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Project Title: Using Density Functional Theory to Predict Heterogeneous Catalysts for the Selective Formation of cis-2-Butene from 1,3-Butadiene

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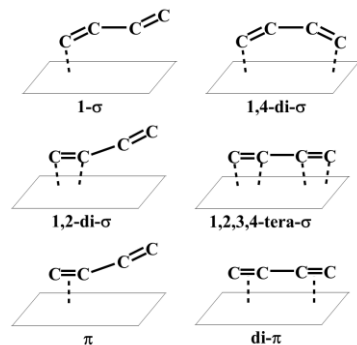


Figure 1: Schematics of possible adsorption modes of 1,3-butadiene with the generic metal surface.

with the underlying metal atom between carbon 1 and carbon 4. A π interaction would have a surface atom beneath the double bond between carbon 1 and carbon 2. It has been shown that depending on the substrate the binding mode of 1,3-butadiene preference can be modulated. For example, 1,3-butadiene adopts di- π bonding on the Pt(111) surface but it adopts di- σ mode on Pd(111) surface. We have calculated the adsorption modes of several olefins on the Cu(111) surface.

To determine the binding modes for cis-1,3-butadiene, trans-1,3-butadiene, 1-butene, cis-2-butene, and trans-2-butene, the organic molecule was optimized with the C2-C3 bond placed over a Bridge (Br) site, a hollow hexagonal close-packed (H_{hcp}) site, a hollow face centered cubic (H_{fcc}) site, or a top site on the Cu(111) surface. These binding sites can be seen in Figure 1. These periodic DFT calculations were conducted using the VASP.5.3.3 software package using the vdW-RevPBE functional, which includes non-local correlation. A summary of our calculations can be seen in Table III. The corrugation energy is determined by looking at the energetic difference between the most and least energetically preferred sites. A smaller corrugation energy indicates that the potential energy surface is relatively shallow for the adsorbate sticking to the surface which leads to a greater mobility of the adsorbate molecule on the surface. The corrugation energies also give insight on if the adsorption is considered chemisorption or physisorption. Typically molecules with a smaller corrugation energy are considered physisorbed.

The binding energy was calculated was determined by:

$$BE = E_{\text{surf-ads}} - E_{\text{ads}} - E_{\text{surf}}$$

, where BE is the binding energy, $E_{\text{surf-ads}}$ is the energy of the surface-adsorbate system, E_{ads} is the energy of the optimized gas phase adsorbate molecule, and E_{surf} is the energy of the relaxed 64 Cu atom slab. A negative value indicates an energetically unfavorable situation whereas a positive value indicates a favorable energy of adsorption. One can also get a clear picture of chemisorption vs.

Narrative:

In this study, we plan to tackle this problem by utilizing Density Functional Theory (DFT) calculations to uncover new heterogeneous catalysts and catalytic pathways on pure and doped copper, silver, and gold surfaces. However, before this goal can be accomplished, an understanding of the interaction between the surface and the adsorbate of the unadulterated Cu, Ag, and Au surfaces must be understood and modeled properly. Currently, we are investigating the interaction of the isomers of butadiene, and the isomers of butene on the Cu(111) surface using DFT.

It is clear that the adsorption mode of the adsorbate on the surface of the catalyst must first be considered before it can be hydrogenated. There are several adsorption modes that 1,3-butadiene can adsorb to a metal surface. A schematic representation of these modes is shown in Figure 1. We adopt the standard notation that indicates the carbon that interacts with the surface, along with how the double bonds interact with the surface. For example, a 1,4-di- σ interaction (shown in the top right of Figure 3) would have a σ interaction with the underlying metal atom between carbon 1 and carbon 4. A π interaction would have a surface atom beneath the double bond between carbon 1 and carbon 2. It has been shown that depending on the substrate the binding mode of 1,3-butadiene preference can be modulated. For example, 1,3-butadiene adopts di- π bonding on the Pt(111) surface but it adopts di- σ mode on Pd(111) surface. We have calculated the adsorption modes of several olefins on the Cu(111) surface.

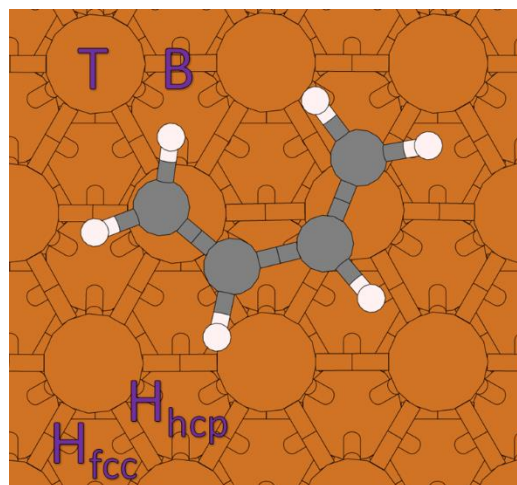


Figure 2: A structure model of cis-1,3-butadiene with the C2-C3 bond over a H_{hcp} site. Top (T), Bridge (B), hollow face centered cubic (H_{fcc}) site, or hollow hexagonal close-packed (H_{hcp}) sites are indicated. The grey/white/orange spheres represent carbon/hydrogen/copper atoms, respectfully.

physisorption by considering the binding energy. For example, benzene on Au(111) is considered to be a physisorbed adsorbate with an experimental binding energy of about 15.9 kcal/mol. In the case of all our adsorbate molecules listed in Table III, it is clear they are all physisorbed as evident by their small corrugation energy and small binding energies.

