PROPYLENE EPOXIDATION ON CUO AND LI PROMOTED CUO
CATALYSTS: A DENSITY FUNCTIONAL THEORY STUDY

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ABSTRACT

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Propylene oxide is a significant intermediate chemical which has many derivatives used as raw materials in many industries such as automobile, cosmetic, medicine etc. However, its current production methods, chlorohydrin process and hydroperoxide process, are not preferred since they are economically and environmentally disadvantageous. Considering these negative effects, heterogeneous catalyst for direct propylene epoxidation is still being investigated. With an objective of filling this catalyst gap in the literature, propylene epoxidation mechanism on CuO (001) and Li promoted CuO catalysts are investigated theoretically by means of DFT calculations where VASP code is used. The ultimate goal is to determine the possibilities of the formation of the probable products and to find the energy profiles for both of the catalysts. With this aim, the most probable product formed on CuO catalyst is explored and the effect of Li promoter is observed for the propylene epoxidation mechanism.

To begin with, for partial propylene oxidation on CuO (001) surface, there are two possible reaction pathways for propylene. One of the pathway is propylene oxide or acetone formation through oxygen bridging intermediate surface. Differs from the other studies in literature, oxygen bridging surface is discovered in this study which refers to the chemical adsorption of propylene on the catalytic surface. The other path is acrolein formation through allyl radical on CuO surface. For the first pathway, the activation barriers between the oxygen bridging and propylene oxide is found as 2.89

eV. In addition to that, energy barrier between the oxygen bridging and acetone is calculated as 2.47 eV. These high barriers show that it is not possible to obtain both propylene oxide and acetone on CuO surface. Then, analysis of the second pathway is conducted. After optimizing the geometries of allyl radical and acrolein formation, it is detected that there is no activation barrier between these two structures. Thus, these results clearly show that for the first propylene send to the CuO surface, formation of acrolein product has the highest possibility. It is predicted result for this reaction since the propylene tends to form acrolein on the heterogeneous catalysts due to its allylic hydrogen containing group. After desorption of the acrolein, study continues with the investigation of water on this surface. Two alternatives are tried for the water formation mechanism. One of them is using lattice oxygen to obtain water. The other alternative is adsorbing oxygen molecule to the vacancy that arise from the desorption of oxygen from the surface, and used this oxygen molecule for water formation. For both of these options, results remain unchanged that hydrogen atoms do not want to attached to the same oxygen atom. It is concluded that water is not formed directly on the CuO surface, this catalyst has an ability of splitting water. Afterwards, second propylene is send to the lattice oxygen of the surface and propylene oxide is formed directly. During the research in literature, experimental studies about CuO catalyst show that formation of acrolein and combustion products are observed for propylene epoxidation mechanism. With this information in mind, both possible products, acrolein and propylene oxide, are investigated with respect to their tendency to combust. Calculations for combustion indicate that combustion products of acrolein is two carbon dioxide and one carbon monoxide; however, the energy requirement for this combustion path is really high. In addition to this, combustion results of propylene oxide has a lower energy barrier (1 eV) with the highly oxidizable products of ethenone and formaldehyde. It seems that combustion of propylene oxide is more possible than the acrolein combustion in the gas phase which is consistent with the information gained from the literature. With the objective of increasing the propylene oxide selectivity on the CuO surface, Li is substituted in the catalyst. After optimizing the Li substituted CuO surface, propylene oxide and acrolein formation on this catalyst are investigated for propylene epoxidation. It is clearly seen that Li promoter block the route for acrolein formation by increasing its activation energy to 1.17 eV. Moreover, promoter of Li increases the possibility of propylene oxide formation by decreasing the activation barrier to 0.49 eV. To conclude, it can be said that compared with the CuO catalyst, Li promoted CuO catalyst is more active for propylene oxide formation.

ÖZ

PROPİLEN EPOKSİDASYONUNUN BAKIR OKSİT VE LİTYUM İÇEREN BAKIR OKSİT KATALİZÖRLERİ ÜZERİNDE YOĞUNLUK FONKSİYONELİ TEORİSİ İLE İNCELENMESİ

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Aralık 2014 , 76 sayfa

Günümüzdeki propilen oksit üretimi maliyeti yüksek ve çevreye zararlı proseslere dayalıdır. Bu proseslerin yerine geçebilmesi için heterojen katalizör yüzey üzerinde doğrudan propilen epoksidasyonunun sağlanması istenmektedir. Bu amaç doğrultusunda, CuO(001) ve Li ile desteklenmiş CuO (001) yüzeyleri üzerinde propilen epoksidasyonu Yoğunluk Fonksiyoneli Teorisi (YFT) hesaplamaları kullanılarak Vienna Ab initio Simulasyon Paketi (VASP) ile analiz edilmiştir. Bu çalışmanın nihai amacı, tepkime sonunda oluşacak ürünlerin oluşma olasılıklarını saptamak ve çalışılan katalizörler için enerji profili oluşturmaktır.

CuO katalizörü üzerinde propilen oksidasyonu için birbiri ile rekabet eden iki rota mevcuttur. İlki, oksijen köprüsü olarak adlandırılan ara yüzey oluşumu üzerinden propilen oksit ve aseton elde edilmesidir. Diğer yol ise allil radikalini takiben akrolein eldesidir. İlk rota için yapılan aktivasyon bariyeri analizlerinde, bariyer propilen için 2.89 eV iken aseton için 2.47 eV olarak bulunmuştur. Böylelikle üst yüzeyi oksijen ile kaplı olan CuO(001) yüzeyi, propilen oksit ve aseton oluşumu için etkisiz olarak görülmüştür. Bu yüzey üzerinde, arasında hiç enerji bariyeri saptanmayan allil radikali ve akrolein oluşum olasılığının daha yüksek olduğu tespit edilmiştir. CuO yüzeyine gönderilen ilk propilen sonucunda yüzeyde akrolein oluşum ihtimali en yüksektir, bu da propilenin içerisinde bulunan allil hidrojen içeren gruptan kaynaklanmakta-

dır. Yüzeyden akrolein uzaklaştırıldıktan sonra, reaksiyon döngüsünü tamamlamak için su oluşumu çalışılmıştır. Yüzeyde su oluşumu için iki alternatif değerlendirilmiştir. Bunlardan ilki yüzey oksijeniyle su oluşumu, ikincisi ise yüzeyden akrolein uzaklaştırılmasıyla oluşan boşluğa getirilen oksijen molekülü ile su oluşumudur. İki seçenek de denenmiş ve sonucun değişmediği görülmüştür. Yüzey üzerinde bulunan hidrojenler aynı oksijene tutunmayı reddetmektedir. Böylelikle suyun yüzeyde oluşmadığı aksine dağıldığı saptanmıştır. Daha sonra reaksiyonun devamı için, ikinci propilen yüzeye gönderilmiş ve yüzey oksijeni yardımıyla direkt olarak propilen oksit oluştuğu görülmüştür. Literatür araştırmaları doğrultusunda, aynı reaksiyon için CuO yüzeyi ile yapılan deneysel çalışmalarda akrolein ve yanma ürünlerinin oluştuğu belirtilmektedir. Bu sebep ile, çalışmanın devamında akrolein ve propilen oksitin gaz fazda oksijen molekülü ile yanma reaksiyonları incelenmiştir. Bu çalışma sonucunda, akroleinin yanarken yüksek enerji gerektirdiği ve sonucunda iki karbondioksit ve bir karbonmonoksit oluşumu gözlendiği belirtilmiştir.Diğer taraftan, propilen oksit incelendiğinde, yanma reaksiyonu için 1 eV kadar az bir enerji ihtiyacı olduğu ve reaksiyon sonucunda yanıcı moleküller olan ethenone ve formaldehit oluştuğu görülmüştür. Böylelikle propilen oksit molekülünün akroleine göre yanmaya daha yatkın olduğu söylenebilir. Son olarak, propilen oksit eldesini arttırmak amacı ile CuO yüzeyindeki iki bakır yerine Li eklenmiştir. Yüzey optimizasyonundan sonra, yüzey üzerinde akrolein ve propilen oksit eldesi araştırılmıştır. Açık olarak söylenebilir ki, eklenen Li, akroleine giden yolu aktivasyon bariyerini 1.17 eV'a çıkararak engellemiştir. Bunun yanı sıra, propilen oksit oluşma olasılığını, enerji bariyerini 0.49 eV'a düşürerek arttırmıştır. Sonuç olarak, Li destekli CuO yüzeyinin propilen oksit oluşumu için sadece CuO yüzeyine göre daha aktif olduğu söylenebilir.

Anahtar Kelimeler: Propilen Epoksidasyonu, Bakır oksit katalizörü, Li destekli bakır oksit yüzeyi, Yoğunluk Fonksiyoneli Teorisi (YFT)

To my family and my soulmate

ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

This chapter intends to provide fundamental concepts about the main aspects of the subject. The reader can gain general knowledge about the definition and classification of catalysts. More specific information is obtained about the heterogeneous catalysts. This section also provides background information about the molecular modeling of the heterogeneous catalysts by means of DFT method. Furthermore, propylene epoxidation reaction mechanism is mentioned with its possible products. Lastly, objective of this study is explained throughout the information given within this chapter.

1.1 Catalysis

Catalysis is a field that effects on so many different aspects of science especially chemistry and chemical engineering. Catalysis is the general concept for the function of accelerating the chemical reaction by a catalyst. Catalysis has become a key element for the chemical processes from the early part of twentieth century up to present. It is increasingly growing that today more than 95% of the production of goods from various raw materials in chemical industry is produced with a catalytic process.

1.1.1 Catalyst

Catalyst is a compound which accomplishes speeding up the reaction of the chemical, whereas remains the same after the occurrence of the reaction. However, during the catalytic process, catalyst is interacted with the reactants by bonding them with

chemically. Reactants are linked to the catalyst and products are released from another form of the catalyst, this is a catalytic cycle which is shown in the Figure 1.1. Intermediate surfaces of the catalysts are experimentally not possible to observe during the cyclic process. Catalysts are used not only for production of materials but also in recycling processes, energy processes and environmental processes. [9]
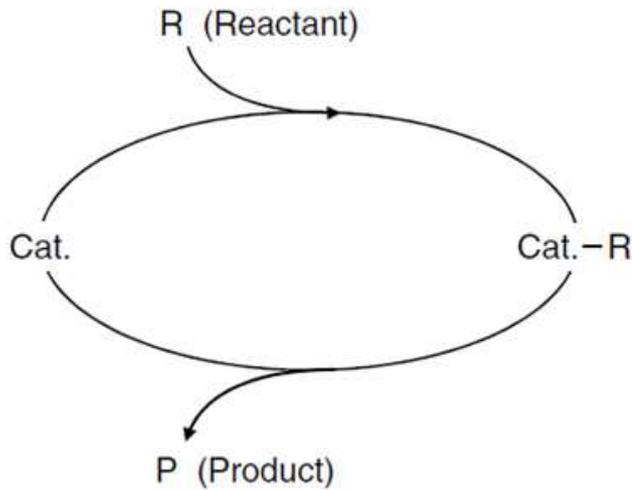
Figure 1.1: Catalytic cycle for a reaction [9]

From a chemical point of view, catalyst can change the reaction pathway towards the lower energy which directly impinges on the mechanism of the reaction. A very simple form of a reversible chemical reaction is represented as

$$A \longleftrightarrow B \tag{1.1}$$

in which A is the raw material and B is the product or vice versa. [1]

The relationship between the reaction rate and the concentration of the reactants are shown as in (1.2). If the reactions are assumed as first order. [1]

$$\text{Reaction Rate (forward)} = k\,[A]$$
$$\text{Reaction Rate (reverse)} = k'\,[A] \tag{1.2}$$

As it is obviously seen from the equation, reaction rate relies on the rate constant and the concentration terms. A catalyst increases the value of rate constant so as to lowers the activation energy as dictated by the Arrhenius Equation (1.3). ,this allows the reaction occurs more rapidly. [1]

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$$k = Ae^{Ea/RT} \tag{1.3}$$

Activation barrier is the energy that is required by the reagents to get started to a reaction. The reason of this energy requirement is generally for breaking the existing bonds to link new chemicals. The reactants should overcome this energy barrier to transform into the products. The major role of the catalyst is to decrease this activation energy indicated by the arrows in the Figure 1.2 . As seen from the illustration, lowering the barrier does not always end with the same product formation, sometimes catalyst may also cause the modification of the product distribution. Dotted line and solid thick line show the path of uncatalyzed and catalyzed reactions end with the same product, respectively. The solid line in the Figure 1.2 refers to the reaction occurred with a catalyst but product that is formed at the end is different. [5]
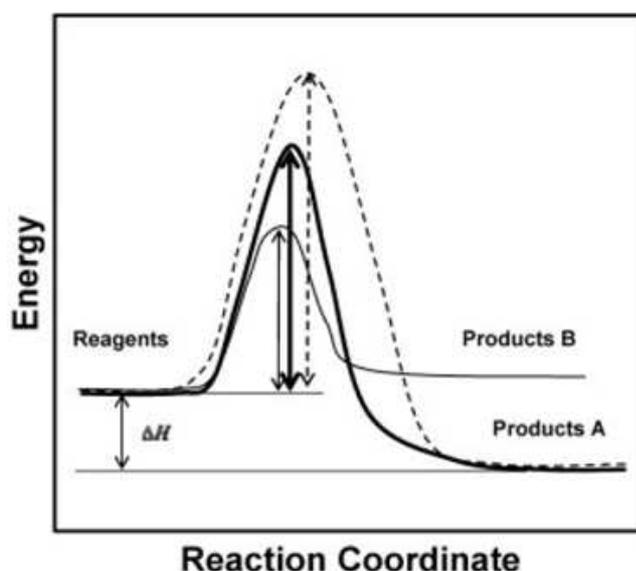
Figure 1.2: Effect of the catalyst on the pathway of a reaction [5]

In here, it is really important to emphasize the relation between the reaction kinetics and thermodynamics. Both forward and reverse reaction rates are equal at the equilibrium. Catalyst cannot change the thermodynamic equilibrium while altering the reaction progress towards this equilibrium state. The rate to approach the equilibrium composition is faster in the presence of a catalyst; however final equilibrium composition is the same.[1]

There are three fundamental properties of catalyst; activity, selectivity and durability

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which mainly determine the convenience of the catalyst for the commercial usage. [1]

Catalytic activity is the key factor since the rate of reaction accelerates more with the more active catalyst. It represents the increment of the chemical reaction rate related with the help of the catalyst as mentioned in the above sections. Even though, it is stated in the theory that the catalyst remains constant during the reaction, now it is experimentally known that catalyst may alter chemically due to the competing reactions. This alteration may cause decrease in its activity, this situation is called as catalyst deactivation. [1]

Apart from speeding up the reaction rates, another important capability for the catalyst is the selectivity. With this ability, catalyst can direct the reactants to the desirable products among the possible products so it selects its own pathway. So if one can choose the wrong type catalyst, unexpected products can be formed although the same reactants are used. [1]

The other significant point for the effective catalyst is its durability which means the life of the catalyst. Durability is taken into consideration since catalyst may be deactivated or destroyed by side reactions even they are not consumed by the reaction itself. From the economical point of view, when the life of the catalyst is not long enough; using fresh catalyst for each reaction or frequently reactivating the catalyst cost too much and the commercialization of the catalyst is not possible. [1]

1.1.2 Classification of Catalysts

The catalysts can be sorted according to many factors such as field of application, main component of the catalyst or state of the reaction. [15]

In the classification given in the Figure 1.3, groups are made according to the aggregate state. There are three considerable main groups; homogeneous catalysts, biocatalysts and heterogeneous catalysts. [9]

Homogeneous catalyst is the class of catalyst whose phase is same with the phase of the reactants in the catalytic system. Both the homogeneous catalyst and the reactants
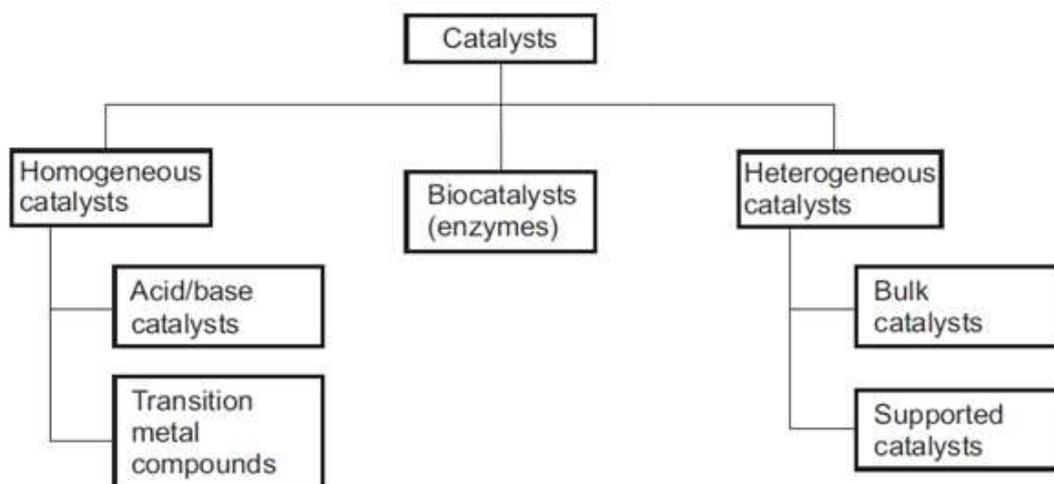
Figure 1.3: Classification of the catalysts in terms of the state of the reactants [9]

can be in gas or liquid phase depending on the state of the process. Some examples of homogeneous catalysts are organometallic complexes and metal salts of organic acids. [9]

Unlike homogeneous catalysts, heterogeneous catalysts are not in the same phase with the reactants in the catalytic process, there exist a phase boundary between them. Heterogeneous catalysts are mostly in solid phase; whereas, reaction occurs in the state of gas or liquid. [9]

Homogeneous catalysts and heterogeneous catalysts differ from each other with so many aspects. In homogeneous catalysts, each atom of the catalyst is active because of the high level of dispersion; however, the dispersion degree is much smaller in heterogeneous type since the only active site is the surface of the catalyst. In consequence of more collisions with the reactants, homogeneous catalysts have the higher activity and reach higher selectivity. In addition to that, the mechanism of the heterogeneous catalysis is not comprehensible as the mechanism of homogeneous catalysis due to the well defined active site. For homogeneous catalysts, reaction temperature is not usually exceed to $200^\circ C$; however, heterogeneous catalyst has higher thermal stability that it can also be active at the temperature over $200^\circ C$. The essential problem of the homogeneous catalysts is to remove catalyst from the products, separation methods such as distillation and liquid-liquid extraction are used in order to overcome this problem. New methods are improved in the last few years to make the separation of catalyst easy from the products. Dissimilarly, in heterogeneous catalysis, since the

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phases are different, separation takes place immediately or by simple physical methods. To sum up, each type of catalysts has its own specific properties that makes them useful, so they are not treated as opponents. [9]

The third category of the catalysts are biocatalysts which are also named as enzymes. It can be understood from its name of biocatalyst, enzymes are used for biological reactions. Biocatalysts are generally composed of protein molecules with high molecular weights. Thus, they have characteristics of being sensitive and unstable so they are not suitable for all conditions of reactions. The main reason of treating the catalysts as three separate groups is that the enzymes do not belong to any other group with its distinctive properties. [9]

In the scope of this thesis, heterogeneous catalyst is investigated for a specific reaction mechanism; therefore, heterogeneous catalysts are explained in the next section.

