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Computational Investigation of Binding Trends of H_2O, O-H and O on Stepped Rhodium (211) Surfaces Using Density Functional Theory

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Abstract

Since the industrial revolution, an increased demand on fossil fuels as the predominant source of global energy have brought upon many harmful consequences, such as environmental pollution, climate change, and depletion of Earth's non-renewable natural resources. Proton-Exchange Membrane (PEM) fuel cells are being researched as an alternative to generate electricity and hydrogen gas is used as fuel. However, hydrogen gas is not abundant in nature and has to be derived from hydrogen containing molecules like fossil-fuel hydrocarbons. Complex alcohols and carbohydrates are a sustainable alternative. These compounds contain long chains of hydrogen, oxygen, and carbon atoms. Transition metal catalysts, such as rhodium (Rh), can be used to break the C-H, O-H, and C-C bonds of these molecules to release hydrogen gas as byproduct. However, a better understanding of the catalytic reaction mechanisms is needed to fully utilize complex alcohols for hydrogen generation. For this research, the computational method periodic density functional theory (DFT) is used to investigate the lowest energy conformations as well as the binding energies of H_2O, O-H, and O to the Rh (211) stepped surface. There are different types of catalytic metal lattice structures, such as planar, stepped, and kink surfaces. Recent studies have shown that the stepped and kink surfaces are more reactive and allow compounds to bind much stronger to the metal surface. The results will be compared to previous research done on a planar Rh(111) surface to further understand the catalytic properties of the stepped rhodium surface.

1. Introduction

Our increased dependence on fossil fuels, as the source of energy, has brought upon rapid depletion of natural resources. In addition to fossil fuel depletion, burning of them to get energy has led to increased amount of greenhouse gases into the atmosphere that are causing many environmental issues. Recently, researchers started considering hydrogen gas as an alternative source of energy. Proton-Exchange Membrane (PEM) fuel cells use elemental hydrogen as a source of energy for electricity generation. This is the most sensible alternative because hydrogen is the most abundant element on Earth, but unfortunately it is rarely found in its elemental form. It is found in hydrogen containing molecules like hydrocarbons and alcohols. These compounds are made out of long chains of hydrogen, oxygen, and carbon atoms forming complex alcohols and carbohydrates[1]. Hydrogen provides energy by breaking the H-H bond in reaction with O_2 that releases water as byproduct. Researchers have considered different transition metal catalysts to assist the breaking of these C-H, O-H, and C-C bonds of different chain lengths of alcohols to release hydrogen gas as a product[2]. Extensive research has been done in the past by researchers in India and China with transition metal catalysts such as Ni, Pt, and Pd. The results have shown increased release of energy with minimal byproducts from transition metal catalysis. Each metal favors different types of intermediates, from alkoxy to formaldehyde. Most of the research performed has been to understand the adsorption energies and binding geometries of these intermediates in the gas phase[3,4,5]. It has been shown that C-H bond cleavage is a lot more favored than the O-H bond cleavage, and the intermediates, such as hydroxymethyl are the preferred intermediate[3]. Over the years Pt(111) and Pd(111) have shown promising results in terms of adsorbent energies and binding geometries, in favor of breaking off a hydrogen and releasing energy with minimum input of activation energy[3,4]. As part of this research, the knowledge obtained from previous research on metal catalysts, such as Pt and Pd, will be used to get similar results with other noble metals, such as rhodium. Bare Rh surface will be used to find the lowest energy conformations of water, hydroxide and oxygen. There are many different types of catalytic metal surfaces, such as planar (111), which is mainly investigated in the previous literary research, stepped, and kink surfaces. Recent studies have shown that the stepped and kink surfaces are a lot more reactive and allow compounds to bind much stronger to the metal surface, due to extra layers of metals and increased electron density of the surface. Density functional theory (DFT) package will be used for calculations and investigation of the reaction mechanisms using a stepped rhodium catalyst surface.

