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UNDERSTANDING BaTiO$_{2.5}$H$_{0.5}$ (BTOH) LATTICE HYDRIDES IN THE
HYDROGENOLYSIS OF POLYETHYLENE

By

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A capstone project submitted for Graduation with University Honors

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ABSTRACT

Plastics are often made up of organic molecules, such as polyethylene, which contain carbon-carbon bonds that are difficult to break down as they require significant energy input. Additionally, most plastics are not properly recycled. This ultimately results in substantial amounts of waste that pollutes our environment. Recent studies indicate that a process called hydrogenolysis can be used to help solve this problem by converting single-use plastics into potentially useful fuels or chemicals. Specifically, through selective hydrogenolysis of polyethylene, high-energy carbon-carbon bonds that are found within the molecule can be cleaved using an H_2 molecule. Researchers have also observed that catalysts can be used to further enhance this hydrogenolysis reaction. We are particularly interested in a new type of material known as a perovskite oxyhydride, $BaTiO_{2.5}H_{0.5}$ (BTOH). That being said, this study examines how polyethylene interacts with the surface of a BTOH perovskite oxyhydride and explains how surface hydrides from BTOH can depolymerize polyethylene. The results from this study will provide insight into developing more effective depolymerization catalysts using mixed metal oxides and improving depolymerization methods via low-energy input.

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INTRODUCTION

Background

The production and consumption of single-use plastics has constantly undergone environmental analysis since the start of this practice in the 1950's (Geyer et al., 2017). Such scrutiny is primarily attributed to the improper recycling methods employed for disposing single-use plastics and the resulting large-scale creation of waste associated with its production. A study conducted by Geyer et al. (2017) found that as of 2015, only 9% of plastics have been recycled out of the 6300 million metric tons that has been generated, and the majority (~79%) ends up in landfills. This overall poses a problem to the environment in that many plastics are non-biodegradable and will not decompose over time. The reason plastics cannot be broken down is because of their chemical nature and properties. Single-use plastics are commonly composed of long-chain, hydrocarbon polymers like polyethylene or polypropylene. These molecules are rich in carbon-carbon (C-C) bonds that are strong and require a large energy input in order to be broken—i.e., around +3.6 eV (Huang et al., 2018). Essentially, plastics are difficult to depolymerize because they contain high-energy C-C bonds that cannot be easily made into simpler molecules.

The basic approach to solving this problem with plastics and diminishing its effects on the environment is to simply melt and remold plastic waste into other useful products via mechanical recycling. This approach, nonetheless, has its disadvantages in that plastics have a limited number of uses. Serrano et al. (2012) found that after successive trials of mechanical recycling there was a significant decrease in the quality of plastic that was produced. This reached a point where other treatments were needed to remove additional waste. All things

considered, researchers have looked into other plastic degradation methods, specifically those that focus on polyethylene depolymerization. One method of interest is a process called pyrolysis, in which thermal heat is applied to substances as a way of causing chemical changes (Soltes & Elder, 1981). Typically, temperatures used during pyrolysis are above 400°C in order to ensure cleavage of high-energy C-C bonds (Zhang et al., 2020). Though pyrolysis is adequate for depolymerizing polyethylene, studies show that it is not the favored method for plastic degradation. This is because at such high temperatures pyrolysis is a considerably energy intensive process, indicating an energetically unfavorable reaction process (Rorrer et al., 2021). In addition to this, it was observed that pyrolysis creates a mixture of chemical products with varying chain lengths—i.e., it has low product selectivity (Serrano et al., 2012).

A more promising avenue for plastic degradation is a process termed hydrogenolysis or rather selective hydrogenolysis of polyethylene. This is where an H_2 molecule is reacted with an organic molecule like polyethylene and resultantly cleaves a C-C bond in the process (Celik et al., 2019). The reason this method is favored for plastic degradation is because hydrogenolysis can depolymerize polyethylene at milder reaction conditions with decreased energy input and higher product selectivity (Rorrer et al., 2021). To elaborate, Rorrer et al. (2021) found that selective hydrogenolysis of polyethylene performed at temperatures between 200-250°C and H_2 pressures between 30-50 bar allowed for selective depolymerization of polyethylene molecules in plastics. Celik et al. (2019) also notes that liquid products—that is, lubricating oils and waxes—made from hydrogenolysis of polyethylene are of higher quality. This means that products made from hydrogenolysis serve a more useful purpose to people and their everyday lives. That being said, hydrogenolysis is considered as a better alternative to methods like

pyrolysis because it does not have the potential to cause thermal destruction to molecules and more likely selects for desired products.

