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Density Functional Theory Study of Ethanol Dehydrogenation Energies over Kinked Rhodium Surfaces

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Abstract

Combatting climate change requires affordable and carbon neutral energy sources. Hydrogen powered fuel cells have shown potential for filling this role but currently, the most affordable source of hydrogen originates from a carbon positive source. Extracting hydrogen from renewable organic matter using metal catalysis is a way to obtain hydrogen gas for fuel cells in a carbon neutral manner. However, a dehydrogenation catalyst that is competitive with the carbon positive process has not yet been found. To try to find a competitive catalyst, organic molecule decomposition reactions have been researched computational investigations of platinum catalysis over many different surface geometries of platinum. Since rhodium is in the same noble metal group as platinum and there is little data concerning its dehydrogenation capabilities, it was studied to elucidate its' potential as a dehydrogenation catalyst. The free energies for dehydrogenation reactions were calculated using the Vienna Ab-Initio Simulation Package to model ethanol and rhodium interactions over many locations on the catalytic surface. For this study, the research group looked at the (653) (kinked) surface's dehydrogenation reaction energy for the first time. The reaction energy for this surface was found to be lower than that of the (211) surface, which is currently the most efficient rhodium dehydrogenation catalyst. This study also discovered that when predicting dehydrogenation energy for a rhodium surface, the surface's Miller index is the defining characteristic that will determine the reaction energy, instead of the local surface features of a metal catalyst.

1. Background

Affordable and abundant fuel sources are necessary for the provision of transportation and electrical power. Nonrenewable fossil fuels such as coal, oil, and natural gas currently fulfill most this need. Unfortunately, these fuels are consumed in combustion reactions that release carbon dioxide as a major product. Since these fuels are being combusted in large quantities, the accessibility of electricity is ultimately contributing to pollution, environmental destruction, and, in conjunction with other unsustainable environmental practices, climate change. Finding a fuel that does not produce carbon dioxide to replace fossil fuels is crucial to halting these environmental issues. The scientific community around the world is aware of this need and is actively looking for solutions to the looming adverse effects of climate change, but many nations are reluctant to implement clean energy sources because of the economic expense in their production.

Research into fuel cells may provide an answer to the growing demand for both an affordable and a non-polluting source of electricity generation. Rather than inefficient combustion reactions generating energy as work, fuel cells directly utilize the chemical combination of hydrogen and oxygen gases, which is a process that produces an electrical current but releases no pollutants or carbon dioxide as a byproduct. While the fuel cells themselves are efficient and nonpolluting, the most profitable method of obtaining the hydrogen gas needed for the fuel cells utilizes natural gas. This process is called methane reforming and is cost effective, but like fossil fuel combustion reactions, releases carbon dioxide as a product to obtain the hydrogen gas. This only shifts the dependence of one fossil fuel onto another.[1]

Methods for producing hydrogen gas from renewable, clean sources are too costly to operate on an industrial scale and this is thus promoting inquiry into more cost-effective catalytic reformers.[2] If sources of plant matter (abundant in organic molecules) that contain large amounts of hydrogen atoms can be used for the production of hydrogen fuel, the use of fuel cells can become a carbon neutral source of energy. This will subsequently help fight climate change.

In this study, the process to create renewable sources of hydrogen gas is researched by analyzing reaction energies for dehydrogenation catalysis interactions over a (653) Miller index surface, utilizing ethanol (an organic molecule) as the primary reactant. In the process of dehydrogenation, the decomposition of organic molecules to hydrogen gas is hindered by an energy barrier, which is determined by the transition states of the molecules between their reactant and product states. When a catalyst is introduced, the molecules can bind to the surface of the catalyst in a process known as adsorption, which lowers the reaction energy barrier due to energy stabilization from the catalyst.[3] As a result, reactions require less activation energy to go to completion and can occur at lower temperatures. As the temperature required for a reaction gets closer to ambient conditions, a lowering of production costs occurs, which leads to more affordable sources of hydrogen gas. While it has been shown that introducing a catalyst will lower the energy barrier for many hydrogen obtaining catalytic reactions, the cost-effectiveness has not yet matched that of forming hydrogen gas from methane reforming. Before new dehydrogenation catalysts can be created and tested, a fundamental understanding of the catalytic reaction mechanism is needed. Quantum mechanical calculations can elucidate the ways organic molecules will break bonds in catalysis and give more insight to the fundamental mechanics of the catalysis reaction. From this mechanistic insight, trends in the decomposition of organic molecules and thus, the most cost effective way to produce hydrogen gas can be elucidated.

