THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

MECHANISM DETERMINATION FOR THE ELECTROCATALYTIC OXIDATION OF 1,2-
PROPANEDIOL OVER GOLD AND PLATINUM

JULIE MILLER
SPRING 2015

A thesis
submitted in partial fulfillment
of the requirements
for a baccalaureate degree
in Chemical Engineering
with honors in Chemical Engineering

Reviewed and approved* by the following:

Michael Janik
Associate Professor of Chemical Engineering
Thesis Supervisor

Enrique Gomez
Assistant Professor of Chemical Engineering
Honors Adviser

* Signatures are on file in the Schreyer Honors College.

ABSTRACT

The selective electrocatalytic oxidation of 1,2-propanediol to lactic and pyruvic acid was studied over gold and platinum catalysts. Previous experimental studies have indicated that the feedstock would oxidize to lactic acid at low overpotentials but would not form pyruvic acid until higher overpotentials were reached. The exact mechanism of these reactions is hard to determine experimentally as the surface reaction intermediates cannot be directly measured. This research utilized density functional theory (DFT) to more accurately determine the mechanism of this oxidation. DFT is a modeling method that uses quantum mechanics to compute the relative energies of each intermediate in predicted hypothesized mechanism. By compiling these energies, a favorable pathway from reactants to products can be determined. On both gold and platinum catalysts, the preferred pathway is through first deprotonating (oxidizing) the terminal oxygen, followed by the deprotonation of the terminal carbon to form lactaldehyde before proceeding to lactic acid. At high potential, further oxidation to pyruvic acid is also favorable. Over a gold catalyst, the unstable intermediate between each step are not strongly bound to the catalyst. This leads to high levels of conversion being unfavorable until high potentials are reached. On a platinum catalyst, the intermediates bind more strongly to the surface and thus higher conversion is obtained. It was also observed that deprotonation and oxidation is far more favorable than breaking carbon-carbon bonds, and oxidation becomes more competitive as the potential increases.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Chapter 1

Introduction

As traditional petrochemical fuel source reserves diminish, interest in renewable fuel sources increases. Biodiesel is of special interest as it can readily be used as liquid fuel and thus can be utilized in the engines of cars and other methods of transportation. Current production methods of biodiesel involve oils and fats undergoing a transesterification reaction with an alcohol to produce fatty acid methyl ester and glycerol.[1] Glycerol is not a major component of biodiesel, and thus represents an unwanted byproduct of the reaction. As the production of biodiesel has increased, so has the production of glycerol without a corresponding increase in demand. This leads to glycerol being readily available and reasonably inexpensive. Glycerol is therefore an appealing feedstock for the production of value added chemicals.[2]

Heterogeneous catalysts can selectively oxidize glycerol.[3] This method leads to high selectivity but a loss of chemical energy, through heat generation, and it offers little control over product distribution. An alternative method, involves the selective reduction of glycerol to 1,2-propanediol. 1,2-propanediol has been experimentally shown to be a suitable feedstock for the production of lactic acid and pyruvic acid. The oxidation of propanediol to value-added products can be performed in an galvanic electrochemical cell – a fuel cell – simultaneously producing electricity while oxidizing propanediol to lactic and/or pyruvic acid. Through the control of the fuel cell operating potential, the distribution of products can be manipulated. The chemical energy in the reaction is also not lost as heat, but converted to electrical current.

As the distribution of products relies heavily on the cell potential, it is important to understand the mechanism of this conversion. Li and co-workers have studied electrochemical propanediol oxidation experimentally in both membrane-electrode assemblies and in model "single-electrode" studies.[4] Over Au catalysts and at low potentials, this reaction tended to produce large amounts of lactic acid. At higher potentials, pyruvic acid was the favored product. Li et al. observed that higher potentials lead to higher conversion percentages, but also to higher production of one and two carbon products resulting from carbon-carbon bond breaking.[4] Better understanding of the mechanism would not only assist in optimizing the selectivity of this reaction to either lactic or pyruvic acid, but help to minimize the formation of these unwanted byproducts.

Li et al. compared the relative oxidation rates and product selectivities between gold and platinum catalysts. The platinum catalyst was shown to have a higher conversion percentages, but very little conversion to pyruvic acid. This indicates that the surface is more reactive.[4] A better understanding of the reaction mechanism over both of these surfaces would allow for alloy catalysts to be designed that could be both more reactive, and more selective to the desired product.

In addition to being directly relevant to the oxidation of propanediol, mechanistic examination can provide insight into the selective oxidation of polyols more generally. Propanediol can be thought of as a model compound for glycerol, among others, and can inform catalyst design for their selective oxidation into other value-added chemicals. The discovery of more uses for the glycerol byproduct of biodiesel production would make this renewable fuel more economically desirable.

Standard experimental procedures are unable to determine the mechanism of these reactions as the concentrations of the numerous possible surface intermediates cannot be measured. The final concentrations of fluid phase products can be measured, but this gives little information about how these products are formed. A quantum mechanical approach is thus far more useful in determining the mechanism of product formation in complex, multistep electrocatalytic reactions. Density Functional Theory (DFT) is a quantum mechanical modeling method. The electron density of the structure is analyzed to determine the electronic structure of matter. The electronic structure of every intermediate surface species is optimized to determine the total energy of the system. This allows the gold or platinum surface to be considered as a system with the absorbed species to determine the most energetically stable conformation. This allows for the favorable pathway to be determined.

The main objectives of this study were to determine how favorable carbon-carbon bond breaking is relative to further oxidation of intermediate species and to compare the stability of intermediate species over gold and platinum catalysts. The Au (111) and Pt(111) surface facets were studied as these are the most stable facets of fcc metals. A secondary objective was determining how the applied potential affects the reaction mechanism and the resulting production percentages of different products.