Research has also shown that catalysts can be used to increase the reaction rate of selective hydrogenolysis of polyethylene. Specifically, Rorrer et al. (2021) observed that liquid alkane products were formed in mild conditions when selective hydrogenolysis of polyethylene was aided by a ruthenium-based catalyst. The catalyst, in particular, is composed of ruthenium nanoparticles that are supported onto a carbon surface (Ru/C). Additionally, it is known to achieve 92% to 100% conversion into liquid and/or gaseous products via low-energy input (Rorrer et al., 2021). This study overall suggests that catalysts can be applied to hydrogenolysis reactions with polyethylene as a way of promoting reaction activity and product formation with low-energy input.

The catalyst of interest in this experimental study is a type of perovskite oxyhydride with the chemical formula of $BaTiO_{2.5}H_{0.5}$ (BTOH). To preface, a perovskite is a mineral that derives from calcium titanate ($CaTiO_3$) and has applications in devices such as computer chips, solar panels, and batteries. Perovskites have a standard ABO_3 crystalline structure where A is any alkali, alkaline earth, or rare earth cation; B is any transition metal cation; and O is oxygen. Perovskite oxyhydrides, in comparison to perovskites, are very similar in structure as the only difference is that some oxygen atoms are replaced with hydrogen atoms. Furthermore, BTOH perovskite oxyhydride stems from a reaction of barium titanate ($BaTiO_3$) with calcium hydride (CaH). The reason this material can be used as a catalyst, as opposed to its simpler perovskite form, is because the surface hydrides located within the structural lattice that replace oxygen anions increases the material's overall catalytic activity (Wang et al., 2020). To further explain, a study conducted by Kobayashi et al. (2017) that compared $BaTiO_3$ and $BaTiO_{2.5}H_{0.5}$ showed that

added hydride anions in the $BaTiO_{2.5}H_{0.5}$ support provided additional catalytic properties. The study goes on to say that when gaseous N_2 and H_2 were suspended over both individual surfaces, only $BaTiO_{2.5}H_{0.5}$ was able to produce ammonia (NH_3). It was then concluded that the hydride anion along with the titanium atom played a critical role in the catalytic activity of $BaTiO_{2.5}H_{0.5}$. Tang et al. (2018) also found that a hydride-reduced form of $BaTiO_3$—specifically, $BaTiO_{2.4}H_{0.6}$—acting as a support for Ni- and Ru-based catalysts was instrumental in increasing the reaction rate of CO_2 methanation at low temperatures. Evidence shows that this increase in reaction activity is likely due to the influence of a hydrogen atom present in the $BaTiO_{2.4}H_{0.6}$ support, which potentially causes hydrogen spillover—the surface migration of hydrogen atoms from the metal catalyst to the non-metal support surface (Prins, 2012). This essentially means that the hydrogen atoms found in $BaTiO_{2.4}H_{0.6}$ were more successful at implementing the reaction process via lowering the activation energy barrier compared to lattice oxygen atoms in $BaTiO_3$ because the hydrogen atoms are more mobile. That being said, the information gathered from these studies raises the question of whether or not a BTOH perovskite oxyhydride can be used to enhance other reaction processes such as selective hydrogenolysis of polyethylene.

Purpose

This experimental study aims to examine how polyethylene molecules interact with the surface of perovskite oxyhydride material, $BaTiO_{2.5}H_{0.5}$ (BTOH). Specifically, the objective is to observe if hydride anions contained in the BTOH lattice can depolymerize polyethylene in a less costly, energy efficient manner. This will be achieved by breaking a high-energy C-C bond in polyethylene and hydrogenating the terminal carbons of the cleaved bond with the surface hydrides. Through this, the relative energies of different reaction states can be analyzed, and thus provide pertinent information on the energy required to progress the depolymerization of

polyethylene. The results gathered from this study can then be used to contribute insight into developing more effective depolymerization catalysts using mixed metal oxides and improving depolymerization methods involving low-energy input.

