only a very small energy difference between all of the stable sites with all of the sites exhibiting physisorption characteristics. For the T-SB site, the average length for the C-C bonds in the adsorbate are 1.39 Å with the C-O bond distance increasing by ~0.02 Å from gas phase phenol to 1.39 Å. Also, the O-M distance was 2.40 Å for this site. Compared to the parallel adsorption of phenol on the Fe (110) surface, perpendicular phenol has a significantly weaker adsorption by ~1 eV and the average C-C bond length is equivalent to that

of gas phase phenol. Finally, the T-SB adsorption site results in a phenol configuration with no appreciable deformation to the carbon ring while the C-O bond is still distorted.

The perpendicular adsorption of phenol on the Pd (111) surface will also occur through the oxygen functional group as the C-H bonds are known to be deflected by the surface.[13, 37] Adsorption through the oxygen group will have the oxygen interacting with the B, F, H, or T sites. As with the Fe (110) surface, the aromatic ring can have multiple configurations based on how the H_s interacts with the surface (via the B, F, H, or T sites). These adsorption sites are shown in Figure 2b and their corresponding adsorption energies (relative to gas phase phenol) are shown in Table 2. These results show that the most stable adsorption site for phenol on the Pd (111) surface is the T site with H_s in the B position. For this site, the average lengths for the C-C bonds in the adsorbate are 1.40 Å with a C-O bond distance of 1.38 Å. Also, the O-M distance is 2.47 Å for this site. Compared to the parallel adsorption of phenol on the Pd (111) surface, perpendicular phenol has a significantly weaker adsorption by ~1.1 eV with both the C-C and C-O bonds remaining largely unaffected by the surface interaction. These results suggest that the perpendicular adsorption of phenol on the Pd (111) surface is physisorption, similar to that found on the Fe (110) surface.

3.3 Van der Waals Corrections

The most stable adsorption sites identified in sections 3.1 and 3.2 were examined using van der Waals corrections (optB88-vdW functional) as these corrections were shown to have a large effect on the adsorption strength of the molecules, bringing the calculated adsorption energies of aromatics into greater agreement with experimental values.[25] In this section, we only examine the most stable adsorption sites calculated using the PW91 method as previous work by Hensley et al.[4] and Liu et al.[24] have shown that the preferential adsorption site does

not change with the inclusion of van der Waals corrections. The resulting adsorption energies and molecular structure details are shown in Table 3 for the LB 30°-T and T-SB sites on Fe (110) and the B 30°-B2 and T-B sites on Pd (111). The molecular structure details calculated using van der Waals corrections for gaseous phenol are also shown.

With the inclusion of the van der Waals corrections, it is clear that each of the adsorption configurations studied have been significantly stabilized, as shown in Table 3. For the Pd (111) surface, the parallel configuration's adsorption energy was found to increase by ~0.9 eV while the perpendicular configuration's adsorption energy increased by ~0.4 eV due to the stabilization effect of the van der Waals corrections. On the Fe (110) surface, the parallel configuration's adsorption energy was found to increase by ~0.8 eV while the perpendicular configuration's adsorption energy increased by ~0.4 eV due to the stabilization effect of the van der Waals corrections. This increase in the stabilization of the phenol adsorbates on both surfaces is similar to that seen for benzene's adsorption on Pt (111), Au (111)[25], and Fe (110)[4] using the optB88-vdW functional for van der Waals corrections. The most significant difference in van der Waals stabilization for phenol adsorption as compared to benzene's adsorption is in the perpendicular adsorption mode where the increase in the adsorption energy is not as significant as the other cases. This decrease in the van der Waals stabilization effect is likely related to the number of atoms in the adsorbate interacting with the surface as both benzene's and phenol's parallel adsorption on the surface has a large interaction with the carbon π -bonds and the surface metal states while only the oxygen atom interacts with the metal during phenol's perpendicular adsorption.