2. Methodology

To obtain the geometric input codes on the XYZ coordinate system, the molecular structures of H_2O, OH, O, and methanol-pentanol were visualized in CrystalMaker, a software that provides the data for DFT calculations. A unit cell of stepped Rh (211) was constructed using CrystalMaker, where the H_2O, OH, O, and varying chains of hydroxyalcohol molecules interacted with the surface. The coordinates from the constructed geometry of the molecules were converted into a VASP input file for DFT optimization. These molecules were placed on 10 different binding sites throughout the Rh surface, including: atop, bridge, and hollow positions on upper and lower, and the edge surfaces of the step as shown in Figure 1. The lowest energy conformations of H_2O, OH, O, and hydroxyalcohols were found. The lowest energy molecules were used to also test the effect of the angle and the positions of hydrogens on the molecules for the H_2O, OH, O. The initial calculations for geometry optimization were done using Monkhorst-Pack grid resolution of 3x3x1 (k points), to optimize the geometry and find the lowest energy conformation of each binding site. Once the optimum energy was found, k points for each of the molecules with the lowest energy conformation were increased to 5x5x1 for more accurate energy calculations. The calculated free energy from DFT was used to calculate the reaction energy using equation 1 and binding energy using equation 2:

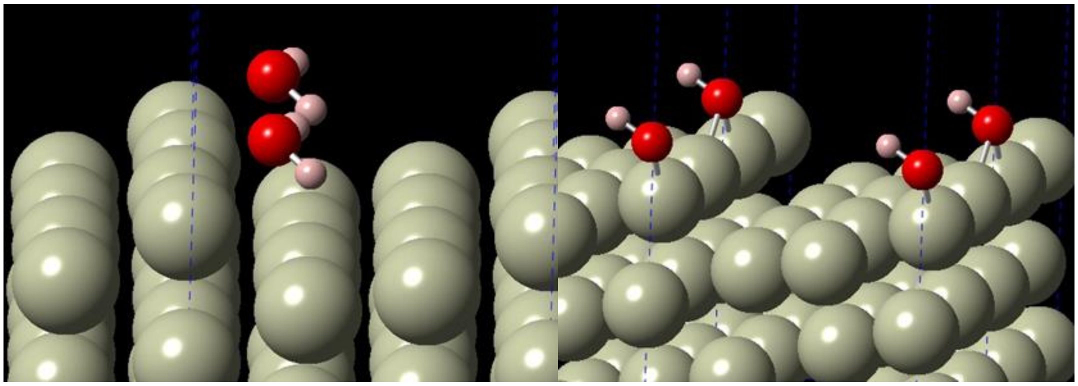
$$E_{\text{reaction}} = (E_{\text{dehydrogenated absorbate}}* + E_{\text{hydrogen}}*) - (E_{\text{absorbate}} *+ E_{\text{bare surface}}) \quad (1)$$

$$E_{\text{bind}} = E_{\text{absorbate}}* - (E_{\text{bare surface}} + E_{\text{absorbate in gas phase}}) \quad (2)$$

where * represents the molecules absorbed to the metal surface[6].

3. Results and Discussion

Following David Lingerfelt's and Kulchanok Panichakornkul's, both members of Wasileski research group, investigations that showed the more favored relationship between stepped Rh(211) surface and the alcohol and alkoxy molecules[1,2], this research investigated the most favored positions of H_2O, OH, and O molecules. It was found that the lower atop site is mostly favored for the H_2O molecule, while OH and O molecules favored the edge bridge and hollow positions of the stepped surface respectively. The lowest energy conformations of the molecules are shown in the Figure 2.



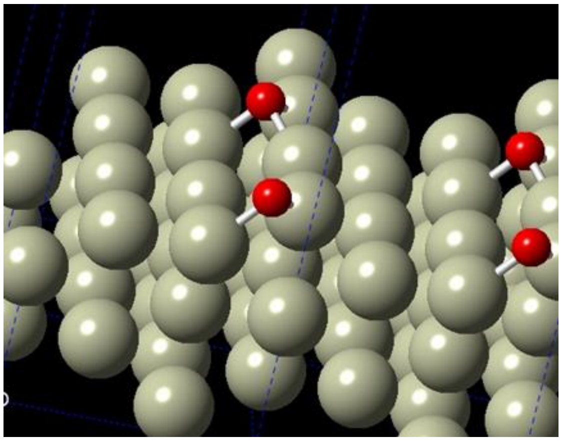


Figure 2. Lowest energy conformations for water(first picture), hydroxide (second picture), and oxygen(third picture) on the stepped Rh (211) surface

The optimized conformations and energies were calculated for all three molecules in 5x5x1 k points in order to compare them to Lingerfelt's and Panichakurnkul's results. The free energy calculated was used to find the binding energies for the molecules using the equation 4. The calculations are summarized in the Table 1. The water molecules moved up the Rh surface and the molecules seemed to have been asymmetric. H_2O molecules were found to prefer the atop position the most due to the need to be closer to the surface in order to be more stable. OH atoms on the other hand have an unpaired electron making atop less favorable, forcing it into a bridge position to stabilize. The O atoms have two unpaired electrons, making them extremely unstable and favor the Rh metal edge due to the partial positivity of the hollow.

