STUDY OF THE ADSORPTION AND DEHYDROGENATION STEPS OF ETHANOL ON A Pt-Sn SURFACE WITH DENSITY FUNCTIONAL THEORY

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Doctoral Thesis
Doctorate in Engineering – Energy Systems

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MEDELLÍN
2011
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The development of Direct Ethanol Fuel Cells (DEFCs) is important for obtaining alternative energy converters. Within this objective, there is an interesting topic that is considered fundamental to the development of these devices: the ethanol reaction mechanism in the anode of the DEFCs. Some groups have investigated this process, but still there are many difficulties to achieve a complete understanding of the ethanol reaction mechanism. Using experimentation procedures is difficult to identify the reaction intermediates and the reaction paths, whereas the theoretical investigations are still in development.

These facts encourage both experimental and theoretical investigations to understand completely the ethanol reaction process in the DEFCs. Currently, the most commonly investigated catalytic surfaces are Pt-Ru, Pt-Sn, and Pt-Ru-Sn mixtures and some catalytic mixtures that contain nickel, Pt-Ru-Ni and Pt-Sn-Ni. Nevertheless the experimental studies cannot elucidate entirely the reaction intermediates and reaction paths. So to date there are not known satisfactory explanations of the catalytic processes existent in the ethanol adsorption and decomposition processes on different catalytic surfaces. Because of this, the theoretical investigation could help to elucidate the complex reaction mechanism involved in the ethanol reaction in the DEFCs. Considering this, it is carried out in this work the study of the initial steps of the ethanol reaction mechanism on a Pt-Sn catalytic surface.

Specifically the potential energy surface (PES) of the adsorption and dehydrogenation steps of ethanol decomposition on a specific catalytic surface (Pt$_{3}$Sn$_{1}$ in atomic ratio) is investigated in this work, using self-consistent periodic slab calculations based on density functional theory. This research reveals that ethanol does not have an unique mode of adsorption on this catalytic surface, as well as the dehydrogenation pathway does not only proceed via the ethoxy species formation, but also via the 2-hydroxyethyl species formation. Additionally it is showed that acetaldehyde desorbs in the process of dehydrogenation of ethanol. These results allow to understand in detail the first steps of the ethanol oxidation on a specific catalytic surface, which constitutes a contribution to clarify the problem of selectivity in catalysts for DEFCs.

**Keywords:** Ethanol oxidation, platinum-tin catalyst, adsorption, reaction mechanism, fuel cells, density functional theory.
RESUMEN

El desarrollo de celdas de combustible alimentadas con etanol (DEFCs) es importante para obtener convertidores alternativos de energía. Teniendo en cuenta este objetivo, un tema fundamental para el desarrollo de estos dispositivos es el mecanismo de reacción de etanol (EtOH) en el ánodo de las DEFCs. Varios grupos han investigado este proceso, pero todavía hay dificultades para comprender totalmente el mecanismo de reacción de EtOH. Esto se debe a la dificultad en la experimentación para identificar los intermediarios y los caminos de reacción y también porque la investigación teórica de estos sistemas está apenas en auge.

Lo anterior justifica la investigación tanto experimental como teórica para entender completamente el proceso de reacción de EtOH en las DEFCs. Actualmente las superficies catalíticas más estudiadas para este propósito son: Pt-Ru, Pt-Sn y Pt-Ru-Sn, entre las tradicionales, y también algunas en desarrollo que incluyen níquel como: Pt-Ru-Ni y Pt-Sn-Ni. Los métodos de investigación experimentales no han podido determinar los caminos e intermediarios del mecanismo de reacción de EtOH sobre estas superficies catalíticas, por lo que a la fecha no hay explicaciones completamente satisfactorias de las etapas de adsorción y descomposición de EtOH. La investigación teórica puede contribuir en la elucidación de este complejo mecanismo de reacción, por lo que en este trabajo se lleva a cabo el estudio de las etapas iniciales del mecanismo de reacción de EtOH en una superficie catalítica platino (Pt) – estaño (Sn).

Específicamente en este trabajo se calcula la superficie de energía potencial (PES) de las etapas de adsorción y deshidrogenación de etanol en una superficie catalítica Pt$_3$Sn$_1$ en relación atómica, usando cálculos de campo autoconsistente con la teoría de funcionales de la densidad (DFT) sobre superficies ideales. La investigación muestra que el EtOH no tiene un único modo de adsorción sobre la superficie catalítica, asimismo muestra que los caminos de descomposición de esta molécula, no sólo se dan a través de la formación de especies etoxi, sino también se descompone mediante la formación de 2-hidroxietil. Además se muestra que se forma acetaldehído en la descomposición de EtOH, el cual se desorbe de la superficie. Estos resultados permiten comprender detalladamente las primeras etapas de la oxidación de EtOH en una superficie catalítica específica, lo cual es una contribución al entendimiento del problema de selectividad en catalizadores para DEFCs.

**Palabras Clave:** Oxidación de etanol, catalizador platino-estaño, adsorción, mecanismo de reacción, celdas de combustible, teoría de funcionales de la densidad (DFT).
Acknowledgements

I wish to express my gratitude to Professor Bibian Hoyos, who supported this work with his advice and guidelines as friend and professor. Likewise I am very grateful with Professor Farid Chejne, who accompanied my Ph.D. giving me encouragement. Both of them of the Universidad Nacional de Colombia – Sede Medellín.

It was very important for me and for the development of this work, the time that I shared in Germany in the University Duisburg-Essen with Professor Eckhard Spohr and with his group of Theoretical Chemistry. That period of time encouraged my knowledge and understanding of Density Functional Theory and the Heterogeneous Catalysis. Thanks to Eckhard, Mehmet, Daniel, Gabriel and Hendrik for the support and the good times.

Finally I wish to express my sincere thanks to the Universidad Nacional de Colombia – Sede Medellín, specifically to the Programa de Becas de Estudiantes Sobresalientes de Posgrado (PBESP) for the financial support to carry out my studies. Also I wish to express my sincere thanks to the German Academic Exchange Service (Deutscher Akademischer Austausch Dienst – DAAD) for the financial support to stay in Germany, developing a primordial part of my doctoral work.
INTRODUCTION

The selective conversion of oxygenated hydrocarbons is important for several chemical processes as the production of propylene glycol from lactic acid, oxidation of alcohols in fuel cells, hydrogen production. Particularly searching for alternative energy converters, the selective conversion of oxygenated hydrocarbons is the great interest for the development of the Direct Ethanol Fuel Cells (DEFCs). These devices are an interesting solution for the environmental pollution [1-4].

The investigation of the catalytic processes in DEFCs is mainly carried out experimentally, with different physical techniques as: X-ray photoelectron spectroscopy (XPS), differential electrochemical mass spectrometry (DEMS), Fourier-transform infrared spectroscopy (FTIRS), scanning tunneling microscope (STM), infrared reflection spectroscopy (IRS) and electrochemical thermal desorption mass spectrometry (ECTDMS), fundamentally [5-14].

According to these physical techniques, there are different reaction mechanisms proposed for the ethanol reaction on each catalytic surface. In the literature are proposed several reaction mechanisms, some of these are formulated in general way and others seek be representative of the ethanol reaction process on a several catalytic surfaces as Pt/C, PtRu/C, PtSn/C, PtRuSn/C, PtRuNi/C, PtSnNi/C [5, 8, 9, 15].

In general, in the proposed reaction mechanisms in the literature is difficult to identify all the intermediates and the reaction paths involved in the complex process of the ethanol reaction on a catalytic surface [5, 16, 17]. The principal steps identified in different investigations are: the ethanol adsorption, the alcohol decomposition, carbon monoxide (CO) adsorption (catalyst poisoning), the complete oxidation of the CO toward CO₂ and the formation of different intermediates (acetaldehyde, acetic acid, water and others) [3, 5-8].

Each of these steps are influenced by several factors, among them the catalytic surface composition and the different metals alloyed in the catalytic surface according to the synthesis method are maybe the most important ones [11, 18, 19]. Likewise the most studied catalysts as anodes for DEFCs are the Pt-Ru and Pt-Sn mixtures [5, 19, 20] with a better performance of the catalytic mixtures that contain tin [12, 18].

It is found to date that Pt-Sn mixtures are a better catalysts than Pt-Ru mixtures due to the modification of the electronic structure of the platinum by the presence of tin, which causes the formation of different species and the interaction of these with the catalyst in the ethanol reaction process toward the formation of CO₂ [9, 11, 19-22]. This electronic
modification of the catalytic surface and of the ethanol molecule is the central research problem of this work, which proposes to explore it through a theoretical investigation with the utilization of the density functional theory (DFT).

In this sense, the general objective in this research is to carry out the simulation of the adsorption and dehydrogenation steps in the ethanol reaction mechanism on a Pt-Sn catalytic surface with DFT. Consequently the specific objectives of this work are:

• To simulate the adsorption step of the ethanol reaction on an ideal Pt-Sn slab, identifying the corresponding adsorption energies.

• To simulate the dehydrogenation of the ethanol molecule on an ideal Pt-Sn slab, identifying the corresponding activation energies with the nudged elastic band method (NEB).

• To propose the most probable stable intermediates in the ethanol adsorption and dehydrogenation steps on an ideal Pt-Sn slab.

• To propose the most probable reaction paths in the ethanol dehydrogenation on an ideal Pt-Sn slab.