METHODS

Experiment Setup

The relationship between the $BaTiO_{2.5}H_{0.5}$ (BTOH) and polyethylene is observed by analyzing the relative energies throughout the hydrogenolysis reaction. This begins by creating a BTOH bulk model and performing energy calculations to determine its ideal structural components. Specifically, the optimal lattice parameters, k-mesh or KPOINT values, and kinetic energy cutoff or ENCUT values are calculated. These values, which are necessary to determine the most stable and energetically favorable bulk structure, are used to configure the appropriate BTOH slab structure for this experiment. Energy calculations involving the BTOH slab are subsequently performed. This includes calculating the energies of the unreacted polyethylene adsorbed onto the surface of the BTOH slab, the fragmented polyethylene cleaved by surface hydrides and adsorbed onto the surface of the BTOH slab, and the fragmented polyethylene cleaved by a gas phase H_2 molecule and adsorbed onto the surface of the BTOH slab. The reaction energy of hydrogenolysis with polyethylene is also calculated in the absence of the BTOH slab. This is achieved by calculating the energies of individual constituents in the hydrogenolysis reaction—i.e., polyethylene, H_2, and the fragmented polyethylene product. The bond dissociation energy is also calculated for a cleaved C-C bond in the polyethylene molecule. All reaction energies in this study were calculated following this equation: $E_{(Reaction)} = E_{(Products)} - E_{(Reactants)}$.

In order to understand how BTOH surface hydrides interact with polyethylene molecules, the relative energies of constituents in the hydrogenolysis reaction and the reaction energy for hydrogenolysis of polyethylene itself must be determined, specifically by employing computational methods. These energies are obtained by performing density functional theory (DFT) calculations via the Vienna ab initio simulation package (VASP), which also models materials like BTOH on an atomic level (Kresse & Furthmüller, 1996). Experimental parameters applied to all calculations include Perdew-Burke-Ernzerhof (PBE), a general-gradient approximation (GGA) that is used for the exchange and correlation energy of electrons; DFT-D3, a van der Waals correction for density functionals; and projector augmented-wave (PAW) potentials, a method that is used characterize and/or manipulate frozen core electrons (Perdew et al., 1997; Grimme et al., 2010). The kinetic energy cutoff or ENCUT used to stabilize the plane waves in a basis set was set at 450 eV. Additionally, spin polarization was used for all calculations in this experiment.

Design of Bulk and Slab Model

The $BaTiO_{2.5}H_{0.5}$ surface structure or slab that is used in this experiment is modeled after a generated $BaTiO_{2.5}H_{0.5}$ bulk. This bulk model, in particular, was made by inserting a hydrogen atom in place of a central oxygen atom located within a 2 x 1 x 1 unit cell of $BaTiO_3$ perovskite. The slab model was created within a 2 x 2 unit cell and has a (211) surface with two hydrogen vacancies; such vacancies were likely caused by the hydrogen atoms reacting with polyethylene. The Brillouin zones of the $BaTiO_{2.5}H_{0.5}$ bulk and slab structures were sampled using a Monkhorst-Pack scheme—that is, a *k*-mesh of 2 x 4 x 4 and 2 x 2 x 1, respectively (Monkhorst

& Pack, 1976). The optimized lattice parameters used to specify the size of the $BaTiO_{2.5}H_{0.5}$ bulk

are as follows for a double-cubic unit cell: $a = 8.06$ Å, $b = c = 4.03$ Å (Wang et al., 2020). These

values align with that of experimental values a = b = c = 4.03 Å for a single cubic cell. With this

in mind, the parameters that are used in the $BaTiO_{2.5}H_{0.5}$ bulk are representative of an

energetically stable bulk structure, and thus play an important role in providing the $BaTiO_{2.5}H_{0.5}$

surface structure (slab) with an optimal framework for future calculations. As shown in Figure 1,

the slab model used in this experimental study—along with other polyethylene and H_2

configurations—were visualized using the Xming display server. This server was also used in