Observations of the changes in the energy barrier can be carried out by first modelling molecules and catalysts computationally. Modelling in this way can show preliminary energy differences that arise when certain aspects of the catalyst are changed. This is able to direct the search for an efficient catalyst as a chemical ansatz. Quantum mechanical calculations first create energy potential interactions between atoms and then allow the atoms to move to more favorable positions as metal and adsorbate species according to a premade functional theory. By changing various parameters, such as molecule orientation over the catalyst or molecule type, the potential differences of the modelled system lead to different stabilization values for the reaction energy and can give valuable information about the catalytic strength of dehydrogenation reactions. If a highly efficient catalyst structure is elucidated from the computational research, experimental tests can then be performed to determine if the structure is possible to create. If so, additional real-world tests to observe actual dehydrogenation reactions will determine if the process is effective enough on an industrial scale to produce clean and inexpensive hydrogen gas from a system based on computational study.

To begin the computational study of these catalysts, virtual models of adsorption interactions are created for a wide array of molecules and catalyst surfaces. Then, Density Functional Theory (DFT) quantum computations simulate the molecule-catalyst adsorption energies. As the simulation proceeds, the atoms interact with each other and conform to the most stable configuration of energy values. Once the most stable configuration has been found, the potential energy locations are optimized and reoriented in modelling software so conclusions can be drawn from the final optimized positions of the atoms. The reason for these calculations' use is two-fold. First, having the same basis for the calculations that collect data throughout the research group's history is vital for comparing results. Secondly, DFT calculations are incredibly useful for observing the effects of catalysis[3] and thus, there is a broad use of DFT calculations for dehydrogenation catalysis reactions,[2,4,5,6,7,8] which allows results to be compared between research groups easily.

For determining catalytic effects, ethanol has been used often due to its ability to model many bonds that are prevalent in organic molecules, but also due to promising research in ethanol steam reformation for dehydrogenation that is being tested with a multitude of catalysts.[9] These studies have been bolstered by investigations of the same rhodium structures for planar[2] and stepped[6] surfaces by other research groups. The results from these research groups confirm findings on planar surfaces in the Wasileski research group, as well as correlate similar trends in the enhanced catalytic activity of stepped (211) surfaces in comparison to planar (111) ones. In the field of ethanol catalysis, rhodium is only one of the many metal systems that are being investigated. In the platinum group metal field of focus, Sutton and Vlachos[10] have performed numerous DFT assays on planar arrangements of metals begin to define which metals are more likely to act catalytically and the specific trends in bond cleavage for ethanol.

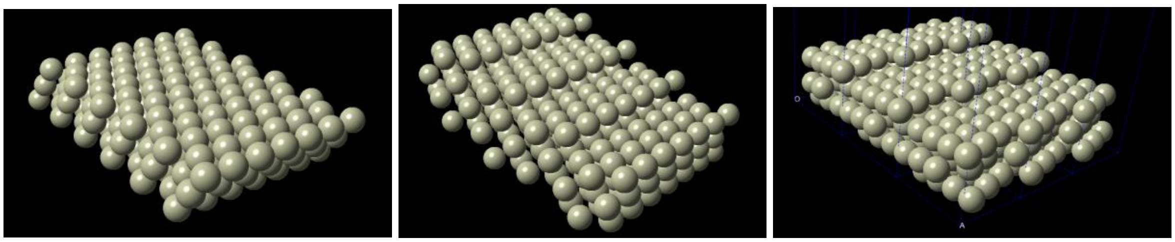

Figure 1. Left Picture - A (111) Miller index surface, referred to as a flat or planar surface. Middle Picture -A (211) Miller index surface, referred to as a stepped surface. The stepping pattern is exhibited by the tiered 111 Miller planes that end and from the tiered pattern form a set of ridges or steps. Right Picture - The (653) Miller indexed rhodium surface.