1.1.2.1 Types of Heterogeneous Catalysts

As seen from the Figure 1.3, there are two types of heterogeneous catalysts; bulk catalysts and supported catalysts. [9]

Bulk catalysts, stated in other words unsupported catalysts, can be metals and metal alloys, metal oxides, carbides, nitrides, ion exchange resins, metal-organic framework and metal salts. [27]

Support catalysts can be composed of unsupported catalysts such as metal and metal oxides. Supports mostly have a porous structure in order to increase the surface area and obtain highly disperse active site. Al_2O_3, SiO_2, $MCM-41$, TiO_2, ZrO_2 and MgO are some of the most preffered support materials. [27]

1.1.2.2 Steps of Heterogeneous Catalysis

During the chemical reaction, reactants are following the path towards the products along the reaction coordinate, sample diagram of energy change with respect to the reaction coordinate is represented in the Figure 1.4. As it is seen from the graph,

there are some minimum and maximum points which refers to the intermediate compounds (I^1 and I^2 are two intermediate surfaces formed during this sample reaction) and transition states, respectively. Actually, what the heterogeneous catalyst does is to provide a alternative pathway from reactants to products with a lower activation energy. [4]
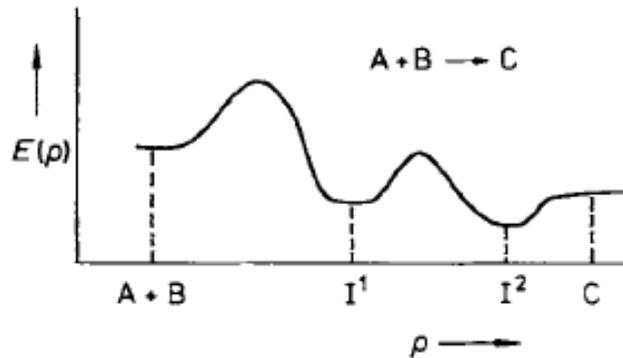
Figure 1.4: Reaction profile for a heterogeneously catalyzed reaction [4]

The heterogeneously catalyzed reaction consists of elementary processes proceeded along the reaction coordinate. These constituent steps are adsorption of reactants, surface reaction and desorption of products. [4]

The flux of the reactants striking the catalyst surface is firstly adsorbed over the active site of the catalyst. Adsorption of the reagents can take place in two forms according to their strength of bonding; physisorption and chemisorption. Physisorption which is called also as physical adsorption representing the interaction of the reacting molecules with the surface by Van der Waals forces. There is no chemical bonding in the physical adsorption. Because of this low binding energy, physisorbed molecules are away from the surface. However, in chemisorption, the adsorbate attached to the catalytic surface with a strong chemical bond that is why it is also called as chemical adsorption. Both physisorption and chemisorption processes are shown as an example in the Figure 1.5. In heterogeneously catalyzed chemical reactions, process of physisorption is generally treated as a precursor of the chemical adsorption. [4]

As a result of adsorption process, new bonds are formed on the catalytic surface with the process of surface reaction. Each of the surface reactions can be explained by the three mechanisms; Langmuir-Hinshelwood mechanism, Rideal-Eley mechanism and Mars-Van-Krevelen mechanism. [4]
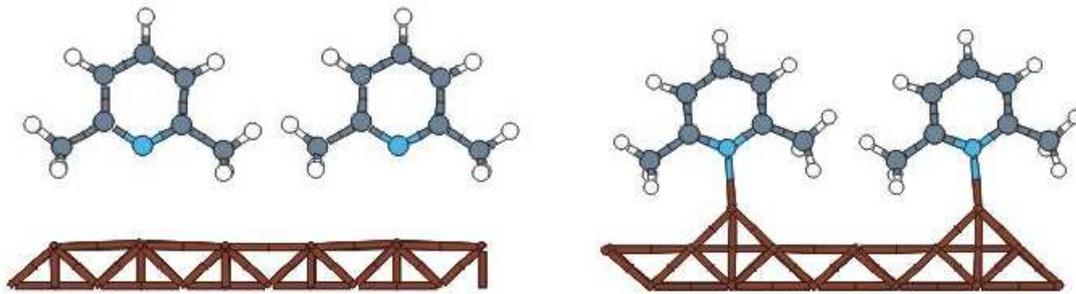
Figure 1.5: Reaction profile for a heterogeneously catalyzed reaction

After the products are formed on the surface, they are unattached from the catalytic surface with a final process of desorption.

The dynamics of the surface reaction can be investigated at three different levels such as macroscopic, mesoscopic and microscopic as seen from the scheme in the Figure 1.6. [15]
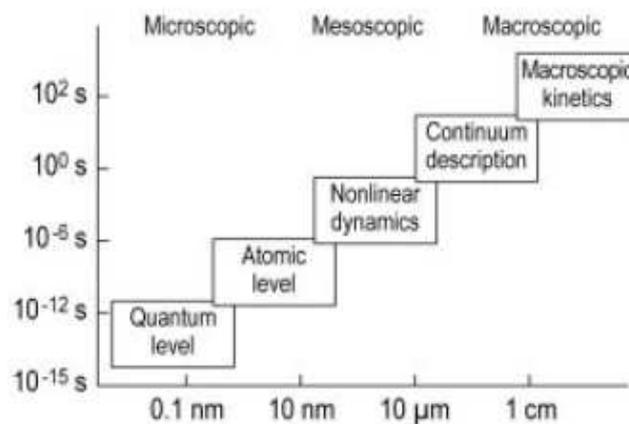
Figure 1.6: Levels of the investigation of the surface reaction [15]

However, at macroscopic and mesoscopic levels, elementary steps cannot be examined as detailed as at the microscopic level. Especially in atomic and quantum level, the mechanism of the reaction can be observed step by step. This thesis is analyzing the reaction mechanism in its topic from the theoretical point of view at microscopic level. [15]

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1.2 Molecular Modelling in Heterogeneous Catalysis

Computational chemistry deals with the chemical problems to generate solutions or widens the horizon of chemistry science by using computers instead of performing experiments.

When the computational chemistry is checked against the experimental studies, using computer rather than performing an experiment brings advantage of being inexpensive since there are no expenses such as chemicals and laboratory equipments. In addition to that, theoretical chemistry gives you freedom for simulating whatever molecule you like, even combining or separating atoms that you select from a molecule; however, in experiments, testing the chemicals are restricted according to the opportunities. Lastly, it is more secure to perform computational calculations, but laboratory experiments are always more risky especially for human health. [8]

Depending on the study that is conducted with the computational chemistry, it generally requires longer time with respect to the experimental studies.

Experimental studies are not substituted with the computational chemistry; however, they are guided with the outcome of the computational calculations perfectly. The scientists benefit from the advantages being offered by the theoretical studies to make better predictions and preparations for performing the actual experiments. They both explain and rationalize the known chemistry, besides all these they have the capability of exploring new and unknown chemistry. [8]

Cheminformatics, statistical mechanics, molecular mechanics, semi-empirical methods and ab-inito quantum chemistry are within the scope of computational chemistry. In the scope of this thesis, ab-initio quantum chemistry is used to achieve the results.

1.2.1 Ab-Initio Quantum Chemistry

Ab-initio varies from the other computational methods with its feature of being directly derived from the quantum mechanical theory. Since it is only based on theory not any experimental data, the method takes the name 'ab-initio' which means 'from the beginning'. [7]

The ab-initio quantum chemistry is a phenomenally successful method for small systems which has tens of atoms, unknown chemical systems with no useable experimental observations and systems requiring strict precision. [7]

The main body of ab-initio quantum chemistry is considered as solving the electronic Schrodinger equation which describes the quantum behavior of atoms and molecules such as their electronic energy and electron density. The computational complexity of Schrodinger equation is directly related with the number of electrons in the problem since it deals with the interacting particles in the system. In the simplest form of Schrödinger Equation (1.4); $\hat{H}$ is Hamilton operator for a molecular system with N electrons and it includes both kinetic and potential contributions. [7]

$$\hat{H}\psi = E\psi \tag{1.4}$$

The capability of solving the crucial problems of the large, condensed-phase systems by the Schrodinger equation is of prime importance for many scientific fields, Nobel Prizes given to John Pople and Walter Kohn in 1998 show the emphasis on this topic up clearly. John Pople and Water Kohn are awarded with the 1998 Noble Prize in Chemistry with his improvement of 'compuational methods in quantum chemistry' and 'density functional theory', respectively. [7]

As it is mentioned, ab-initio quantum chemistry solely depends on the solution of Schrodinger equation. There are two main approaches to solve the Schrodinger equation; the firts one is *wavefunction based approaches* and the second approach is the *density functional theory*. [7]

To begin with the wavefunction based approaches, the very first and simple method is Hartree-Fock (HF) theory. Within this theory, the wavefunction is expressed by a single Slater determinant. Since it is a single-particle wavefunction, the motion of the elctrons do not taken into account so its limit is always above the electronic correlation energy. Therefore, HF method is unqualified for reactive chemical systems in which energy of interaction between electrons has a significant role. Neglecting the electron correlation is a major problem for this method, although it may produces acceptable outcomes for many quantum systems. [7]

To overcome the electron correlation problem of HF method, some other wavefunction based approaches are developed which are called as correlated wavefunction based calculations. Some of these correlated approaches are Mohlar-Plesset perturbation theory (MPn, where n is the order of correction), the Generalized Valence Bond (GVB) method, Multi-Configurations Self Consistent Field (MCSCF), Configuration Interaction (CI) and Coupled Cluster theory (CC). [42]

Each of these methods are preferred for the different kind of computational problems. To illustrate, MP2 is commonly preferred method by biologists and material scientists for investigating non-bonded interactions between molecules and force fields in molecular mechanics in both small and large systems. In addition this method, CC method is generally applied in order to optimize the geometry and obtain the basis set convergence of the systems with small molecules in the gas phase. [7]

The second and the most successful approach to solve Schrodinger equation is Density Functional Theory (DFT) method which is especially used for studying the chemical reaction between individual atoms and molecules in medium to large systems. [7]

By comparing the two approaches with each other, wavefunction based approaches are more complicated since density functional theory method uses electron density which is more simpler to find the energy instead of wavefunction. Also DFT method is not as expensive as wavefunction based approaches in terms of computational cost. DFT method has better precision for molecular structures. [8]

Within the context of this thesis, since the chemical reactivity is the main concern, DFT method is selected as a tool for quantum chemistry calculations specified in the following sub-title in detail.

1.2.1.1 Density Functional Theory

Density functional theory (DFT) is widely used as a research tool by scientists within the departments of chemistry, physics, biology, material science and different engineering disciplines such as chemical engineering. In this part of the thesis, general information and certain technical details will be given about the application of this powerful tool. [29]

DFT tool owes its rapid development in recent years to two largely scientific fields. The first and most frequently used path is to apply quantum mechanics in order to understand the complex atomic systems at the level of individual atoms and molecules. With the help of DFT method; molecular modelling, finding ground state energies of the molecules and studying chemical reactivities are possible and simpler. As a second subject, DFT method is also actively used in the field of statistical mechanics; especially for inhomogeneous fluids and phase transition problems. [16]

The purpose of applying DFT method in this study is to solve computational chemical problem related with the first path mentioned above; especially simulations of catalytic energy surfaces in molecules and possible reactions occur between these molecules.

In accordance with this purpose, DFT method deals with the chemical reaction theories applied with the help of the physical laws which include complicated mathematical equations.

If needs to be explained in detail, it is mentioned that the density functional theory uses the electron density to describe an interacting molecular system instead of many-body wavefunction different from the other traditional ab-initio methods. [34]

The electron density is a basic term in quantum chemistry which is defined as the probability of finding an electron at a specific location in space. After a brief description of an electron density, the term called 'functional' is explained in order to understand the density functional concept more clearly. As it is understood from its name, functional comes from the common word 'function'. Function is a formula which depends on one or more variables to define a number. In a similar way, functional assigns an output of a single number, but its input is a function. In DFT method, functional of the electron density is the energy of a molecule. Electron density is also a function of the position of electrons depends only on x,y and z coordinates regardless of the magnitude of the system. However; in the wavefunction methods, 3N variables are used for an N-electron system which means as the number of electrons increases, computations will become more complicated. Therefore, electron density functional is a powerful quantity for resolution of ground state energies of the molecular properties in reactivity studies. [34]

$$\text{Functional} \, y = F[f(x)]$$
$$\text{Electron density} = \rho(x, y, z) \tag{1.5}$$
$$\text{Energy} = F[\rho(x, y, z)]$$

At the core of the DFT method, there are two mathematical theorems; Hohenberg-Kohn theorem and Kohn-Sham equations. The Hohenberg-Kohn theorem states that " The ground-state energy from Schrodinger's equation is a unique functional of the electron density." This statement means that Schrodinger equation can be solved by the electron density which has three variables rather than 3N variables-wavefunction. Henceforward, the main objective of the DFT method is to find the output of the F functional which refers to the energy of the molecule. Second statement of Hohenberg-Kohn theorem makes the first statement more clear with an expression of " The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation." It is understood from this statement that different electron density values should be tried until the ground state energy become minimum. The density that makes the functional reaching minimum energy is called as true electron density. [29]

The Hohenberg-Kohn theorem is developed by Kohn and Sham and more practical version of DFT method is explored. To solve the Kohn-Sham equations, the Hartree potential is required to describe and to describe this potential , electron density should be known. To find the electron density, Kohn-Sham equation should be solved in order to find the wave functions. Thus, this is a cyclic problem which can be solved by iterative approximation. As a first step of these iterations, electron density is defined. After all these cyclic calculation steps are completed, the electron density calculated from the Kohn-Sham equation is compared with the initial density estimated. If the densities are equal to each other, this means that this is the ground state electron density from which the total energy of the structure can be found. These are the steps how the DFT method is worked for investigating the reaction mechanisms on catalytic surfaces. [29]

1.3 Propylene Epoxidation Reaction Mechanism

In this sub-title, reaction mechanism of the propylene epoxidation which is investigated in this study by utilizing DFT method is explained in detail.

1.3.1 Propylene Epoxidation

General representation of the selective oxidation of olefins to epoxides are given in the Figure 1.7.
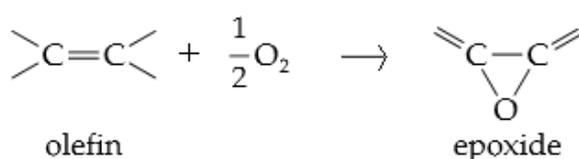
Figure 1.7: Chemical illustration for epoxidation of olefins

In propylene epoxidation reaction, the olefin is C_3H_6 molecule which is known as propylene and the epoxide is C_3H_6O named as propylene oxide. Propylene oxide in this reaction is formed by the oxidation of carbon-carbon double bonds in the propylene. Thus, carbon atoms with double bond become attached to the same oxygen atom.

Propylene, which is the reactant of this reaction, is generally produced by the steam or catalytic cracking process as a byproduct in oil refining and natural gas processing. Apart from the production of propylene oxide, it is also used for producing several chemicals such as acrolein, acrylonitrile and acetone. [33]

Propylene oxide, also known as propene oxide, is an important versatile chemical used in the production of many compounds such as polyether polyols, polyurethane polyols, propylene glycols, glycol ethers and polyalkylene glycol. By taking part in the production of these important chemicals, it serves for a wide range of industries; automotive industry, building trade, food industry, tobacco industry and cosmetics industry. Propylene oxide is currently produced with the methods seen from the Figure 1.8 by the big companies Dow Chemical Co, LyondellBasell Chemical Co and Shell. [33]

14
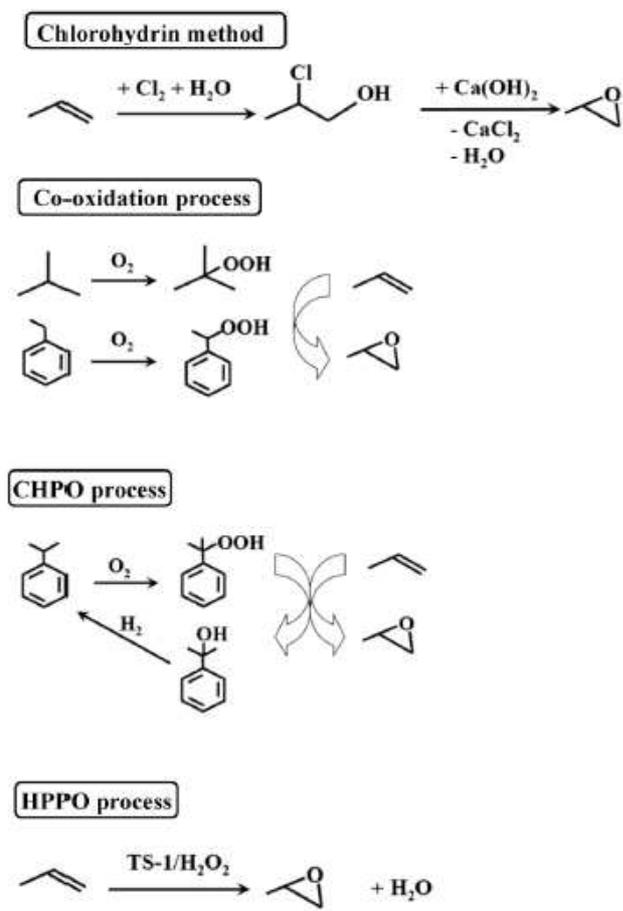
Figure 1.8: Current production methods of propylene oxide [25]

Commonly used conventional methods for propylene oxide production are chlorohydrin method and co-oxidation techniques which require corrosive chlorine in its process and expensive organic peroxides as oxidants, respectively.