Table 1. Binding energies and bond lengths between O atom and the Rh surface.

Molecules	H2O	OH	O
Binding energy (eV)	-0.477	-3.391	-4.885
Rh-O Bond length (Å)	2.300	2.100	1.900

The results were compared to Lingerfelt's planar surface and Panichakurnkul's carbon chains of alcohol and alkoxy molecules in Figure 3 and Figure 4. Based on the data it has been found that the stepped Rh surface produces lower energy conformations than the planar surface. This is due to the uneven distribution of the electron density on the surface[2]. The water molecules were found to have a lower binding energy than the alcohols bonded to various carbon chains. However the binding energy of the OH was found to be higher than any of the alkoxy molecules optimized by Kulchanok Panichakornkul. This could be due to the unpaired electrons on the OH which make it unstable in comparison to more stable alkoxy molecules.

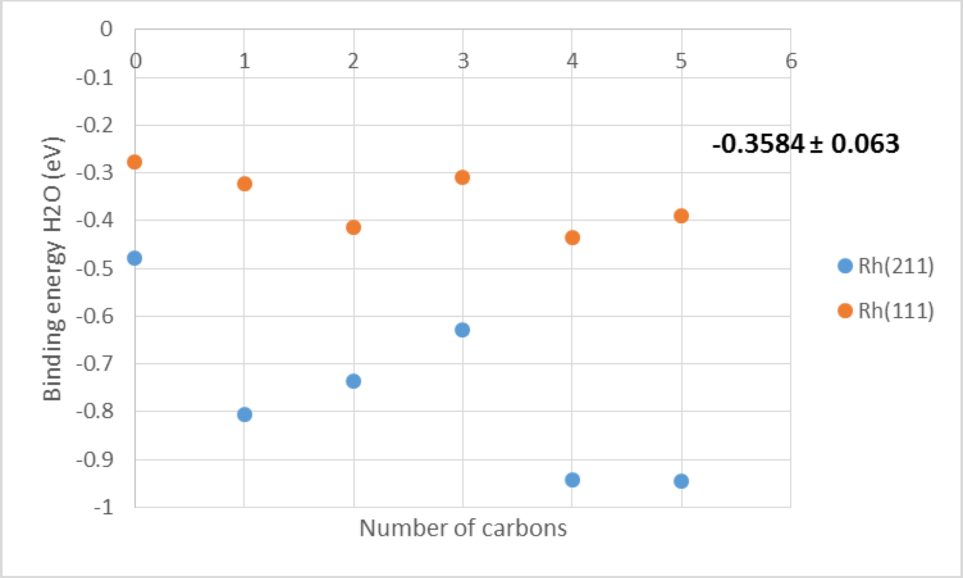


Figure 3. The binding energies of varying chains of alcohols based on the differences between Rh(211) and Rh(111) surfaces.

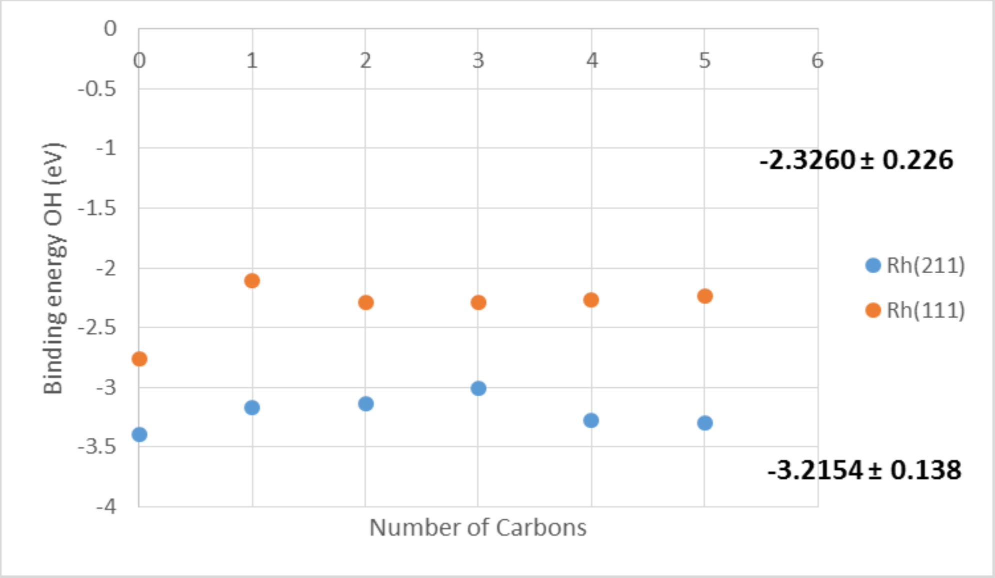


Figure 4**.** The binding energy of alkoxy based on the difference between Rh(211) and Rh(111) surfaces.