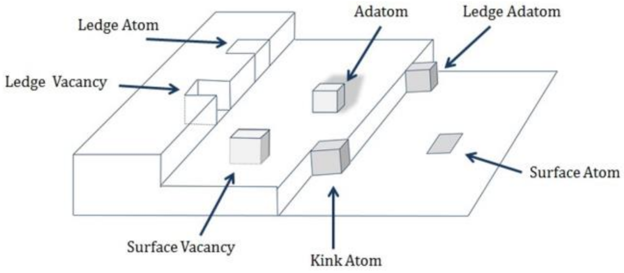

Figure 2. A picture list of defect sites that can occur on a metal surface.[15] This study focuses on ledge atoms, prevalent on the stepped (211) surface and kinked (653) surface, and kink atoms on the (653) surface and the (653) surface derivatives.

Shape control within the field of experimental nanoparticle production has shown that it is possible to control the shape of nanoparticle surfaces, based on the seed particles used and the reaction environment itself.[11] As agglomeration kinetics are better understood over time, papers such as the Personick and Mirkin[12] study and Yu et al.[13] which investigate the creation of nanoparticles and the kinetics of the catalytic interactions with nanoparticles, will only continue to increase their importance in the design of catalysts. Especially as the mapping of the surface of catalysts are made (such as the study by Barnard and Chang[14]), DFT calculations will play an important role in the preliminary searches for effective catalysts. While the Wasileski group focuses on platinum group metals, it is important to note experimental findings show that viable candidates are not restricted to these groups of metals. The catalytic tests run by Biswas and Kunzru[9] uses catalytic oxides to drive their real-world tests of ethanol steam reforming and show alterations of the surface of catalysts can induce dramatic changes in the energy requirements for catalytic activity. Overall, the contributions of each research group to this field are continuing to build the database of knowledge on the specifics of catalytic activity and the methods of creating new catalysts. Combining trends in activity from all of these studies can help direct the search for the best catalysts for ethanol steam reforming.

For this research project, a (653) surface structure (fig. 1) was created for a rhodium catalyst. This surface was chosen due a hypothesis created from the observed change in reaction energy between the (111) surface and the (211) surface, in which the reaction energy was more negative (and thus more favorable) for the (211) surface. The hypothesis was that the (211) surface had the lower reaction energy because the ethanol dehydrogenation was occurring on the low-coordinated atoms of the (211) surface. The surface ledge atoms that dehydrogenation occurs at on the (211) surface interact with fewer metal atoms than the surface atoms on the (111) planar surface and were thus, “low coordinated” atoms. On the (653) surface, the “kink” atoms that repeat over the surface (fig. 2) have an even lower coordination than the (211) ledge atoms and if the hypothesis was correct, these kink atoms should make the (653) reaction energy more negative than the (211) surface. Each surface atom in the repeating rhodium unit cell was tested for the favorable free energy resulting from interactions between the surface with an ethanol molecule and the resulting ethoxy radical. Multiple orientations of the ethanol molecule were tested over each of the surface atoms, to elucidate the reaction energy to a high degree of accuracy.

2. Experimental

The Shiva supercomputer housed in the Zeis building on the University of North Carolina at Asheville's campus was used to perform the DFT calculations for this project. To create the coordinates needed for the Vienna Ab-Initio Simulation Package (VASP)[15,16,17] first, a (653) rhodium catalyst unit cell was created using the visualization software, CrystalMaker. This program allows atoms to be located and oriented by the user so that desired starting locations of molecules can be chosen by researchers. Then, these locations can be returned in orthogonal coordinates that are able to be processed by computational calculations. The unit cell must be large enough that it can encompass an ethanol molecule easily and be designed to form a repeating kinked structure pattern. An ethanol molecule was placed close to the metal surface where adsorption can occur and the modeling of the ethanol molecule's position was based around possible orientations of the metal to oxygen interaction (fig. 3). For example, some calculations have the ethanol molecule perpendicular to the surface, some include a single carbon metal interaction in conjunction with the oxygen to metal interaction, and so forth (fig. 3). To calculate how well the surface can remove hydrogen from the molecule, is was also necessary to use CrystalMaker to also model an ethanol molecule derivative called an ethoxy radical. This ethoxy radical has the same number, kind, and orientation of atoms, except in that it is missing one hydrogen atom from the oxygen on the ethanol molecule. The choice to remove the hydrogen atom from the oxygen as the dehydrogenation reaction was due to previous study by the Wasileski research group that found the most favorable hydrogen dehydrogenation reaction was the removal of the hydrogen bonded to ethanol's oxygen atom over a rhodium surface.