The first production technique represented in the Figure 1.8 is method of chlorohydrin which is a multistep process begin with the oxidation of propylene with the hypochlorous (HOCl) to produce chlorohydrin intermediates and then dehydrochlorination of two chlorohydrin to form propylene oxide together with a side product of calcium hydroxide. At the end of this process, large amount of waste product such as halogen-containing waste water and stoichiometric amount of salt side product are generated. These undesired products cause environmental problems and equipment corrosion problems. To overcome this problem, an effective waste treatment system can be designed to handle with the calcium chloride brine waste water; however, this solution needs additional costs. [25]

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The second method utilized in propylene oxide production is co-oxidation process which uses organic oxide compounds such as tert-butyl hydroperoxide and ethylbenzene hydroperoxide in order to transfer the oxygen to propylene. Unfortunately, in this technique, large quantities of byproducts like tert-butanol and styrene are formed together with the propylene oxide. This is not an economical process due to the fact that the amount of propylene oxide and coproducts are unbalanced. [25]

To summarize, these processes are neither economical nor environmental since large amount of undesired products are formed that should be treated or scrapped. [25]

In addition to these processes, there is no commercial production of propylene oxide from direct oxidation of propylene [38] which is thus expected to be developed. For this reason, research on investigation of suitable heterogeneous catalyst for direct propylene oxidation still maintains its importance.

There are two competing reactions for oxidation of propylene; partial oxidation and total oxidation. The chemical reactions for both partial and total oxidation are given by (1.6) and (1.7), respectively.

$$C_3H_6 + 1/2O_2 \rightarrow C_3H_6O \qquad\qquad (1.6)$$

$$C_3H_6 + (9/2)O_2 \rightarrow 3CO_2 + 3H_2O \qquad\qquad (1.7)$$
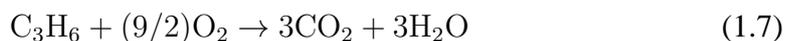
Generally, the total oxidation reactions are more exothermic from the thermodynamical point of view, whereas partial oxidation of hydrocarbons such as propylene are kinetically limited reactions. [19]

1.3.2 Possible Products of the Propylene Epoxidation Mechanism

In the Figure 1.9, the chemical representation of propylene molecule is given with its strong and weak C-H bonds. Blue lines represent the stronger bonds related with the double bond atoms and red lines refer to weaker bonds in the methyl group. Thus, it is not easy for the propylene to partially oxidize because of the fact that hydrogen atoms in the methyl group are willing to move away.

16
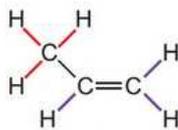
Figure 1.9: Chemical formula of the propylene molecule

Hence, many probable products such as acrolein and acetone besides propylene oxide can be formed at the end of the partial oxidation of propylene as seen in the Figure 1.10.
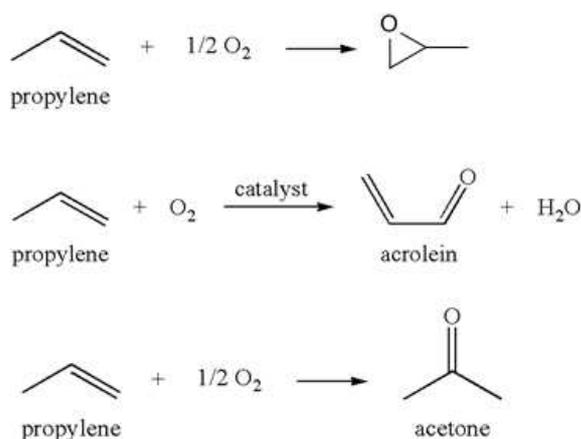
Figure 1.10: Possible reactions for the oxidation of propylene

In these studies, allylic hydrogens containing group in propylene constitute an impediment for direct propylene oxide formation since they have a great tendency to form acrolein.

Acrolein, named also as propylene aldehyde, 2-propenal, acrylic aldehyde and allyl aldehyde, is a crucial chemical which is produced commercially from propylene with multicomponent catalyts. In addition to that, acrolein also occurs in our daily life with the combustion of fossil fuels and during the heating of cooking oils. This compound is used mainly in the production of acrylic acid as a starting material of acrylate polymers. The most significant use of acrolein is in the production of DL-methionine which is a fundamental amino acid added to poultry feeds. It is also a helpful chemical for controlling the plugging and corrosion due to its antimicrobial activity. [39]

1.4 Purpose of the study

Propylene oxide which is a significant intermediate chemical for many industries is produced commercially with environmentally and economically disadvantageous methods. The solution is to find a heterogeneous catalyst for the propylene epoxidation reaction. However, although many experimental and theoretical studies are conducted, the suitable catalyst for propylene oxide formation from propylene has not been developed yet. This thesis aims to investigate the CuO and Li promoted CuO heterogeneous catalysts for propylene epoxidation reaction by means of DFT method.

CHAPTER 2

LITERATURE SURVEY

This chapter gives information about the literature studies conducted related to the propylene epoxidation. The content of this chapter also includes the ethylene epoxidation as part of a continuing effort to understand the mechanism of the epoxidation of olefins. Both experimental and theoretical studies about investigating specifically the Ag and Cu catalysts with or without promoters are mentioned within this chapter.

2.1 Studies conducted for ethylene epoxidation

In petrochemical industry, hydrocarbons such as methane, ethylene, propylene and higher olefins serve as a raw materials for especially oxidation reactions in which they are converted to valuable chemical intermediates like acetylene, ethylene oxide and propylene oxide or acrolein, respectively. In the presence of heterogeneous catalysts, oxidation reactions occur between the hydrocarbon and the oxygen species of the catalytic surface.

While heterogeneous catalyst for epoxidation of propylene research is in progress, direct ethylene oxidation for ethylene oxide (EO) production can be succeed by the Ag catalyst. [13] With high-resolution X-ray photoelectron spectroscopy (HRXPS) experiments and DFT studies conducted for ethylene oxide on Ag, important surface intermediate called oxametallacycle, Oxygen-Metal-Metal-Ethylene (OMME), is discovered [18]. Other experimental and theoretical studies conducted for ethylene epoxidation on Ag-Cu bimetallic catalysts prove the existence of intermediate surface OMME and show higher performance by comparing with the pure Ag catalyst

[12, 17]. Ethylene oxide and oxametallacycle formation geometries can be seen from the Figure 2.1.
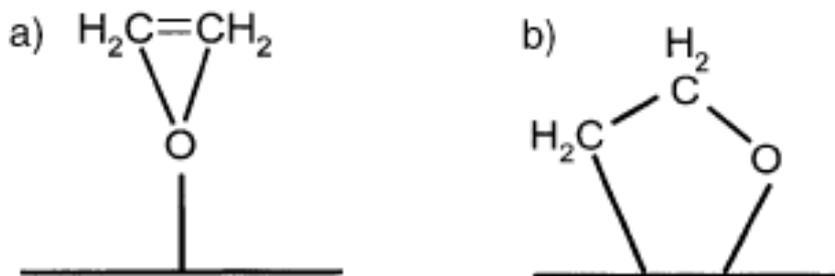
Figure 2.1: (a) Ethylene oxide (b) OMME[18]

2.2 Studies conducted for propylene epoxidation

As it is mentioned in the introduction part, for propylene epoxidation mechanism, there are two main product alternatives; propylene oxide and acrolein. According to literature research, propylene oxide is formed through the intermediate surface and acrolein is produced towards the allylic hydrogen stripping from the raw material propylene. Unlike propylene oxide which has no commercial catalyst yet, acrolein has patents of catalyst systems including Mo, Bi and Co used in its production [3].

2.2.1 Studies conducted for propylene epoxidation on Ag catalyst

Based upon the successful studies conducted for ethylene epoxidation, Ag catalyst was also investigated for propylene epoxidation. However, it is found as ineffective catalyst for the epoxidation of propylene with $2-5\%$ conversion, whereas the conversion is $85-87\%$ for ethylene epoxidation on Ag catalyst. There is a sharp decrease in the conversion value just by the replacement of hydrogen with methyl group in the propylene molecule as shown in the Figure 2.2.

The reason of this difference is because of the allylic hydrogen in the propylene which is more active than the olefinic carbon. On Ag catalyst, allyl radical formation from the propylene is observed instead of propylene oxide since allylic hydrogen is stable

20
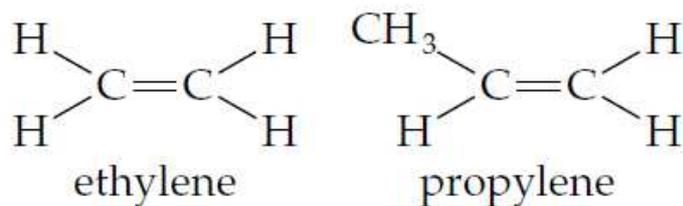
Figure 2.2: Molecular structure of ethylene and propylene

on the catalytic surface. Both the olefins without an allylic hydrogen and the olefins with unstable allyl radical have the possibility to be converted to epoxide with high conversion on Ag catalyst [22]. One of the experimental studies conducted on Ag catalyst was resulted with propylene oxide selectivity of 0.42%, whereas approximately 30% selectivity of propylene oxide was reached on the Ag-CuCl catalyst which is the highest percentage among the different types of promoters such as AgCuCl2, AgFeCl2, AgMnCl2 and AgAuCl3 [20]. In line with experiments conducted, a theoretical study [6] proves that activation barrier for propylene oxide formation is three times higher than the barrier of allyl formation on Ag catalyst. After Ag is concluded as poor catalyst, Cu (111) and Ag (111) surfaces were examined theoretically for propylene epoxidation and it is concluded that Ag leads to allylic hydrogen stripping, whereas Cu tends to form surface intermediate oxametallacycle. Oxametallacycle is called OMMP for the propylene epoxidation reaction which refers to Oxygen-Metal-Metal-Propylene interaction [31]. There are two types of OMMP formation; OMMP-1 and OMMP-2. In OMMP-1, C1 bonds to adsorbed oxygen whereas C2 bonds to metal surface atom. In OMMP-2, adsorbed oxygen is bounded to C2, while C1 bonds to metal surface atom. Another theoretical study [32] claimed that Ag is not as effective as Cu in alkene epoxidation.

2.2.2 Studies conducted for propylene epoxidation on Cu catalyst with/without promoter effect

Lower basicity of copper catalyst tends to form OMMP so this clearly shows that Cu catalyst should become a focus for propylene epoxidation with some new structural or compositional alternatives.

When Cu doped Ag surface was investigated, it is seen that probability of oxametalla-

cycle formation increases in comparison to Cu only and Ag only catalysts [23]. However, an experimental study conducted in 1960 resulted that 45% of reacted propylene form acrolein by using the mixture of 15 catalysts including Cu and Al [40]. Following study conducted through the application of the techniques of combinatorial catalysis [21] claims that Cu, Mn, and W metal catalysts has a probability of acrolein formation from propylene in the oxygen rich conditions.

Cu supported by silica catalyst (1 wt$\%$ Cu/SiO_2) prepared by the method of microemulsion gives promising experimental results in the presence of dioxygen for propylene epoxidation. This catalyst has three observed products; propylene oxide, acrolein and combustion products. Acetone is also another product, but it is produced in negligible amounts. As seen from the graph in the Figure 2.2, the greatest selectivity is obtained at $225°C$ for the product of propylene oxide. [35]
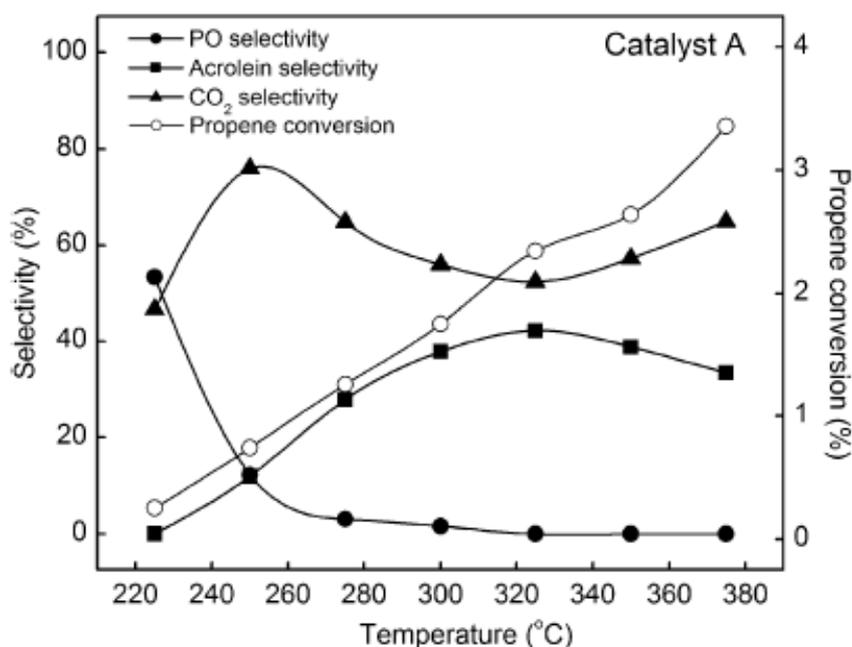
Figure 2.3: Selectivities of the products with respect to the temperature

To analyze the Figure 2.3, while the production of propylene oxide is decreasing, the acrolein formation is rising up until the temperature reached at $325°C$. In addition to that, selectivity of CO_2 decreases in direct proportional to propylene oxide. It is obviously understood from this fall that propylene oxide is inclined to combustion more than acrolein is [35]. In a XRD study [26], oxidation of copper is investigated with respect to temperature. It is stated that Cu is prevailing catalyst up to the tem-

peratures less than $250°C$ and then it is converted to CuO at higher temperatures. By combining the results of the studies [35] and [26], it can be said that Cu is effective catalyst for propylene oxide formation at a certain temperature range. Formation of acrolein and combustion products are more possible on CuO catalyst at temperature above $250°C$.

After it is concluded that Cu(0) can work for propylene oxide formation from propylene, another experimental study [44] in which catalysts are prepared by sol-gel method is conducted for investigating the effects of Cu(I) catalyst for propylene epoxidation. In this study, it is found that Cu (I) can form active sites for propylene epoxidation in the presence of rich oxygen since Cu(I) is more stable than Cu(0) in oxidation reactions. Cu(I) catalyst supported by SiO_2 is also modified by K^+ atom in [44] and modified CuO_x-SiO_2 catalyst enhance the selectivity of propylene oxide. Another study [10] also deals with the CuO_x-SiO_2 catalyst for propylene epoxidation reaction in the presence of oxygen, but in this case it is modified by Cs^+. This study claims that without modification, CuO_x-SiO_2 catalyst can form the allyl intermediate followed by acrolein. However, by the effect of the promoter Cs^+, the selectivity of propylene oxide increases. Acrolein formation through allylic hydrogen stripping was also observed on CuO_x/SBA-15 catalyst; however, addition of K^+ alters the reaction path to propylene oxide formation [37]. Another modification is done with vanadium to unsupported Cu catalyst [41], it ensures that the vanadium promoter increases the performance of the propylene epoxidation since it helps to activate the electrophilic oxygen species.

In a theoretical DFT study [14], Ru-Cu surface is compared with the Cu surface for propylene epoxidation reaction. Cu surface shows better performance compared with the Ru-Cu surface because of the reason that it has lower energy barrier through oxametallacycle formation, whereas Ru-Cu surface has a tendency to form allyl radical intermediate. Additionally, there is an experimental study [28] conducted with trimetallic catalyst RuO_2CuO_xNaCl supported with silica which gives PO selectivities around 50% at a temperature of around $250°C$, this multimetallic catalyst shows promising results for propylene epoxidation.

This study is conducted with the intent of investigating the possible route for partial

oxidation of propylene on CuO (001) and Li promoted CuO (001) surfaces theoretically by using the DFT method.

CHAPTER 3

COMPUTATIONAL METHODOLOGY AND SURFACE MODELS

In this chapter, computational method that is utilized for performing the density functional theory calculations is explained for the investigation of catalysts for propylene epoxidation reaction mechanism. Computational strategy that is followed during the study is also mentioned. In addition to that, modelling of CuO (001) and Li substitute CuO (001) catalysts which are analyzed for the propylene epoxidation mechanism throughout the study are described. Final equilibrium geometries of these surfaces, which are optimized with the help of information gathered from the literature, can be found within this chapter.

3.1 Computational Methodology

Periodic, plane wave density functional theory (DFT) calculations are performed with Vienna ab initio Simulation Package (VASP). The reciprocal spaces of the supercells are represented with a $4 \times 4 \times 1$ k-point Monkhorst-Pack mesh. The generalized gradient approximation (GGA) using the PW91 functional is used to calculate exchange correlation energy in order to utilize plane wave basis sets. In calculations, the cut-off energy is $500 \ eV$ to make certain of the precision.

Optimizations of each geometries are conducted until the net atomic forces are smaller than $0.015 eV/Å$. After optimizing the initial and final geometries of the each elementary steps, activation barrier energies are found by utilizing the Climbing Image - Nudged Elastic Band (CI- NEB) method. With the help of CI-NEB method, saddle

Table 3.1: Strategy that is followed during the study of the propylene epoxidation reaction

Steps	Description
Step 1	Preparation of the catalytic surfaces
Step 2	Adsorption of propylene on catalytic surfaces
Step 3	Optimization of intermediate surface geometry
Step 4	Optimization of propylene oxide formation
Step 5	Optimization of acetone formation
Step 6	Optimization of allyl radical formation
Step 7	Optimization of acrolein formation
Step 8	Analysis of activation barriers between optimized geometries

points in the reaction path are determined. Therefore, reaction profile for the studied reaction mechanism can be plotted with respect to relative energies.