measuring bond lengths and bond angles to ensure proper maintenance of structures and observe
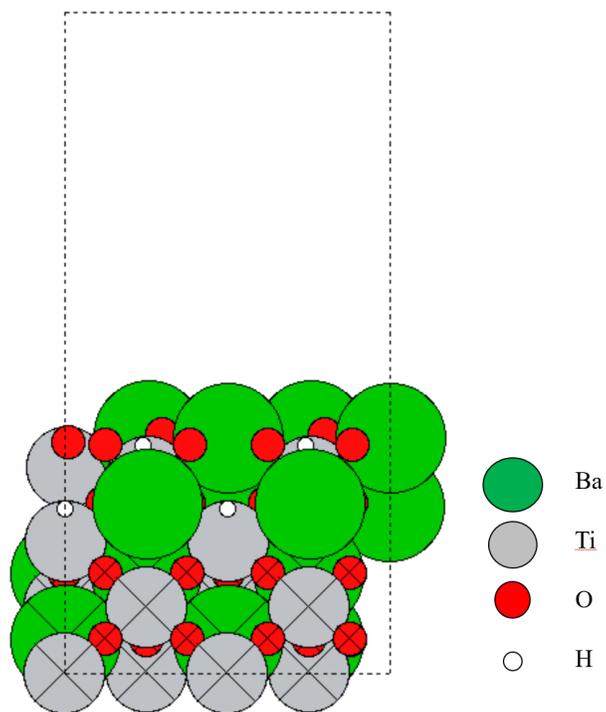
successive structural changes throughout the experiment.

Figure 1. The Xming generated model of the $BaTiO_{2.5}H_{0.5}$ (BTOH) slab with

the corresponding legend for the atoms represented in the structure.

RESULTS

  A total of four reactions and their respective reaction energies were analyzed in this study. To obtain these energies, the energies of each reaction unit was determined individually—i.e., the reactants or initial state structure and product or final state structure for each reaction—using density functional theory (DFT) calculations. Those energy values were then plugged into the equation $E_{(Reaction)} = E_{(Products)} - E_{(Reactants)}$ to find the overall reaction energy. The table and figures below are used to help further explain the collected data.
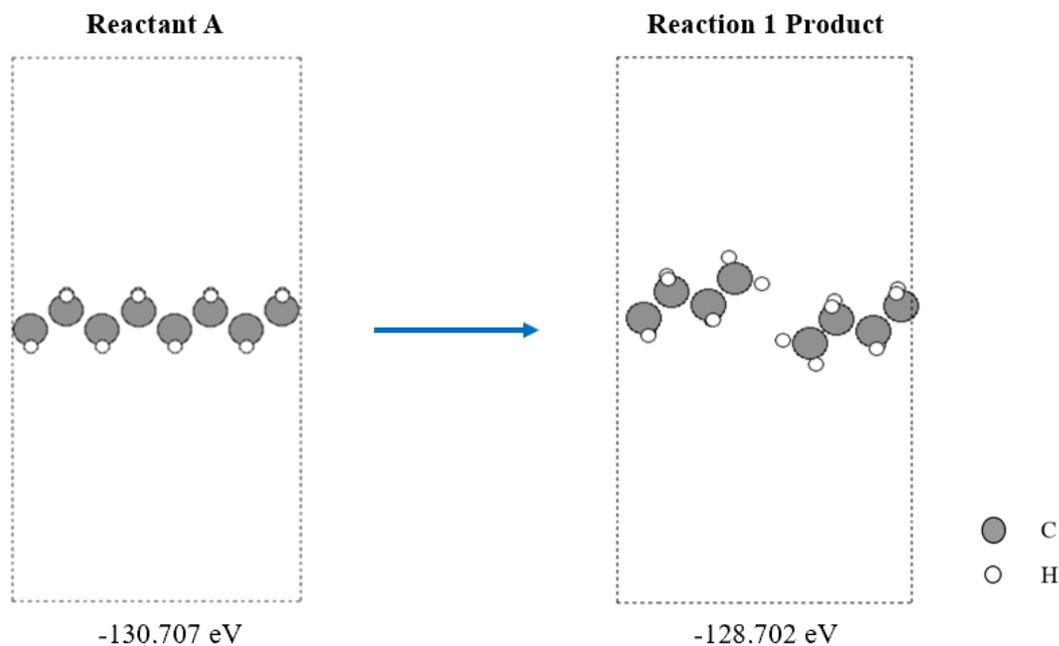

Figure 2. The Xming generated models of components in Reaction 1. Reactant A has a DFT calculated energy of -130.707 eV. Reaction 1 Product has a DFT calculated energy of -128.702 eV. The corresponding legend for the atoms represented in the structures are shown on the lower right.

