# Periodic DFT Calculations for the Investigation of Carbon-Carbon Bond Cleavage Reactions of Ethene, Ethenol, Propene, and Propenol Over Rh(211) Stepped Versus Rh(111) Planar Lattice Structures

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## Abstract

As the need for fossil fuels increase, there is greater urgency for a more sustainable fuel source to generate energy. Fuel cells use oxygen and hydrogens gas as fuel to form water and electricity at high efficiency. However, hydrogen gas is not a naturally occurring compound and is typically generated from other hydrogen-containing molecules such as hydrocarbons. Plant-derived alcohols and carbohydrates have the potential to be a more sustainable hydrogen source via C-C, C-H and O-H bond cleavage reactions facilitated by a metal catalyst, typically as nanoparticles containing flat planes, stepped edges, and other defects in the surface structure. A fundamental understanding of catalytic reaction mechanisms at these different surfaces are needed for optimal catalyst design and periodic density functional theory (PDFT) calculations can be used to investigate energetic, structural, and electronic effects for elementary steps of the reaction mechanism over extended catalyst surfaces. In this research, C=C double bond cleavage reactions in alkenes and alkenols as a function of chain length were investigated by PDFT on a stepped (211) rhodium catalyst surface, and compared to previous results on a planar (111) surface[1]. It was found that the reaction energies at the stepped surface are ~14 kJ/mol more favorable for ethene and propene C=C cleavage compared to the planar surface. The reaction energy is similarly more favorable at the stepped surface for alkenols, but is more variable depending on surface-OH interactions. Reaction energetics and the structural dependence of C=C bond cleavage mechanisms for alkenes and alkenols from 2-4 carbon chain lengths will be presented along with insights into the differences between reactions at stepped and planar catalyst surfaces.

**Keywords: Alcohols, PDFT, Reaction Energies**

## 1. Background

Copious amounts of finite fossil fuels are depleted from the earth's crust in the form of coal, oil and other hydrocarbon fuels each day to the point where the Earth is unable to replenish in a timely manner. To help lower the dependence on fossil fuels alternative sources, such as biomass sources, are being investigated. Fuel cells have the capability to produce electricity from hydrogen and oxygen gas as fuel, creating a byproduct of water[2]. The need for hydrogen gas has inspired this research topic, because hydrogen gas is not a naturally occurring compound, and must be generated from hydrogen containing compounds.

When plants undergo photosynthesis carbon dioxide and water are converted into carbohydrates which contain hydrogen atoms in the form of alcohol functional groups (OH) on hydrocarbon chains and rings. When the O-H and C-H bonds are broken hydrogen gas ($H_2$) can be formed[3]. Bond cleavage of the hydrocarbon chain is also necessary to break the carbohydrates into small CO or $CO_2$ fragments.

C-H, O-H and C-C bond cleavage reactions are facilitated through the assistance of a transition metal catalyst by stabilizing interactions between metal atoms and the potentially weakened bonds of the compound. Through varying differences in transition metal catalysts, determining the optimal one to use for each carbon length chain would be a grand achievement in the field of chemistry. With the discovery of the prime catalyst for the highest reactivity rate, a sustainable source of hydrogen fuel could be possible.

Previous research has been performed by Dr. Sally Wasileski's research team, to determine the potential mechanisms to produce hydrogen gas for fuel cells. These mechanisms look into the dehydrogenation of O-H and C-H bonds along with C-C bond cleavage, known as cracking. The focus has been to determine how chain length affects the energies of C-C, C-H, or O-H bond cleavage[1,4,5,6]. The cleaving of these bonds have seen to be facilitated best by four different transition metals, Ni, Pt, Pd and Rh[2,3]. Out of these four compounds, Rh has continued to be investigated due to its catalytic ability.