Chapter 2

Methods

The Vienna Ab Initio Simulation Package (VASP) was used to perform the density functional theory calculations. It is a molecular dynamic and ab initio total energy program.[5-7] The projector augmented wave method was used along with a plane wave basis set with a cut-off energy of 400 eV. The exchange and correlation energies were determined through the use of the Perdew-Wang functional form of the generalized gradient approximation.[8] The k-points grid was created using a 3 x 3 x 1 Monkhorst-Pack grid.[9] For an optimized structure to be reached, the forces on the atoms had to fall below a threshold of 0.05 eV Å^{-1}. The gold and platinum catalytic surfaces were modeled using 4 metal layers in a vacuum slab model with a 3 x 3 unit cell with lattice parameters 8.65 x 8.65 x 21.20 Å^3 and 8.32 x 8.32 x 22.63 Å^3 respectively.

A method for determining the relative energies of the intermediate states was developed to assess the favorability of each electrochemical step. A single oxidation step in a surface reaction can be written as the protonated species bound to the surface being converted to the deprotonated, bound species plus the energies of the proton and electron oxidation products. The reaction energy can thus be modeled by comparing the energies of the reactants and the resulting products of each step. This relation is shown in equation 1:

$$\Delta G_{rxn} = G_{A*} + G_{H+} + G_{e-} - G_{AH*} \tag{1}$$

The left hand side of the equation represents the energy of reaction in the forward direction while components of the right hand side represent the energies of the individual products and

reactants. The energies of the absorbed species can be calculated using VASP DFT calculations.

However, the energy of the solvated proton depends on the applied potential. Using the redox half-cell of the Reversible Hydrogen Electrode (RHE), this energy can be determined as shown in equation 2. At zero potential on the RHE scale, the free energy of an electron and proton pair is equal to that of a H_2 molecule at its standard state.[10] Equation 3 shows how the free energy of the proton can thus be calculated.

$$H_2 \leftrightarrow 2H^+ + 2e^- \tag{2}$$
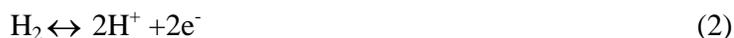
$$G_{H_2} = 2G_{H^+} \text{ at 0 V-RHE} \tag{3}$$

The proton and electron pair energy is equal to that of half of the H_2 molecule at the RHE equilibrium potential, and we reference then the energy of the electron relative to this O V-RHE value. The rate of reaction is also a function of the electrode potential. Therefore equation 1 can be rewritten to account for the energy of the electron as shown in equation 4.

$$\Delta G_{rxn}(\mu_{RHE}) = G_A + [\frac{1}{2}G_{H_2} - e^- \mu_{RHE}] - G_{AH} \tag{4}$$

Here e- represents the charge of an electron while μ is the electrode potential in volts relative to the RHE equilibrium. The energies from this general equation are not definite energies and need to be considered in terms of the specific reaction steps, specifically the oxidation of 1,2-propanediol to lactic and pyruvic acid. This sequence of reactions can be written as shown in equation 5 to represent 1,2-propanediol as the reactant and the product being the intermediate product in question.

$$C_3O_2H_8 + * + H_2O \rightarrow C_3O_xH_y * + n(H^+ + e^-) + (3-x)H_2O \tag{5}$$
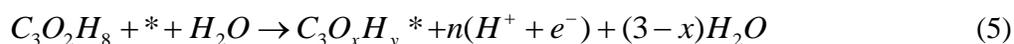
In this equation, * denotes the surface site, x is the number of oxygen atoms in the intermediate, y is the number of hydrogen atoms in the intermediate, and n is the number of electrons transferred. The energies of the proton and electron in this equation can be represented as a function of the potential in the same way they were in equation 4. This allows for the determination of the relative energy of

any surface intermediate species from the energy of 1,2-propanediol, the surface, and water as shown in equation 6.

$$RE(\mu_{RHE}) = G_{C_3O_xH_y^*} - G_* - G_{1,2-propanediol} + (3-x)G_{H_2O} + n[\frac{1}{2}G_{H_2} - e^-\mu_{RHE}] \qquad (6)$$

RE is the relative energy in eV, G_* is the energy of the bare surface, and $C_3O_xH_y^*$ represents the surface absorbed species. This equation can be used for any 3 carbon intermediate. While studying the results of carbon-carbon bond breaking, the formula had to be altered as shown in equation 7.

$$RE(\mu_{RHE}) = G_{C_1O_{x1}H_{y1}^*} + G_{C_2O_{x2}H_{y2}^*} - 2G_* - G_{1,2-propanediol} + (3-x1-x2)\ G_{H_2O} + n[\frac{1}{2}G_{H_2} - e^-\mu_{RHE}] \qquad (7)$$

$C_1O_{x1}H_{y1}^*$ represents the absorbed one carbon species, $C_2O_{x2}H_{y2}^*$ represents the two carbon product.

Many structures were studied during this research, so an alphanumeric nomenclature was adopted to identify different species. The numeric portion represents the oxidation step at which the species occurs. 1,2-propanediol is designated as 0 and each subsequent step increases by one with each electron transferred in the reaction. The letter denotes which pathway the step belongs to. A denotes the pathway initiated by deprotonating the oxygen attached to the terminal carbon while B denotes that initiated by the secondary OH oxidation. Appendix B and C use this nomenclature and the structure of each species is shown visually.