There are several distinct differences in the parallel adsorption of phenol on the Fe (110) and Pd (111) surfaces. First, the OH functional group prefers the configuration atop a surface

atom in the Fe surface while the functional group prefers the less interacting B site on the Pd (111) surface. This greater degree of OH-M interaction on the Fe (110) surface over the Pd (111) surface can be seen in the increase in the C-O bond distance on the Fe (110) surface while the C-O bond length remains constant on the Pd (111) surface. Also, the overall distortion of the phenol adsorbate is greater on the Fe (110) surface as seen in the ~ 0.2 eV increase in the distortion energy on Fe (110) relative to Pd (111). Second, while the adsorption of phenol is stronger on the Pd (111) surface, the average adsorbate-metal distance is smaller on the Fe (110) surface by ~ 0.1 Å. Overall, these results show that the Fe (110) surface produces a greater distortion of the parallel phenol's molecular structure, specifically the C-O bond, while phenol is bound stronger on the Pd surface as compared to the Fe surface.

For the perpendicular adsorption of phenol on the Fe (110) and Pd (111) surfaces, phenol was found to physisorb on the surfaces due to the significant decrease in both the adsorption energy and distortion energy for this system relative to the parallel configurations. On both surfaces, the C-O bond increases relative to its gas phase length; however, the C-O bond increase is 0.01 Å larger on the Fe (110) surface. Comparing the overall distortion of the adsorbate (E_{dist}), it is clear that neither surface significantly distorts the perpendicularly adsorbed phenol. In the perpendicular adsorption configuration, the Fe surface produces a slightly stronger adsorption energy for phenol as well as a smaller metal-adsorbate distance than the Pd surface. Overall, these results suggest that the C-O bond is weakened to a greater extent and there is a greater degree of surface-adsorbate interaction on the Fe surface compared to the Pd surface for perpendicularly adsorbed phenol.

Table 3. Adsorption energies, distortion energies, and molecular structure results for phenol adsorbed both parallel to and perpendicularly on the Fe (110) and Pd (111) surfaces, as well as

the molecular structure results for gaseous phenol.^a These results were calculated using van der Waals corrections with the optB88-vdW functional.

Gas Phase							
Site	E_{ads} (eV)	E_{dist} (eV)	$d_{\text{C-C}}$ (Å)	$d_{\text{C-O}}$ (Å)	$\theta_{\text{C-H}}$ (°)	$\theta_{\text{C-O}}$ (°)	$d_{\text{A-M}}$ (Å)
Gaseous Phenol	–	–	1.40	1.37	0, 1	2	–
Fe (110)							
Site	E_{ads} (eV)	E_{dist} (eV)	$d_{\text{C-C}}$ (Å)	$d_{\text{C-O}}$ (Å)	$\theta_{\text{C-H}}$ (°)	$\theta_{\text{C-O}}$ (°)	$d_{\text{A-M}}$ (Å)
LB 30° – T	-1.99	1.22	1.45	1.41	20, 28	13	2.04
T – SB	-0.62	0.02	1.40	1.40	0, 1	1	2.37
Pd (111)							
Site	E_{ads} (eV)	E_{dist} (eV)	$d_{\text{C-C}}$ (Å)	$d_{\text{C-O}}$ (Å)	$\theta_{\text{C-H}}$ (°)	$\theta_{\text{C-O}}$ (°)	$d_{\text{A-M}}$ (Å)
B 30° – B2	-2.23	1.04	1.44	1.37	17, 26	18	2.15
T – B	-0.59	-0.02	1.40	1.39	0, 1	1	2.38

^a adsorption energy, E_{ads} ; distortion energy, E_{dist} ; C-C bond length, $d_{\text{C-C}}$; C-O bond length, $d_{\text{C-O}}$; dihedral angle of hydrogen atoms, $\theta_{\text{C-H}}$; dihedral angle of the oxygen atom, $\theta_{\text{C-O}}$; and the perpendicular distance from adsorbate to surface, $d_{\text{A-M}}$.

3.4 Electronic Analysis

The electronic interactions between the phenol adsorbate and the metal surfaces were examined by calculating the differential charge density distribution (equation 1), partial density of states (PDOS), and several of the highest occupied molecular orbitals, along with the LUMO level, partial charge density distributions for the most favorable adsorption sites for the parallel and perpendicular adsorption of phenol on the Fe (110) and Pd (111) surfaces. The results from these analyses are shown in Figure 3 (differential charge density), Figures 4 and 6 (PDOS), and Figures 5 and 7 (partial charge distributions). For the PDOS analysis, only the results from a single adsorbate bonded surface metal atom (d-states), a carbon atom (p-states), and the oxygen atom (p-states) are shown. All other adsorbate bonded surface metal atoms' PDOS and aromatic ring carbons' PDOS were found to be nearly equivalent. Also, the spin up and spin down states for the C, O, and Pd atoms were found to be identical. Therefore, only the spin up and spin down states for the surface Fe are shown. All other graphs show only the spin up states and all of the PDOS results presented here were calculated using the optB88-vdW functional, despite the

nearly identical results for the PDOS without any van der Waals corrections (Figure S2). This lack of a change in the electronic structure of our models is consistent with work by Yildirim, et al.[38] which showed that, unless the van der Waals corrections switch the adsorption characteristic from physisorption to chemisorption, the van der Waals corrections do not significantly change the model system's electronic structure.