With transition metal catalysts there are three general surface lattice structures on which the catalytic reactions occur: planar, stepped and kinked. Each of the structures have a varying amount of reactivity for bond cleavage. The (111) planar and (211) stepped surface structures for the face-centered cubic structure of rhodium can be viewed in figure 1. Reaction energies are predicted to vary due to different electron densities from the planar surface to the upper terrace, edge, or lower terrace of the step or kink.
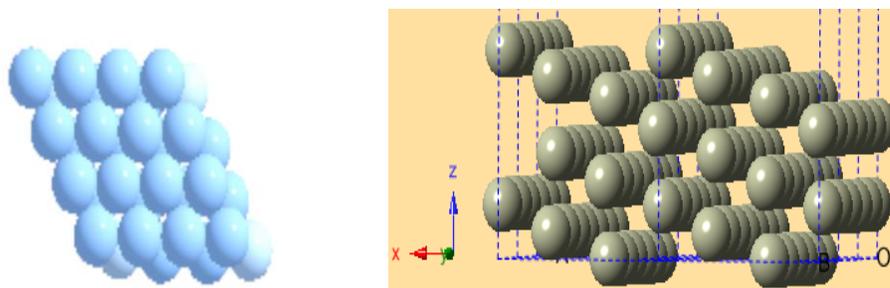


Figure 1: Represents the planar (111) surface, left, and the stepped (211) lattice structure, right.

The difference between planar and stepped surfaces is that a stepped surface is comprised of two different planar layers staggared at the surface to create a step between layers. The benefit of layers is that adsorbate compounds can interact with different electron densities on the top terrace, at the step and on the bottom terrace[7]. When previously studied, the stepped surfaces were observed to have stronger adsorption and lower reaction barriers for catalytic reaction[8].

The objective of this research is to investigate the C-C bond cleavage of alkenes and alkenols at the Rh(211) stepped surface and compare to previous results on the Rh(111) surface in order to determine how the catalytic activity changes with surface catalyst structure for bond cleavage reactions. Alkenes and alkenols were chosen because the C atoms in the double bond strongly interact with the catalyst surface, and previous results show that initial alcohol dehydrogenion is preferred before C-C bond cleavage[9].

## 2. Methodology

All research is performed computationally using periodic density functional theory (PDFT) models, which allows for each elementary step in a reaction mechanism to be investigated over an extended metallic catalyst surface. The step is created by a repeating unit cell of 27 metal atoms, separated by a vacuum layer to create the (211) step. There are 10 different high symmetry adsorption sites on a 211 stepped surface. These positions are upper terrace (atop, bridge or hollow), lower terrace (atop bridge or hollow), and 4 sites at the step edge (atop and bridge on the edge face and two hollow sites at the intersection of the step with the bottom terrace. Each of the 10 possible positions are shown by red circles in figure 2. The optimum geometry of reactant and product states are determined by optimizing the molecule or molecular fragment geometry bound at each of these sites (to 0.0001 eV geometry convergence) and selecting the geometry that produces the lowest energy.
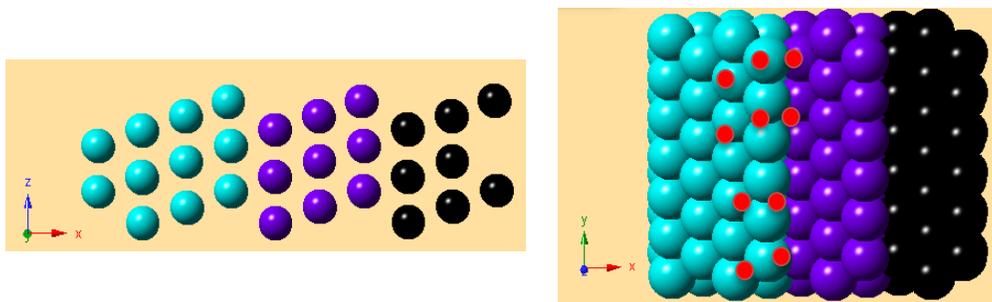
Figure 2: Represents 10 binding positions of a compound on a stepped surface.