Chapter 3

Results and Discussion

The electrochemical oxidation over gold and platinum FCC crystal structures with (111) surface geometries was studied. The results of the study on the main oxidation pathways over gold is discussed in detail in a previous thesis and are summarized in Appendix A[11]. Using this research as a starting point, the energy required to break a carbon-carbon bond was determined along with the energies of the same oxidation pathway over a platinum catalyst.

Carbon-Carbon Bond Breaking over Gold

To determine whether or not carbon-carbon breaking would be favorable at a given step along the reaction diagram, all possible one carbon products and two carbon products were optimized adsorbed on the surface. Several trends were identified during the mechanistic study over gold. Among these was that structures that were able to form stable gaseous phase molecules would only interact weakly with the surface while radicals would bond first through an unsaturated carbon then through an unsaturated oxygen. This trend was also shown in the absorption of the products of the carbon bond breaking.

Using equation 7, the relative energy of breaking the bond was determined and compared to the energy required to oxidize the compound at each stage. The results of this are summarized at one potential in figure 3-1. While several possible conformations were investigated for each step, only the results of the most favorable conformations are included in the figure. From this diagram it is clear that at every oxidation step, breaking the carbon-carbon bond is not favorable compared to further oxidation.
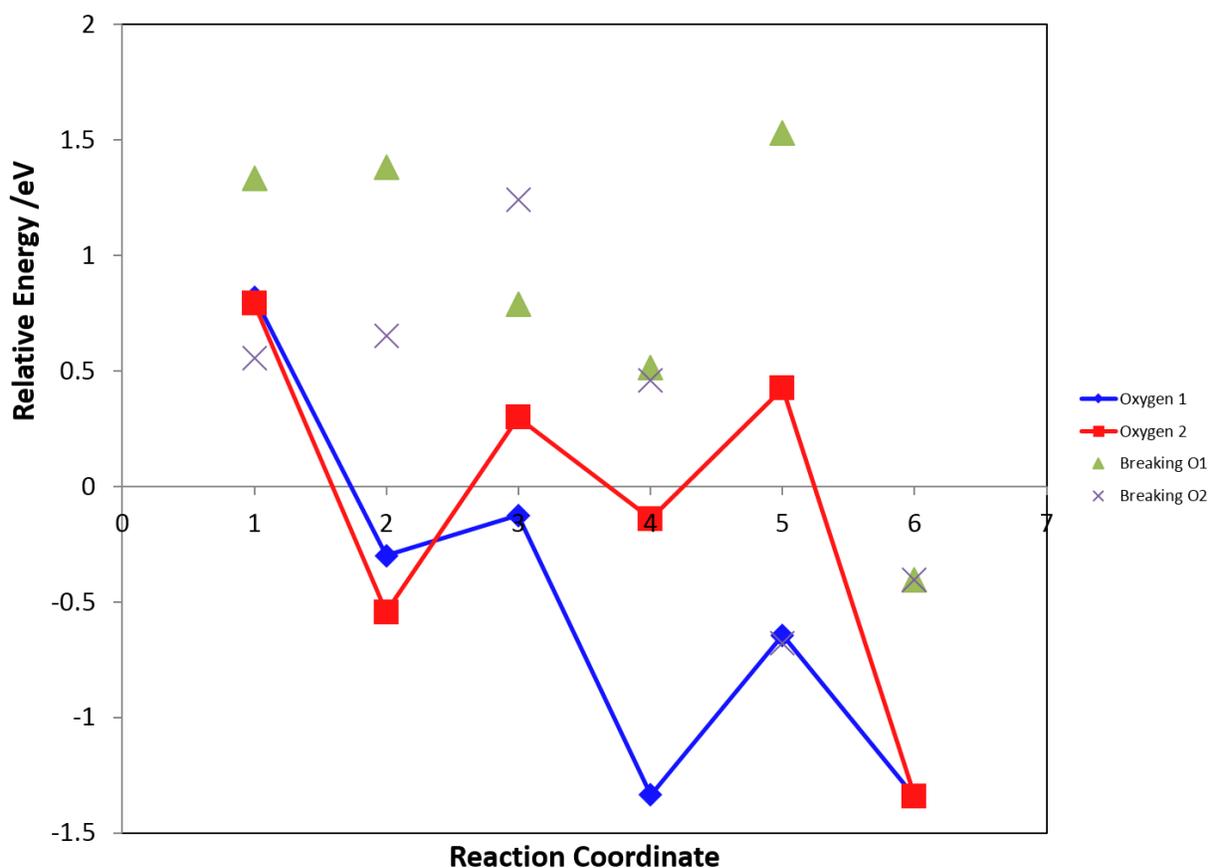
Figure 3-1: Reaction energy diagram for 1,2 propanediol oxidation over the Au(111) surface. The red and blue lines represent the most favorable elementary reaction steps for oxidation to C_3 products initiating with deprotonation of the terminal (blue) and secondary (red) alcohol group. The data points represent the relative energy of surface intermediates, calculated with Equations 6 and 7. Data points are also included for the formation of C-C bond breaking products. Comparison of the stabilities of C-C breaking fragments with intermediates along the preferred reaction paths indicates that carbon –carbon bond breaking is not competitive with further oxidation on the gold catalyst.

Platinum Reaction Energy Diagram

The computational results over gold indicated two possible pathways for the mechanism of this reaction. The results for this are shown in Appendix A. These same structures were optimized over the platinum surface to determine if these same pathways would be followed. The relative energy of each species was determined by calculating the energy of the molecule absorbed on the surface and comparing it to the energies of the bare surface, propanediol in a gaseous state and water. Each species was optimized with the unsaturated atom absorbed at each of the three high symmetry sites on the (1 1 1) fcc facet. In general, unsaturated carbons were positioned atop the surface level atoms, and unsaturated oxygen atoms were positioned in a hollow site between three of the surface level platinum atoms.