These specific points are developed in this work, devoting the first chapter to a detailed exposition of the research problem, showing the main difficulties in the elucidation of the ethanol reaction mechanisms, both experimentally and theoretically. After this chapter, there is a review of the most relevant concepts and techniques, which were employed in this work and in the simulation of the processes of adsorption and dehydrogenation of ethanol.

The third chapter is concerned with the discussion of the results obtained for the adsorption and dehydrogenation steps of ethanol on a Pt-Sn catalytic surface. Consequently this chapter deal with the simulation of the catalyst, the adsorption step of ethanol on the surface, also the dehydrogenation of this compound and the calculation of the reaction barriers, from which a detailed potential energy surface (PES) of this process is proposed.

Finally, the last part of this text summarizes the main found insights in the development of this study of the adsorption and dehydrogenation steps of ethanol on a Pt-Sn catalytic surface using DFT, as a first step to obtain a research method to establish better trends in the design of selective catalysts toward the complete electrooxidation of ethanol for polymeric fuel cells.
1. RESEARCH PROBLEM

There are different proposals that attempt to explain the reaction mechanism of ethanol on a Pt-Sn surface, but these explanations are not entirely satisfactory as it is showed below. There are two kinds of proposals: the empirical works and the theoretical works. To date the most of works about ethanol decomposition on catalytic surfaces are empirical and specifically the Figure 1 depicts one of the most complete empirical proposals for the reaction mechanism of ethanol on a Pt-Sn catalyst developed.

![Figure 1. Experimental reaction mechanism of ethanol decomposition on a Pt-Sn catalyst proposed by Simoes et al., 2007 [8].](image)

In the Figure 1 the process of ethanol reaction on a Pt-Sn surface begins with the assumption that ethanol molecule adsorbed on the surface, but how do this process occur on the surface? From the ethanol adsorption, through different decomposition steps of the molecule, there are different possibilities (reaction paths) to reach the complete decomposition of ethanol into carbon dioxide (CO$_2$). The problem is in practice that this complete decomposition of ethanol is not reached and several intermediates are produced: 1-hydroxyethyl (Step 1), hydroxyethylene (Step 7), acetaldehyde (Step 2), acetic acid through the addition of an external hydroxyl group (Step 5) and so on. Nevertheless, does this ethanol decomposition really occur in this way? Are these initial steps of adsorption and dehydrogenation of ethanol completely described? It is important to see more in detail the information that proceeds from these empirical proposals.
According to this, the most important characteristics of the empirical works are discussed on the basis of the Figure 1:

• As it is reported from experimental works [5], the reaction mechanism for the ethanol oxidation is not the same on each catalytic surface because of the different synthesis procedures of the catalysts, catalytic surface composition, different metallic mixtures for the catalytic alloys and the voltage present at the anode. This indicates that it is complicated to establish with all these changing factors, the intermediates and reaction paths of this problem of heterogeneous catalysis via experimentation. Additionally, in the literature was reported that the physical and chemical techniques employed in the experimentation are unable to determine completely this process [8, 11, 23].

• Furthermore in the mechanism of the Figure 1, it was proposed that there is hydrocarboxylic (COOH) species formation, but the problem with this proposal is that in the literature was reported that these species were not found in all analysis carried out with FTIRS, these species only were detected predominantly with SEIRAS [24].

• Similarly in this reaction mechanism, the acetyl species (CH$_3$CO) are presented as a stable intermediate in the reaction paths for ethanol dehydrogenation, nevertheless in other investigations these are considered as a metastable compound [25].

• Likewise a fundamental point in the ethanol reaction mechanism is to achieve the complete oxidation to CO$_2$, which depends of the initial steps of the ethanol reaction, and not only of the final C-C bond splitting as it is demonstrated in a recent experimental work [11], due to the first steps establish the stable compounds and the possible reaction paths. Taking into account this fact, the central point of research in this work is to describe and analyze the initial dissociative adsorption of the ethanol molecule on the catalytic surface.

• From the experimental work is proposed that there are difficulties with the use of experimental techniques in the whole identification and understanding of the ethanol reaction process because of the screening of the platinum over another metals and compounds, which affects their identification [27]. In the same way it is very difficult to distinguish by spectroscopic techniques between acetic acid and acetaldehyde [6, 11].

• Furthermore this anodic process has a low reaction rate compared with the reduction reaction in the cathode in a DEFC [3, 8, 11]. This is a fundamental reason to try to understand what are the possible causes of this behavior.
These points show the difficulty of the whole identification and understanding of the ethanol reaction process due to: the complexity to identify the intermediates [5, 8, 11], the different and possible reaction paths and also by the physical limit of detection of the physical and chemical techniques to investigate this problem [3, 5-8, 11, 26]. Currently it is established that the different spectroscopy and spectrometry techniques can not completely elucidate the ethanol reaction mechanism [11, 28]. These experimental conditions are complex and demonstrate the requirement to accomplish the investigation of the ethanol reaction on a metallic surface with theoretical studies.

The DFT is an adequate theory that allows to deal with such complex systems accurately to establish their electronic structures, bonding energies and reaction paths for catalytic processes as the ethanol reaction on a Pt-Sn surface [29-37]. Thus, the key interest of this work is to study the intermediates formation and the reaction paths in the initial steps of this catalytic process for the anodic catalyst in the DEFCs. In this sense, this work aims to analyze the possibilities for improving the DEFCs with the design of selective catalysts for the complete oxidation of ethanol, which avoid the formation of adverse compounds for DEFCs performance (acetic acid, acetaldehyde and carbon monoxide) [6, 8, 11, 27, 38, 39].

With this empirical context, it is important to discuss the theoretical works reported to date for this process. It is remarkable to mention that there are not many works about this topic, actually there is only one work [1] to date with a similar system compared with the system under investigation in this work. Among the main aspects of this reported work is relevant to mention that it is carried out with differences in the calculation method. The most important differences are the number of layers considered to describe the catalyst and the way to describe the energies of the system through the functional used in the theoretical method of calculation.

Likewise, the most important aspects from the chemical point of view presented in the reported work [1] are:

- The inclusion of tin (Sn) may decrease the size of the surface Pt ensembles and consequently the hydrocarbon species may adsorb more weakly on Pt-Sn catalysts.

- It is proposed that ethanol proceeds through ethoxy and 1-hydroxyethyl intermediates via parallel pathways considering their transition state energies (56 and 68 kJ/mol relative to ethanol gas phase and clean slab respectively). But the effects of the addition of Sn in the catalyst affect the adsorption energies, leading to changes in the nature of the reaction pathway for the initial dehydrogenation, such that the ethanol dehydrogenation takes place primordially through ethoxy species on Pt$_3$Sn$_1$. 


Other important detail exposed in the reported work is that the experimental results show that the rates of hydrogenation and dehydrogenation reactions between ethanol and acetaldehyde are faster on PtSn-based catalysts than on a pure Pt catalyst. This fact is explained in other reported works by the presence of tin, as it was mentioned previously in the analysis of the experimental works.

The description of this system is still in development and it is very important for the improvement of the DEFCs. In consequence is primordial to complement this information, reason why is fundamental to ask what else is possible to say of the adsorption and dehydrogenation steps of ethanol on this surface? What other details is possible to find about this process? And of course, how these steps are different of the proposed in the reaction mechanisms of ethanol on pure platinum (Pt)?

Considering this last question, it is relevant in this section to say some words about the adsorption and dehydrogenation steps of ethanol on pure Pt. The most important and recent works [40, 41] consider that the ethanol oxidation is dominated by one-step concerted dehydrogenation pathway to produce acetaldehyde, in consequence the major product of the electrooxidation of ethanol on pure Pt is acetaldehyde. This is important because experimental studies revealed that DEFCs with Pt-based electrodes are inefficient, because ethanol is partially oxidized to acetaldehyde, though at small coverages it is found that the adsorbed acetaldehyde can completely decompose without any desorption. From these results is primordial to ask what happens with the formation of acetaldehyde on a Pt-Sn based catalyst? How much does the production of acetaldehyde change on a Pt-Sn catalyst with respect to a pure Pt catalyst?

Other relevant detail exposed in the works that propose the ethanol reaction mechanism on pure Pt [40, 41] is that the selectivity of the catalyst is not sensitive to the electrical potential. If this is right, the logical conclusion is that the calculations without the simulation of the electrode potential are a good approximation for the description of the adsorption and dehydrogenation process of ethanol on a catalytic surface, as it was made in the present work. If this assumption is not right simply this work would be the first step to include in future works the simulation of the electrode potential and other aspects of the decomposition of ethanol, which were not taking into account in this work as it is described in the next chapter.

These aspects of the ethanol decomposition on a pure Pt catalyst lead to two additional questions related with the present work: i) how are ethoxy, 1-hydroxyethyl, 2-hydroxyethyl and acetaldehyde produced on a Pt-Sn catalyst? and ii) what reaction paths from the direct dehydrogenation of ethanol on Pt-Sn are more favorable toward a complete oxidation of
ethanol? These aspects and questions are analyzed and evaluated in this work, using a theoretical approach described in the following chapter.
2. THEORETICAL METHOD

2.1. Density Functional Theory: Background

Taking into account the objectives of this work, methods as molecular dynamics (MD) or Monte Carlo methods (MC) are not suitable to carry out the description of this system because of the difficulty to extend these methods for different catalytic systems, due to the adjustment of the potentials. Likewise it is necessary in this work to calculate the adsorption energy and the activation energy fundamentally, and these quantities are dependent of the electron interactions, hence, the quantum mechanics is the most properly and accurate theory to study these phenomena, which is not easy to describe with the classical physics and chemistry [42]. About this, among the different quantum mechanical methods, namely, semi-empirical methods and ab initio (from first principles) methods, DFT has been probed to describe problems similar to the ethanol oxidation on a Pt-Sn surface, achieving results with high accuracy in solid state physics and in quantum chemistry [43-46]. In connection with this work, DFT has been probed to study the chemical and electrochemical reaction mechanisms, generally providing high accuracy for these kind of problems [47].