The reaction energies for the alcohol molecules and water for Rh(211) and Rh(111) surfaces are shown in Figure 5. The trend is the same that shows that the stepped surface has a lower reaction energy, while the planar surface is not as favored. However the H_2O reaction energy is a lot lower than any of the alcohols. This could be due to the fact that H_2O depend on the surface to stabilize it, while alcohol molecules have the carbon chains to stabilize them.

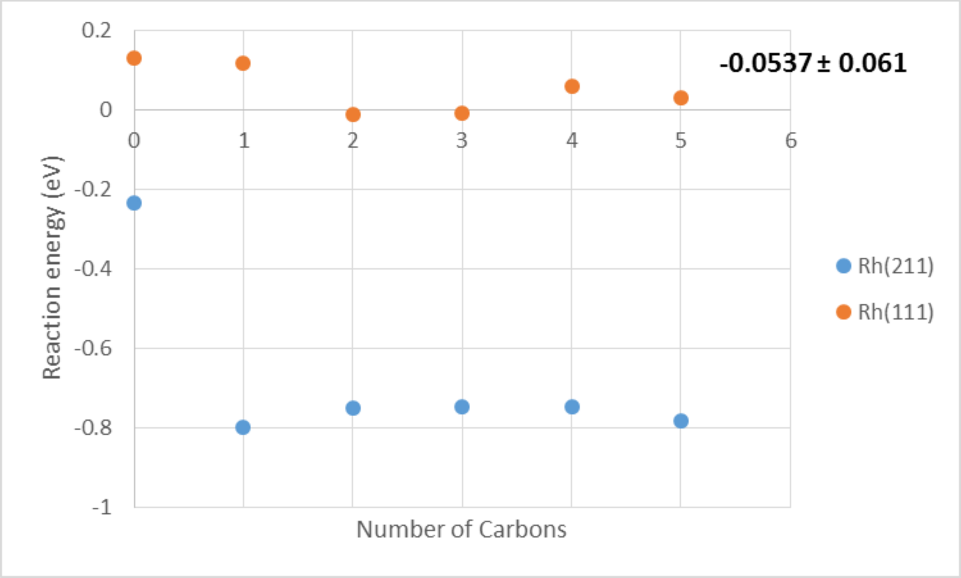


Figure 5. Reaction energies of water and alcohols on the difference between Rh(211) and Rh(111) surfaces.

After the optimization of the various angles on the lowest energy conformations of H_2O, OH, and O it has been found that the angle might not play a very significant role in the lowering of the free energy of these particular molecules. However, the lowest energy angles for O (137°) and OH (140°) are shown in Figure 6 due to their reinforcement of the previously made statement that the unpaired electrons on the O atom prefer to be in a bridge or hollow position.

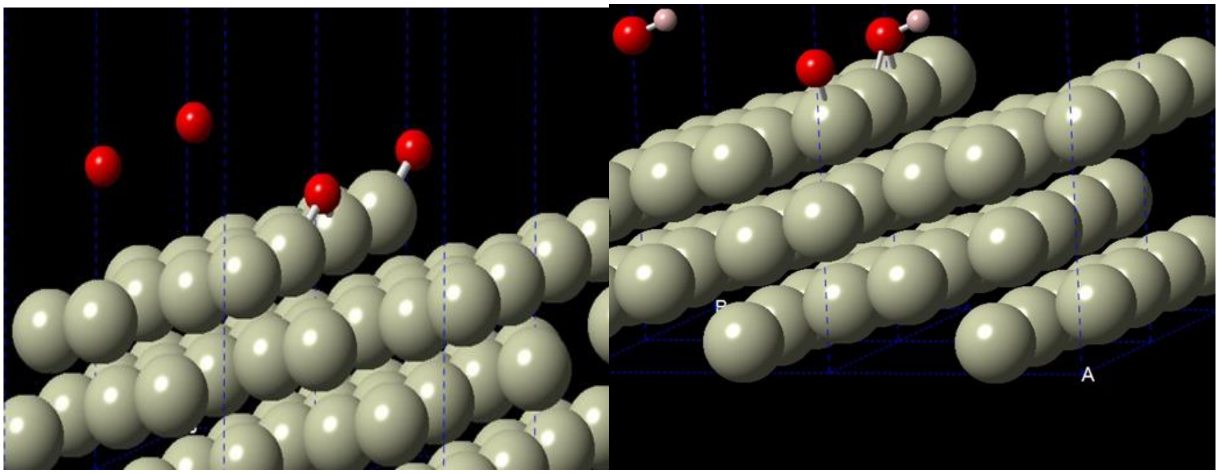


Figure 6. Most favored Rh-Rh-O angles for lowest energy conformations of hydroxide (left) and oxygen (right)