For cis- and trans-1,3-butadiene the H-C-H bond angles of the outermost carbons change from 117.1/117.3° in the gas phase to approximately 115.5/116.9° for the cis-/trans-isomers, respectively. However, the central carbons (C2 and C3) C-C-H bond angle remained unchanged when adsorbed at an angle of approximately 119°. This shows that the hybridization of C1 and C4 is switching from a more sp² hybridization to a more sp³ environment while C2 and C3 remain relatively unchanged from their more sp² hybridization which provides evidence for the 1,4-di-σ binding mode for both isomers on Cu(111).

We have decided to focus on cis-1,3-butadiene due to the prominent bond elongation/shortening. We are currently considering the following:

- Comparing different density functionals. We are investigating the possibility of using the less computationally expensive Grimme3 empirical dispersion rather than nonlocal correlations.
- Determining the impact of coverage, i.e. the amount of molecules on the surface, on the bond modulation and hydrogenation mechanism.
- Determine the impact of the surface's composition on the bond modulation and hydrogenation mechanism.
- Determine the minimum required of the depth of the surface to obtain chemical accuracy. By utilizing a model with less atoms, but not compromising the chemical accuracy of the model, computations can be conducted more quickly.

The results of our preliminary calculations investigating the interaction of 1,3-butadiene and butene isomers on the Cu(111) is currently being prepared as a manuscript for the *Journal of Physical Chemistry C* with a submission goal of the end of the 2020 academic year.

Impact on Career

Thanks to the generous funds the PRF, I have been able to purchase several new computing servers and the TURBOMOLE software package which have enabled me to conduct computational investigations that would have been impossible for me to complete without the funding. Being at a small primarily undergraduate institution (PUI) undergoing financial challenges, these funds effectively increased by research budget by 10-fold. I have been able to recruit more research students to conduct research by having the ability to pay them which would have never been an option. Additionally, these servers & programs have enabled me to produce preliminary data for a National Science Foundation – Environmental Chemical Science Grant for \$119,373 for the years of 2019-2021. Additionally, I have made it to the 2nd round of applications for the Cottrell Scholar Award which funds the PI with \$100,000 in unrestricted research funds thanks to preliminary data also generated by the servers/software purchased via the PRF funds. A total of 4 research manuscripts have been recently submitted to peer-reviewed journals, all of which were supported by the PRF funds. The PRF funding was also highlighted as my nomination and acceptance of the St. Bonaventure University Junior Faculty Award for Professional Excellence.

Impact on Students

I was able to fund 6 undergraduate researchers for the 2018-2019 grant year. 4 of these students worked with me over the summer enabling them to conduct research. Additionally, through this funding we were able to recruit Jonathan Antle, a transfer student from Jamestown Community College, to join the St. Bonaventure Biochemistry Department as a student starting the Fall 2019. Alex Izydorczak presented her research at the ACS National Conference at Boston in 2019. She has been accepted into a Ph.D. program in chemistry at SUNY, University at Buffalo. She co-authored a paper with me that is currently under review.

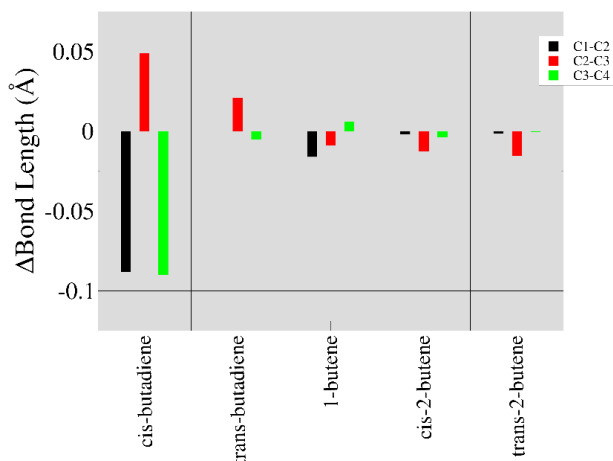


Figure 3: Deviation of bond lengths of the isomers of 1,3-butadiene and butene adsorbed on Cu(111) compared to the gas phase, as reported in Å. A negative/positive value denotes an elongation/shortening of the bond upon adsorption.