Specifically, in the study of the adsorption and dehydrogenation steps of ethanol on a Pt-Sn surface, the specific adsorption (chemical bonding) on the surface plays a primordial role, as well as the cleavage of bonds, processes that depend of the density of electronic states, which are very well described by DFT [4, 16, 24, 42, 48-50]. In this sense, it is really important to show several characteristics of DFT, which allow to demonstrate why DFT is the most appropriate theoretical method to study and describe the initial steps of ethanol decomposition on a Pt-Sn surface.

In first term DFT is a theory oriented to the description of the molecular orbitals (MOs), it means that within the framework of DFT, the atomic orbitals (AOs) could interact to form the MO. This description of the MO originates the concept of hybridization, which is a concept to describe the chemical bonding and its cleavage through the lineal combination of the AO vectors. This characteristic is not exclusive of the DFT, in general it comes from the ab initio methods.

Another important characteristics are deduced from the formulation of the DFT, whose proposal is that the Kohn-Sham equations are equivalent to the Schrödinger equation, with the physical difference that the primordial quantity is the electron density distribution $\rho(r)$, a real quantity, instead of the wave function, which does not have a direct physical interpretation [32, 42, 45, 46, 48]. These characteristics and others are commented from the
central equation:

\[ \hat{H} \Psi(x) = E \Psi \]  

(1)

This mathematical expression is the so well known Schrödinger equation, which is the primordial basis to deal the problems of electronic structure. This equation is wrote for the many electron wave function \( \Psi \). The symbol \( \hat{H} \) is the hamiltonian operator corresponding to the total energy of the system:

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_i Z_i \frac{e^2}{|R_i - r_i|} \]  

(2)

This form of the hamiltonian operator involves the Born-Oppenheimer approximation (BOA), in which the nuclei are considered fixed in the space, so the expression (2) depends only parametrically of the positions of the nuclei. The consequence of this approximation is that the kinetic energy of the nuclei is zero and the potential energy due to nucleus-nucleus repulsion is merely a constant. The BOA postulates are also valid to DFT [32, 42, 45, 46].

Nevertheless, the equations (1) and (2) involve two problems to be solved in the framework of the traditional wave function methods: the first one is the difficulty to find the mathematical form of the wave function that describes exactly each electron and consequently the total multiparticle wave function, which has a dependence of 4N variables: 3 spatial coordinates and one spin coordinate, where N is the number of electrons. The second one is the number of resulting equations in these wave function based methods, problem called by Kohn as the problem of the exponential wall [42], where for systems with 10 atoms or more with N-electron wave functions, the simultaneous solution of the multiparticle wave function is very demanding in computational time for each system.

In contrast to this problem, DFT can handle the order of \( 10^2 \)-\( 10^3 \) atoms. DFT allows to handle this number of atoms because of the utilization of the electron density distribution defined by:

\[ \rho(r) = \sum_i^N |\phi_i(r)|^2 \]  

(3)

Where the \( \phi_i \) functions are a basis set of functions to describe the spatial orbitals. This concept was introduced in the Thomas-Fermi theory (1920) and it facilitates the description
of quantities as the total energies for atoms [42, 51]. In principle, this is because of the theoretically complete and exact description of the electron structure using this concept, as it is demonstrated by Hohenberg and Kohn in the formulation of density functional theory [42, 46, 52, 53]. The electron density (distribution), a pure number, allows to reduce the difficult problem called the exponential wall to handle 4N-dimensional wave functions (N is the number of electrons), into a problem of only 3-dimensional density function.

Inside this framework, the DFT is an approximation with the electron density as the fundamental variable. Using the concept of electron density distribution, DFT allows the calculation of the total energy of a system and its geometries with high accuracy (chemical accuracy) because the Kohn-Sham equations consider all possible contributions to the total energy of the system, even the unknown contributions, reason why the BOA do not restricts these calculations.

Inside the Kohn-Sham formulation of DFT, there are two important parts [52, 53]. The first part is known as the first theorem of Hohenberg and Kohn (HK). This theorem shows that for a system of interacting electrons under the influence of an external potential, the ground state density ($\rho_0$) of the system determines this potential uniquely [42, 46, 51]. It is deduced from this lemma a corollary, which is that if the electron density determines the potential for a determined number of electrons, then the electron density determines the complete $\hat{H}$ for the system of the interacting electrons and consequently all the properties derivable of this $\hat{H}$ at the ground state [42, 46, 51]. For any property $O_0$ derivable of the $\hat{H}$ in a system:

$$\rho_0(x,y,z) \rightarrow O_0$$

(4)

This expression means that any ground state property (observable) $O$ can be calculated, if the ground state density is determined, in other words, any ground state property of a molecule, for instance the energy of the ground state, is a functional $F$ (a rule that assigns a number to a function) of the ground state-electron density. It is important to note at this point, that this first theorem does not explain how to find the functional $F$ such that:

$$F[\rho_0]=O_0$$

This would be for any property. Applying this equation specifically to the total energy:

$$E[\rho_0]=E_0$$

(5)

The second part of the work of Hohenberg and Kohn takes into account the variational principle, originally proposed by Rayleigh and Ritz (Rayleigh-Ritz minimal principle). This
second theorem demonstrates using the total energy of the system as reference quantity, that any trial electron density \( \rho_t \) will produce a corresponding energy value, higher or equal than the true value of the ground state energy \( E_0 \) produced with the true electron density \( \rho_0 \), which can be expressed with the following inequality:

\[
E_v[\rho_t] \geq E_0[\rho_0]
\]  

(6)

In this expression any electronic energy functional \( E_v \) under the influence of an external potential produced by the nuclei \( V(r) \), which depends of a trial electron density \( \rho_t \), has an energy value higher or equal than the true ground state energy \( E_0 \). From this second HK-theorem is important to consider that the true functional in the inequality (6) is unknown, but it is possible to use approximations through the minimization of approximate proposed functionals \([32, 45, 48, 51]\).

The HK-theorems delineate the way in which DFT works in practice: it is necessary to express the total energy functional for a molecule as the sum of different terms, among them only one contain the unknown functional. This sum of terms depends of the electron density, so it is also necessary to suppose initially the electron density distribution. In this way it is possible to calculate the molecular orbitals and refine the calculation through a self-consistent field method (to find the same electric field in two successive steps of iteration). To see this in detail, the Hohenberg-Kohn ground state energy functional is:

\[
E_{HK}[\rho_0] = \langle T[\rho_0] \rangle + \langle V_{Ne}[\rho_0] \rangle + \langle V_{ee}[\rho_0] \rangle
\]  

(7)

This is the total energy of molecule calculated as the sum of the functional of kinetic energy, the functional of the potential energy due to the interaction electron-nuclei and the functional of the potential energy due to the interaction between electrons. From this equation and supposing a system of non interacting electrons as reference, with the same electron density for the ground state than the real system, it is derived the following one-electron equation (Complete derivation in \([32, 45, 46]\)):

\[
\left[ -\frac{1}{2} \nabla_i^2 - \sum Z_A \frac{1}{r_{1A}} + \frac{1}{2} \rho(r_2) \right] \Psi_{i}^{KS}(\mathbf{r}) + V_{XC} \Psi_{i}^{KS}(\mathbf{r}) = \epsilon_i^{KS} \Psi_{i}^{KS}(\mathbf{r})
\]  

(8)

Where the first term inside the brackets comes from the kinetic energy of the reference system, the second is result of the interaction nucleus-electron (coulomb interaction of the system), the third comes from the classical electrostatic repulsion of the system (Hartree term), the fourth term is the exchange-correlation potential as result of the unknown part of
the functionals of the correlation kinetic energy and of the exchange-correlation potential energy for the interaction electron-electron. The values $\varepsilon^K_S$ in (8) are the Kohn-Sham energy levels, analogous to the Schrödinger equation.