Calculation steps that are followed throughout the study is given in the Table 3.1.

The very first step of the study is preparing the bulk structure of the CuO surface followed by the preparation and optimization of catalytic CuO (001) and Li substituted CuO (001) surfaces. Modeling of these surfaces are explained in detail in the next sections. After that, in step 2, physical adsorption of propylene on CuO and Li promoted CuO surfaces are optimized. Then, in step 3, optimization of intermediate surface geometry is performed on the surfaces which refers to the chemical adsorption of propylene. Steps 4 to 7 represent the investigation of the final equilibrium geometries and energies of all possible products including propylene oxide, acetone, allyl radical and acrolein on the optimized catalytic surfaces.

Subsequent to the optimizations of possible geometries on the catalytic surfaces, energies of activation between these optimized geometries according to the path of reaction mechanism are determined by using CI-NEB method. This method requires

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two input file consisting of optimized geometries of both initial and final state among which calculation of energy barrier can be made. Method of CI-NEB is qualified for finding the minimum energy path of the reaction. This method can distribute images along this energy path between initial and final geometry. The number of images that is created between these geometries depends on the researcher. In this study, 8 images are constituted from initial to final state and with the optimized energies of all these created images, graph of activation barrier can be plotted with ten data points.

As a final step, before representing the overall energy profile for the reaction mechanism on the catalytic surfaces, desorption energies of the possible products are calculated. Desorption energy is equal to the subtraction of the summation of the energy of the surface just after desorption and the energy of the product in the gas phase from the energy of the adsorbed product on the surface. For this calculation, the final equilibrium energies of the products in gas phase which are optimized in vacuum are found.

Throughout this study, energy of reference state for CuO surface is taken as shown in (3.1) given below.

$$E_{reference} = E_{CuO} + E_{Propylene} \tag{3.1}$$

Reference state is used to plot the energy profile for the propylene epoxidation mechanism with respect to relative energies of the optimized surfaces.

3.2 Preparation of CuO surface

CuO compound, which is called as copper oxide in general, is specifically known as copper (II) oxide or cupric oxide. In the catalytic surface of CuO, there is almost square planar molecular configuration that four oxygen atoms coordinate the one Cu atom.

In experimental studies, CuO surface is synthesized by different techniques such as sol-gel, hydrothermal and spray prolysis methods which are conducted in liquid phase and Radio Frequency (RF) sputtering, pulsed laser deposition (PLD) and chemical

vapor deposition (CVD) methods which take place in the vapor phase. [36]

In this theoretical study, CuO catalyst is formed at the molecular level. At first, bulk structure of CuO is prepared by using the lattice parameters of the crystal structure from literature. In literature, it is mentioned that CuO belongs to monoclinic crystal structure system in which lattice constants are $\alpha = 90°$, $\beta = 99.54(1)°$, $\gamma = 90°$.
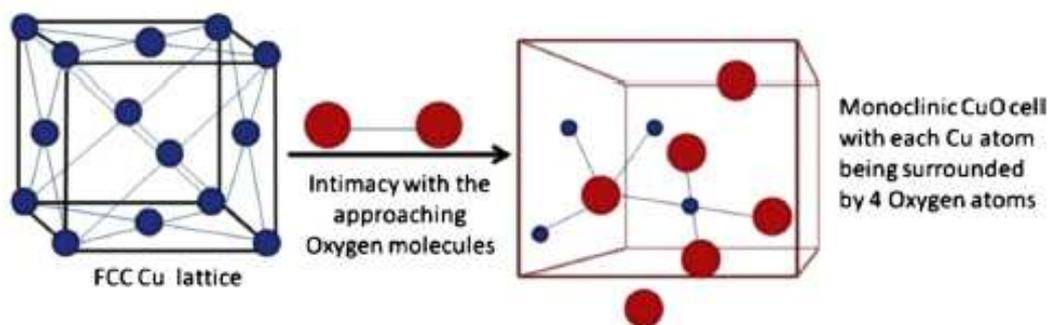
Figure 3.1: Schematic representation of CuO formation at the molecular level.[43]

As illustrated in the Figure 3.1, Cu atoms in the form of FCC lattice turns into the monoclinic CuO cell with approaching oxygen molecules. In the representation, Cu and oxygen atoms are expressed by blue and red balls, respectively. With the lattice parameters obtained, bulk form of CuO slab is optimized with the utilization of the VASP code.

Afterwards, CuO crystallic surface is built by using the optimized lattice parameters taken from the final bulk structure with utilization of Material Studio program. The surface can then be cleaved any types of planes that will be studied. After cleaving the surface, it is required to specify the number of layers, adjust the periodicity and built a vacuum region. Vacuum region is inserted in order to eliminate the interaction between the z direction.

At the beginning, crystal plane type of the CuO surface that is cleaved is selected. There are many plane alternatives for CuO surface, some of them are represented in the Figure 3.2. From these alternatives, surface is cleaved as 001 plane in this study.

In an experimental study, it is claimed that among the planes in the Figure 3.2, CuO (001) surface is found as active crystal plane. In addition to that, it is stated that CuO (001) crystal planes has the highest activity so it can provide more reactive sites to be

28
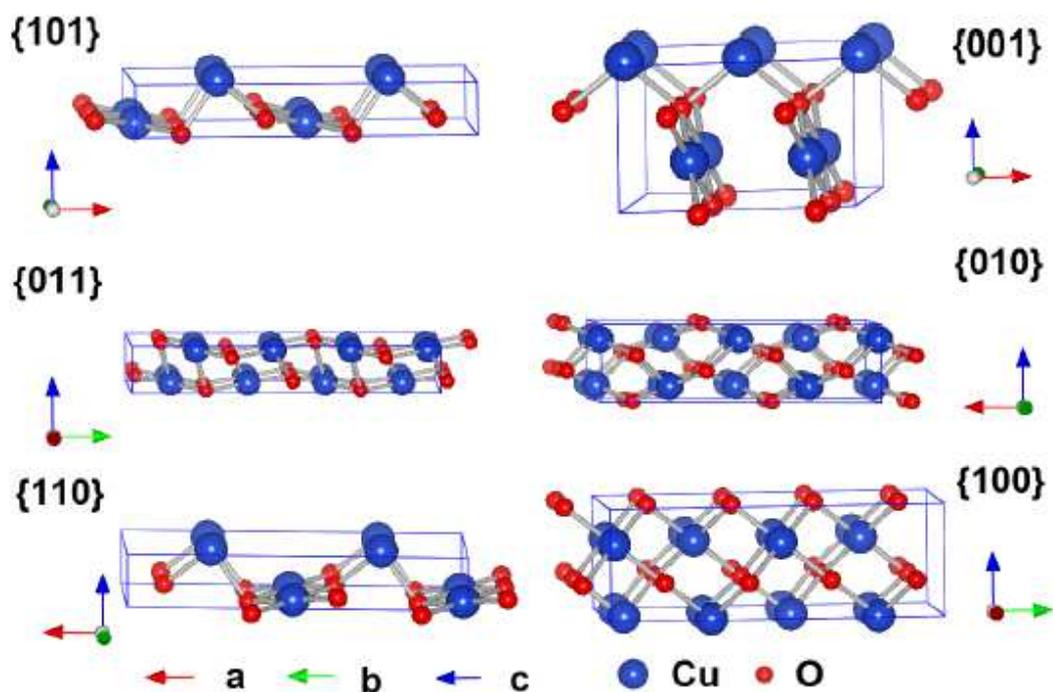
Figure 3.2: Side views of relaxed crystal planes of CuO.[30]

involved in an interaction with Li atom. The study also demonstrates that the (001) plane requires less energy to accomplish reactions [30] Another experimental study [24] mentions an important point that CuO (001) surface react faster compared with the other planes so they have difficulty in collecting accurate data while performing the experiments. To conclude, there are two reasons for cleaving the (001) plane for CuO surface; one of them is its advantage of being interacted with Li atom and the other reason is its difficulty for collecting experimental data rapidly.

CuO (001) surface can be prepared in two different configurations; oxygen- terminating CuO (001) surface or copper-terminating CuO (001) surface. In [11], oxygen-terminated and copper-terminated CuO (001) surfaces are compared and it is resulted that oxygen- terminated surface is more stable. As seen from the final geometry of CuO (001) surface in the Figure 3.2, the surface is optimized as oxygen-terminating in this study.

CuO (001) is modeled as a slab containing four atomic layers as represented in the Figure 3.3 both of which is $2x2$ enlarged. The bottom layer of the slabs is kept fixed to represent the bulk structure whereas all other atoms are relaxed. A vacuum distance

of 15 Å is used over the slabs and the reactive species are optimized on only one side of the CuO slab.

(a)

(b)
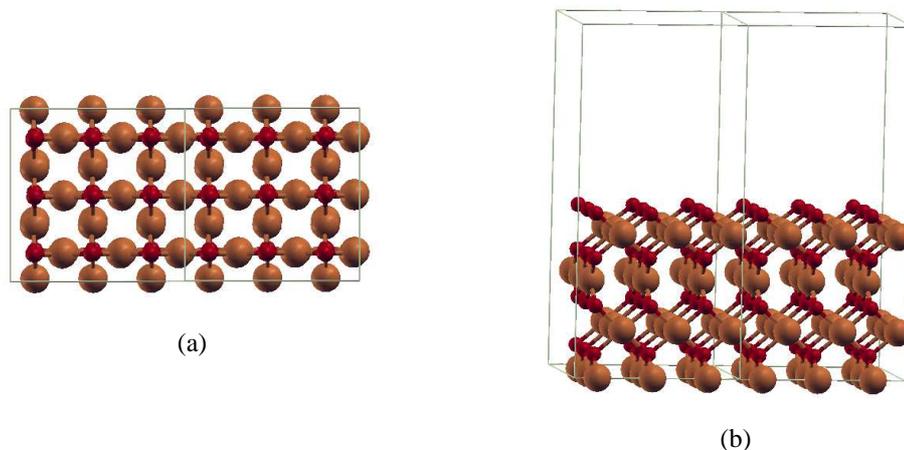
Figure 3.3: (a) Top view of CuO (001) slab, (b) Side view of CuO (001) slab

3.3   Preparation of Li promoted CuO surface

Li atom is decided to substitute into the optimized CuO (001) surface with a function of promoter. Li promoter is aimed to interact with the active atoms on the surface and alter the crystal structure besides the chemical effect on catalytic surface.

Li atom can not be directly substituted with Cu atom positioned in the surface due to the fact that overall charge on the catalytic compound should be zero. In an effort to maintain the charge balance, the number of electrons lost must be equal to the number of electrons gained between the atoms in order to neutralize the system. In this case, two Li atoms with an overall charge of +2 are replaced with the two Cu atoms and one oxygen atom with a total charge of +2.

Two of the copper atoms removed from the catalytic surface and two Li atoms are located to fill the vacancies. However, there are many configurations for which of the oxygen atom is removed from the surface.

Three different configurations for oxygen removal are attempted as seen from the following estimated geometries. In the Figure 3.4a, oxygen which is located on the removed Cu atoms moves away from the surface. As a second alternative, oxygen that is attached to a Li from one side is removed from the catalyst shown in the

30

Figure 3.4b. Last configuration is to send the oxygen located in the middle of the surface which is not connected to any Li atom as shown in the Figure 3.4c.
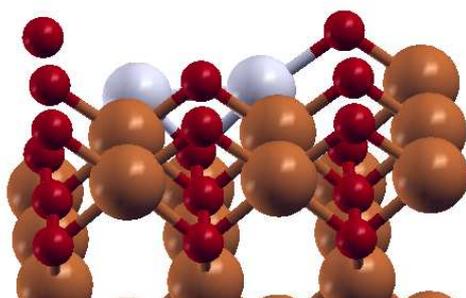
(a)
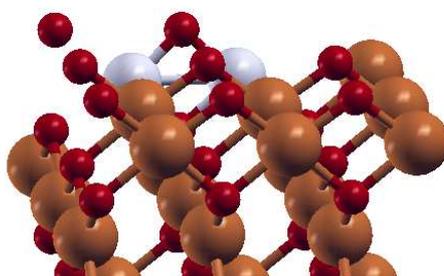
(b)
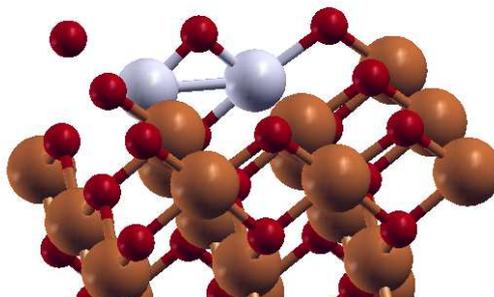
(c)

Figure 3.4: Alternative configurations for Li substitution on CuO surface

According to the optimization results of these three alternatives, the most stable Li promoted CuO (001) surface is the first configuration with a lowest energy. Optimized surface is represented schematically in the Figure 3.5.

Calculation is performed to check the possibility of this Li substitution in terms of their final equilibrium energies. It is found that the energy of the summation of optimized CuO slab and 2 Li (gas phase) is lower than the total energy of optimized geometry in the Figure 3.5 and Cu_2O (gas phase). Therefore, optimized Li promoted

31
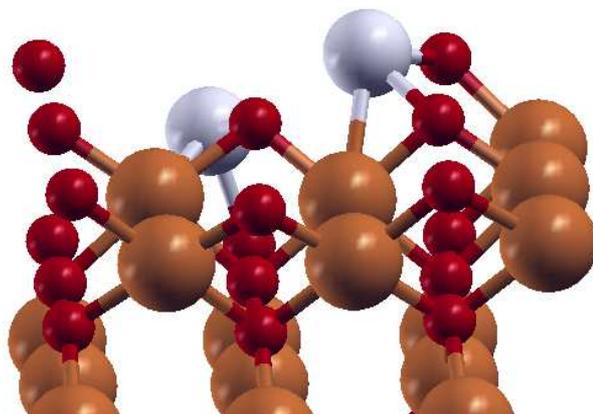
Figure 3.5: Optimized geometry of Li promoted CuO (001) surface

CuO (001) surface in the Figure 3.5 is used during the investigation of the propylene epoxidation reaction mechanism.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, results for the propylene epoxidation mechanism are given for CuO and Li substituted CuO catalysts. A thorough analysis of this reaction mechanism is done for CuO catalyst and the effect of Li promoter is investigated for possible main products of propylene oxide and acrolein. Discussion of the results are presented with the comparison of the activation energies for the probable products together with the energy profiles.

4.1 Results of the propylene epoxidation mechanism on CuO catalyst

For partial propylene oxidation on CuO (001) surface, the calculations indicate that there are two possible reaction pathways.
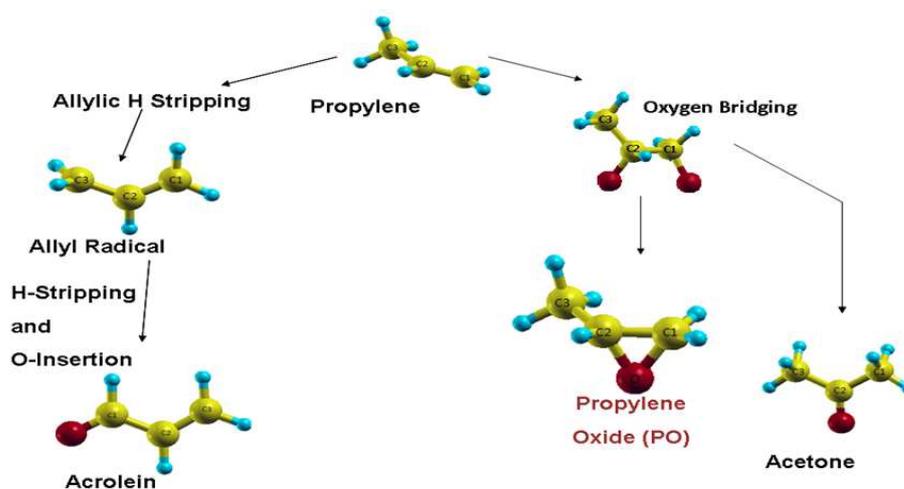
Figure 4.1: Possible pathways for propylene epoxidation reaction

One pathway is propylene oxide or acetone formation through oxygen bridging intermediate surface and the other one is acrolein formation through allylic hydrogen stripping on CuO surface as represented in the Figure 4.1.These two possible pathways with all possible products are analysed and discussed within this chapter.