Figure 2 represents the first reaction analyzed in this study. This first reaction shows the depolymerization of polyethylene without the assistance of external factors, such as catalysts or H_2 molecules used in hydrogenolysis. The figure displays unreacted polyethylene as Reactant A, which has a DFT calculated energy value of -130.707 eV. It also shows the cleaved polyethylene as Reaction 1 Product with a DFT calculated energy value of -128..702 eV.
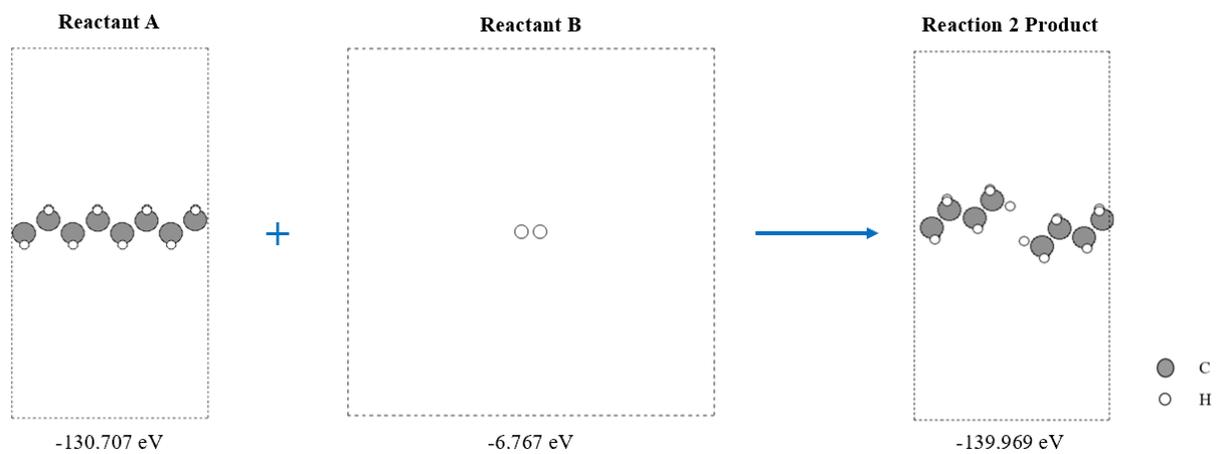
Reactant A	Reactant B	Reaction 2 Product
-130.707 eV	-6.767 eV	-139.969 eV

○ C
○ H

Figure 3. The Xming generated models of components in Reaction 2. Reactant A has a DFT calculated energy of -130.707 eV. Reactant B has a DFT calculated energy of -6.767 eV. Reaction 2 Product has a DFT calculated energy of -139.969 eV. The corresponding legend for the atoms represented in the structures are shown on the lower right.

Figure 3 represents the second reaction that is studied in this experiment. This second reaction is a hydrogenolysis reaction with polyethylene. The figure, in particular, shows a polyethylene molecule (Reactant A) with an single H_2 molecule (Reactant B). This H_2 molecule is used to cleave the C-C bond in polyethylene. The reactants have a DFT calculated energy value of -130.707 eV and -6.767 eV, respectively. The figure also shows the resulting structure of the hydrogenolysis reaction labeled as Reaction 2 Product. This structure has a DFT calculated