These terms in (8) are multiplied by the Kohn-Sham spatial orbitals:

$$\Psi^K_S = \sum_{s=1}^{m} c_{si} \phi_s \quad i = 1, \ldots, m$$  \hspace{1cm} (9)

It is necessary in these equations to choose a basis set to expand the KS-orbitals in (9). This basis set, in the most of implementations of DFT, are plane waves, because this representation is adapted naturally to the behavior of waves and because the computational cost of implementation of this representation is lower and easier, for instance, than spherical waves [46, 54]. So the general form for the plane waves is:

$$\phi_i(r) = e^{i_k r} u_i(r)$$  \hspace{1cm} (10)

where the $k$ is a wave vector and $u_i$ is a periodic function. The plane waves represent the orbitals in the Fourier space, where it is defined a particular region of minimal representation of the system known as the irreducible Brillouin zone. In this space the k-points are the points that conforms the grid of discretization of the system. To calculate this grid of discretization, the standard method is the Monkhorst-Pack [55]. Using the Kohn-Sham orbitals calculated with the equation (9), it is possible to calculate and recalculate the electron density in the self consistent scheme of the DFT:

$$\rho = \sum_{i=1}^{2n} |\Psi^K_S(1)|^2$$  \hspace{1cm} (11)

Analyzing the equation (8), it is noted that to complete the Kohn-Sham scheme of DFT, the exchange-correlation term must be calculated, which is possible through the following expression:

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}$$  \hspace{1cm} (12)

Likewise in (12) it is primordial to choose the adequate approximation for the exchange-correlation functional ($E_{xc}$). This selection depends of the system to study. There are many approximations to quantify this term and its quantum effects, as the local density
approximation (LDA), the generalized gradient approximation (GGA), meta GGA, beyond LDA, etc. in each case considering spin polarized or not system [42, 46, 50]. Despite the formulation of these approximations, a complete understanding of the exchange-correlation energy is still in development [48]. Analogous to the mathematical form of the external potential term, in the generalized gradient approximation (GGA) it is proposed:

$$E_{xc}[\rho, |\nabla \rho|] = \int \rho(\mathbf{r}) F_{xc}(\rho, |\nabla \rho|) d\mathbf{r}$$  \hspace{1cm} (13)

Where $F_{xc}$ is any approximate function. The advantage of this approach is the improvement of the calculation of the binding energies, because of the inclusion of soft variations of the electron-density with its gradient. There are many attempts in the construction of a such kind of functionals, among the most important the functionals of Perdew-Wang (PW86 and PW91), Becke and Perdew (PW), Perdew-Burke-Ernzerhof (PBE) and Lee-Parr-Yang (LYP) [56-60]. The equations (8), (9), (11) and (12) are the main equations (K-S equations) that support DFT.

An additional approach in DFT is the approximation of the pseudo-potential. This approximation consists in the replacement of the complicated interactions of the electrons in the core region by a soft pseudo-potential (effective potential), whereas the major contribution to this pseudo-potential comes from the valence electrons, which are described with nodeless wave functions. This approach has the advantage of a lower number of plane waves to describe the electronic system [57, 61].

2.2. Nudged elastic band method

In this work is primordial to identify the stable adsorbed compounds and to identify the most likely reaction paths. In general, DFT provides the way to identify the most stable compounds directly with the total energy calculations, nevertheless to identify the most likely reaction paths and specifically the minimum energy path (MEP) is necessary to use a coupled method using DFT.

Many different methods could be useful to find the reaction paths, the minimum energy path (MEP) and the saddle points: i) conventional approach, ii) drag method or adiabatic mapping and iii) dynamic-reaction-coordinate methods. The first and second methods are very demanding computationally and they need a suitable reaction coordinate beforehand to obtain an adequate guess of the MEP, this is very difficult to achieve in practice [62-64]. On the other hand, the dynamic-reaction-coordinate methods are divided in two types: i) methods of iteratively refinement of the transition state from an initial guess using a local reaction coordinate, and ii) methods of a chain of intermediate states to approximate the
whole MEP [49, 62-64]. The first type of methods are very limited by the initial assumption of the transition state, it is very complex and difficult for different systems. For its part, the chain-of-states methods do not yield the transition state itself, only intermediate states close to the transition state, but they are robustness in terms of convergence and allow to describe more complicated reactions with several saddle points along the MEP [49, 62-64]. In this category is found the nudged elastic band method (NEB).

NEB is one of the most used methods to scan the potential energy surface (PES) searching for the transition state due to i) it converges to a MEP with a suitable number of images for the path representation, ii) it is not very demanding computationally because only requires evaluation of the interaction energy and the first derivative of the energy with respect to coordinates, iii) the NEB convergence to the MEP is decoupled from the discrete representation of the path (flexible path representation), iv) NEB is guaranteed to give a continuous path even when multiple MEPs exist, v) NEB can easily make use of parallel computers, it is inherent to the algorithm method and vi) NEB requires very little communication between the computing nodes [62].

By these characteristics, NEB method is appropriate to calculate the energy barriers in the ethanol oxidation on a Pt-Sn surface with respect to the other methods. Furthermore there are several investigations similar to this in which NEB method has been probed successfully to find the transition states in complex chemical and electrochemical systems [16, 24, 33, 34, 50]. The latter demonstrates why NEB method is a suitable technique to calculate the energy barriers in this work. In the following a concise description of this method is exposed (Figure 2).

Figure 2. Illustrative diagram of the nudged elastic band method [65].
To scan the PES searching for the transition states and the values of the energy barriers, the NEB, as it is depicted in the Figure 2, constructs a chain of images $R_i$ (possible states) along a specific reaction pathway with an initial image (initial reactant state) and a final image (final products state) [24, 62-65]. These images (intermediate states) describe a minimum energy path for a specific reaction.

In this method the initial configurations of the reaction path are generated from a linear interpolation between the initial state and the final state. This method adds an interaction between the adjacent images $R_i$, the net spring forces $F_i^\parallel$ to ensure the continuity in the reaction path (elastic band). On the path only the tangential component of the spring forces (Equation 15), parallel to the local tangents $\hat{T}_i$ at the images are regarded, neglecting the perpendicular component of this spring force, which tries to take the elastic band out of the MEP when there is a curve in the path [63, 65]. In this term of the NEB method all images are well distributed along of this minimum energy path (MEP) because of the spring force constants $k$ (Equation 15).

Likewise the NEB method also takes into account the forces due to the real potential gradient acting on the path $F_i^\perp$ (Figure 2 - Equation 16). The perpendicular component of this force leads the images toward the MEP, whereas the tangential component of this gradient force leads the images toward the reactant or product state, so this parallel component of the gradient force is neglected. This description is depicted by the equations [65]:

$$F_i^{\text{NEB}} = F_i^\parallel + F_i^\perp$$ (14)

$$F_i^\parallel = k \left(|R_{i+1} - R_i| - |R_i - R_{i-1}|\right)\hat{T}_i$$ (15)

$$F_i^\perp = -\nabla V(R_i) - (-\nabla V(R_i)\cdot\hat{T}_i)\hat{T}_i$$ (16)

Where $V$ is the potential acting on the path. The equation 16 can be interpreted as the sum of potentials of the different images in the calculation of the MEP and the equation 15, as the energy to keep adjacent the images of the MEP. The equations 14-16 are solved variationally [65], allowing to calculate the saddle points and the minimum energy path, when the convergence in the forces is reached. Finally the highest point (saddle point) along the MEP is considered as the transition state in the reaction path and the free energy barrier is determined [16, 24, 62-65].
2.3. Electron localization function

The electron localization function (ELF) is used in this work to analyze the chemical bonding. Furthermore of the determination of the chemical stability of the compounds and its possible reaction paths, it is important to understand if there is really a chemical bonding between each stable configuration of the ethanol molecule and the atoms on the surface because of the likely weak interaction between them. The electron localization function is a measure of the probability to find an electron in the spatial neighborhood of a reference electron located at an arbitrary point and with the same spin [66].

The concept of electron localization developed by Becke and Edgecombe is different to the electron density: the electron localization function shows the spatial regions where the electrons are localized, whereas the electron density function only shows how the density varies in the space, in other words, the ELF can show a clear separation between the valence and core electrons, whereas the electron density function can not show clearly all shells [67].

Thus, the graphics of ELF are representations of the regions of localization, which means, graphics of the orbital structure of molecules and solids [66]. Mathematically the ELF has higher values in the regions where an electron has a low probability to find another electron of the same spin (good localization), whereas the ELF has lower values in the regions where an electron has a high probability to find another electron of the same spin (poor localization) [66-69].

According to this, ELF is defined mathematically as a dimensionless scalar number [66-68]:

\[
ELF = \frac{1}{1 + \left( \frac{D_\sigma(X, Y, Z)}{D_\sigma_{\text{gas}}(X, Y, Z)} \right)}
\]

In this equation the ratio \( \frac{D_\sigma}{D_{\sigma_{\text{gas}}}} \) has the form [66]:

\[
\frac{D_\sigma}{D_{\sigma_{\text{gas}}}} = 0.3483 \rho_\sigma^{5/3} \left[ \sum_i |\nabla \Psi_{i\sigma}|^2 - \frac{1}{8} \frac{\text{\nabla} \rho_\sigma^2}{\rho_\sigma} \right]
\]

In these equations (17 and 18) \( D_\sigma \) is a term related with the Taylor expansion of s-spin pair probability and \( D_{\sigma_{\text{gas}}} \) is the corresponding s-spin pair probability for the electronic reference
system (a fully delocalized reference state: homogeneous electron gas), where the \( \sigma \)-spin can be \( \alpha \) or \( \beta \) spin [66-69]. \( \Psi_{\sigma} \) are the molecular orbitals (MO) and \( \rho_{\sigma} \) is the \( \sigma \)-spin electron density. In this way ELF provides a precise definition of electron localization, identifying the regions of large or small contributions to the kinetic energy term in (18).

### 2.4. General Aspects of the simulation and Limitations

In the ethanol oxidation process on a Pt-Sn surface, clearly it is necessary consider some simplifications, but it is important to note that this is the first step toward a more accurate description and modeling of this problem. In this sense, it is important to remark the primordial simplifications of this simulation using DFT:

- There was not consideration of the multi-phase boundary between noble metal catalyst, carbon support, aqueous phase and polymer electrolyte. In this work the physical model for this problem was only an ideal slab for the catalytic alloy.