4.1.1 Propylene adsorption on CuO surface

As mentioned in the previous chapter, first step is the adsorption of the propylene on the CuO catalyst. Pyhsisorption of propylene on the catalytic surface as seen from the Figure 4.2 is achieved exothermically. The distance between the closest carbon molecule (carbon-1) and the CuO surface is 2.95Å obtained from the optimized geometry.
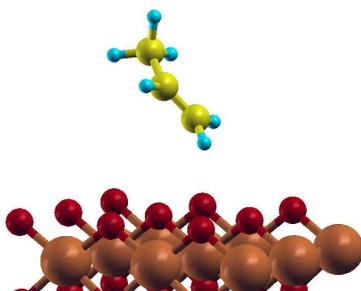
Figure 4.2: Physical adsorption of propylene on CuO surface

Physical adsorption of propylene on the CuO surface is 0.55 eV more exothermic relative to the refence state (Propylene(g) + CuO) as represented in the Figure 4.3. Sample calculation to find the relative energy of the optimized geometries is given in the Appendix A.1. There is no energy barrier between these two geometries.
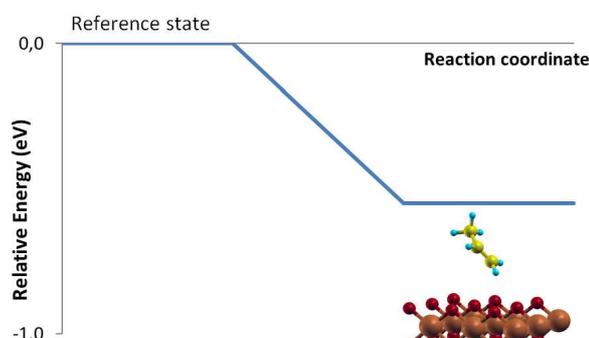
Figure 4.3: Relative energy of propylene physisorption on CuO surface

Following the adsorption of propylene in gas phase on the catalyst surface, energy of formation of surface intermediate on CuO catalyst is investigated. This surface intermediate formation refers to the chemisorption of propylene on the surface of the catalyst. Different from the other catalysts whose surface intermediate is oxametallacycle, newly observed intermediate surface called 'Oxygen Bridging' shown in the Figure 4.4 is obtained on CuO surface.
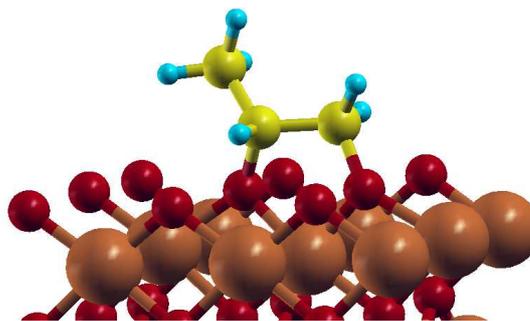
Figure 4.4: Chemical adsorption of propylene on CuO surface

In some of the experiments or theoretical studies, catalytic surface is covered with oxygen and then reactant is adsorbed on the surface. So, there is an alternative of adsorption of oxygen on CuO surface before the chemical adsorption of propylene. In the presence of both oxygen and propylene at the beginning of the reaction, it is checked whether the propylene adsorbed firstly or not with respect to their energies.

There are two possible geometries for oxygen adsorption on the CuO surface. One is the adsorption of oxygen molecule on a lattice oxygen atom on the surface seen from the Figure 4.5, which resulted as moving away of oxygen molecule from the surface as seen in the Figure 4.6 in contrast to adsorption.
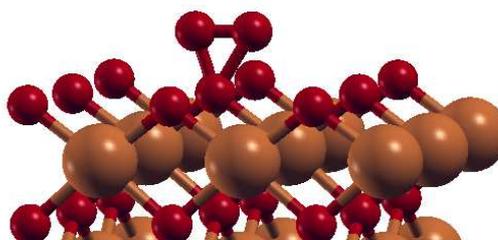
Figure 4.5: Estimated geometry for oxygen adsorption on lattice oxygen
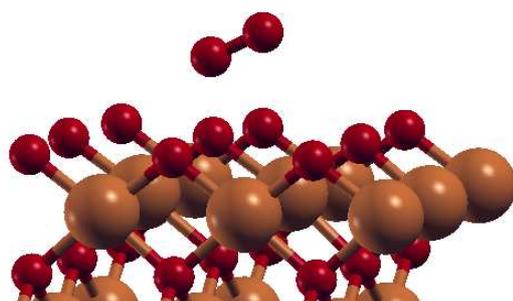
Figure 4.6: Optimized geometry for the physisorption of oxygen molecule

The other possibility is to adsorption of oxygen molecule from the copper side of the CuO surface as shown in the Figure 4.7. This alternative ends with an adsorption of oxygen molecule separably on the catalytic surface with a ground state energy of $-345.72eV$ represented in the optimized geometry in the Figure 4.8.
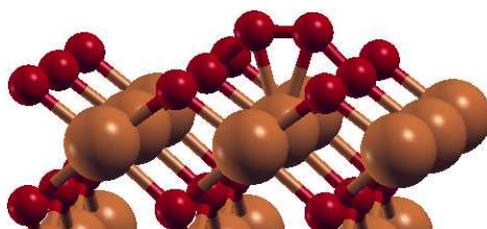
Figure 4.7: Estimated geometry for oxygen adsorption on Cu site
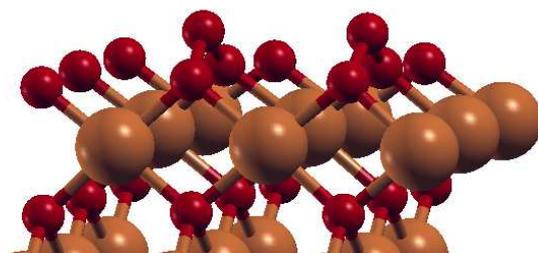
Figure 4.8: Optimized geometry for oxygen adsorption on CuO surface

At the beginning of the reaction, in the presence of both propylene and oxygen molecule in the gas phase, it is understood that both molecule have the tendency for adsorping the CuO surface. These two options are compared according to their energy of adsorption which shows the favorable reaction path for the progress of the study.

First option is to adsorption of the propylene molecule in the presence of oxygen. The energy of this alternative equals to the summation of the energy of the Oxygen Bridging intermediate surface $(-386.92eV)$ with the gas phase energy of the oxygen molecule $(-8.78eV)$ which is $-395.70eV$.

Second option is to chemical adsorption of the oxygen molecule on the surface with an energy of $-345.72eV$ in the entity of propylene in the gas phase $(-48.83eV)$ with a total energy of $-394.55eV$. When it is looked at the results, propylene molecule is inclined to adsorption of the studied surface more than oxygen molecule is if they exposed to the surface as a reactant at the same time.

There is also one last alternative that is checked before moving on with the propylene adsorption on the CuO surface. Propylene has a potential of reacting with oxygen in the gas phase before adsorbing on the catalyst. However, according to the experimental studies conducted on propylene epoxidation reaction propylene requires high energy to take place in gas phase combustion reaction.

Therefore, since it is proved that there is no chance for coverage of the surface with oxygen molecule or combustion of propylene in the gas phase, study continues with the propylene molecule adsorption on the CuO catalytic surface.

There is no difference for propylene between the oxygen atoms in the surface to being attached since the surface is symmetrical in terms of the location of the surface atoms and the calculations are done for infinite surface estimation without considering the edge effects.

4.1.2 Possible pathways for partial oxidation of propylene on CuO surface

After propylene is physically adsorbed on the CuO catalytic surface, there are two competing reactions for partial propylene oxidation. One of these two reaction pathways ends up with the products, propylene oxide or acetone; whereas, the other pathway is concluded with formation of acrolein or allyl radical.

4.1.2.1 Propylene oxide and acetone formation through 'Oxygen Bridging' intermediate surface

As it is mentioned previously in this chapter, through oxygen bridging intermediate surface, there are two possibilities for propylene oxidation, propylene oxide formation and acetone formation.

Before reaction profile analysis for these products, energy barrier between the geometries of physical adsorption of propylene on surface and 'Oxygen Bridging' intermediate geometry is found as $0.5eV$ seen from the graph in the Figure 4.9.
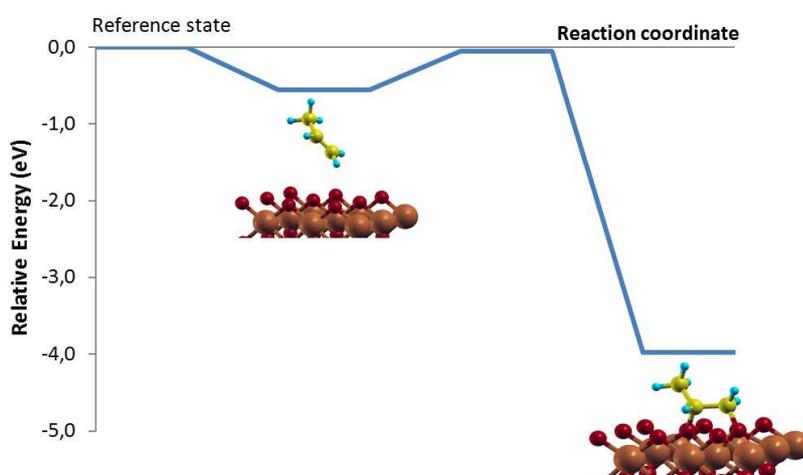
Figure 4.9: Activation barrier between propylene adsorption and oxygen bridging on CuO

Propylene oxide, which is one of the main products, is formed on the CuO surface by breaking the chemical bond between the carbon-1 and oxygen atom in the oxygen bridging intermediate surface and then being attached of carbon-1 to the same oxygen with the carbon-2. This epoxide geometry is optimized as shown in the Figure 4.10.
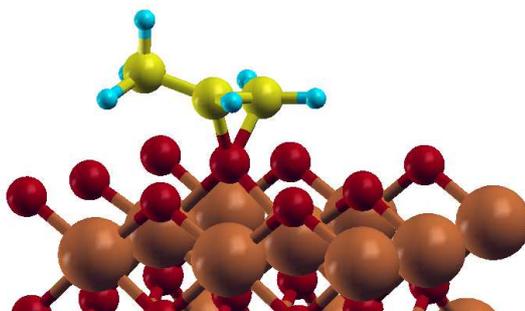
Figure 4.10: Propylene oxide formation on CuO catalyst

Activation barrier for propylene oxide formation through oxygen bridging intermediate surface is 2.89 eV as represented in the Figure 4.11. Images created during the activation barrier calculation between oxygen bridging and propylene oxide pathway is given as sample in the Appendix A.2.
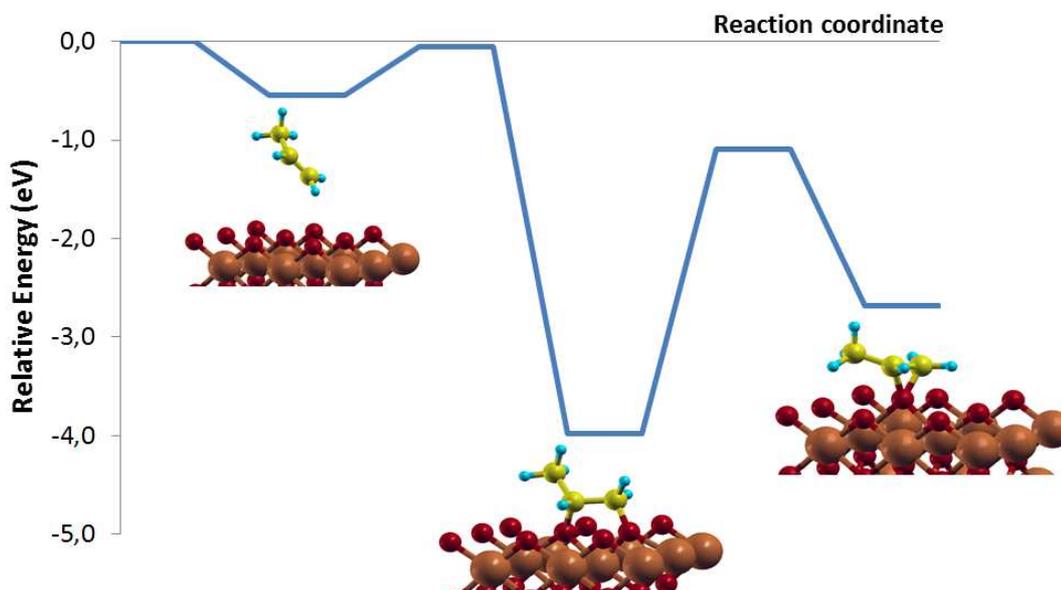
Figure 4.11: Activation barriers up to formation of propylene oxide on CuO surface

This result clearly shows that it is not possible to obtain propylene oxide on CuO surface from propylene.

Acetone, which is another possible product according to this reaction mechanism, is formed by just breaking the carbon-1 and oxygen atomic bond in the oxygen bridging surface as demonstrated in the Figure 4.12.
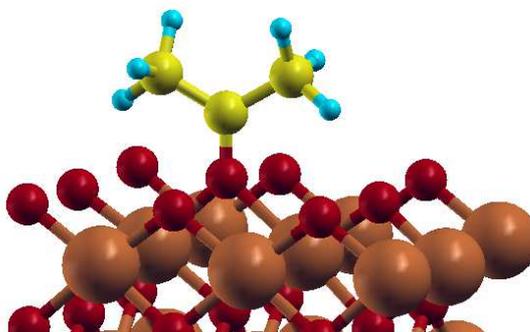
Figure 4.12: Acetone formation on CuO

When possibility of acetone formation is investigated, it is found that activation bar-

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rier through oxygen bridging intermediate surface is $2.47eV$ as shown in the Figure 4.13.
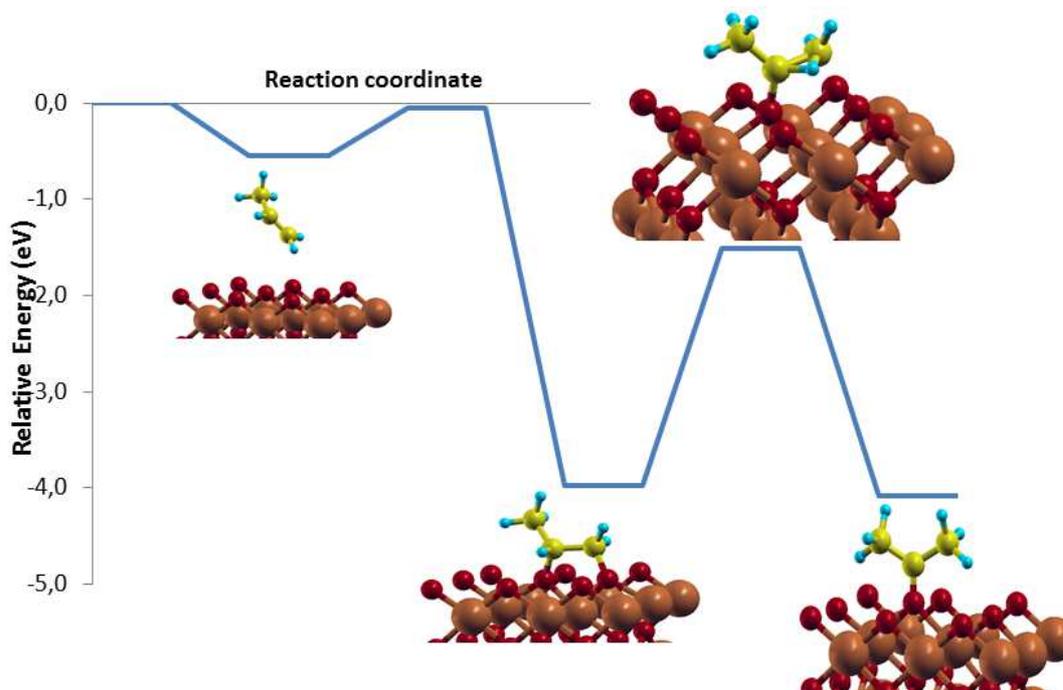
Figure 4.13: Activation barriers up to formation of acetone on CuO surface

Whether this barrier is lower than the propylene oxide barrier, the activation barrier is still too high. As a result of this calculation, it is claimed for the CuO catalyst that acetone formation is also not probable.

When it is compared the activation energies between propylene oxide formation and acetone formation from intermediate surface, there is a slight difference which may cause from the attachment of the carbon-1 atom to the oxygen atom to form propylene oxide.

These activation barriers show that oxygen bridging surface intermediate is a stable surface intermediate which makes propylene oxide and acetone formation almost impossible through oxygen bridging formation.

Although activation barriers are too high to overcome, desorption energies are calculated for products of propylene oxide and acetone from the catalytic surface CuO as represented in the Table 4.1. Desorption of these products occur with breaking the bond of the lattice oxygen atom from its surface by the help of the carbon atom/s.

Table 4.1: Desorption energies of products of the first pathway from the CuO catalyst

Products	Desorption energies from the CuO surface (eV)
Propylene oxide	1.4
Acetone	1.6

The reason of this small difference between the desorption energies is related to the number of the carbon atom attached to this ruptured oxygen. While the desorption of propylene oxide, both carbon 1 and 2 are linked to the oxygen; whereas, only carbon-2 helps oxygen to break its bond with the surface in the desorption of acetone from CuO catalyst.

4.1.2.2   Acrolein and allyl radical formation through allylic hydrogen stripping

Instead of following the pathway through oxygen bridging intermediate surface, propylene has another alternative to strip one of its hydrogen while attaching to the surface seen from the Figure 4.14. In this optimized geometry, which is called as allylic hydrogen stripping, one hydrogen from the carbon-3 atom abstract from the propylene molecule and attach an oxygen atom on the surface.
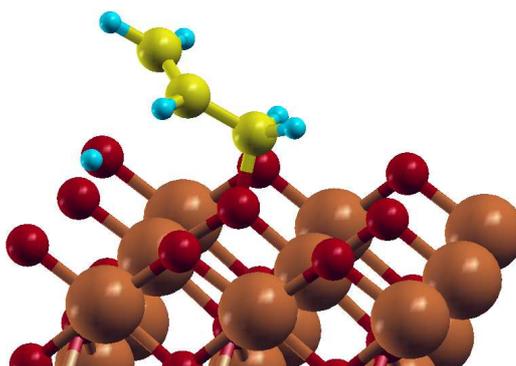
Figure 4.14: Formation of allyl radical on CuO

From propylene adsorption on CuO surface to allylic hydrogen stripping, activation barrier is 0.68 eV which can be seen from the graph in the Figure 4.15. It is predicted

that CuO surface has a great affinity for the H atom by negative charge on its surface oxides.
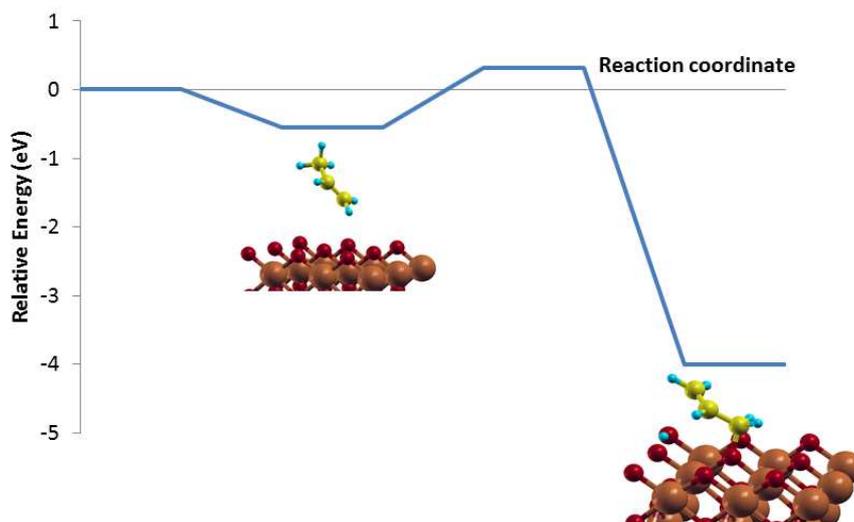
Figure 4.15: Activation barrier between the propylene adsorption and the allyl radical formation

After allylic hydrogen stripping, the possibility of the allyl radical desorption from the CuO surface is also checked and it is found that it requires high energy which is approximately $4eV$.