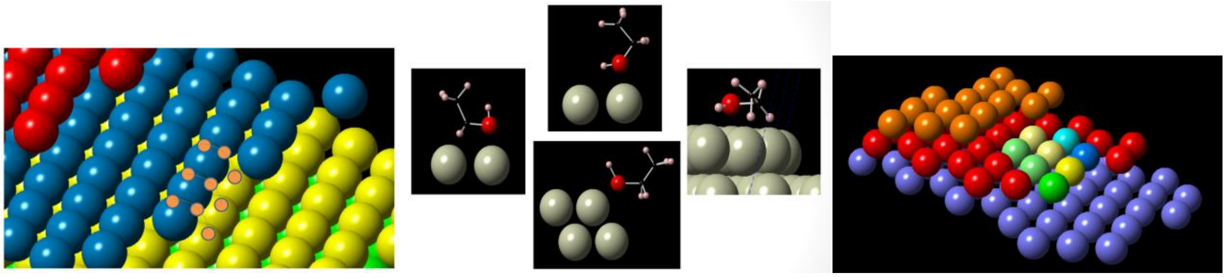

Figure 3. Left picture: Positions over the step area that the oxygen atom on the ethanol molecule was modeled over as indicated by orange dots. Middle picture: An example of orientations of the ethanol molecule over the surface Right Picture: Visual showing positions for graphic nomenclature where the green atom is referred to as the obtuse atom, the yellow atom is referred to as the middle atom, and the blue atom is referred to as the acute atom. This nomenclature extends from the ledge and into the planar areas of the (653) surface as show by the lighter colors.

The calculations were performed using VASP to run the DFT base calculations using the PW91 functional. The DFT calculations begin with the assumption that the energy of the system can be modelled effectively by treating non-valence electrons as a single electron density for each atom. Then, the unit cell created in Crystal Maker is repeated so a surface of a catalyst can be simulated by allowing these unit cells to interact with each other and creating a continual surface like one that would be found on a nanoparticle or industrial scale catalyst. The PW-91 functional was chosen by previous researchers in the Dr. Wasileski research group due to its effectiveness in accurately modelling catalytic interactions. Finally, calculation time can be greatly reduced through the linear correlation of activation energy to the final energy of the products that are known as Bronsted-Evans Polanyi relations.[18]

Once calculations are input into VASP and the programmed calculation completes, the free energy value for the modelled system is returned. The stability of adsorption states is determined by these values, with lower free energies corresponding to more stable states. For example, if a molecule over one position on the surface has a higher free energy than another position over the surface, the latter position will be the most likely spot that a molecule will adsorb. The most favored spot that the ethanol will adsorb to will be the one that the overall catalytic reaction energy can be calculated from. The reaction energy is then calculated in a simple products-minus-reactants equation of the free energy. The systems modelled as reactants for this formula are the bare metal surface and the adsorbed ethanol molecule. The product systems are an adsorbed ethoxy molecule and an adsorbed hydrogen molecule. Once the most favorable binding site is located, the reaction energy for the entire surface is a result from the products-minus-reactants equation. Finally, the overall reaction energy for the dehydrogenation reaction over the surface can be calculated by combining the most favorable sites for binding and the resulting reaction energy from modelling a catalytic reaction at this location.