- The electrode potential was not simulated, so in this work only a neutral slab was considered. This is necessary to have a “clean” (without interferences) first calculation of the initial steps of the mechanism and after that is possible to include the electrode potential.

- There was not consideration in this work of the effect of different surface defects on the catalyst, particularly one and two dimension surface defects, but a complete scanning of the Pt-Sn surface in the slab approach was carried out.

These approaches with respect to the realistic system are the first step toward the real description of the ethanol oxidation in the electrochemical environment of the fuel cells, which tries to be the basis for a realistic scenario to describe the mechanism of ethanol dehydrogenation in the electrooxidation reaction of the DEFCs.

Taking into account the above general details of the simulation, specifically in this work, the catalytic surface was considered as an ideal surface, which means an infinite slab with periodic boundary conditions (slab approach) [29, 30]. The crystal-structure geometry of this slab initially was face-centered cubic (1 1 1). This structure was selected because in the physical characterization of the platinum-tin alloys for DEFCs, several studies showed this crystal structure for Pt-Sn alloy [70-71], however this is an approximation if one consider that the fcc (1 1 1) structure corresponds to metallic platinum and that the tin oxides could have another structure or could be even amorphous.
With respect to the surface segregation effects related with the catalyst, these are very important to obtain an active catalyst [30, 57], nevertheless in this work they were not considered the inhomogeneous atom distributions close to the surface (segregation). It was only considered in this work the substitution of the platinum atoms by tin atoms in the above mentioned slab geometry with a bulk composition of \( \text{Pt}_3\text{Sn}_1 \) atomic ratio, composition selected because it allows the validation of this work, by comparison with the related papers in the literature [1], which are not numerous to date with this specific system and with the general details of this process reported from experimental research and discussed in the previous chapter [2, 6-11, 18].

Likewise, the point defects of the catalyst were not considered in this work, however it could be treated in the future for a Pt-Sn slab in the following way: i) the vacancies could be treated with the removal of one or more atoms of the crystal structure and ii) the interstitials could be considered with the selection of different planes for the crystal structure.

With respect to the surface coverage, it is a requirement in this work to isolate the behaviour of a single molecule of ethanol to understand without interferences the first steps of its oxidation mechanism. In future works based on this one, it would be possible to simulate different coverage conditions with ethanol molecules or even with ethanol-water mixtures to establish the behaviour of the ethanol in aqueous phase at different conditions of coverage. The effect of the temperature was not treated in this work because of the complexity of this system and due to the requirement to work with the minimum possible number of interference parameters.

Summarising, in this work were explored only the atop, bridge and hollow sites on the Pt-Sn surface with the bulk composition 3:1 Pt:Sn in atomic ratio, using the slab approach for a low coverage of ethanol on the surface. To carry out this, all calculations were performed with the utilization of density functional theory in the Viena Ab Initio Simulation Package (VASP) implementation [72]. The generalized gradient approximation (GGA) with the functional of Perdew-Burke-Ernzerhof (PBE functional) was utilized for all calculations of total energy to manage the exchange-correlation effects.

The ionic cores were described by ultrasoft-pseudopotentials and the Kohn-Sham one-electron valence states are calculated with plane waves. The convergence criteria for this plane waves expansion was 450 eV. It was not possible to use a lower value for this cut-off because of the convergence of the total energy is achieved only from this value.

All calculations were not spin-polarized (there is not net spin polarization). The Brillouin
zone (zone of the reciprocal space in which the system is represented) is sampled with a 3 x 3 x 1 Monkhorst-Pack scheme on the basis of converged total energies. The electron-density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0$ eV) and Pulay mixing of the resulting electronic density [72].

For all simulations it was considered a unit cell with $2\sqrt{2} \times 2\sqrt{2}$ atoms of size with a bulk composition of Pt$_3$Sn$_1$, which indicates that the coverage is for all cases 1/8 of mono layer. In this unit cell the catalyst was simulated with different number of metal layers to test the convergence with respect to the size of the system: metallic slabs with three, five and seven layers of Pt$_3$Sn$_1$ - bulk atomic ratio were tested.

For this supercell geometry it was employed periodic boundary conditions. It is important to mention that in this supercell the vacuum between two successive slabs was for all systems around 15.8 Å. Only the two upper layers in each case was allowed to relax, the rest of layers were kept fixed at their optimized bulk positions because there is not change in the values of the total energies. At the beginning the surface relaxation was done with a full relaxation. All geometry optimizations were carried out with a total force tolerance of 0.01 eV/Å as break condition for the ionic relaxation loop.

The initial guess for the geometry optimization of the slabs was the same as pure Pt, namely (1 1 1) facet of the face-centered cubic metals. The adsorption of the ethanol and its intermediates was carried out only in one of the two exposed surfaces of the slab, as it is showed in the next chapter, where the initial steps of ethanol decomposition are described and analysed.
3. RESULTS

3.1. Simulation of the catalyst

The first part of this work is focused in the simulation of the catalyst with the slab approximation [29]. The first crystal constructed was a pure Pt crystal. This crystal of Pt (1 1 1) has a lattice parameter of 3.977 Å in this work, compared with 3.925 Å of the experimental value reported in the literature [73]. After that, a Pt$_3$Sn$_1$ crystal was built from the Pt (1 1 1) calculated crystal. In this structure of pure Pt are embedded the Sn atoms to reach the desired atomic ratio of Pt:Sn 3:1, according to the experimental phase diagram of the possible Pt-Sn alloys (Figure 3a) reported in the literature [73] and considering that this atomic ratio is one of the most studied experimentally.

![Figure 3. a) Experimental phase diagram of Pt-Sn alloys. Taken from: Zhou et al., 2009 [73] and b) Built crystal of Pt$_3$Sn$_1$.](image)

From this calculation it was obtained the Pt$_3$Sn$_1$ crystal (Figure 3b: Pt in gray, Sn in black) with a lattice parameter of 4.070 Å (Experimental value: 4.000Å, GGA: 4.076Å, LDA: 3.967Å) [73], which presents an expansion of the crystal lattice of 2.36% with respect to the Pt-crystal, whereas in the literature the experimental expansion of the crystal lattice is about 1.91% with respect to Pt-crystal [73]. It is important to note that the final structure of the Pt$_3$Sn$_1$ crystal is a cubic structure Pm$ar{3}$m, similar to the initial guess, which was a face-centered cubic structure. It is found that this structure is in agreement with other simulations and with the experimental structure of this alloy [73]. Additionally, these calculations demonstrate that this approximation to the problem is good enough, considering the obtained relative error of 1.75% with respect to the experimental value (This work 4.070Å vs. Experimental value [73]: 4.000Å).
After the construction of this crystal, it was checked the convergence of the total energy value of the system with respect to the cut-off of the kinetic energy (Figure 4a), which is a criteria to limit the expansion in plane waves of the system. Likewise it was checked the convergence of the total energy of the system with respect to the number of k-points (Figure 4b), the number of points in the grid of the reciprocal space to describe the system.

The Figure 4a shows that the accuracy of the calculation with respect to the cut-off is high: between 450 and 850 eV, there is only a change of 0.007 eV in the calculated value of the total energy for the Pt$_3$Sn$_1$ crystal. Likewise the Figure 4b shows the consistency in the calculation of the total energy for the Pt$_3$Sn$_1$ crystal with different number of k-points. The Figure 4b shows that the lower limit to work with this system is 15 k-points, which involves a maximum change of 0.2 eV. From these convergence curves, it was chose a 550 cut-off and a 3x3x3 k-points scheme to work initially in the simulation of the Pt$_3$Sn$_1$ crystal. A higher number of k-points increases dramatically the computing time and there is not an appreciable difference in the total energy values.

![Figure 4. a) Convergence curve of the cut-off and b) Convergence curve of the k-points number.](image)

After the selection of the initial cut-off and the initial k-points scheme, it was necessary to choose the planes to build the slab (a portion of solid with infinite periodicity in the $X$ and $Y$ spatial directions, but discontinuous in $Z$ to form a free surface) (Figure 5). Analyzing the cutting planes of the built crystal, there are two possibilities to construct the slab in which the adsorption and dehydrogenation steps of ethanol will be studied. The first one is the Slab 1 in the Figure 5, which has a surface composition of 3:1 Pt:Sn in atomic ratio. The second one is the Slab 2 in the Figure 5, which has a surface composition of 1:1 Pt:Sn in atomic ratio. The Pt$_3$Sn$_1$ - crystal and the resulting slabs are depicted in the Figure 5 (Pt in gray, Sn in black).
These slabs have a different configuration in the surfaces to be exposed to the ethanol molecule (plane \( XY \), Figures 5 and 6). For the \( Slab\ 1 \), the lengths of the vectors that describe the unit cell are: 8.36 Å in \( X \)-direction, 7.77 Å in \( Y \)-direction and 24.36 Å in \( Z \)-direction. Whereas for the \( Slab\ 2 \) the lengths of the vectors are: 8.36 Å in \( X \)-direction, 8.36 Å \( Y \)-direction and 24.36 Å \( Z \)-direction. These length vectors of the unit cell determine that the \( Slab\ 1 \) is asymmetric (8.36Å x 7.77Å) with respect to the plane \( XY \) and the \( Slab\ 2 \) is symmetric (8.36Å x 8.36) with respect to the same plane (Figure 6). The free space in the slabs was found by convergence.
From Figure 6 - Plane XZ, it is important to note that the layers of each slab have a different arrangement in the Z-direction. For the Slab 1 in Z direction there are two atoms of Sn per layer and it causes a configuration A-B-A-B-A in Z direction, due to these two atoms of Sn in the plane XY are in alternative positions between one layer and the next one (Figure 6). For the Slab 2 there are four atoms of Sn in the plane XY and it causes an arrangement C-D-E-D-C for the layers in the plane XZ (Figure 6), where C is a layer with four atoms of Sn, D is a layer which only contains Pt atoms and E is a layer with four Sn atom but in a different position in the plane XY with respect to the layer C (Figure 6).