Acrolein, which is one of the possible main products of this reaction mechanism, is obtained on the catalytic surface by stripping of the second hydrogen from the carbon-1 atom and attaching of this hydrogen to an oxygen atom on the surface of the catalyst. Acrolein geometry achieved on CuO surface according to optimizations is represented in the Figure 4.16. At this final equilibrium geometry, two of the surface oxygens are covered with two hydrogen atoms.
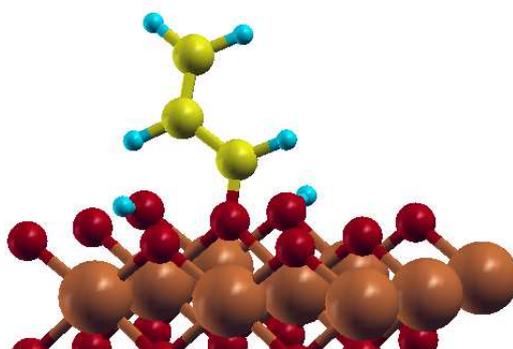
Figure 4.16: Acrolein formation on CuO

Furthermore, the energy of activation between the allylic hydrogen stripping and the acrolein formation on the surface is investigated. Results show that there is no barrier between these geometries as seen from the Figure 4.17, ally radical on the surface directly turns into the product of acrolein.
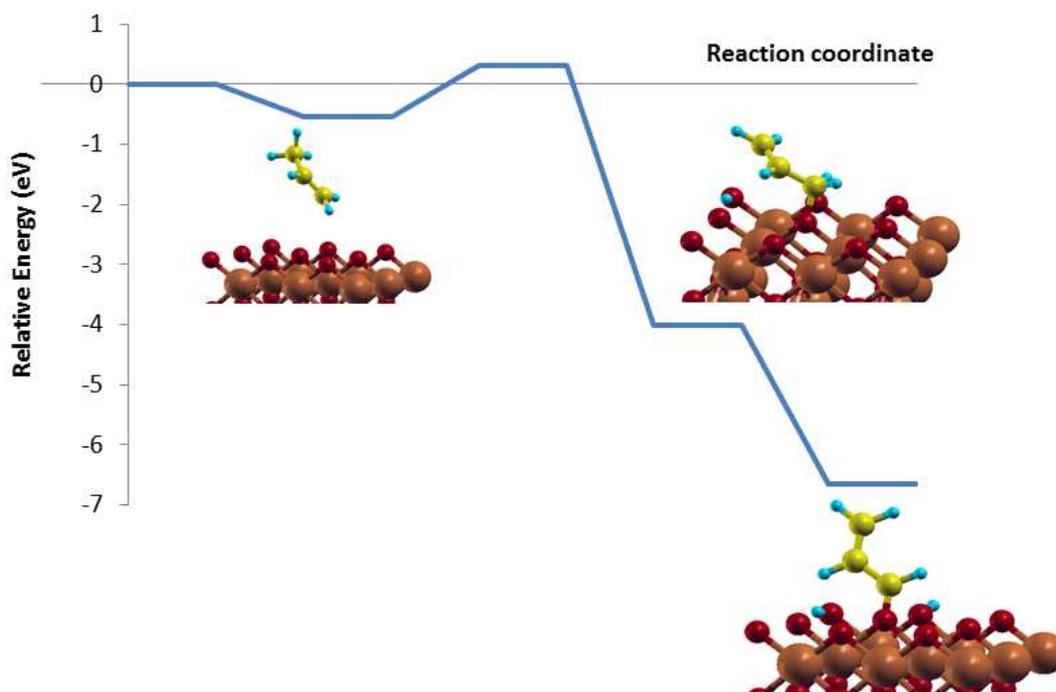
Figure 4.17: Activation barrier between the ally radical and the acrolein on CuO

After finding that acrolein is formed on the catalytic surface without any energy requirement from allyl radical geometry, desorption of the acrolein from the surface is calculated as approximately $1eV$.

To summarize the energies of the optimized geometries and to compare the activation barriers between these probable products, energy profile for the partial propylene oxidation on CuO surface is given in the Figure 4.18.

To conclude, according to the energy diagram, acrolein seems the most probable product among the propylene oxide and acetone for the propylene epoxidation reaction on CuO catalytic surface.
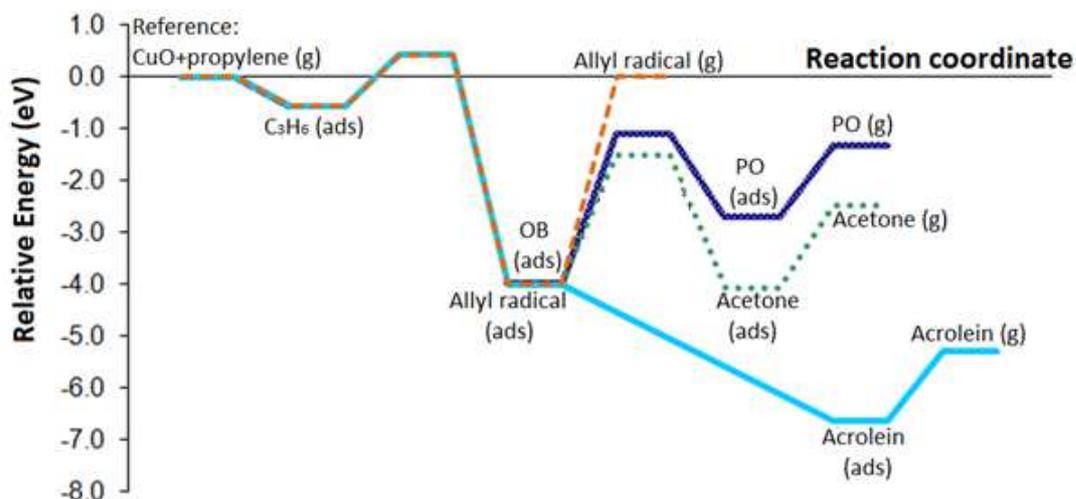
Figure 4.18: Energy profile for the partial propylene oxidation on CuO surface

4.1.3 Formation of water on CuO surface

Up to now, it is clearly understood that CuO surface is suitable catalyst for acrolein formation when it come across with the first propylene molecule. After the desorption of this acrolein molecule from the CuO catalyst, two stripped hydrogen from the propylene left on the surface and one oxygen is missing which goes away with the acrolein as represented in the Figure 4.19.
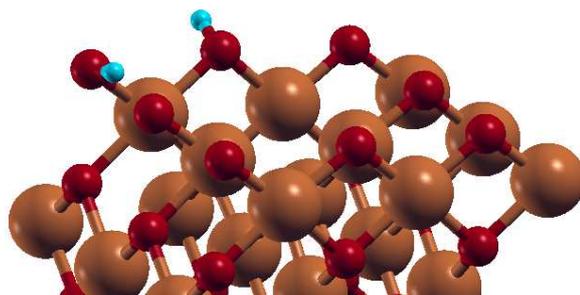
Figure 4.19: Optimized geometry of CuO surface after the desorption of acrolein

It is thought that water molecule should be formed in order to complete the reaction cycle after desorption step. There are two possible ways for the formation of water on the surface; the reaction of two hydrogens with one of the lattice oxygen or with adsorption of an oxygen molecule.

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4.1.3.1　Formation of water on CuO surface without addition of oxygen molecule

For water formation by using the surface oxygen, both of the hydrogens should be attached on the same lattice oxygen. Then, water molecule is obtained as a side product by the desorption of these two hydrogen and one lattice oxygen from the surface. So, two options for the two hydrogen atoms which should be linked together are discussed in the Figure 4.20 and Figure 4.21 in the presence of vacancy.
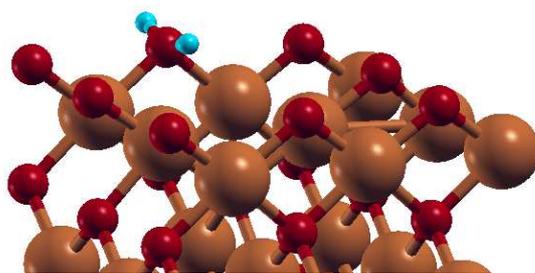
(a)
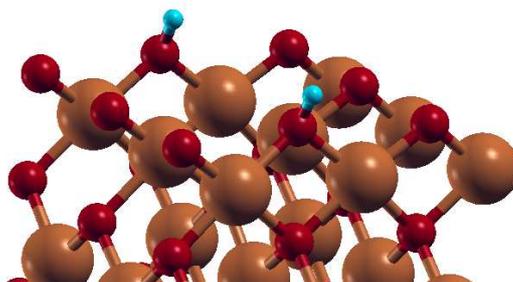
(b)

Figure 4.20: (a) 1st estimated geometry of the hydrogen atoms, (b) Optimized geometry of the hydrogen atoms for the 1st alternative

Both in the Figure 4.20 and in the Figure 4.21, images of (a) represents the estimated geometry of hydrogen atoms modelled with a purpose of the formation of water. However, results show that hydrogen atoms move away from each other to link to the different lattice oxygen atoms as shown in their equilibrium geometry structure from the images of (b).

From these Figures 4.20 and 4.21 it is obviously understood that there is no chance to form H_2O with lattice oxygen on the surface since hydrogen atoms preferably separate from the same lattice oxygen.

(a)
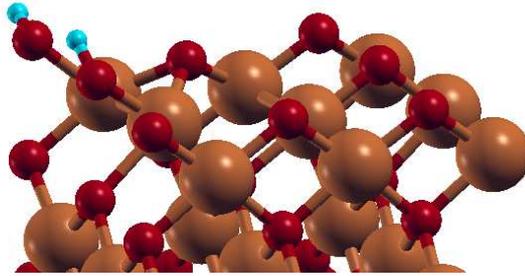
(b)

Figure 4.21: (a) 2nd estimated geometry of the hydrogen atoms, (b) Optimized geometry of the hydrogen atoms for the 2nd alternative

4.1.3.2 Formation of water on CuO surface with addition of oxygen molecule

Since estimations done with lattice oxygen result in failure of water molecule formation on the CuO surface, it is decided to form water by addition of an oxygen molecule to the vacancy to create an excess oxygen atom. For adsorption of the oxygen molecule to the oxygen vacancy on the surface, probable geometries are optimized to find the one that has the minimum energy.

From the alternatives optimized as shown in the Figure 4.22, the most stable geometry is found as in the Figure 4.22c among the others. Afterwards, several alternatives are tried with an aim of investigating the water formation on the energetically most preferable surface as in the Figure 4.22c.
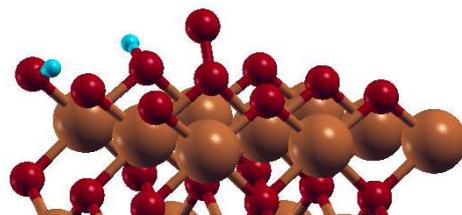
(a)
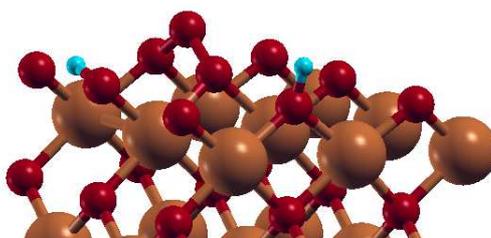
(b)
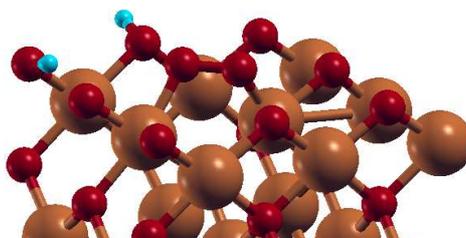
(c)

Figure 4.22: Oxygen molecule adsorption after the desorption of acrolein from the surface

First alternative is that direct water formation on CuO surface. Energy barrier between the Figure 4.22c and Figure 4.23 is investigated as $2.65eV$. So, it is obviously seen that direct formation of water is not possible since it requires high energy.
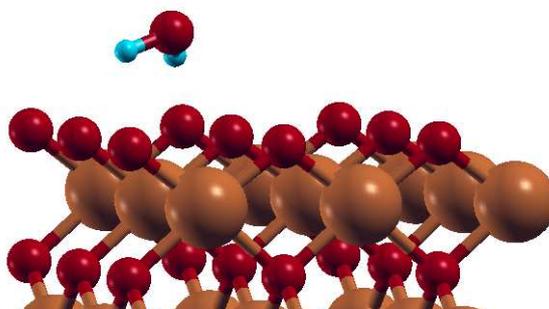
Figure 4.23: Optimized geometry for desorption of water from the surface

Second alternative is to form water by using the lattice oxygen once again; however, in this case there is oxygen molecule adsorbed on the surface instead of vacancy. Although the molecular structure does change, the results of the optimizations are still the same that hydrogens fall apart from each other as seen from the Figure 4.24. One more time, it is claimed that forming water with two stripped hydrogen and a lattice oxygen is not probable on this geometry.
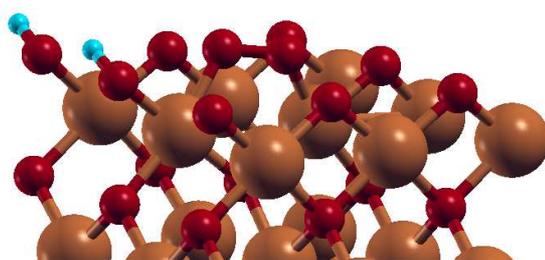
(a)
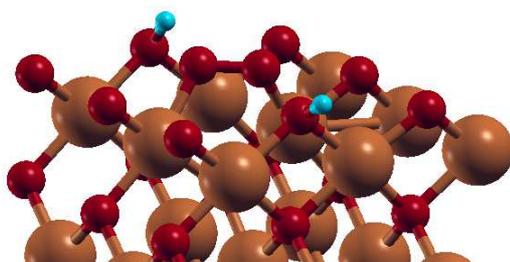
(b)

Figure 4.24: (a) Optimized geometry of the hydrogen atoms in the presence of oxygen molecule- 1st alternative, (b) Optimized geometry of the hydrogen atoms in the presence of oxygen molecule- 2nd alternative

As a third alternative, it is decided to generate water molecule by the help of atomic oxygen. For this purpose, it is thought to check whether atomic oxygen is obtained from the Figure 4.22c surface represented in the Figure 4.25 or not. Calculations indicate that desorption of atomic oxygen from this surface to attain the final equilibrium geometry of Figure requires 5.5 eV energy. This high level of energy expresses that it is too hard to obtain oxygen atom so as to form water from the surface of the Figure 4.22c.
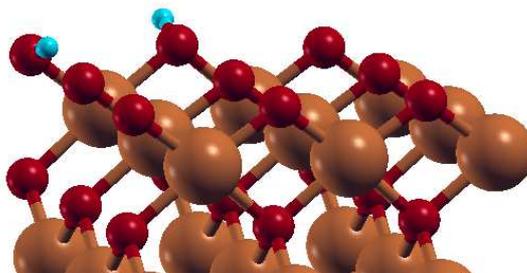
Figure 4.25: Two hydrogens adsorbed separately on CuO surface

The fourth and the last alternative is to use desorbed OH radicals to obtain water molecule on the surface. Estimated geometry for the desorption of OH radicals is given in the Figure 4.26a; however, final equilibrium structure as represented in the Figure 4.26a is quite far away from its initial guess. In final geometry, OH radicals are attached to each other and both of them are linked to the copper metal.
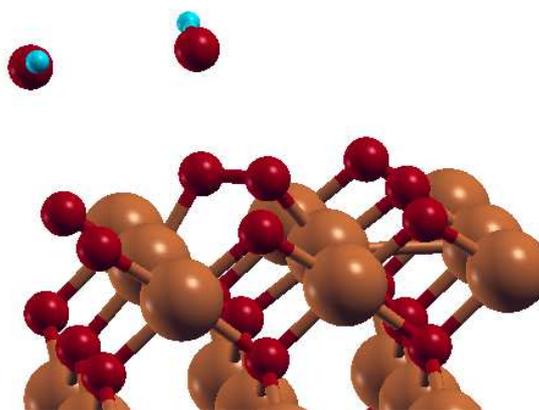
(a)
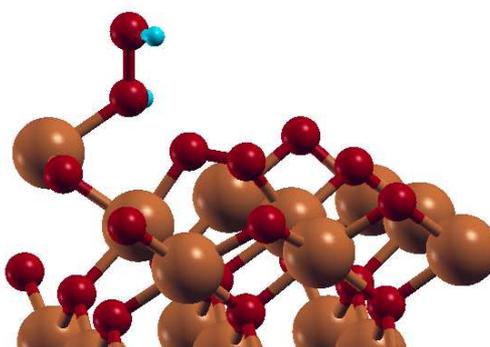
(b)

Figure 4.26: (a) Estimated geometry for the desorption of OH radicals, (b) Optimized geometry for OH radical desorption

After achieving the optimized surface in the Figure 4.26b, another possibility of formation of water arise. So as to check the probability, the required energy from the Figure 4.22c to the Figure 4.26b is investigated and it is found as approximately 10 eV. It can be said that this alternative way of water formation on the surface is nearly impossible due to its high energy barrier.