Figure 3. Differential charge density distributions for phenol adsorbed on (a) Fe (110) in the LB 30°-T site, (b) Pd (111) in the B 30°-B site, (c) Fe (110) in the T-SB site and on (d) Pd (111) in the T-B site. The isosurface was set at 0.0045 electrons/Å³ and the green or blue areas represent a gain or loss of charge. The calculations were performed with the optB88-vdW functional and the sphere coloring is identical to that presented in Figure 1.

The differential charge density results for the parallel adsorption of phenol of the Fe (110) and Pd (111) surfaces both show that a large degree of charge transfer occurs between the surfaces and the aromatic ring. The differential charge density distribution shown between the aromatic ring and surface are similar to that found for the adsorption of benzene on Fe (110) with van der Waals corrections[4] and on Pd (111) and Pt (111) without van der Waals corrections[37], as well as Pt (111) with van der Waals corrections[25]. It should be noted that for the differential charge density for the adsorption of benzene on the Pd (111) surface[37] the

authors only showed the distribution for benzene adsorbed on the Pt (111) surface, but they comment that the electronic interaction is the same on the Pd (111) surface as on the Pt (111) surface. The major difference in the differential charge density distributions comes from observing the interactions between the hydroxyl functional group and each metal surface. On the Fe (110) surface, a small amount of charge transfer is observed between the oxygen and the nearest Fe atoms. However, on the Pd (111) surface, the hydroxyl's hydrogen atom shows an interaction with the metal surface and the oxygen is slightly lifted away from the metal surface. The total amount of charge transferred between the surface and phenol upon adsorption (Q , equation 2) was found to be 1.36 e and 1.69 e for the Fe (110) and Pd (111) surfaces, respectively. These values for Q are consistent with previous work performed by Delle Site, *et al.*[39] where the parallel adsorption of benzene was studied on several Ni surfaces. The increase in the amount of charge transferred between the adsorbate and surface on Pd (111) accounts for the stronger adsorption energy of phenol relative to the Fe (110) surface.

The charge transfer between the surface and adsorbate, as seen from the differential charge density, has significantly decreased for the perpendicular adsorption of phenol on the Fe (110) and Pd (111) surfaces when compared with the parallel adsorption of phenol on those same surfaces. On both surfaces, as phenol adsorbs, charge is transferred between the surface and the oxygen atom. This charge transfer with the surface causes a small loss of charge from the hydroxyl group's hydrogen and the C-O bond as the highly electronegative oxygen gains charge to compensate for those binding with the surface. The major difference in the differential charge density distributions for the perpendicular adsorption of phenol on these surfaces is that there is a small gain of charge between the surface and adsorbate on the Fe (110) surface, while the Pd (111) surface shows no charge gain between the adsorbate and surface, but instead shows that the

surface Pd gains a small amount of charge. The total amount of the charge transferred between the surface and phenol upon adsorption (Q , equation 2) was found to be 0.43 e and 0.45 e for the Fe (110) and Pd (111) surfaces, respectively. These values for Q are consistent with previous work performed by Ghiringhelli, *et al.*[12] where the perpendicular adsorption of phenol was studied on several Ni surfaces. The nearly identical amount of charge transferred between the adsorbate and the Fe (110) and Pd (111) surfaces accounts for the nearly identical adsorption energy of phenol on both surfaces.