Taking into account these two slab geometries, the convergence curve of the total energy of the system with respect to the free space between two contiguous slabs is calculated both for the Slab 1, as for the Slab 2. This free space between two contiguous slabs for each system (Slab 1 and Slab 2) allows to prevent the interaction between the upper and lower surfaces in each system (Figure 7).

![Figure 7. Complete view of the slab geometry for the Slab 1.](image)

![Figure 8. Vacuum convergence test for the Slab 1 and the Slab 2.](image)
The Figure 8 depicts the convergence of the total energy of each system with respect to the free space in each slab. It shows that it is necessary to consider a region of vacuum between two successive slabs of 15.8Å for the Slab 1 and 16.5Å for the Slab 2 to avoid the interaction between the exposed surfaces in each slab. These values of the free space were established because of the variation in the total energy is about 0.003 eV, when the free space is around of 16Å or more. In this way the geometries of the two slabs were obtained to carry out on each of them the adsorption of ethanol that is showed in the next section.

3.2. Adsorption of ethanol on the Pt$_3$Sn$_1$ slabs

In order to investigate the ethanol adsorption, different configurations of the molecule were tested (Figure 9), as well as different sites of adsorption were explored on the Slabs 1 and 2 (Figure 10). The following color code was used for the identification of the atoms in this text: The carbons, C$_\alpha$ of the methyl group and C$_\beta$ bonded to the hydroxyl group of the molecule, are in yellow. The oxygen is depicted in red. Whereas the different hydrogen atoms are in light blue. As it was stated in the previous section the Pt-atoms are in gray and the Sn-atoms are in black.

![Figure 9. Configurations of the ethanol molecule: a) Methyl group up, b) Molecule parallel to the surface and c) Methyl group down.](image)

The configurations of the EtOH molecule depicted in the Figure 9 were tested to find the configuration of the best fitting on the surface for the adsorption, comparing their total energies. Three different configurations of the EtOH molecule were tested: i) one perpendicular configuration of EtOH pointing to the surface with the hydroxyl group (Figure 9a), ii) one parallel configuration of the EtOH with respect to the surface (Figure 24).
9b) and iii) one perpendicular configuration of EtOH with the methyl group pointing to the surface (Figure 9c). These configurations of EtOH were tested in the region of the surface in which there are Pt atoms and Sn atoms, trying to identify some trend of adsorption on the surface.

As result of the exploration of these ethanol configurations, it was observed that the ethanol molecule always takes a configuration combined between the configurations of the Figure 9a and the Figure 9b. This configuration of ethanol is oriented toward the Sn atom on the surface through the oxygen of the molecule, and also is oriented toward the Pt atom/s through the hydrogens of the molecule. On the other hand, the configuration of the Figure 9c always rotates to take the combined configuration between the configurations of the Figure 9a and the Figure 9b, which is due to the chemical stability of the methyl group, as it is showed in the data of the adsorption and dehydrogenation steps of this work.

Using the combined configuration of ethanol described previously, the catalytic surface was explored as it is depicted in the Figure 10. As we shall see next in this text, the exploration of these different points of adsorption on each surface reveals the trends of adsorption of the ethanol molecule, called adsorption modes of ethanol in this text. These modes of adsorption were called A, B, C, D and E depending of the geometry of the ethanol molecule and the adsorption point on the surface, as it is specified later in this text. For now, it is important to describe the explored adsorption points on each slab.

In the Slab 1 the explored sites on the surface were: the atop site of Sn (t1), the atop site of Pt (t2), the bridge site between Pt and Sn (b1), the bridge site between Pt and Pt (b2) and the hollow site (h1). For the Slab 2 the explored points were t1, t2, b1 and h1 as it is depicted in the Figure 10. These points were selected to scan the most of possibilities of adsorption on each surface.

![Figure 10. Explored points of adsorption for a) Slab 1 – Plane XY and b) Slab 2 – Plane XY. (Notation: t1: Sn atop site, t2: Pt atop site, b1: Pt-Sn bridge site, b2: Pt-Pt bridge site, h1: hollow site)](image-url)
In addition to the exploration of the three commented configurations of the ethanol molecule and the adsorption sites of the two surfaces depicted in the Figure 10, three different number of layers in the catalytic slab (3, 5 and 7 layers) were employed to simulate the catalyst in $Z$ direction. This was made to prove the consistency of the calculated adsorption energy on each point of adsorption with respect to the variation of the number of layers in the slab. The adsorption energy in this work is defined from the calculated total energies as it is showed in this expression:

$$E_{ads} = E_{sys} - E_{slab} - E_{EtOH}$$ (19)

Where $E_{ads}$ is the adsorption energy, $E_{slab}$ is the total energy of the single slab and $E_{EtOH}$ is the total energy of the isolated ethanol molecule. This expression shows the energy consumed in the process of adsorption as it is used in the literature [1, 3, 41, 73-75]. On the basis of this equation, all adsorption energies were calculated with respect to EtOH gas phase and clean slab.

Once the adsorption was reached on each adsorption point, the geometries and their corresponding values of adsorption energies were established to compare the differences of the potential energy surface for the adsorption of ethanol on the two surfaces of the Slab 1 and of the Slab 2. Thus in first place, a general comparison of the adsorption energies of ethanol between these two surfaces with different surface composition was made, including the adsorption energies for a different number of layers for each catalytic slab (Figure 11).

The results of the simulation of the adsorption of ethanol demonstrate for both of these two slabs (Slab 1 and Slab 2), that depending on the system, there is a number of layers minimum after which converges the adsorption energy. This is a routine calculation for this
kind of simulations, but the interesting part is that for these two investigated Pt-Sn surfaces, the convergence in the adsorption energy is reached with more than only three layers depending on the surface composition. So in the Slab 1 it is necessary to work with 5 or more layers (Figure 11a), whereas in the Slab 2, only with 7 layers or even more is possible to reach consistency in the calculation of the adsorption energy, as it seems to indicate the Figure 11b.

The changes in the adsorption PES in the Slab 1 between the system with 3 layers, and the systems with 5 and 7 layers obeys to the strong reconstruction of the surface (strong loss of geometry for the slab) when a slab of only three layers is used, whereas for 5 or more layers, this kind of strong reconstruction was not observed. In fact, the atoms of the slab with 5 or 7 layers only have a maximum displacement in any direction between 0.01 and 0.03 Å. In consequence the adsorption energy of the systems with five and seven layers for this slab are very similar, which confirms the convergence of the adsorption energy with respect to the number of layers of catalyst from 5 layers and not from just three.

The situation is different for the Slab 2, where the E_{ads} has a good agreement between the slabs with 3 and 5 layers, whereas this energy is more negative for the slab with seven layers (Figure 11b). It is clear for this slab that the description of the PES for the adsorption of EtOH is different with a slab of three or five layers, in comparison with a slab of 7 layers. In the Slab 2, the calculated adsorption PESs suggest that it is necessary to work with systems of 7 layers or even more, simulating the catalytic slab for this specific alloy and surface composition. It is important to remark that only one point of adsorption was calculated for the Slab 2 with seven layers, taking into account, as it is demonstrated with high accuracy for the Slab 1, that the convergence of the E_{ads} with respect to the number of layers in the slab is described better when the number of layers increase for this systems.

This last point establishes the selection of one of these two slabs to continue with the second part of this work, that is the dehydrogenation of the ethanol. From the Figure 11 was demonstrated the fact that in the Slab 1 an accurate representation of the adsorption PES is reached from 5 catalytic layers and more, whereas for the Slab 2, an accurate representation of the adsorption PES seems to be obtained with 7 layer or more. In consequence, from the analysis of the Figure 11, it is showed that an accurate description of the adsorption and subsequent steps of ethanol dehydrogenation in the Slab 2 would require calculations with a simulated catalyst of 7 layers, which is very demanding computationally.

Based on this, hereafter it is presented the results for the adsorption of ethanol only on the Slab 1. It is important to note that this slab has a surface composition of 3:1 Pt:Sn in atomic ratio, which is a composition easier to compare different values and trends with theoretical
and experimental works. Despite of this choice, it would be possible in a future work to continue with the analysis of the Slab 2 and with another slabs with different global compositions to establish the effect of the change of composition in the reaction mechanisms in selective catalysts.

3.2.1. Analysis of the adsorption energy of ethanol on a Pt₃Sn₁ surface: In the analysis of the adsorption of ethanol (EtOH) on a Pt₃Sn₁ surface, three different tools for the analysis were employed in this work. The first of them is the analysis of the PES for the adsorption and dehydrogenation of ethanol, the second one is the analysis of the adsorption geometries of the ethanol and its intermediates, and the third one is the analysis of the ELF to establish if there is specific adsorption of ethanol on the catalytic surface or not, because this point is very difficult to check experimentally and because there is not agreement with respect to the kind of adsorption of ethanol on the catalysts. This process is assumed in the proposals of the ethanol reaction mechanisms of the experimental works.