To better visualize the favorability of each path and the effect potential has on the reaction, reaction energy diagrams were made at various potentials. Figure 3-2 shows two of these diagrams. The two paths represent the initial oxygen binding mechanism through deprotonation of the terminal oxygen or the secondary oxygen. Only the most favorable configuration at each intermediate along each path is shown.
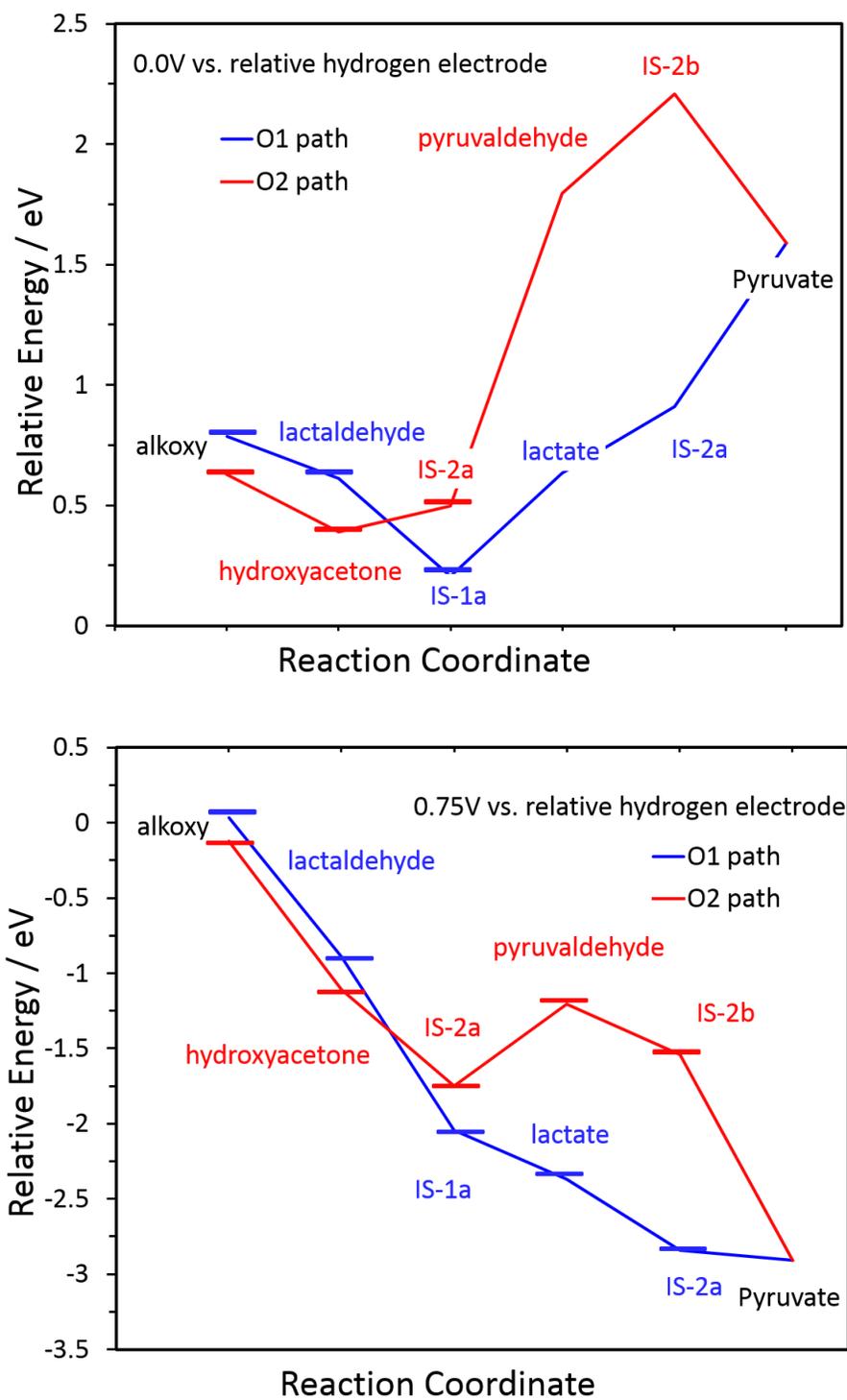
Figure 3-2: Determined reaction pathways showing the relative energies of each intermediate over a platinum catalyst at 0 V-RHE and 0.75 V-RHE.

Comparison or propanediol oxidation between the gold and platinum surfaces

The previous study over a gold catalyst found that the likely path of the reaction mechanism proceeded through deprotonation of the primary carbon then reaction to lactaldehyde before proceeding to lactic acid and finally pyruvic acid. This thesis concludes that this is also the preferred path over a platinum catalyst. The main difference between the two catalysts is that the unsaturated intermediates are able to be stabilized more by the platinum surface than the gold surface. The reaction mechanism as illustrated by the optimized structures of each intermediate is shown in figure 3-3.