3. Results

The ethanol over metal, ethoxy over metal, and hydrogen over metal calculations were performed over the rhodium (653) surface. From these calculations, the most stable location for the ethanol and ethoxy to bind to was found to be the obtuse ledge atom. Because this is the most likely place for the ethanol molecule to interact, the products and reactants used for the reaction energy calculation were found from this location. Once the free energies were output by VASP, the reaction energy for an ethanol's oxygen dehydrogenation was found to be -0.223 eV. As shown in figure four, this reaction energy is significantly higher than the reaction energy for the planar (111) surface, but is also significantly lower than the (211) surface. Similar trends in the binding energy appear for the surfaces as well (fig. 4)

The energy of binding for the ethanol molecule to the surface is shown in figure 5. The more energetically stable the adsorbate species is at a certain location, the more it will attract the ethanol to that location. Thus, reactions will occur at this area due to the ethanol molecules quickly moving to be bound at this most favorable site. The overall trends in the ethanol binding energy are given by figure 7. The resulting orientations of the ethanol molecules after the quantum calculations were completed show the ethanol molecules in a low-coordinated position, nearly always tending to favor interactions with only one rhodium atom and being as far as possible from all other surface atoms.

Ethoxy binding energy was much higher than ethanol binding energies (fig. 6), however in comparison to previous rhodium surface studies, the step sites on the (653) surface were much lower than the (211) step sites and only marginally better than the (111) plane. In comparison to the (111) plane, the terrace sites on the (653) surface were lower in energy than the (111) planar surface. In comparison to the ethanol binding over the (653) surface, ethoxy binding preferentially occurred in high coordination sites, with the ethoxy radical bound by its oxygen to multiple rhodium atoms. This most favorable site excluded the carbons from interacting with the (653) surface the most. The aggregated trends for the favorable location for ethoxy binding is shown by figure 7.

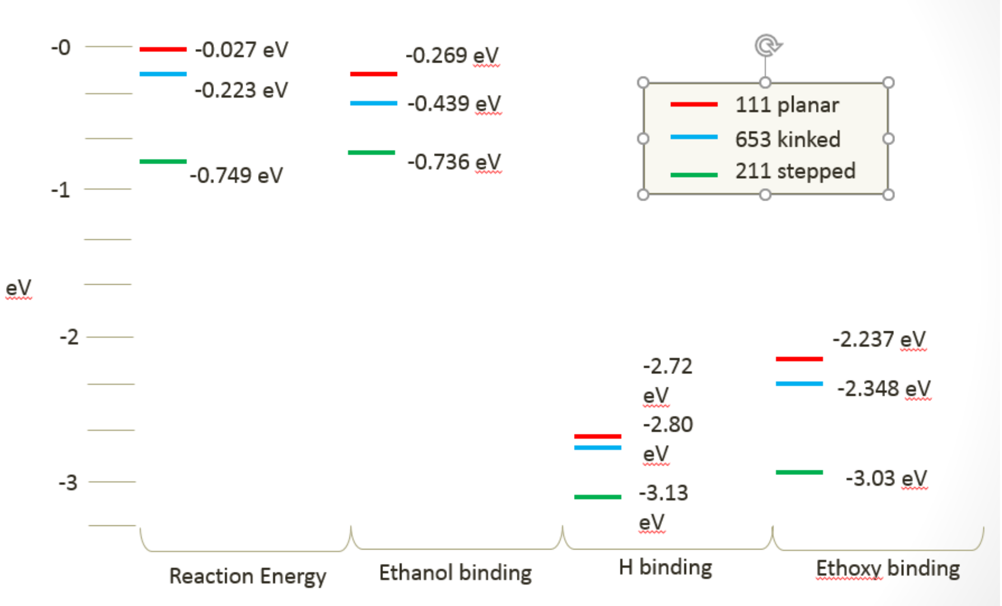

Figure 4. Ethanol binding, hydrogen atom binding, and ethoxy binding energies to the surface of rhodium catalysts. The overall reaction energies follow the trends in binding energy for each of the surfaces.