After these unsuccessful attempts for water formation on the CuO surface, as a reverse approximation, it is decided to determine how water molecule is adsorbed on CuO catalyst. The initial estimation for the geometry after adsorption can be seen from the Figure 4.27.
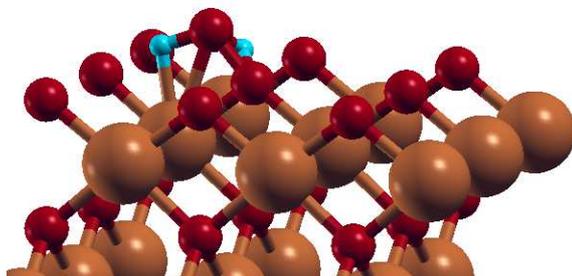
Figure 4.27: Estimated geometry for adsorption of water on CuO surface

Starting with this initial guess, final equilibrium geometry is achieved as represented in the Figure 4.28 which directly explains the reason of these ineffective attempts for water formation. Water molecule splits into its atoms on CuO surface which is also stated in [2]. Therefore, it can be stated that for the first propylene sends to the surface of CuO, there is no formation of water besides the product of acrolein.
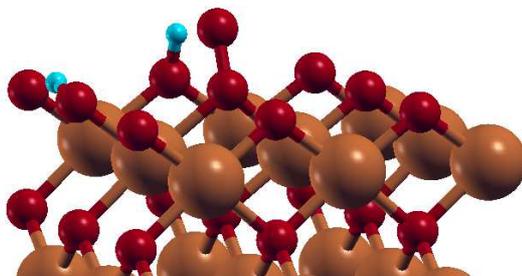
Figure 4.28: Optimized geometry of the structure in the Figure 4.27

4.1.4 Adsorption of the second propylene after the desorption of acrolein from the surface

The attitude of water on the surface leads to send the second propylene molecule to the catalyst just after desorption of the acrolein and then filled the vacancy with oxygen molecule.

At first, the geometry is estimated as if propylene is attached to the adsorbed oxygen molecule seen from the Figure 4.29a. As a result of the calculation of this estimation, fully optimized geometry indicated in the Figure 4.29b claims that propylene has not a tendency for adsorption or, in other words, adsorbed oxygen molecule refuses the propylene due to its saturated form. So, it can easily seen from the equilibrium geometry that propylene stays in the gas phase instead of connecting to the adsorbed molecule.

(a)

(b)
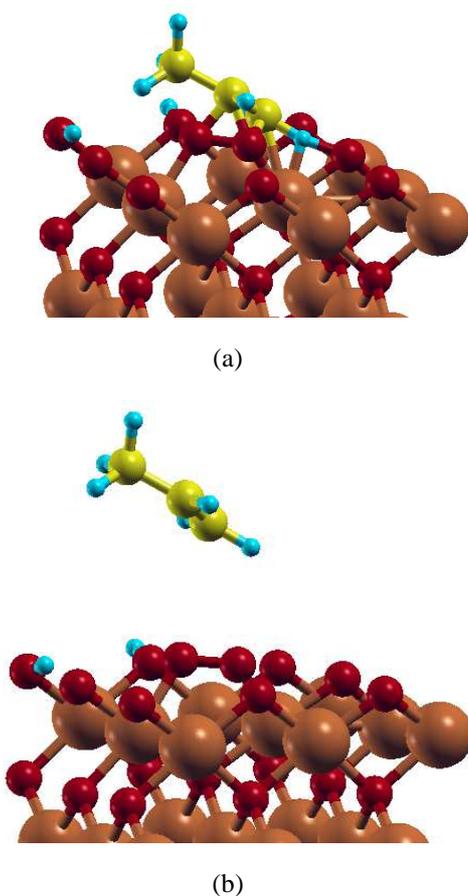
Figure 4.29: (a) Estimated geometry for the adsorption of 2nd propylene on oxygen molecule, (b) Optimized geometry for the estimated structure of (a)

Another possibility is attaching of the second propylene to the lattice oxygen of the surface rather than the adsorbed oxygen molecule. Initial geometry is estimated as illustrated in the Figure 4.30a below. After the optimization of this initial geometry is carried out, outcome geometry is quite unimagined. As it is seen from the Figure 4.30b, final equilibrium geometry is propylene oxide molecule in the gas phase. Carbon-1 and carbon-2 atoms involving in the propylene are connected to the surface oxygen and desorbed immediately.
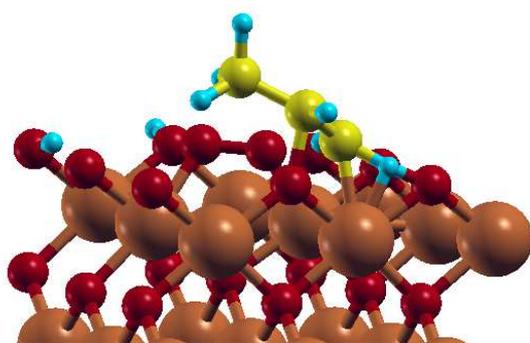
(a)
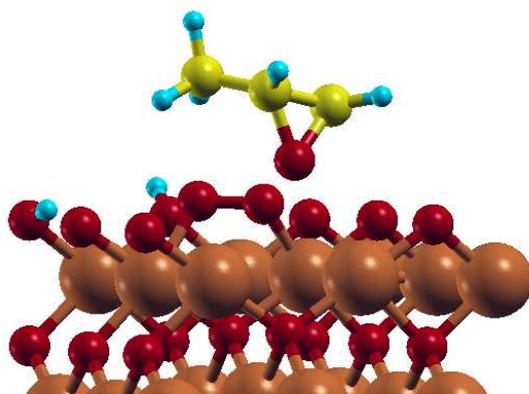
(b)

Figure 4.30: (a) Estimated geometry for the adsorption of 2nd propylene from Cu side, (b) Optimized geometry of propylene oxide desorbed from the surface

Up to now, it is investigated that acrolein is the main product for propylene epoxidation reaction mechanism on CuO catalyst. In addition to the acrolein, it seems that there is also a possibility for propylene oxide formation for continuing flow of propylene reactant. However, experimental results stated in [24] for propylene epoxidation mechanism on CuO surface insist that CuO catalyst leads to complete combustion

since it is more reactive in producing highly oxidized products. It is commented that due to its distribution of fully oxidized surface, it is more prone to the combustion reaction for propylene epoxidation according to experimental results. It is also assumed in the study that the combustion products probably form due to the oxidation of acrolein. A further experimental study [35] conducted for propylene epoxidation on copper surface points out that acrolein is more resistant to combustion than propylene oxide. This argument is supported by the experimental data that between the temperature of $275°C$ and $325°C$, as the selectivity of propylene oxide decreases, formation of combustion products are also declining; whereas, production of acrolein show an increase. Opposite of the former study, this study claims that formation of combustion products are directly related to the propylene oxide rather than acrolein.

Therefore, according to literature findings, it is decided to investigate the combustion of both acrolein and propylene oxide.

4.2 Combustion reaction mechanisms with molecular oxygen in the gas phase

In the studies related with the combustion, products are oxidized with the oxygen molecule instead of oxygen atom. As mentioned above, it requires higher energy to obtain the atomic oxygen on the surface.

4.2.1 Combustion of the product: Acrolein

Figure 4.31: Acrolein and oxygen molecule in the gas phase

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At the beginning of the reaction of acrolein combustion, molecular oxygen is adsorbed in the gas phase with acrolein as represented in the Figure 4.31.

Molecular oxygen attracts the two hydrogens from carbon-2 and carbon-3 as a first step of this combustion reaction as seen from the optimized Figure 4.32. However, attracting the hydrogens is not that easy for the oxygen molecule. When the energy requirement is checked between these Figures; Figure 4.31 and Figure 4.32, it is seen that the activation barrier is really high such that it is impossible for atoms to overcome this energy.
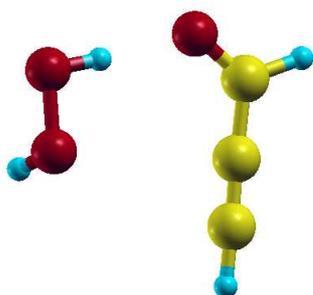
Figure 4.32: Hydrogen removal from the acrolein

Nonetheless, optimizations are continued to investigate the further steps of the acrolein combustion reactions.

Afterwards, one of the hydrogen from C_3H_2O is attached to the OH bond Figure 4.33a and then the remaining hydrogen from C_3HO is connected to the other OH bond Figure 4.33b and consequently as seen two water molecules are formed. These steps containing removal of hydrogen can occur without activation energy barrier.

(b)

(a)
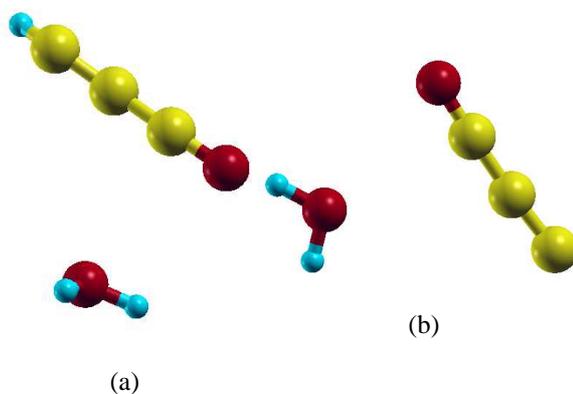
Figure 4.33: (a) C_3HO formation, (b) C_3O formation

In an attempt to see the further mechanism of the combustion reaction of acrolein, after getting rid of all the hydrogens, two more oxygen molecules are attached to C_3H molecule Figure 4.34a. In the Figure 4.34b, there are two CO_2 and one CO molecule as products of these combustion mechanism. Between these two figures, there is also no activation barrier.

(a)

(b)
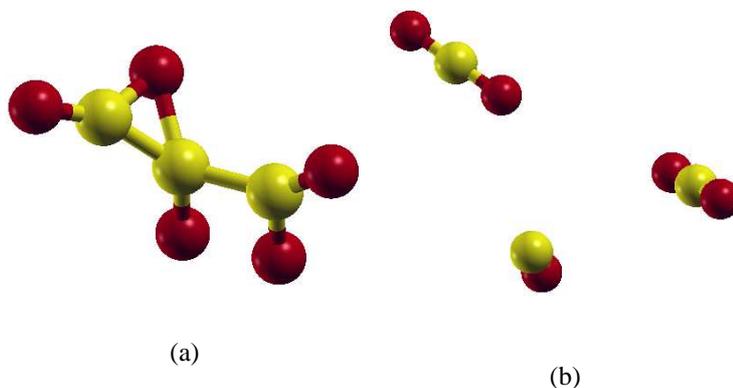
Figure 4.34: (a) Oxygen adsorption on C3O Molecule, (b) Formation of CO2 and CO

The combustion reaction of the acrolein is simulated with the optimized geometries as mentioned above which represents the chemical equation (4.1).

$$C_3H_4O + 3O_2 \rightarrow CO + CO_2 + 2H_2O \tag{4.1}$$
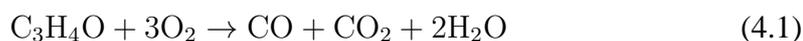
However, the probability of the combustion of acrolein seems too low since the first step of the reaction requires high energy. Thus, the acrolein is probably obtained as a product instead of oxidizing after the propylene epoxidation reaction on CuO surface.

4.2.2 Combustion of the product: Propylene Oxide

Another possible product that can be oxidized after desorption from the surface is propylene oxide. As a first step of this combustion mechanism, oxygen molecule is directly attached to the propylene oxide molecule as indicated in the Figure 4.35 without any barrier.
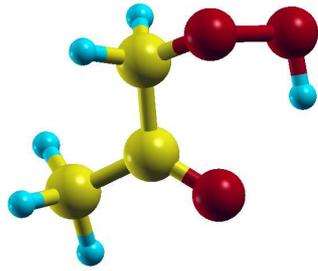
Figure 4.35: Oxygen adsorption on propylene oxide

As a second step, OH radical is removed from this molecule and water is formed by the reaction of one of the hydrogen from carbon-1 atom with this OH radical as illustrated in the Figure 4.36.
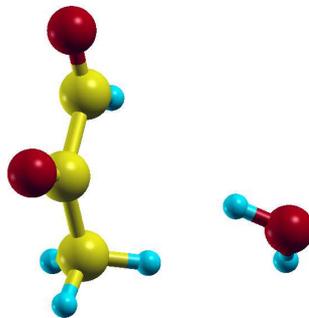
Figure 4.36: H_2O formation in the combustion of propylene oxide

Final molecules that are obtained at the end of the combustion pathway of propylene oxide with respect to the chemical equation (4.2). below are formaldehyde (CH_2O), ethenone (C_2H_2O) and water (H_2O) all of which are shown in the Figure 4.37.

$$C_3H_6O + O_2 \rightarrow CH_2O + C_2H_2O + H_2O \qquad (4.2)$$

Both ethenone and formaldehyde are known as highly reactive molecules, thus they are rapidly oxidized according to (4.3) and (4.4).

$$C_2H_2O + 2O_2 \rightarrow H_2O + 2CO_2 \qquad (4.3)$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (4.4)$$
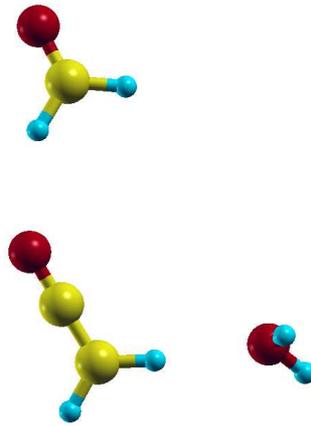
Figure 4.37: Ethenone, formaldehyde and water formation

The activation barriers between all of these steps are investigated as plotted in the Figure 4.38. To overcome the energy of activation, the required energy is approximately $1eV$.
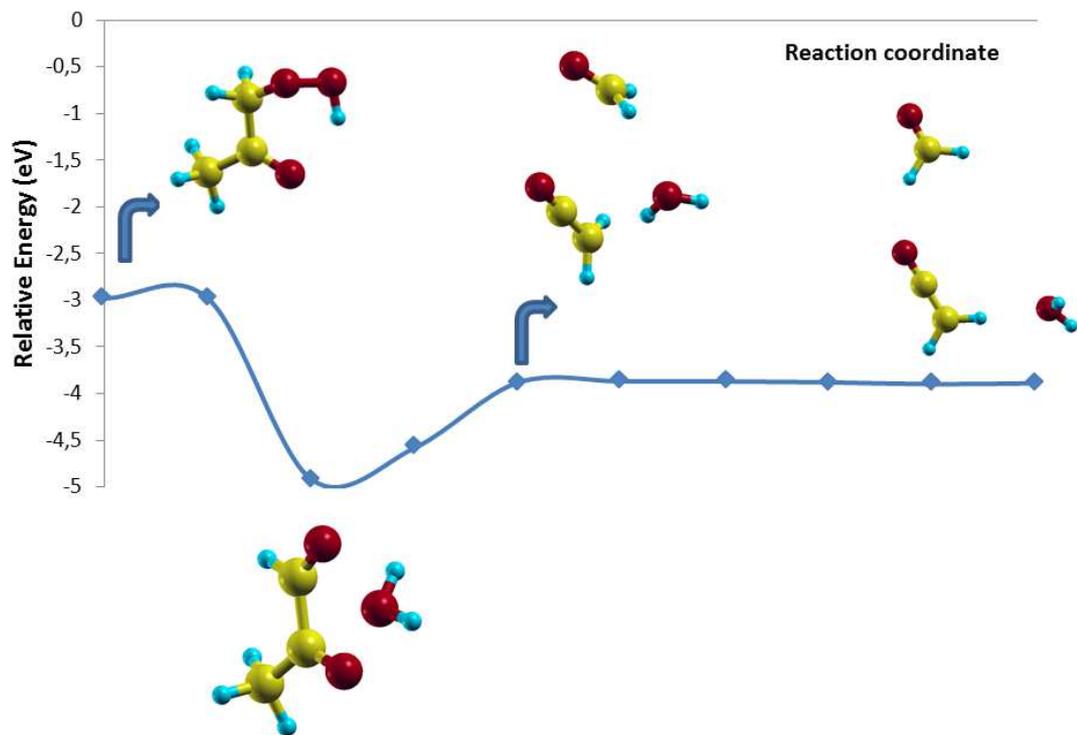
Figure 4.38: Activation barrier for the combustion of propylene oxide with an oxygen molecule

Hence, propylene oxide has a higher possibility to take place in combustion reaction after desorping from the CuO surface.

4.3 Results of the propylene epoxidation mechanism on Li promoted CuO catalyst

Li is substituted to the CuO surface in order to block the route leading to the allylic hydrogen stripping which prevents the formation of the propylene oxide formation. Firstly, pyhsisorption of propylene on the optimized Li substituted CuO surface as seen from the Figure 4.39 is achieved. Represented final equilibrium geometry shows that the distance between the carbon-1 atom and closest Li atom is 2.45Å.
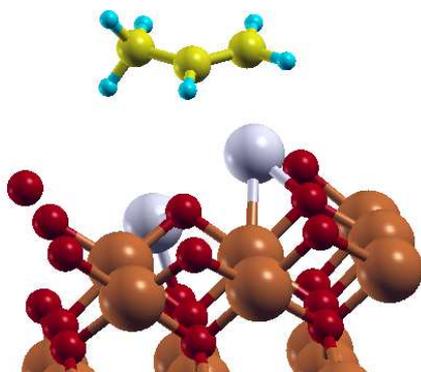
Figure 4.39: Physical adsorption of propylene on Li promoted CuO surface

To see the promoter effect of Li for propylene epoxidation reaction on CuO surface, possible main products; propylene oxide and acrolein are investigated in this study.