O1 Surface Binding

~- absolute energy difference between oxidation states (eV)
*- absolute energy relative to starting material
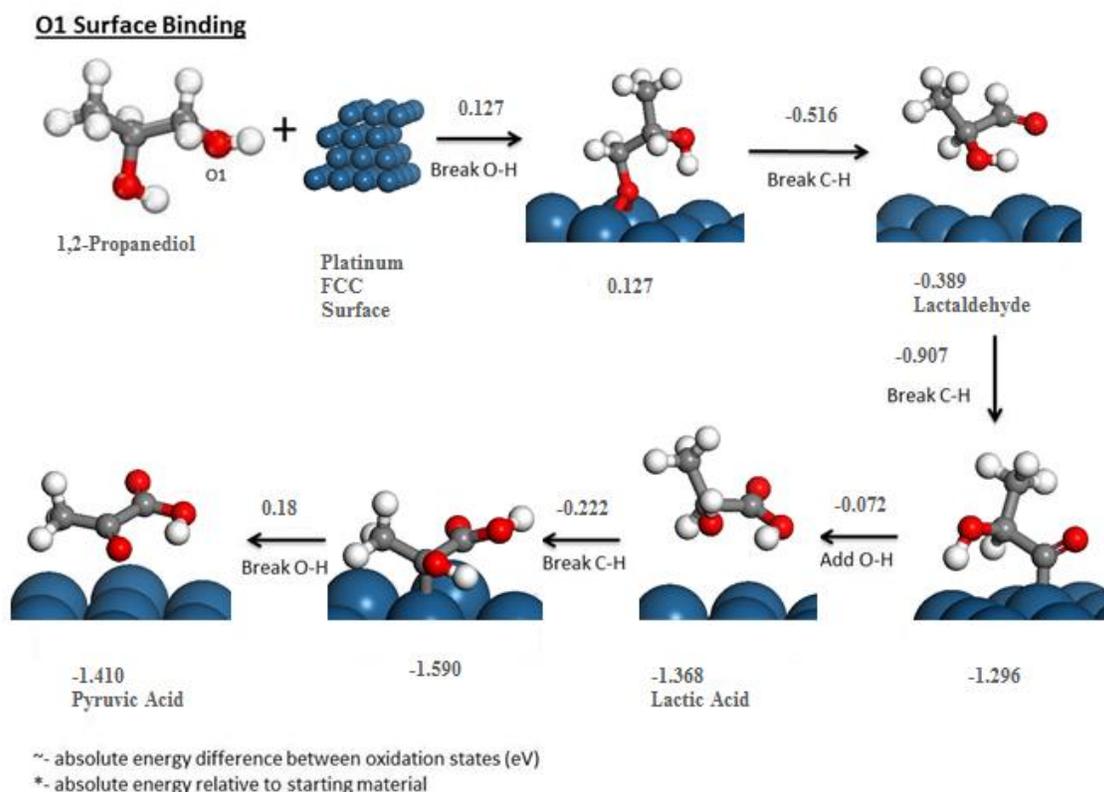
Figure 3-3: The favorable reaction pathway for the oxidation of 1,2-propanediol to pyruvic acid at a potential of 0.5 V-RHE. The preferred pathway is initiated by the deprotonation of the terminal oxygen.

Comparison with Experimental Results

The results from Li et al. indicate a gold catalyst is more selective to pyruvic acid while platinum was found to be more reactive at all potentials[4]. This agrees with the results of this study. Gold was found to have a high energy barrier between lactic and pyruvic acid that decreased as the potential was increased. There were several such barriers throughout the gold reaction mechanism that would lead to lower conversion rates. The platinum catalyst on the other hand was shown to be better able to better stabilize the unsaturated intermediates. This would lead to higher conversions of the feedstock. It is also shown in the experimental results that conversion percentage increases with increased potential over both

surfaces. This agrees with the results of this study; as the potential increases, the energy of activation for all the steps in the reaction decreases and makes reaching the products more favorable.

The one disagreement between this study and the experimental results is that computational analysis of the simplified system was not able explain the discrepancy between pyruvic acid selectivity over the platinum and gold catalysts. Platinum is experimentally only able to produce this product at very high potentials. The reasoning for this is likely that the intermediate between lactic acid and pyruvic acid would be greatly destabilized by hydroxyl groups that would likely be present on the surface. The absorption structure suggested by this research would not be able to bond strongly with the surface if there were a one third monolayer of hydroxyl groups.

Chapter 4

Conclusions and Future Work

The reaction mechanism of 1,2-propanediol to lactic and pyruvic acid over a gold and platinum catalytic surface was computationally studied using density functional theory. The relative energies of possible intermediates were compared to a gas phase 1,2-propanediol molecule, the gold or platinum surface, and water molecules using a derived equation. The intermediates with the lowest energies were compiled in reaction energy diagrams to display the likely reaction mechanism at varying potentials. Over both surfaces hydroxyacetone appeared to be a favorable intermediate as it was more stable than lactaldehyde. However, as no hydroxyacetone was present in the experimental results, kinetic barriers likely exist. This means the formation of lactic acid is likely to be through a lactaldehyde intermediate. Further studies of the activation barriers between these oxidation steps would help to clarify the discrepancy between the experimental and computational results.

Carbon-carbon bond breaking was studied over the gold catalytic surface. Breaking this bond is seen to be unfavorable at every stage of the determined mechanism. This agrees with the experimental data as very little one and two carbon products were produced. However, even unfavorable pathways will occur just at slower rates therefor there was a small concentration of formic acid and acetic acid. Further studies could be done over the platinum surface to confirm these findings.

Over a platinum catalyst, the intermediates bound to the surface of the catalyst displayed much higher stability than the same species over the gold catalyst. As this leads to lower reaction energies over the course of the mechanism, this supports the evidence that the platinum catalyst would me much more reactive than the gold catalyst. However, as the platinum catalyst is unable to produce pyruvic acid except at high potentials, it is not as favorable of a catalyst.

The majority of future work in this investigation would focus on producing different catalytic geometries and compositions. The (1 1 1) facet likely does not accurately represent the metallic electrode. A surface with pronounced steps could be studied to see if some of the unfavorable pathway would be stabilized over these steps. Carbon- carbon bond breaking would also likely be more favorable over these steps and this would better explain the traces of one and two carbon products. Bimetallic catalysts would also be a good field of future study. As the platinum catalyst was shown to be more reactive but less selective to the desired product, a partly platinum and partly gold catalyst could feasibly be used to yield higher selectivity and higher conversion percentages.