The results for the density of states for the parallel phenol configurations are shown in Figure 4. In this figure, the states are shown for one of the surface metal atoms that is directly interacting with two carbon atoms as these surface atoms showed the greatest distortion of the metal's PDOS. Also, all the carbon atoms' PDOS were found to be equivalent with the exception of the G2 peak which was not present in the carbon bonded to the oxygen and its para carbon companion. By examining the partial charge densities for gas phase phenol (Figure 5), it is clear that the absence of this peak in those carbon atom PDOS is due to the aromatic π orbital's distribution and that this distribution is similar to that observed for benzene[40]. However, for the benzene molecule, the G2 and G3 orbitals are degenerate, while the hydroxyl functional group in phenol causes a separation in the energy of these two distributions. Therefore, we have chosen to show the PDOS for a carbon ortho to the carbon bonded to the hydroxyl group in order to observe all of the carbon peaks. All other aspects of the carbons' PDOS were equivalent.

Figure 4. PDOS for phenol adsorbed parallel to (a) Fe (110) in the LB 30°-T site and (b) Pd (111) in the B 30°-B site. The spin up and spin down states for the adsorbate bonded Fe atom are shown along with only the spin up states of the C, O, and Pd as the spin down states for these atoms were found to be equivalent to the spin up states. The PDOS for each element are shown for both before (dotted line) and after (solid line) adsorption. These calculations were performed using the optB88-vdW functional and E_{Fermi} has been set to zero.

For the parallel adsorption case, we can see that the metal's d-states for both the Fe and Pd surface have slightly shifted to lower energies and that small peaks appear in the distributions at energies below -5 eV which correspond to overlaps with the phenol adsorbate's C and O p-

states. The shift in the metals' d-states can be seen more clearly by examining the change in the d-band center and width (equations 3 and 4, respectively) upon phenol's adsorption, as seen in Table 4.

Table 4. d-band center (spin up/spin down components) and d-band width (spin up/spin down components) on the metal surface atoms involved in the adsorption of phenol both parallel to and perpendicularly on the Fe (110) and Pd (111). These results are compared to those for the clean surface and were calculated using van der Waals corrections with the optB88-vdW functional.

Fe (110)		
Site	d-band center (eV)	d-band width (eV)
Clean Surface	-2.1/-1.2	2.4/1.5
LB 30° – T	-2.2/-1.6	2.6/2.2
T – SB	-2.1/-1.3	2.4/1.7
Pd (111)		
Site	d-band center (eV)	d-band width (eV)
Clean Surface	-1.8	2.2
B 30° – B2	-2.6	3.0
T – B	-2.0	2.4

For the Fe (110) states, the parallel adsorption of phenol causes a slight shift in the spin down state's d-band center by -0.4 eV and a broadening of both the spin up and spin down states' d-band widths. Similar changes are seen in the Pd (111) d-band characteristics where the d-band center shifts by -0.4 eV and that d-band width is significantly broadened by the adsorbate interaction. Also, the number of states in the Fe or Pd d-states near the Fermi level has slightly decreased and is most evident in the Pd's d-states. These changes in the metals' d-states are consistent both with strong chemisorption and with those of the C and O p-states which show almost no shift in the lower energy states (below -5 eV) while the highest occupied orbitals (G2 and G3) along with the LUMO level (G4) have nearly disappeared as they hybridize with the metal states.

This hybridization of the highest peaks in the C and O p-states with the metal states can be seen more clearly by examining the partial charge density of the system and comparing it to the partial charge density distributions for phenol in the gas phase (Figure 5). The gas phase partial charge density distributions are shown for the three highest energy orbitals (G1 – G3) and the first unoccupied level (G4). Here, we refer to the HOMO and LUMO levels for the gas phase phenol molecule as the G3 and G4 distributions, respectively. The exact energy ranges used to generate the partial charge density distributions shown in Figures 5 and 7 are presented in Table S1 in the Supporting Information.

Figure 5. Top and side views of the partial charge density distributions of the highest energy orbitals for phenol in the gas phase (a), adsorbed on Fe (110) in the LB 30°-T site (b), and adsorbed on Pd (111) in the B 30°-B2 site (c). The isosurface was set at 0.01 electrons/Å³, with

the exception of the F3 and P3 orbitals which had isosurface levels of 0.005 electrons/ $\text{\AA}^3$, and the green areas represent the presence of electrons. The calculations were performed with the optB88-vdW functional and the sphere coloring is identical to that presented in Figure 1.