energy of -139.969 eV. Additionally, it is important to note that the polyethylene molecule shown is not adsorbed onto the BTOH surface.
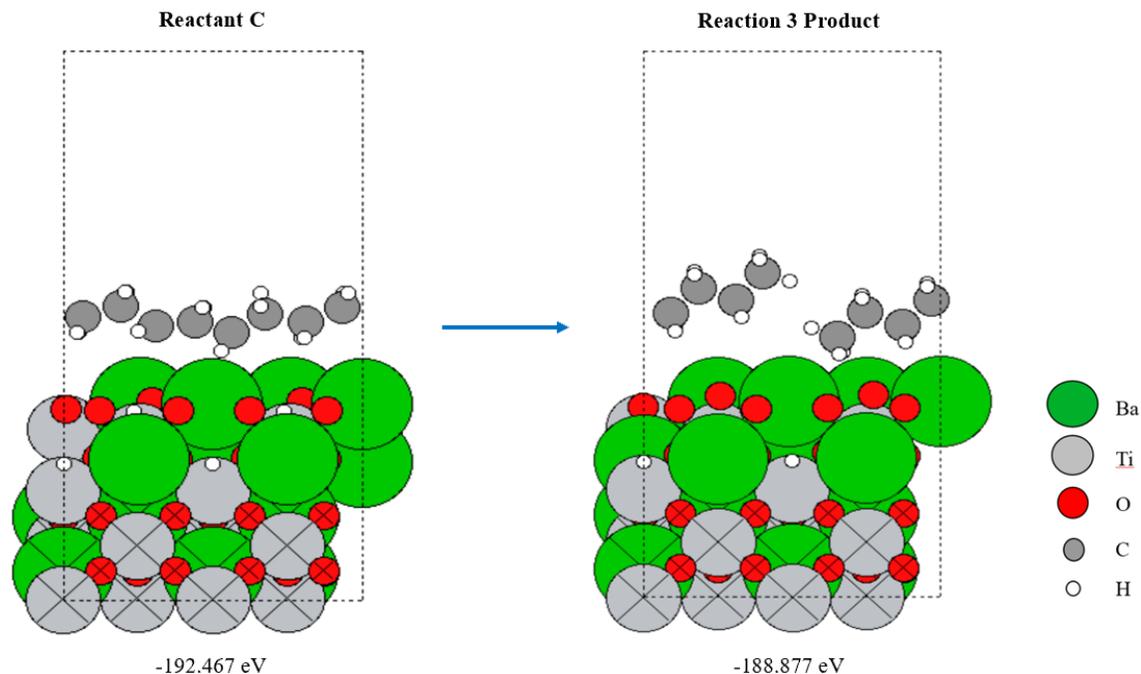

Figure 4. The Xming generated models of components in Reaction 3. Reactant C has a DFT calculated energy value of -192.467 eV. Reaction 3 Product has a DFT calculated energy value of -188.877 eV. The corresponding legend for the atoms represented in the structures are shown on the lower right.

Figure 4 represents the third reaction that is examined in this study. More specifically, it shows the initial state and final state structures involved in the hydrogenolysis reaction of polyethylene with a $BaTiO_{2.5}H_{0.5}$ (BTOH) surface. The hydrogen atoms used to cleave polyethylene are taken from the BTOH slab. Reactant C shows unreacted polyethylene adsorbed onto the BTOH surface with a DFT calculated value of -192.467 eV. Reaction 3 Product shows the final state structure where a reacted polyethylene molecule is adsorbed onto the BTOH

surface and cleaved by hydride anions from the surface. This structure has a DFT calculated value of -188.877 eV.
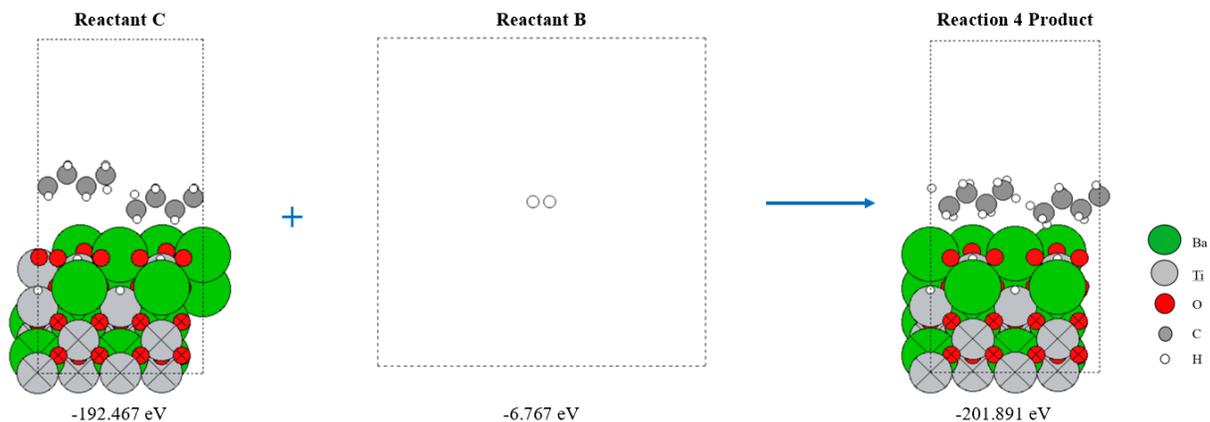