Appendix A

Reaction pathway of 1,2-propanediol oxidation over Au (1 1 1)
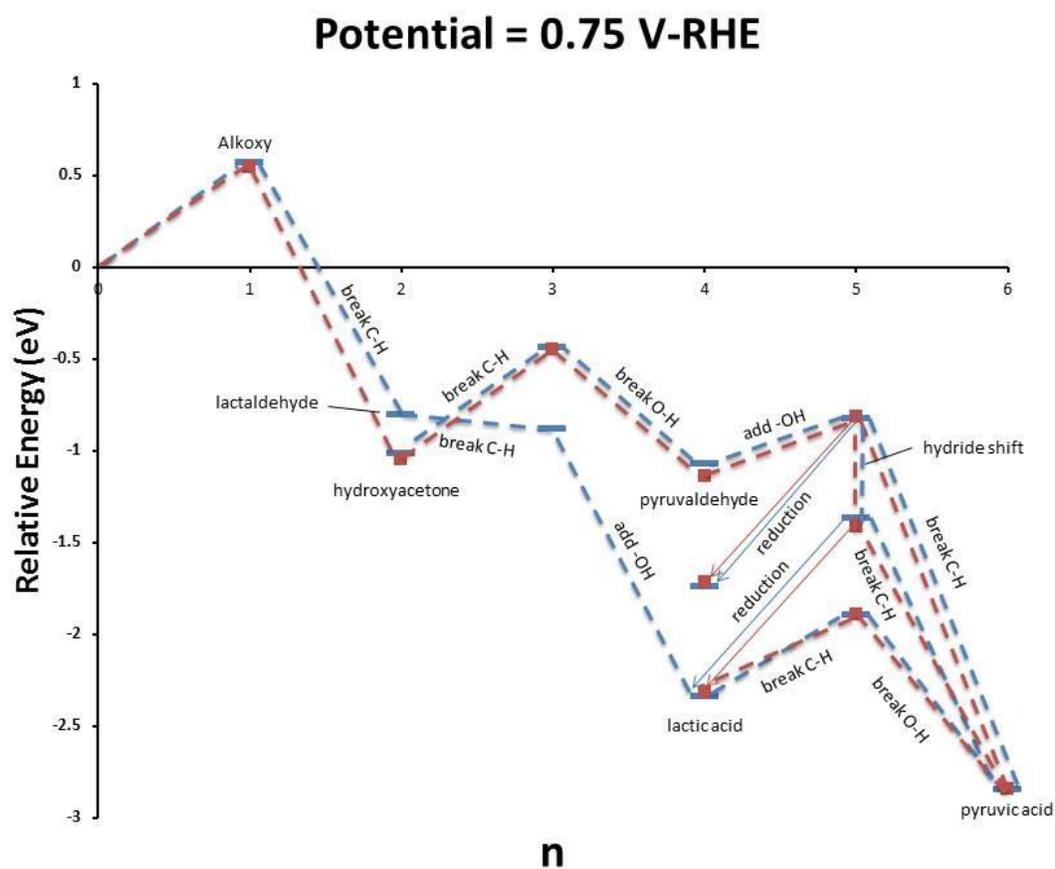
Figure A-1: The determined reaction pathway for the oxidation of 1,2 – propanediol over a gold catalyst. Relative energies calculated at 0.75V RHE.

~- absolute energy difference between oxidation states (eV)
*- absolute energy relative to starting material
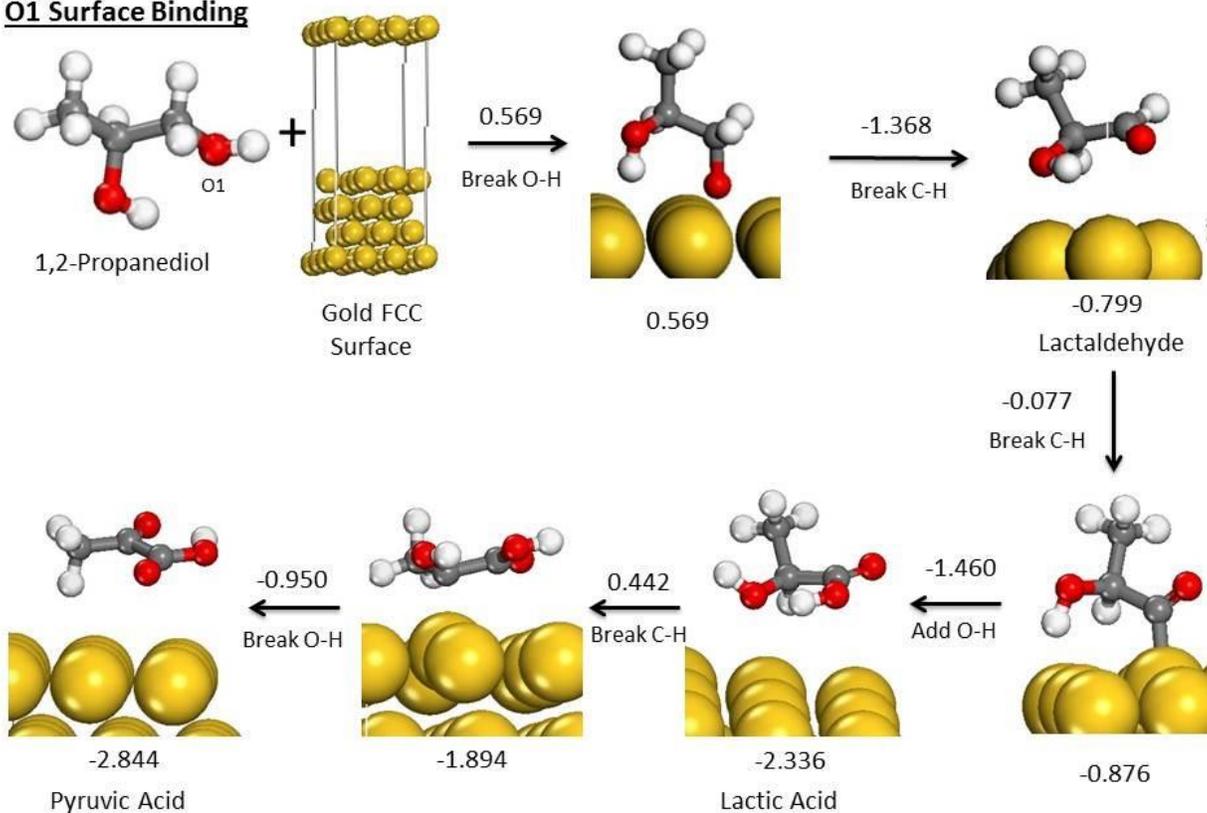
Figure A-2: The favorable reaction pathway for the oxidation of 1,2-propanediol to pyruvic acid over a gold catalyst. The preferred pathway is initiated by the deprotonation of the terminal oxygen.