In first term in this section there is an analysis and discussion of the adsorption energies $E_{\text{ads}}$ of ethanol on the Pt₃Sn₁ surface in the Slab 1. This analysis was made using an arbitrary notation for each different case of adsorption, using the letters A, B, C, D and E depending of the geometry of the ethanol molecule and the points of adsorption on the catalytic surface. Using this notation, the analysis of the $E_{\text{ads}}$ shows that the process of adsorption of ethanol in this catalytic surface has a smooth PES (Figure 12). It is consequent with the experiments, in which it was seen that this adsorption is not strong [11].

![Figure 12. Potential energy surface for the adsorption of ethanol on Pt₃Sn₁.](image)

Likewise, in the literature it has reported that the adsorption energy of ethanol on a similar system with respect to this study is -29 kJ/mol [1]. This indicates that the description of the energy values of the adsorption of ethanol on Pt₃Sn₁ is accurate in this work. Also another important reference value to take into account in this work is the adsorption energy value of ethanol on a pure Pt slab, with reported values of -27 kJ/mol [1] and -17 kJ/mol [40, 41],

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both in the same order of magnitude as the adsorption values calculated in this work, which validates the calculations presented below.

Considering these details, the adsorption PES of ethanol on the catalytic surface Pt$_3$Sn$_1$ is discussed below. The analysis of the adsorption energy values of ethanol (Figure 12 and Table 1) indicates that there is a competitive adsorption among the different modes in which occur this process on the Pt$_3$Sn$_1$ surface. Each one of this modes was found through the exploration of the catalytic surface, finding 5 different modes of adsorption namely A, B, C, D and E. These modes are completely described in the next section, but at this point it is important to make some general comments about these adsorption modes, which are related to the calculated adsorption energy values.

Considering the adsorption energy values and the adsorption sites (Table 1), it is possible to affirm that the most favorable sites for the adsorption in the modes A, B, and C are close to the Sn atoms, as it occurs on the Pt-Sn bridge site and Sn modified-atop site. Also it is possible to have a considerable energy of adsorption in the mode E where ethanol adsorbs on the modified atop site of Pt, with an adsorption energy value comparable to the former modes A, B, and C. The mode of adsorption D has a lower adsorption energy value, which is associated to the fact that the distance of adsorption is 2.64Å, the most large distance of adsorption among the five different adsorption modes.

### Table 1. Energetics and geometries of the adsorption of ethanol on the Pt$_3$Sn$_1$ surface

<table>
<thead>
<tr>
<th>Ads. Modes</th>
<th>Eads (kJ/mol)</th>
<th>Ads. Site</th>
<th>BAS (bonded atom of the surface), CAS (closest atom of the surface)</th>
<th>d O-CAS (Å)</th>
<th>d C-CAS (Å)</th>
<th>d C_α-C_β (Å)</th>
<th>d C_β-O (Å)</th>
<th>d O-H (Å)</th>
<th>d C_α-H (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-31.9</td>
<td>bridge</td>
<td>Sn-Pt</td>
<td>2.52</td>
<td>3.41 (C_1)</td>
<td>1.51</td>
<td>1.46</td>
<td>0.99</td>
<td>1.10</td>
</tr>
<tr>
<td>B</td>
<td>-28.4</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.56</td>
<td>3.45 (C_2)</td>
<td>1.51</td>
<td>1.46</td>
<td>0.98</td>
<td>1.10</td>
</tr>
<tr>
<td>C</td>
<td>-27.7</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.53</td>
<td>3.44 (C_3)</td>
<td>1.51</td>
<td>1.46</td>
<td>0.98</td>
<td>1.10</td>
</tr>
<tr>
<td>D</td>
<td>-12.9</td>
<td>atop</td>
<td>Pt</td>
<td>2.64</td>
<td>3.58 (C_4)</td>
<td>1.51</td>
<td>1.46</td>
<td>0.98</td>
<td>1.10</td>
</tr>
<tr>
<td>E</td>
<td>-29.9</td>
<td>atop-mod</td>
<td>Pt</td>
<td>2.36</td>
<td>3.34 (C_5)</td>
<td>1.52</td>
<td>1.45</td>
<td>1.00</td>
<td>1.10</td>
</tr>
</tbody>
</table>

### 3.2.2. Analysis of the geometries of adsorption of ethanol on a Pt$_3$Sn$_1$ surface:

Additionally to the previous $E_{ads}$ analysis, in this section the geometries of adsorption for those energy values are described and analyzed for the adsorption of ethanol on a Pt$_3$Sn$_1$ surface (Figure 13). For the mode A of the adsorption of ethanol (EtOH), it is showed that the molecule adsorbs mainly through O on the atom of Sn and through the hydrogen of the hydroxyl group on the bridge between Pt and Sn, so that the adsorption is through of the hydroxyl group on the Pt-Sn bridge. In the mode of adsorption B the situation is similar than the mode A, but the adsorption in this case is mainly on Sn through the oxygen atom of the hydroxyl group.

In the case of the mode of adsorption C, the Figure 13 shows that the adsorption is again
between the O atom of the ethanol molecule and the Sn atom of the surface, but there is also bonding between the hydrogen of the methylene group (CH₂) in the ethanol and the Pt in the surface, likewise the hydrogen in the methyl group (CH₃) is close to another atom of the surface, so this mode of adsorption shows a geometry closer to the surface than the others in a general point of view.

In the mode D, the adsorption of the molecule changes with respect to the other modes, here the EtOH molecule adsorbs with the hydroxyl group parallel to the surface but the O atom adsorbs on an atop site of Pt, whereas H atom of this group is in the bridge between Sn and Pt. Additionally one hydrogen of the methylene group and one of the methyl group of the ethanol molecule is quite close to the Pt atoms of the surface.

The mode E shows that it is also possible that the molecule of EtOH adsorbs on a perpendicular position with respect to the surface, in this case the adsorption is mainly between the O atom of the molecule and the Pt atom of the surface.

Figure 13. Modes of adsorption of ethanol on a Pt₃Sn₁ surface (Geometries described in Table 1). (For the slab: Pt in gray, Sn in black. For the EtOH: C in yellow, O in red and H in light blue.)
The Table 1 shows the analysis of the described modes of adsorption. It is important to note
that in three modes of adsorption (A, B and C) the closest atom of the surface (CAS) is Sn,
which interacts with the O of the EtOH. For two modes of adsorption (D and E), the O
atom is closer to Pt atoms than Sn atom on the surface (Figure 13). As consequence of this
and considering the adsorption energy, the most favorable modes for the adsorption (A, B,
and C in Table 1) are close to the Sn atoms.

Also from the analysis of the Table 1, it is important to remark that the distances of
adsorption O-Sn in this work are found for values of 2.52, 2.56 and 2.53 Å for the
adsorption modes A, B and C respectively, whereas the distances of adsorption between O-
Pt have values of 2.64 and 2.36 Å on the adsorption point D and E respectively. In the
reviewed literature it is not reported the O-Sn adsorption distance, but it is reported that the
distance of adsorption for O-Pt it is 2.65 Å [40]. Once again it is clear that the calculations
of these distances show that the description of the adsorption of EtOH is correct and
accurate in this work on the basis of the reported distances for O-Pt, likewise this shows
that presumably the distances O-Sn found in this work are right and this verifies the
existence of other modes of adsorption different to the only reported mode [1, 3], which is
similar than the geometry of the mode E.

Furthermore, the previous analysis of the energy and geometries of ethanol adsorption
shows that in a general way, there are two trends of adsorption of ethanol on this surface:
the first of them in which the molecule adsorbs with the O interacting with the Sn atom on a
modified-atop site or on a bridge Sn-Pt, and the second with the O atom interacting with the
Pt atom. In both cases there is a combined effect of attraction of the O and H atoms toward
the surface, but it is important to note that Sn atoms facilitate the process of adsorption
because of the interaction with the oxygen of the molecule, maybe to form tin oxides [76,
77]. This is different as it occurs in the adsorption of ethanol on a pure Pt surface, so that it
is the importance of the addition of Sn to the catalyst in the process of adsorption.

Also the previous description of the geometries of adsorption shows that the molecule of
ethanol adsors in different positions (competitive modes) and not only in a privileged
position, that is consistent with the complex process of adsorption and subsequent complex
reaction mechanism of ethanol on an alloyed catalysts. Other relevant detail is that the $C_\beta$
(carbon of the methylene group) is closer than $C_\alpha$ (carbon of the methyl group) to the
surface (Table 1), which indicates that the methyl group is chemically more stable than the
other carbon, so the destabilization of EtOH is mainly through the $C_\beta$. It is confirmed by the
distances of the hydrogens to the $C_\alpha$ and the distances between oxygen and the binding
distance of the hydroxyl group, which suffer a slight change (Table 1).
In addition to this analysis, one question is very important considering the smooth PES found for the adsorption of ethanol on a Pt$_3$Sn$_1$ surface, this question has to do with the kind of adsorption that is achieved by the EtOH molecule on this catalyst, what is the structure of this smooth adsorption of ethanol on the Pt$_3$Sn$_1$ catalytic surface? There is an answer to this question in the next section.