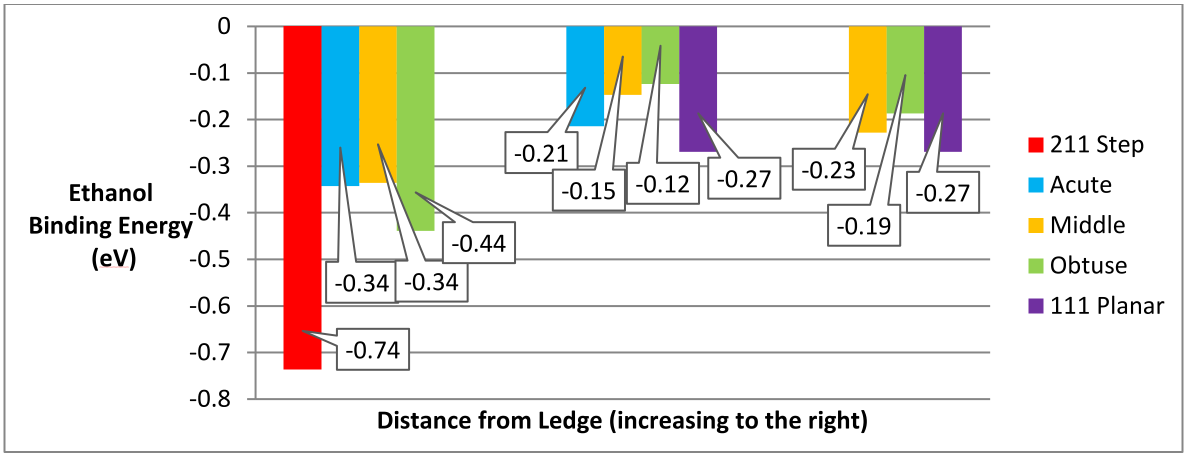

Figure 5. Ethanol binding energy. Groups of binding energies correspond to position of the surface atoms in relation to the ledge of the (653) surface, with the far left group being at the ledge, the middle group being one row back from the ledge, and the right group being two rows back from the ledge. Refer to figure 3 for a visualization of this.

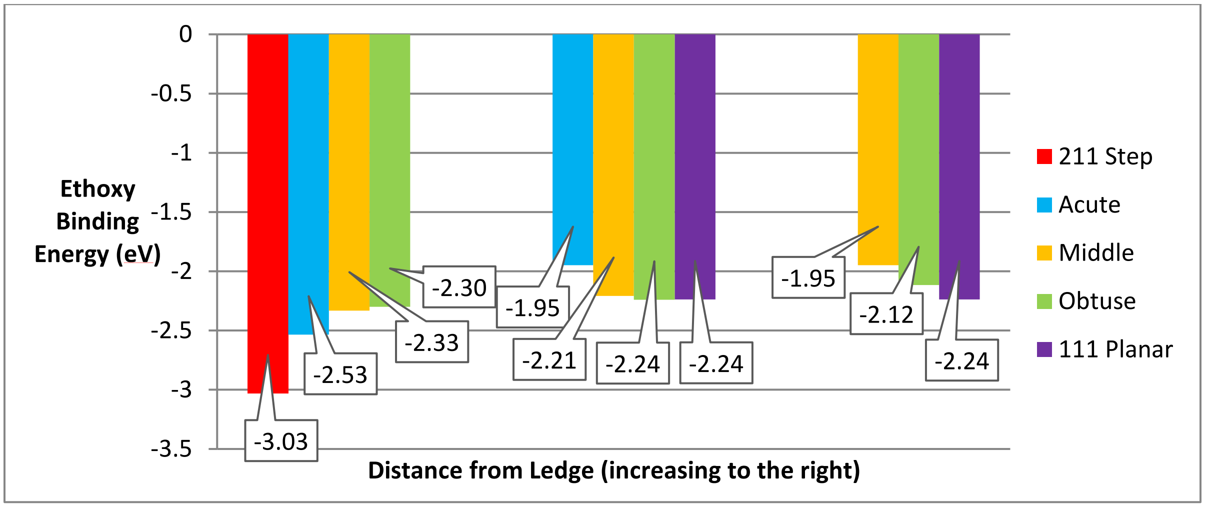

Figure 6. Ethoxy species binding energy. Groups correspond to the description given in figure 5.