For further optimization of the energy conformations, the position of the hydrogens attached to the O atom were visualized and based on the calculated free energy, the lowest energy positions are shown in Figure 7. It was found that the hydrogens better interact with both O atom and the surface if they are positioned away from the Rh surface.

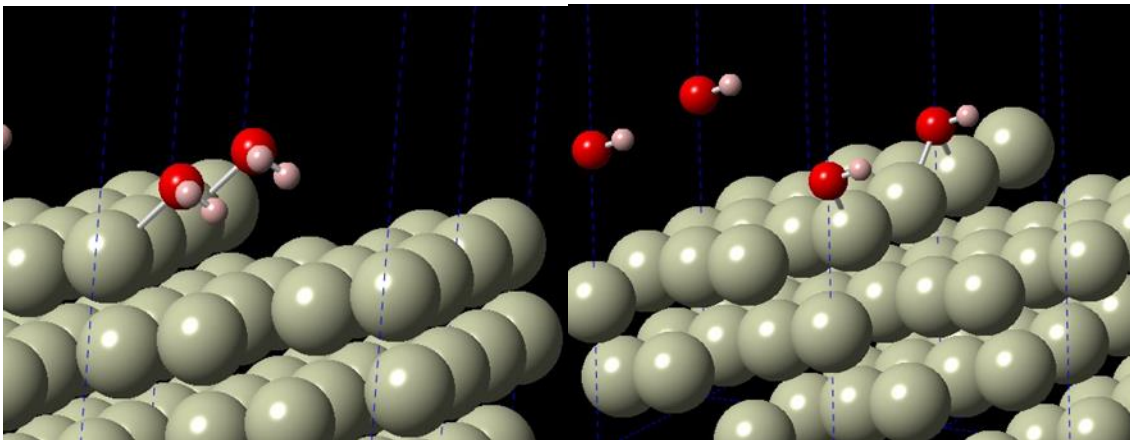


Figure 7. Favored positions of hydrogen on oxygen for lowest energy conformations of water (left) and hydroxide (right).

The single O atom is very unstable and due to its unpaired electrons requires the partial positivity of the hollow position on the Rh surface to stabilize itself. Based on these findings several calculations were run to determine the optimal hollow position for the O atom with the lowest energy. The findings are presented in Figure 8. The most favored position seems to be in-between three atop Rh atoms and an overlapping Rh lower surface atoms. This way the O atom is closely interacting with the surface to keep itself stabilized.

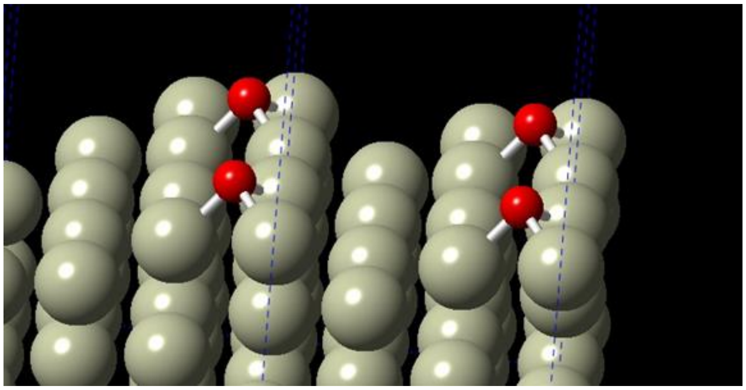


Figure 8. Lowest energy hollow conformation of the O atom.

4. Conclusion

During this research it has been shown that H_2O, OH, and O are less stable compared to the molecules like methanol, or pentanol, due to their unpaired electrons and partial negativity. It was shown that the H_2O molecule appears to be the most stable out of the three and prefers the upper atop position of the stepped surface. The OH and O are less stable and prefer to be either in a bridge or a hollow position, which helps them be more stable. It has also been shown that the stepped Rh(211) surface is better for dehydrogenation reactions, due to its lower energy calculations. Next step in the research will be testing these new positions and possibly angles on bigger molecules like hexanol and heptanol, and seeing how the reactions and energies will change.

5. Acknowledgements

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