To compute the energy of each surface-adsorbate state, PDFT was used, with the PW91 functional, calculated by the Vienna Ab-Initio Simulation Package (VASP) [10,11,12,13]. To visually represent each compound a 3D model is created with Crystal Maker[18]. A plane wave basis set using ultrasoft pseudopotentials was used to represent the electron density in the repeating set of unit cells[14,15]. Figure 3 shows a 3D representation of the stepped (211) surface, created by three layers set at the optimized Rh-Rh bond distance of 2.73 Angstroms with the bottom layer fixed. The distance in angstroms between two Rh atoms at the step is shown. The blue and black atoms both represent the Rh atoms but just signify the different layers. All surface-adsorbate geometry optimizations used the quasi-Newton method at 331 KPOINTS and all final energies were determined from a single point energy calculation at 551 KPOINTS using the optimized geometry.
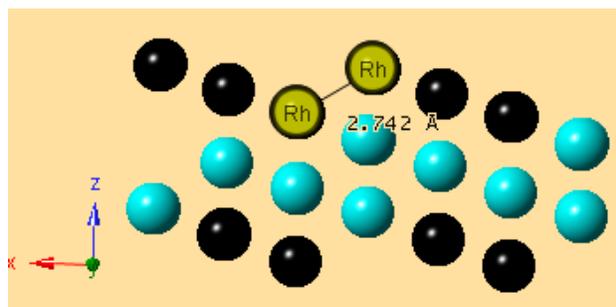
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Figure 3: 3D structure of the stepped (211) Rh surface

For each compound all isomers were considered. Out of the four compounds tested (ethene, ethenol, propene, and propenol), propenol is the only compound that had different isomers. Figure 4 shows the different positons of the double bond and alcohol substituent for propenol.
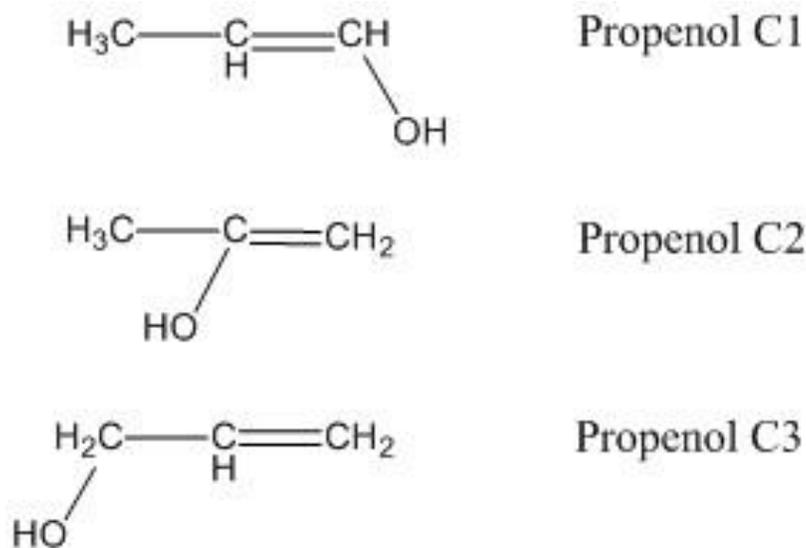
H₃C———C===CH     Propenol C1
       |
       H
                 OH

Figure 4: Propenol isomer structures.

# 3. Results

In order to explore the differences in catalytic activity between (211) and (111) surfaces, the C-C bond cleavage reaction energies are calculated. It has been shown by the Bronsted Evans Polanyi approximation that the activation barrier is directly proportional to reaction energy for C-C bond cleavage reactions. Therefore, the mechanism can be predicted from the more computationally efficient reaction energies[16,17].