Figure 5. The Xming generated models of components in Reaction 4. Reactant C has a DFT calculated energy value of -192.467 eV. Reactant B has a DFT calculated energy value of -6.767 eV. Reaction 4 Product has a DFT calculated energy value of -201.891 eV. The corresponding legend for the atoms represented in the structures are shown on the lower right.

Figure 5 represents the fourth and final reaction analyzed in this experimental study, which is selective hydrogenolysis of polyethylene using a gas phase H_2 molecule. It shows the same initial state structure (Reactant C) used in Reaction 3, where an unreacted polyethylene molecule is adsorbed onto the BTOH slab surface. This is reacted with an H_2 molecule or Reactant B in order to carry out the hydrogenolysis reaction, as opposed to using BTOH hydride anions. In other words, a separate H_2 molecule cleaves the C-C bond in polyethylene instead of hydrogen atoms from the BTOH slab. Reactants C and B have DFT calculated energy values of -192.467 eV and -6.767 eV, respectively. Together, these two result in the final state structure

labeled as Reaction 4 Product, which is the cleaved polyethylene adsorbed onto the BTOH surface. This structure has a DFT calculated energy value of -201.891 eV.

Reaction Number	Chemical Equation	Reaction Energy (eV)
1	A	+2.005
2	A + B	-2.495
3	C	+3.590
4	C + B	-2.657

Table 1. The calculated reaction energies for Reactions 1 to 4. The chemical equation shows the breakdown of the reactants involved in each reaction. Reaction 1 corresponds to Figure 2; Reaction 2 corresponds to Figure 3; Reaction 3 corresponds to Figure 4; and Reaction 4 corresponds to Figure 5.

Table 1 represents the calculated reaction energies for all four reactions and their corresponding chemical equations. The reaction energy values are determined using the DFT energy values of the reactants and products in each reaction. The equation of $E_{(Products)}$ - $E_{(Reactants)}$ is used to solve for the value of $E_{(Reaction)}$, otherwise referred to as the reaction energy. The term $E_{(Reactants)}$ equates to the sum of the reactants, and $E_{(Products)}$ equates to the sum of the products.

For Reaction 1, $E_{(Reactants)}$ is equivalent to the reaction's initial state structure, which has a value of -130.707 eV. $E_{(Products)}$ is equivalent to the reaction's final state structure with an energy value of -128.702 eV. This results in a calculated $E_{(Reaction)}$ value of +2.005 eV for Reaction 1. $E_{(Reactants)}$ for Reaction 2 is the sum of Reactants A and B with a value of -137.474 eV. $E_{(Products)}$ is equivalent to the reaction's final state structure, which has a value of -139.969 eV. This leads to a

calculated $E_{(Reaction)}$ value of -2.495 eV for Reaction 2. For Reaction 3, the $E_{(Reactants)}$ is equivalent to the reaction's initial state with an energy value of -192.467 eV, and the $E_{(Products)}$ is equivalent to the reaction's final state with an energy value of -188.877 eV. This results in a calculated $E_{(Reaction)}$ value of +3.590 eV for Reaction 3. Lastly, $E_{(Reactants)}$ for Reaction 4 is equal to the sum of Reactants C and B, which has a value of -199.234 eV. $E_{(Products)}$ is equivalent to the reaction's final state structure with a value of -201.891 eV. Thus, the calculated $E_{(Reaction)}$ for Reaction 4 is -2.657 eV.