Firstly; propylene oxide, which is one of the desired product for propylene epoxidation reaction, is optimized on Li substituted CuO surface as illustrated in the Figure 4.40. The geometry of the epoxide is formed by using the surface oxygen connected to the one of the Li atoms.
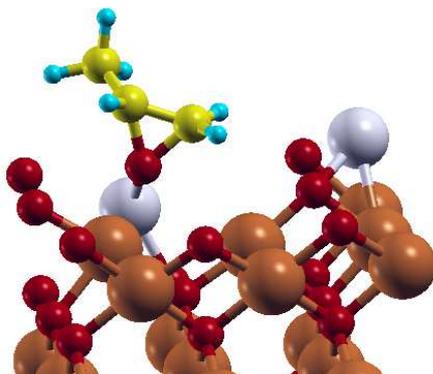
Figure 4.40: Propylene oxide formation on Li promoted CuO surface

Different from the CuO catalyst, there is no intermediate medium obtained such as oxygen bridging surface before propylene oxide formation on the surface. Hence, activation barrier is calculated from physical adsorption of the propylene to the propylene oxide formation on the Li promoted catalytic surface. In addition to that, transition state geometry from the Figure 4.41 clearly shows that oxygen atom located in the middle, which is connected to the Li atom, tends towards the carbon-1 and carbon-2 atoms of the propylene. The energy barrier is found as $0.49 eV$ which makes possible to the formation of propylene oxide through this pathway.
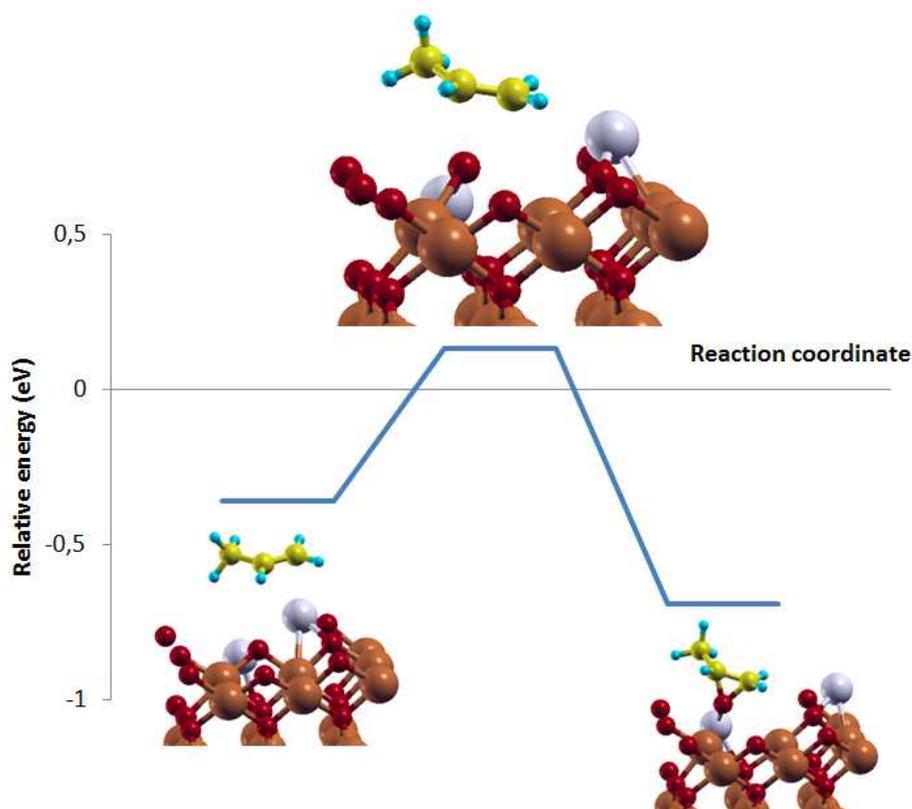
Figure 4.41: Activation energy between propylene adsorption and propylene oxide on Li promoted CuO

The other possible pathway investigated for the CuO catalyst, acrolein formation through hydrogen stripping geometry, is also optimized for the CuO surface in the presence of Li promoter. Final equilibrium geometry achieved for the allylic hydrogen stripping on the promoted surface is shown in the Figure 4.42. This optimized geometry is obtained by removal of one of the hydrogen from carbon-3 atom of the propylene molecule.
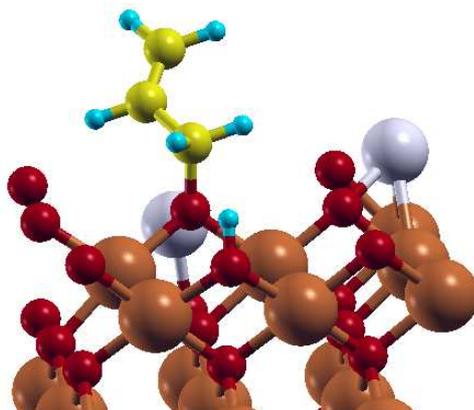
Figure 4.42: Allyl radical formation on Li promoted CuO surface

The activation energy diagram from the propylene physically adsorbed to the formation of allyl radical on Li substituted surface is represented as seen in the Figure 4.43.
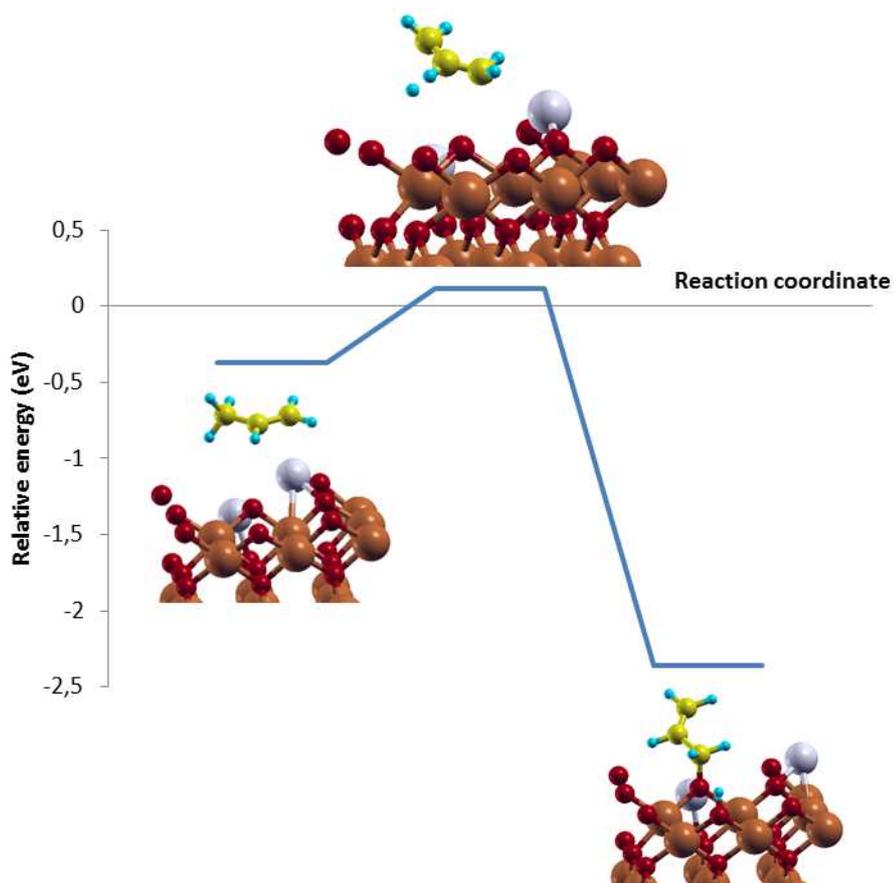
Figure 4.43: Activation energy between propylene adsorption and allyl radical on Li promoted CuO

The required energy to overcome the barrier is $0.49eV$ which is determined by the transition state geometry explicitly seen from its side view in the Figure 4.44. The barrier makes its peak point at the removal of hydrogen from carbon-3.
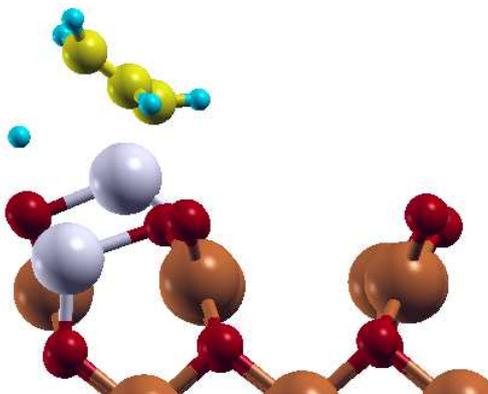
Figure 4.44: Transition state geometry towards allyl radical formation from side view

After analyzing the energies of allylic hydrogen stripping formation, acrolein is optimized on the Li promoted surface by abstraction of the second hydrogen from the carbon-1 atom as indicated in the Figure 4.45.
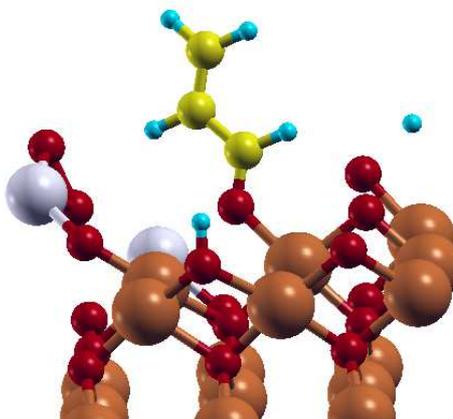
Figure 4.45: Acrolein formation on Li promoted CuO surface

Between the geometry of allylic hydrogen abstraction and the acrolein formation, the activation barrier is found as $1.17eV$. As it is seen from the pathway in the Figure 4.46, there is too much alteration on the surface because of the motion of the surface atoms. The peak energy is observed at the geometry of that oxygen molecule attracts the Li atom and pulls toward itself.
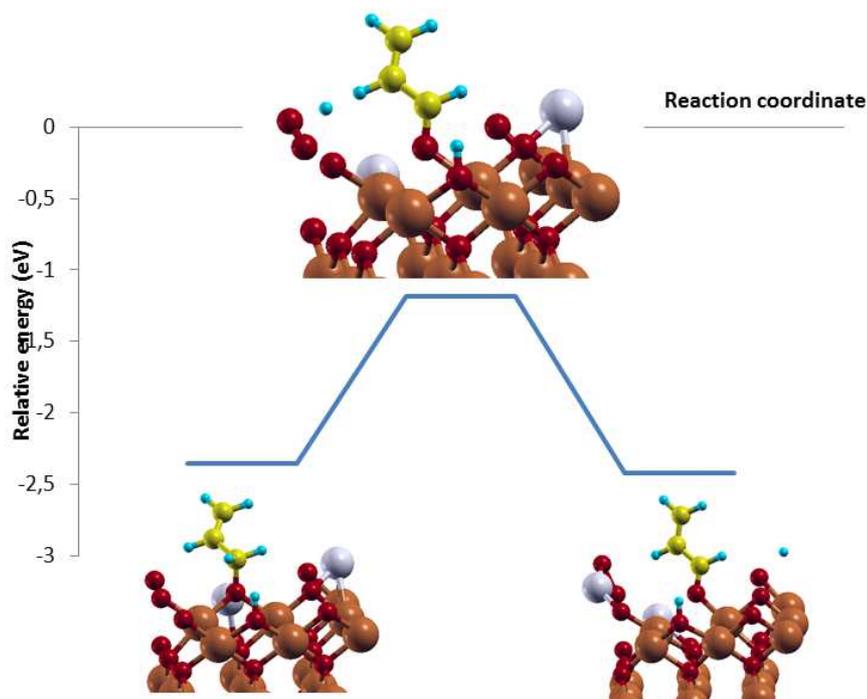
Figure 4.46: Activation energy between allyl radical and acrolein on Li promoted CuO

On Li substituted CuO catalytic surface, propylene oxide seems more favorable product for propylene epoxidation reaction. However, as mentioned in the CuO catalyst, it has tendency for combustion which leads to combustion products such as carbon dioxide and carbon monoxide.

4.4 Discussion of the results of the propylene epoxidation mechanism on CuO and Li promoted CuO catalysts

For the partial oxidation of propylene, activation energy barriers for the pathway of each possible products investigated on CuO (001) and Li promoted CuO (001) catalysts throughout the study are summarized in Table 4.2.

To sum up, the mechanism of the partial oxidation of propylene proceeds via allylic hydrogen stripping to acrolein formation for the first propylene encounter with the CuO catalytic surface. For the second propylene which is sent to the surface, direct propylene oxide formation occurs. These theoretical results are supported by the

Table 4.2: Activation energies for each possible products of the propylene epoxidation reaction

For	CuO (001) Surface	Li promoted CuO (001) Surface
Oxygen bridging to PO	2.89 eV	-
Oxygen bridging to acetone	2.47 eV	-
Propylene adsorption to allyl radical	0.68 eV	0.49 eV
Allyl radical to acrolein formation	0	1.17 eV
Direct PO formation	0.85 eV	0.49 eV

experiment conducted for propylene epoxidation on CuO_x catalyst supported with SiO_2 [10]. The experimental results claim that the reaction of the first pulse of the propylene leads to acrolein formation with a selectivity of 95% together with small amount of CO_x. However, it is observed that selectivity of acrolein is decreasing with the increasing number of successive propylene pulses. In addition to that, combustion products such as CO_2 and CO has an increasing trend contrary to acrolein. These experimental consequences are consistent with the theoretical results given in this study.

Furthermore, experimental study states that after the approximately 62 pulses of propylene, none of the products are formed due to the fact that lattice oxygen atoms are consumed by the formation of acrolein and combustion products. Thus, it is predicted for CuO surface that consuming of lattice oxygen atoms reduces the surface to Cu_2O after a while. On the latter oxide surface, acrolein is favorable product rather than combustion products.

Analysis of CuO catalyst in terms of propylene epoxidation reaction brings about the necessity for substitution of a promoter Li with the aim of increasing the selectivity of propylene oxide formation. When the results in the Table 4.2 are compared, it is clearly seen that the formation of acrolein pathway is prevented. Although there is no

Table 4.3: Comparison of the experimental results of CuO and Li promoted CuO surfaces for propylene epoxidation reaction [10]

Catalyst	Selectivity			
	PO	Acrolein	Others	CO_x
CuO_x/SiO_2	1.8	49	4.6	42
$Li - CuO_x/SiO_2$	12	3.8	0.3	84

activation barrier between allyl radical and acrolein formation on CuO catalyst, the energy barrier is obtained as $1.17 \ eV$ between the same geometries on Li promoted CuO surface. Since the intermediate surface is not attained on the Li substituted CuO catalyst, the activation energies for propylene oxide and acetone through oxygen bridging surfaces are incomparable. In the presence of Li promoter, it is claimed that propylene oxide is directly formed on the catalytic surface with an energy requirement of $0.49 \ eV$. On the other hand, the same optimization for direct propylene oxide formation is done for the CuO surface, the calculation indicates that the energy barrier is $0.8 \ eV$ which is quite high with respect to the result of Li promoted surface. Thus, it is concluded that propylene oxide selectivity increases for propylene epoxidation on the Li substituted CuO surface, whereas the route leading to the acrolein formation is blocked. This conclusion proves the results of the experimental studies in which it is demonstrated that Li enhances the selectivity of propylene oxide by weakens the acidity of the catalytic surface. In an experimental study about propylene epoxidation [10], copper catalyst is promoted with Li and the results show that while the selectivity of acrolein is decreasing, both propylene oxide and CO_2 selectivities are increasing as seen from the Table 4.3.

CHAPTER 5

CONCLUSIONS

Propylene oxide is an important versatile compound whose annual consumption is increasing with a rising demand. In this study, propylene epoxidation mechanism on CuO (001) and Li promoted CuO catalysts are investigated theoretically by utilization of DFT method. The purpose of this investigation is to discover a heterogeneous catalyst for the direct propylene epoxidation reaction in order to obtain highly valuable propylene oxide chemical whose commercial production techniques are problematic.

The optimization calculations indicate that there are two possible reaction pathways for CuO surface. One pathway is propylene oxide or acetone formation through oxygen bridging intermediate surface which turns out to have high activation barriers. The other one is acrolein formation through allylic hydrogen stripping on CuO surface. As a result, energy profile for formation of propylene oxide, acrolein and possible co-products from propylene on CuO surface is identified. Propylene oxide formation through oxygen bridging pathway is not possible due to high activation barrier. On the other hand, acetone formation on CuO slab is highly exothermic. In addition, formation of acrolein from hydrogen stripping has no activation barrier. Likely, desorption of allyl group has high energy requirement. To conclude, according to reaction mechanism, CuO is the suitable catalyst for allyl radical formation resulting in acrolein formation. After desorption of acrolein from the catalytic surface, in order to complete the reaction cycle, water formation is studied and it is found that water is preferably splitted on CuO surface rather than formation. For the second propylene send to the catalyst, it is recognized that propylene oxide is directly formed with the lattice oxygen atom. Then, it is stated that after the number of reacting propy-

lene increases, acrolein selectivity is decreasing. In addition to that, both acrolein and propylene oxide is compared in terms of their ability of complete oxidation. It is shown that propylene oxide has more tendency for combusting so this proves the high amounts of the products of combustion observed in the experimental studies together with acrolein formation.

Lastly, propylene epoxidation is investigated on CuO catalyst in the presence of Li promoter. It is found that Li increases the possibility of propylene oxide formation, whereas it prevents the acrolein formation path by increasing its activation energy. Therefore, it is concluded that Li substituted CuO catalyst is more active by comparing with the CuO catalyst with respect to the propylene oxide formation.

For further studies, it can be suggested that amount of Li atom on the surface can be increased to observe the effect on the formation of propylene oxide. In addition to that, two Li atoms can be substituted to the surface by replacing with only one Cu atom instead of removing an oxygen atom, this alternative surface can be studied for the same reaction mechanism to see the effect of oxygen removal. It is also recommended to study different promising promoters on CuO surface such as Na, Cl and Cs. Also, it can be checked that whether the resulted intermediate surfaces can be observed for propylene epoxidation reaction experimentally by using FTIR technique or not.

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APPENDIX A

APPENDIX

A.1 Sample calculation for relative energy of the optimized geometries

The generalized equation for relative energy calculation is given below.

$$E_{optimizedgeometry} - E_{referencestate} = E_{relativeenergy} \qquad (A.1)$$

The ground state energy of the optimized geometry of propylene adsorption is -383.49 eV. The refence state (Propylene(g) + CuO) has a energy of -382.94 eV.

$$-383.49 - (-382.94) = -0.55 eV \qquad (A.2)$$

So the relative energy of the physical adsorption of propylene on the CuO surface is $0.55 eV$.

A.2 CI-NEB images between oxygen bridging and propylene oxide on CuO surface

During the activation barrier calculations, 9 images created between the oxygen bridging intermediate surface and formation of the propylene oxide is given below.