Appendix B

Optimized structures of 1,2-propanediol oxidation over Pt (1 1 1) surfaces

Table B-1: Most favorable optimized structures of intermediates for the oxidation of 1,2-propanediol with relative energies.

Step Number	Structure Name	Structure	Relative Energy at 0.5 V* (eV)
0	0A		0
0	0B		0
1	1A		0.285
1	1B		0.127
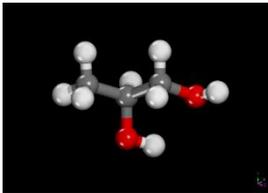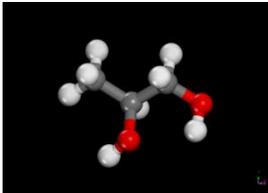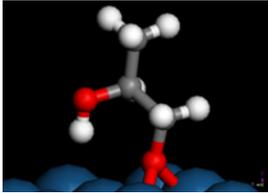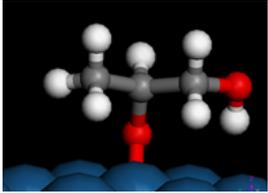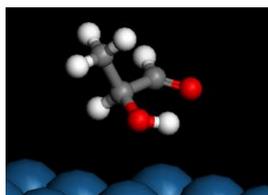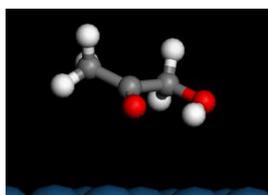
2	2A		-0.389
2	2B		-0.610
3	3A		-1.296
3	3B		-1.002
4	4A		-1.368
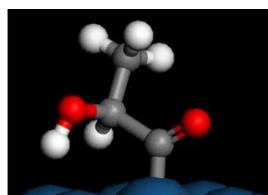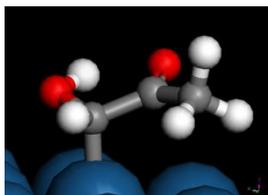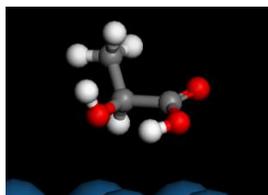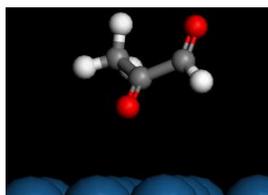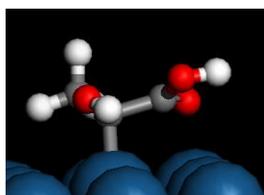
4	4B		-0.206
5	5A		-1.590
5	5B		-0.291
6	6A		-1.410
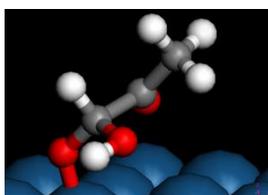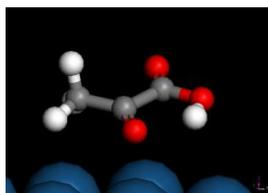
Appendix C

Optimized structures resulting from the breaking of carbon-carbon bonds with the relative energy of the break

Table C-1: Most favorable, optimized products of carbon-carbon bond breaking of the intermediates for the oxidation of 1,2-propanediol.