DISCUSSION AND CONCLUSION

To best interpret these results, Reactions 1 and 2 will be analyzed first. Reaction 1 illustrates the individual polyethylene polymer that is depolymerized without the help of any hydrogen atoms. This produces a reaction energy value of +2.005 eV. Reaction 2, on the other hand, demonstrates a polyethylene polymer that is depolymerized via a hydrogenolysis reaction with an H_2 molecule. This leads to a reaction energy of -2.495 eV. Based on these results, it can be concluded that Reaction 2 is more energetically favorable compared to Reaction 1, as it is an exothermic process. Reaction 1 requires a considerably higher energy input in order to cleave the C-C bond in the polymer chain. This makes Reaction 1 an uphill, endothermic reaction with a difference of +4.500 eV compared to Reaction 2, and thus it is thermodynamically unfavorable. Moreover, it can be observed from these two reactions that hydrogenolysis is a successful method in lowering the activation energy barrier in polyethylene depolymerization as was expected based on previous studies. This also indicates that the H_2 molecule acts as a driving force that moves the reaction towards completion.

Reaction 3 shows the polyethylene polymer adsorbed onto a $BaTiO_{2.5}H_{0.5}$ (BTOH)

surface. In the hydrogenolysis reaction, hydride anions from the surface cleave polyethylene into

what is seen in the final state structure (Figure 4, Reaction 3 Product). This process produces a

reaction energy of +3.590 eV. Reaction 4 also represents the polyethylene molecule adsorbed

onto a BTOH surface. However, this time BTOH does not influence the hydrogenolysis reaction

and rather an individual gas phase H_2 molecule is used to cleave the polymer chain. This leads to

a reaction energy value of -2.657 eV. From these results, it can be seen that Reaction 3 has a

significantly higher reaction energy of ~ 2-fold compared to Reaction 4. Reaction 4 is an

exothermic process, and thus is more energetically favorable in contrast to Reaction 3. This

ultimately means that using BTOH as a catalyst was not successful in lowering the energy input

or activation energy barrier for the hydrogenolysis reaction as was expected based on previous

studies. Instead, it appears that a separate gas phase H_2 molecule acts as a better driving force for

the hydrogenolysis of polyethylene on a BTOH surface as opposed to hydride anions from the

surface itself.

Moreover, the calculated reaction energies show that Reaction 4 is the most exothermic

and thermodynamically favorable process out of all three hydrogenolysis reactions—that is,

Reactions 2 to 4. This indicates that the BTOH surface may play a role in lowering the energy

input in the hydrogenolysis reaction. Nonetheless, both reactions involving a gas phase H_2

molecule contrasts this idea in that the reaction energies for Reactions 2 and 4 differ by -0.162

eV, which is relatively low. Reaction 3, which includes BTOH as well, has the highest reaction

energy value and is the most thermodynamically unfavorable reaction amongst the three. This

means that it is possible that BTOH is able to decrease the reaction energy for hydrogenolysis of

polyethylene, but its effects are not entirely clear nor understood based on the data from this experiment.

The effectiveness of BTOH as a catalyst in polyethylene depolymerization can be further analyzed by comparing Reaction 3 to the standard C-C bond energy and the bond dissociation energy in Reaction 1. Reaction 3 has a calculated reaction energy value of +3.590 eV, and the standard energy value to break a C-C bond is approximately +3.6 eV (Huang et al., 2018). This means that there is a difference of -0.010 eV, which is considerably low in value but could imply that BTOH slightly lowers the overall reaction energy. Reaction 1, which also represents the energy used to cleave a C-C bond, has a reaction energy of +2.005 eV. This implies that Reaction 3 is a more endothermic process by approximately +1.6 eV compared to Reaction 1, meaning that BTOH possibly increases the reaction energy as well. All things considered, it is difficult to determine whether or not BTOH can successfully decrease the energy required to break a C-C bond. This is because the data collected gives rather contradictory results, and thus it is hard to confidently make any conclusions about the effectiveness of BTOH as a catalyst in the breakdown of polyethylene.

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