To calculate the reaction energies of each compound the energies for the reactant structures is subtracted from the energies of the product structures. The products are considered the portions of the surface-adsorbed compounds when the double bond is broken where the reactants is the surface-adsorbed compound and an empty Rh(211) surface, to account for the energy from the interactions of Rh atoms. For example with propene the products are adsorbed $CH_3CH$ and $CH_2$ where the reactants are adsorbed $CH_3CHCH_2$ and the Rh surface. Figure 4 gives the 3D representation of each optimized compound on the stepped (211) surface from a side-on view in the repeating unit cell structure. Figure 5 shows the same optimized compounds on the stepped (211) surface from a top-down view.
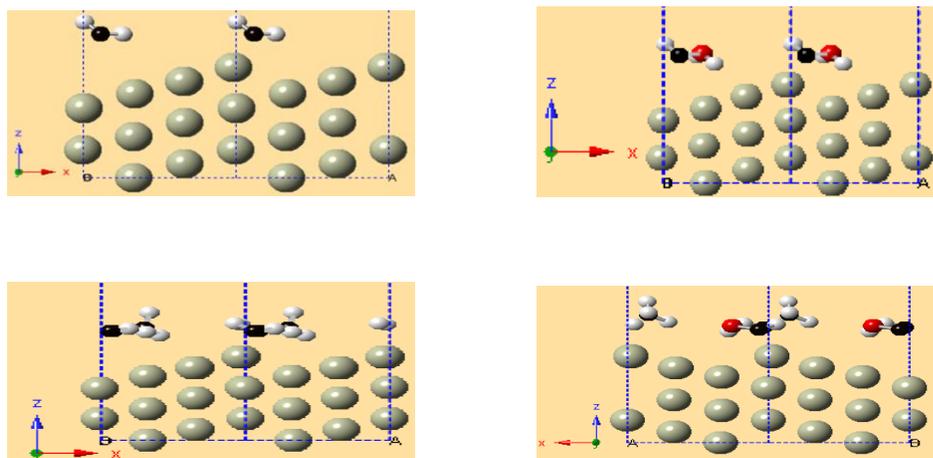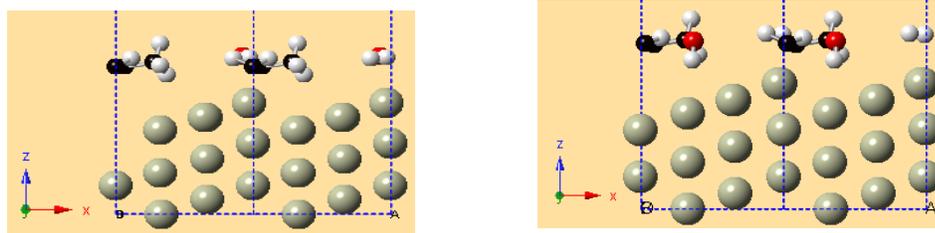
Figure 4: Lowest-energy optimized geometries of adsorbed reactants from a side-on view (order from left to right the compound are ethene, ethenol, propene, propenol C1, propenol C2, and propenol C3). Note that atoms are overlapping in the structure for etheneol.
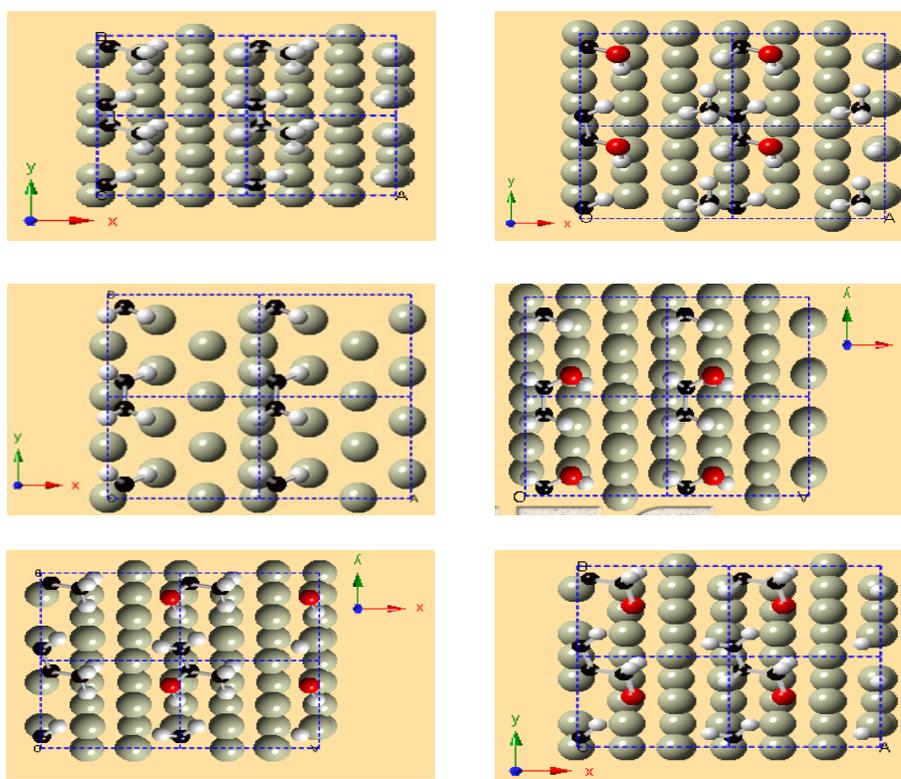