Step Number	Structure Name	2C End	1C End	Relative Energy at 0.5 V* (eV)
1	1A			1.335
1	1B			0.556
2	2A			1.381
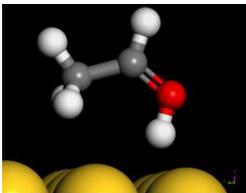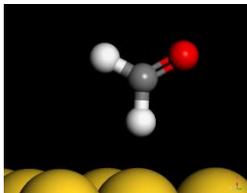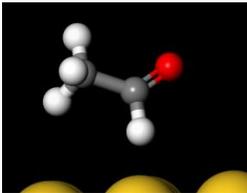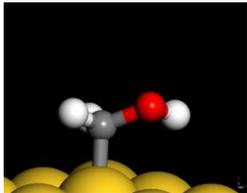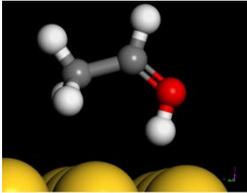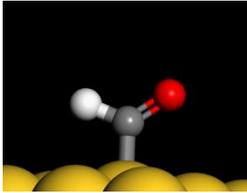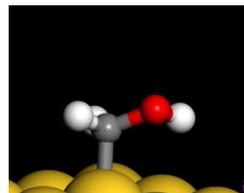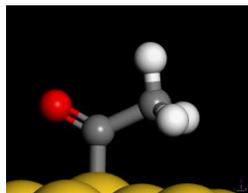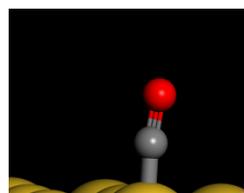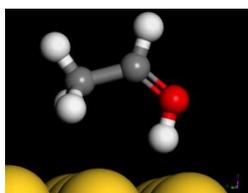
2	2B			0.651
3	3A			0.789
3	3B			1.241
4	4A			0.516
4	4B			0.461
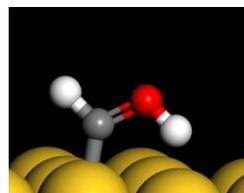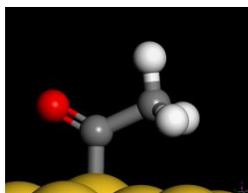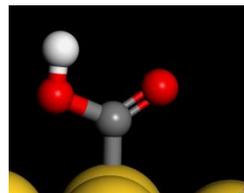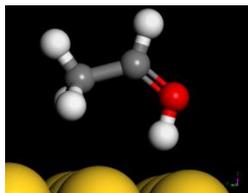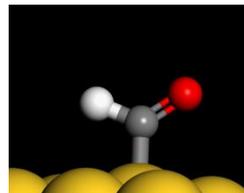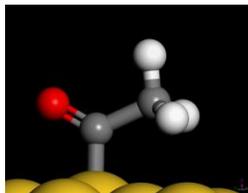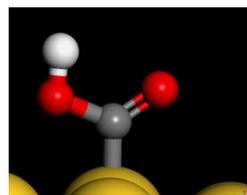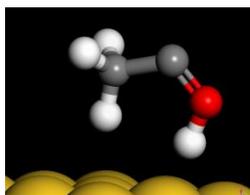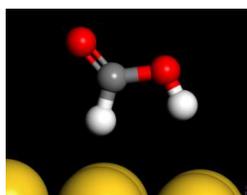
5	5A		1.529
5	5B		-0.680
6	6A		-0.404

BIBLIOGRAPHY

1.   Van Gerpen, Jon. Biodiesel Processing and Production. *Fuel Processing Technology*. **2005**, 86 (10), 1097-1107.
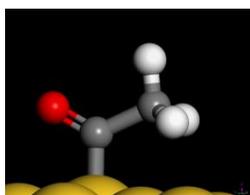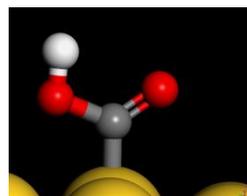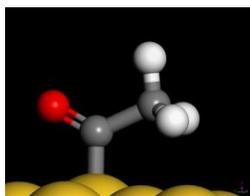
2.   Katryniok, B. et al. Selective Catalytic Oxidation of Glycerol: Perspectives for High Value Chemicals. *Green Chem* [Online]. **2011**.

3.   Zope, Bhushan N.; Hibbitts, David D.; Neurock, Matthew; Davis, Robert J. Reactivity of the Gold/Water Interface During Selective Oxidation Catalysis. *Science*. **2010**, 330, 74-78.

4.   Li, Wenzhen; Chadderdon, David; Xin, Le; Qi, Ji; Brady, Brian; Janik, Michael. Selective Oxidation of 1,2-Propanediol in Alkaline Media Over Supported Au and Pt Nanoparticles in Anion Exchange Membrane Fuel Cell (AEMFC) and Electrocatalytic Flow Reactors. Oral presentation at the national meeting of the American Institute of Chemical Engineers. 7 Nov 2013. San Francisco, CA.

5.   G. Kresse, J. Hafner, *Phys. Rev. B* **47** (1993) 558–561.

6.   G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **6** (1996) 15–50.

7.   G. Kresse, J. Furthmuller, *Phys. Rev. B* **54** (1996) 11169–11186.

8.   J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B*, **46** (1992) 6671.

9.   H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, **13**, (1976) 5188.

10.   Norskov, J.K. et al. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell

        Cathode. *J. Phys. Chem. B*. **2004**, 108, 17886-17892

11.   Brady, Brian.   Determining the electrocatalytic oxidation mechanism of 1,2-propanediol

        using density functional theory. Senior Thesis. 2014.

ACADEMIC VITA

Julie Miller
73 Daniel Drive, Avondale, PA 19311
miller.julie@verizon.net

Education

B.S. in Chemical Engineering, 2015
The Pennsylvania State University, University Park, PA
Schreyer Honors College

Research Experience

University of Michigan, NNIN REU Participant
Department of Electrical Engineering and Computer Science, Dr. Rebecca Peterson
Summer 2014

Penn State University, Soft Materials REU Participant
Department of Chemical Engineering, Dr. Michael Janik
Summer 2013

Penn State University, Fenske Research Lab Assistant
Department of Chemical Engineering, Dr. Michael Janik
Spring 2012-Spring 2015

Honors and Awards

Chemical Engineering Departmental Biofellowship
Omega Chi Epsilon - Chemical Engineering Honors Society
National Member of SWE - Society of Women Engineers

Publications

"Interlayer Dielectric and Interconnect for Heterointegration"; 2014 NNIN REU Research Accomplishments, 50-51, November 2014.

"Selective electrocatalytic oxidation of 1,2-propanediol in continuous-flow alkaline anion-exchange membrane reactors," Pending Publication