The trend in the orbital hybridization between the LUMO and two highest occupied orbitals in gas phase phenol upon parallel adsorption on either Pd (111) or Fe (110) is similar and are discussed here. First, we can see that upon adsorption, the phenol's G1 orbital distribution remains fairly unaffected by the surface interaction. The major change to this orbital (seen as F1 and P1 in Figure 5) occurs on the Pd (111) surface where there is a greater overlap with the surface d-states (see Figure 4) leading to a distribution of electrons to gather between the adsorbate and the surface. Second, the G2 orbital distribution can be found in the F2 and P2 distributions with the G2 distribution dominating the aromatic ring charge density, but with additional oxygen states present caused by hybridization with the G3 (HOMO) orbital, as can be seen in that dumbbell shaped states surrounding the oxygen atom in the G3 orbital distribution. Third, both the F3 and P3 orbitals strongly show the G3 distribution, but with a significant decrease in the number of states present in these orbitals. Fourth, as we move to the F4 and P4 orbitals, encompassing the energy levels of ~ -3 eV to the Fermi level, we can see that there is a hybridization of the HOMO (G3) and LUMO (G4) levels with the LUMO level dominating the aromatic ring distribution, as seen in the extension of the charge distribution to include the C-H bonds, and the HOMO present in the p-type charge distribution around the oxygen atom. Finally, by examining the F5 and P5 orbitals, comprising the energy levels above the Fermi level, and comparing the distribution to the gas phase phenol distributions, it is clear that the F5 orbital is composed entirely of G4 (LUMO) states as seen in the LUMO-like distribution surrounding the aromatic ring and hydroxyl group. Based on these results, it is clear that there is a definite

mixing of the highest two orbitals (G2 and G3), along with the LUMO (G4), upon phenol's parallel adsorption onto both Fe (110) and Pd (111). These results show that on both surfaces the oxygen atom's HOMO character dominates the oxygen charge distribution near the Fermi level, but interacts only weakly with the surface states. This leaves only the LUMO states in the aromatic ring available for electron backdonation from the surface, causing the hybridization of the HOMO and LUMO aromatic states seen in orbital F4. Not even the oxygen's LUMO states above the Fermi level (orbitals F5 and P5) interact with the surface, as shown in Figure S2. The differences in the orbital distributions between the two surfaces are small and mainly present within the first three distributions (F1 versus P1, F2 versus P2, and F3 versus P3). In the first distribution (F1 and P1), it is clear that charge transfer is occurring between the Pd surface and phenol adsorbate while no exchange occurs on the Fe surface. The second (F2 and P2) and third (F3 and P3) distributions have similar differences in that there appears to be a significant decrease in these both the orbitals themselves and the charge transfer between surface and adsorbate on the Pd surface as compared to the Fe surface. Overall, the orbital hybridization that occurs upon phenol's parallel adsorption on the Fe (110) and Pd (111) surfaces is similar and the mixing of the HOMO and LUMO levels below the Fermi level, along with the shift in the metals' d-states to lower energies, is consistent with strong chemisorption.

The results for the density of states for the perpendicularly adsorbed phenol configurations are shown in Figure 6. In this figure, the states are shown for one of the surface metal atoms that is directly interacting with the oxygen atom. The same carbon atom ortho to the C-O bond was chosen for the carbon atom PDOS results as used in Figure 4.

Figure 6. PDOS for phenol perpendicularly adsorbed on (a) Fe (110) in the T-SB site and (b) Pd (111) in the T-B site. The spin up and spin down states for the adsorbate bonded Fe atom are shown along with only the spin up states of the C, O, and Pd as the spin down states for these atoms were found to be equivalent to the spin up states. The PDOS for each element are shown for both before (dotted line) and after (solid line) adsorption. These calculations were performed using the optB88-vdW functional and E_{Fermi} has been set to zero.

For the perpendicular adsorption case, we can see that there is almost no change to the metal's d-states for both the Fe and Pd surface. The shift in the calculated d-band center (Table 4) for the Fe (110) and Pd (111) surfaces are small and the distributions show minimal changes. However,

there is an increase, or broadening, in the d-band width for both metals when phenol adsorbs perpendicularly (~ 0.2 eV for both Pd and Fe) which indicates that a small degree of charge transfer occurs between the adsorbate and surface as seen in the differential charge density distributions (Figure 3). In addition to this, there is no significant shift in the C and O p-states for phenol's adsorption on the Fe (110) surface; however, there is a slight broadening of the HOMO peak in both the O and C p-states on both surfaces which corresponds to the small degree of charge transfer observed in the differential charge density distributions (Figure 3 (c) and (d)). This lack of change in the electronic structure of both the metal and adsorbate is indicative of physisorption which is a weak adsorption that occurs without significant charge transfer between surface and adsorbate. The only significant deviation in the electronic structure is seen in the C and O p-states for the perpendicular adsorption of phenol on Pd (111). For this system, there is a clear shift to higher energies in all the peaks, indicating that phenol's perpendicular adsorption on Pd (111) slightly destabilizes the molecule.