Figure 5: Lowest-energy optimized geometries of adsorbed reactants from a top-down view (order from left to right the compound are ethene, ethenol, propene, propenol C1, propenol C2, and propenol C3).

The lowest energy geometry is similar for all adsorbates studied, in which the C-C double bond is bonded with each C atom in an atop position on the top edge of the step. The difference in bonding between ethene and ethenol is the O-H group of the ethenol prefers to position over and away from the step, which limits interaction of the oxygen atom with the Rh surface. However, with propenol there are three possible isomers, which allow the oxygen atom to interact with the Rh surface in different ways. When the O-H is bonded to the C1 and C2 of the propenol the oxygen atom interacts with the Rh surface due to geometry constrains (see figures 4 and 5). However, in the C3 propenol structure, the OH group can position away from the Rh surface and not interact, in a similar way to ethenol surface adsorption. Table 1 shows the reactions energies produced from the tested compounds for the (211) stepped surface and compared to similar calculations on a (111) planar surface[1]. When comparing the results for reaction energies between the planar

and stepped surface there is an average of 0.15 eV( ~14 kJ/mol) more favorability for the stepped surface than the planar for ethene, propene and ethenol.

Table 1: Reaction energies in eV for cleavage of the C-C double bond.

| Compound | Reaction Energy (eV) for stepped (211) surface | Reaction Energy (eV) for planar (111) surface[1] |
|---|---|---|
| Ethene $H_2C$-$CH_2$ | 0.58 eV | 0.71 eV |
| Propene $H_2C$-$CH$-$CH_3$ | 0.45 eV | 0.61 eV |
| Ethenol $H_2C$-$CHOH$ | 0.19 eV | 0.56 eV |
| Propenol C1 $HCOH$-$CH$-$CH_3$ | -0.07 eV | - - |
| Propenol C2 $H_2C$-$COH$-$CH_3$ | 0.35 eV | - - |
| Propenol C3 $H_2C$-$CH$-$CH_2OH$ | 0.58 eV | - - |

Binding energies were calculated which indicate how strongly the compound interacts with the Rh surface. To find the binding energy, the energy from the compound in the gas phase and the Rh surface is subtracted from energy of the the compound adsorbed to the surface in its optimum geometry. Table 2 shows the binding energies for the following compounds for the stepped surface.

Table 2. Optimized binding energies in eV.

| Compound | Binding Energy (eV) for stepped (211) surface |
|---|---|
| Ethene $H_2C$-$CH_2$ | -1.34 eV |
| Propene $H_2C$-$CH$-$CH_3$ | -1.33 eV |
| Ethenol $H_2C$-$CHOH$ | -1.30 eV |
| Propenol C1 $HCOH$-$CH$-$CH_3$ | -1.06 eV |
| Propenol C2 $H_2C$-$COH$-$CH_3$ | -1.29 eV |
| Propenol C3 $H_2C$-$CH$-$CH_2OH$ | -1.41 eV |

The binding energies are used to determine the strength of interactions between the surface and the compound and how the strength of interaction changes from one compound to another. For example with ethene and ethenol, the binding geometries are similar with the C atoms of the C-C double bond interacting in atop sites and the OH of ethenol not interacting with the step. The corresponding binding energies for ethene and ethenol are essentially the same (-1.34 and -1.33 eV, respectively), confirming the energetic similarity in surface bonding.