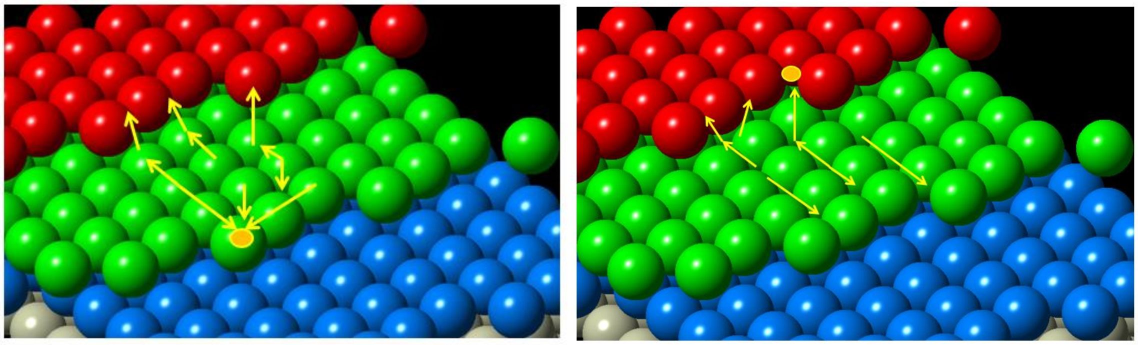

Figure 7. Left picture: Yellow lines indicate the binding energy gradient for an ethanol molecule with direction of arrows indicating a more favorable binding environment. The most favorable position is indicated by the orange dot.

Right Picture: Yellow lines indicate the binding energy gradient for the ethoxy radical with direction of arrows indicating a more favorable binding environment. The most favorable position is indicated by the orange dot.

From the most favorable positions for the ethanol molecule binding and the ethoxy radical binding, the oxygen dehydrogenation reaction was favorable at a -0.223 eV difference between products and reactants. As stated previously, this reaction energy is not as high as the stepped surface, but is much higher than the reaction energy for the planar surface. This trend in energy shows that it is not necessarily the degree of coordination on individual atoms that will make a surface more reactive or less reactive, but is a property inherent of the kind of surface's Miller index. Even though the coordination of the metal atom does not determine the reaction energy, the number of metal atoms bonded to another one of the surface atoms does determine where the most reactive points on a catalytic surface will be (figs. 5 & 6). Atoms with a low bond-order conservation, such as the obtuse atom on the (653) surface, will exhibit a high binding energy with electron rich molecules, such as the ethanol molecule. This could be due to the lack of repulsion against the lone pairs of electrons on the oxygen atom in the ethanol molecule (fig. 7). The ethoxy species showed the opposite kind of trends, with the electron deficiency of the ethoxy radical being fulfilled from electron dense areas, such as at the acute site.

4. Conclusion

The (653) Miller index plane for a bulk rhodium catalyst was found to dehydrogenate ethanol's oxygen molecule with a reaction energy of -0.223 eV. The best site for binding was around the obtuse kink atom at the ledge of the surface, which is a different site in comparison to the planar (111) and stepped (211) surfaces. From these results, it has been shown that while the atoms that interact with fewer other surface metal atoms are more reactive on their respective surfaces, it is the geometry of the surface itself that determines the reaction energy for dehydrogenation. Factors that characterize molecules, such as the degree of oxidation on an atom or the electronegativity of a functional group, are important in determining how the molecules will interact with a surface. Depending on the length of the organic molecule and what kinds of interactions and dehydrogenation reactions should occur first, the surface of the catalyst can be designed to direct decomposition reactions in a much more controlled way. Currently, for ethanol dehydrogenation, it has been shown that the (211) surface is still the most promising for obtaining hydrogen gas efficiently. However, if this high reactivity needs to be moderated, the alteration of the surface to have kink atoms included can provide tunability towards the energy of decomposition and thus, the decomposition pathway for other organic molecules.

Future studies should look at the distinctions between the planar and stepped surfaces to high Miller index surfaces. To allow for nanoparticle modelling, computational studies must discover what the characteristic is that distinguishes the kinked surfaces' energy from the step surface energy. Finally, adatom structures (fig. 2) over a catalytic surface should also be tested to begin to add additional trends for nanoparticle modelling.

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