To further examine the electronic nature of the perpendicularly adsorbed phenol, we calculated the partial charge density for phenol's HOMO (F4 and P4) and LUMO (F5 and P5) levels on both Fe (110) and Pd (111) and the resulting distributions are shown in Figure 7.

Figure 7. Partial charge density distributions of the HOMO and LUMO for phenol adsorbed on (a) Fe (110) in the T-SB site and (b) Pd (111) in the T-B site. The isosurface was set at 0.01 electrons/Å³ and the green areas represent the presence of electrons. The calculations were performed with the optB88-vdW functional and the sphere coloring is identical to that presented in Figure 1.

The HOMO and LUMO distributions for phenol perpendicularly adsorbed onto both surfaces shows no gain of electrons in the space between the adsorbate and surface and the distributions are nearly identical to the HOMO and LUMO distributions found for gas phase phenol. These results agree with the previous results and show that phenol will weakly adsorb through the oxygen functional group without any charge transfer with the surface.

Overall, the electronic analyses performed here support the conclusions formed from the energetic and structural results; namely, that the Fe (110) surface produces a greater degree of distortion of the C-O bond while the Pd surface has a stronger surface-adsorbate interaction. The parallel adsorption of phenol results in a similar distortion and hybridization of the adsorbate's

highest occupied orbitals both with each other and the surface metal's d-states, while the perpendicular adsorption of phenol shows no significant change in the adsorbate's HOMO and LUMO levels. From the differential charge density distributions, it is clear that the greater degree of distortion of the C-O bond is due to the additional charge transfer between the Fe surface and oxygen in the hydroxyl group, while the stronger adsorption energy for phenol on the Pd (111) surface is due to the greater degree of charge transfer between the surface and adsorbate. Also, the stronger adsorption energies for the parallel adsorption sites as compared to the perpendicular adsorption sites are due to the significant increase in the charge transferred between the adsorbate and the surface for the parallel sites as these adsorption sites involve charge transfer between the surface and the aromatic ring. The increased distortion of the C-O bond and surface-O electronic interaction on the Fe (110) surface when compared to the Pd (111) surface suggests that the Fe surface is a more active surface for the deoxygenation phenol to benzene, which was observed experimentally [41].

4. Conclusions

The adsorption of phenol both parallel via the aromatic ring and perpendicularly via the oxygen functional group was studied on the Fe (110) and Pd (111) surfaces using density functional theory. Parallel phenol was found to have a stronger adsorption energy on the Pd (111) surface as compared to the Fe (110) surface, while perpendicularly adsorbed phenol had a nearly identical adsorption energy on both surfaces. However, the Fe (110) surface was found to distort the C-O bond to a greater extent than the Pd (111) surface. The increase in adsorption energy was found to be due to the greater degree of charge transfer between the surface and the aromatic ring in the parallel configurations. From the differential charge density distributions of parallel phenol, the Fe surface was seen to exchange charge with the oxygen atom in the

hydroxyl group while the Pd surface exchanged charge with the hydrogen atom in the hydroxyl group, accounting for the increased C-O distortion on the Fe (110) surface. Overall, our results show that the Fe (110) surface produces a greater degree of distortion of the C-O bond due to the O-Fe interactions while the Pd surface has a stronger surface-adsorbate interaction due to the greater degree of charge transfer between the surface and aromatic ring.

Supporting Information

The Supporting Information contains one table detailing the energy ranges used to generate the partial charge density distributions presented in section 3.4 of the main text, a figure presenting an alternative side view of the orbital distributions of the states above the Fermi level for the parallel adsorption of phenol on both surfaces, the PDOS comparison between the PBE and optB88-vdW functionals for phenol adsorbed on Fe (110) in the LB 30°-T site, and the atomic coordinates of the most favorable parallel and perpendicular configurations of phenol on the Fe (110) and Pd (111) surfaces, as well as the gas phase phenol atomic coordinates, used in the majority of the calculations presented in this work.

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