However, for propene and propenol cleavage on Rh(211), changes in binding energies show that the oxygen atom plays a vital role in the strength of Rh-adsorbate bonds. For propenol C3, the optimum adsorption geometry does not have the oxygen atom directly interacting with the Rh surface, and both propene and propenol C3 have similar binding energies (Table 2). But for propenol C1 and C2, there is a strong decrease in binding energies compared to propenol

C3 (Table 1), indicating that the surface-oxygen interaction acts to weaken the overall surface-adsorbate interaction. These weaker reactant interactions are evident in a more favorable reaction energy C-C bond cleavage for the C1 and C2 propenol isomers than for C3 propenol on Rh (211) (Table 1).

Interaction of the lone pairs of oxygen from the OH group also influences the reaction energy for (111) surfaces. For ethene and propene, which have no influence from oxygen interactions, there is 0.13 eV (~13 kJ/mol) difference in reaction energies between ethene and propene on a stepped (211) surface and a very similar difference in reaction energies of 0.10 eV (~10 kJ/mol) on the (111) surface. The reaction energies are merely shifted to less endothermic on the stepped surface. But comparing the differences between ethene and ethenol on the (211) and (111) surfaces, C-C bond cleavage is 0.39 eV more favorable for ethenol versus ethene cleavage on the (211) surface, which is larger than the 0.15 eV difference on the (111) surface (Table 1). The close proximity of the OH group to adjacent Rh atoms on the (111) planar surface enables/forces interaction of the oxygen atom with the surface. But, the structure of the (211) step allows for repulsion of the OH group away from the surface step; the Rh-O interaction is not forced to occur based on proximity and the OH group prefers to not interact with any Rh surface atoms. As a result, it takes even less energy to cleave the C-C bond of ethenol on the step. Therefore, the stepped (211) surface produces greater differences in reaction energies due to both the surface geometry of the step and the enhanced reactivity of the step.

Although there are no comparative results for the propenol isomers on the (111) surface, it can be speculated that the C2 and C3 propenols on the (111) surface will have similar Rh-C interactions and Rh-O interactions with the surface due to the close positioning of the OH group to the C-C double bond. Unlike the stepped (211) surface, the proximity of adjacent Rh atoms on the planar (111) surface, does not allow for the same lack of interaction with the lone pairs of the oxygen atom and the Rh surface. Therefore, a more similar bond cleavage reaction energy is also expected.


## 4. Conclusion

From the computational results there is a trend produced from the reaction energies within each set of compounds: those containing alcohol substituents and those that do not at 2 and 3 carbon chain lengths. Out of all molecules investigated, all but the propenol C1 are endothermic, expected from the high energy required to break a C-C double bond. However, the reaction energy is less endothermic (smaller positive reaction energy) on the stepped versus planar surface, indicating the enhancement of bond cleavage on the (211) surface, as expected from the literature[3]. For the three possible propenol isomers, the alcohol located on the C1 position is slightly negative, indicating that the location of the OH group and how it can interact with the surface to stabilize or destabilize reactant and product states is important. This work shows that both the catalyst surface structure and fuel structure greatly impacts bond cleavage for reactions that lead to hydrogen generation.


## 5. Future Work

To further understand the influence of chain length and alcohol substituents longer chains such as butene and butenol will be investigated. For these compounds the reaction energy dependency on the double bond and alcohol positions will be investigated with the results then being compared to that of the same compounds over a planar surface.


## 6. Acknowledgements

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