3.2.3. Analysis of the electron localization function for the adsorption of ethanol: The electron localization function (ELF) allows to describe the chemical bonding as it is explained in the previous chapter. In a practical sense, in this work the main objective to make use of this tool of analysis is to show if the ethanol molecule is bonded to the catalytic surface, it means, if hybridization takes place between the molecule and the catalyst or not, or equivalently: Are there high values of electron localization in this region, where the bonding between the ethanol molecule and the atoms of the surface is formed?

To answer this question, ELF contour maps were plotted in the plane that intersects the centers of the atoms that form the bond between the ethanol molecule and the catalytic surface, considering the BAS of the Table 1 and the bonded atom of the molecule, mentioned in the previous description of the adsorption modes. Using ELF in this way, it was checked the existence of specific adsorption for each one of the five modes of adsorption (Figure 14). About this, ELF allows to establish if effectively there is a chemical bonding between the EtOH molecule and the catalyst, which is primordial to establish the advantages and disadvantages of each mode of adsorption, as well as to establish the differences between the interaction of O in the EtOH molecule with the Sn atoms of the surface, in contrast with the adsorption of ethanol on the region of the clusters of Pt of the surface.

In the Figure 14, the ELF contour maps shows that in the modes of adsorption A, B and C exist hybridization of the electronic orbitals of the EtOH molecule and of the respective bonding atom of the surface. In consequence there is specific adsorption between the molecule of ethanol and the catalytic surface. In these modes there is high localization of the electrons in the region of hybridization (high hybridization), this is evidenced in the figures because of the loss of the concentric shape of the electronic orbitals for the bonding atoms of the molecule and of the surface, and also because of the value of the ELF (blue: 0; green and orange: higher than 0.5; red: 1.0).

For the mode of adsorption D, the contour map of the ELF shows that there is not a strong hybridization of the orbitals of the molecule and the catalyst, because the electronic orbitals of the molecule and of the surface tend to keep a more concentric shape and because the color of the bonding region is green, which means a poor localization of electrons in this
region (weak hybridization). This confirms that this geometry of adsorption does not have a strong specific adsorption on the catalyst. Nevertheless it is important to note that the electronic orbitals of the oxygen of EtOH tend to localize electrons toward the Pt atom of the surface and also the structure of the electron orbitals of O is highly modified with respect to the ideal concentric shape.

Figure 14. ELF maps describing the chemical bond between EtOH and the Pt-Sn slab. (Elf values: 0 no electron localization and 1 maximum electron localization.)
For the mode of adsorption E, the hybridization is slightly stronger than in the mode D, but the hybridization is weaker than when the ethanol molecule is adsorbed on sites directly related with Sn atoms. As in the case of the adsorption mode D, in the adsorption mode E the electron orbitals of the oxygen and of the Pt atom of the surface tend to keep their concentric shape, so for both cases D and E is demonstrated that the hybridization with the surface is weaker than the hybridization obtained in the modes A, B and C.

As consequence of the previous analysis, it is found that the specific adsorption of the EtOH is stronger in terms of ELF, on the sites related more directly with Sn than in the sites where EtOH interacts more directly with Pt. This metal, namely Sn, induces a high localization of the electrons in the binding zone and a high modification of the specific electron orbitals in the modes A, B and C, modifying the orbital structure of both, the ethanol molecule and the corresponding atom(s) of the surface. On this basis, it is possible to affirm that the reason why ethanol adsorbs stronger in terms of ELF and consequently reacts stronger in a Pt-Sn surface than in a pure Pt surface is that Sn induces a pronounced change in the structure of the electronic orbitals of EtOH.

3.3. Dehydrogenation of ethanol on a Pt$_3$Sn$_1$ slab

From the results of the adsorption of ethanol, the process of dehydrogenation of this compound is simulated to describe the the most likely stable intermediates and the possible reaction pathways on a Pt$_3$Sn$_1$ catalytic surface. For each mode of adsorption, one cation of hydrogen was removed of the ethanol molecule, first of the hydroxyl group of this molecule, after of the methylene group and finally of the methyl group, as result of this, the investigated intermediates derived from ethanol were ethoxy, 1-hydroxyethyl, 2-hydroxyethyl and acetaldehyde.

3.3.1. Analysis of the relative energies of the intermediates in the dehydrogenation of ethanol on a Pt$_3$Sn$_1$: In this section the relative energies of the ethoxy, 1-hydroxyethyl, 2-hydroxyethyl and acetaldehyde were calculated. These intermediates are the result of the process of dehydrogenation of ethanol in the former five modes of adsorption. The relative energies are defined with respect to the DFT total energies of the ethanol in gas phase and clean slab, calculating on each case the total energy of the hydrogen excess on a separated slab, as it is showed in the following equation [1, 3, 40, 41, 74]:

$$E_{rel} = E_{sys} + nE_{Hremoved} - E_{EtOH} - (n+1)E_{slab}$$

In this equation $E_{rel}$ is the relative energy of the molecule of interest, $E_{sys}$ is the total energy of the whole system (Molecule + Slab), $E_{Hremoved}$ is the total energy of the removed
hydrogens, $E_{\text{EtOH}}$ is the total energy of ethanol in gas phase, $E_{\text{slab}}$ is the total energy of the clean slab and $n$ is the number of removed hydrogens from ethanol.

The relative energies of the intermediates and the adsorption energies of ethanol are depicted in the Figure 15 to determine the most stable compounds after the dehydrogenation of ethanol. This figure shows a comparison of the relative energies of ethanol (CH$_2$CH$_2$OH), ethoxy (CH$_3$CH$_2$O), 1-hydroxyethyl (CH$_3$CH$_2$OH) and 2-hydroxyethyl (CH$_2$CH$_2$OH). A lower (more negative) energy in this figure means a stronger energy of adsorption between the intermediate and the catalyst, so this figure allows to identify the most stable compounds in the dehydrogenation of ethanol. Based on this criterion, only the species with a relatively strong energy (more negative, i.e. more attractive between the molecule and the catalyst) are selected to study the possible reactions in the ethanol oxidation on the Pt$_3$Sn$_1$ catalyst.

In the calculation of the relative energies of the compounds derived of each EtOH adsorption mode in the first dehydrogenation, only was possible to calculate the dehydrogenation of the methyl group of the EtOH molecule for the mode of adsorption D. This was in this way because analyzing the geometries of the EtOH adsorption, the methyl group is quite far of the catalytic surface in the modes A, B, C and E (Figure 13 and Table 1), furthermore this group is very stable chemically, as it was showed in the adsorption of EtOH. In consequence there is not possibility that any hydrogen atom of this group in EtOH is released. Because of this, the geometries of the adsorption modes A, B, C and E do not allow the dehydrogenation of the methyl group and were not calculated.

![Figure 15. Relative energies of ethanol and its intermediates.](image)
Considering the previous annotation and taking into account only the species with an energy value below zero (Figure 15), the most stable compounds derived from the dehydrogenation of ethanol are the ethoxy species obtained from the dehydrogenation of EtOH in the modes A, B and C, likewise the 1-hydroxyethyl and 2-hydroxyethyl obtained from the modes C and D respectively, and finally the acetaldehyde species obtained from the modes A and E. These points result from the attempt to calculate 1-hydroxyethyl, but this process leads to the formation of acetaldehyde. This identification of acetaldehyde as a stable compound is important in this work because it is known that acetaldehyde does not allow the complete oxidation of ethanol and it is a typical product in DEFCs, so in this work is confirmed that acetaldehyde is a product of the dehydrogenation of EtOH on the Pt₃Sn₁ catalytic surface.

Likewise, from the Figure 15 and considering the relative energies more attractive toward the adsorption of a specific compound, as well as the previous general comments, the following reactions could be possible for the step of dehydrogenation in each mode of adsorption (A, B, C, D, E):

- **A**: CH₃CH₂OH → CH₃CH₂O + H⁺ + e⁻ or CH₃CH₂OH → CH₃CHO + 2H⁺ + 2e⁻
- **B**: CH₃CH₂OH → CH₃CH₂O + H⁺ + e⁻
- **C**: CH₃CH₂OH → CH₃CH₂O + H⁺ + e⁻ or CH₃CH₂OH → CH₃CHOH + H⁺ + e⁻
- **D**: CH₃CH₂OH → CH₂CH₂OH + H⁺ + e⁻
- **E**: CH₃CH₂OH → CH₃CHO + 2H⁺ + 2e⁻

It is important to note in this possible set of reactions among the more stable compounds showed in the Figure 15, that for the mode of adsorption A there are two competitive reactions with a single and double release of hydrogen cations, which means that acetaldehyde could be a stable compound in the oxidation of ethanol after the double dehydrogenation of ethanol, but not necessarily it means that this compound remains adsorbed, contrary to this, acetaldehyde tends to desorb of the surface (Figure 16 and Table 2) as it is explained in the next section.

Also on the adsorption mode C, there are two possible competitive reactions to produce ethoxy or 1-hydroxyethyl through the release of only one hydrogen cation. Additionally to this, from the other adsorption modes, the stable intermediates which could be produced are ethoxy from the mode B, 2-hydroxyethyl from D and acetaldehyde from E.

The occurrence of these reactions for these stable compounds depends of the energy barrier associated to each reaction, because of this reason these energy barriers are investigated for each reaction and for each compound that proceed from the different EtOH adsorption modes A, B, C, D, and E, with the use of the nudged elastic band method (NEB).
Figure 16. Intermediates of the ethanol reaction mechanism on a Pt₃Sn₁ catalyst after the first dehydrogenation.
3.3.2. Analysis of the geometries of the intermediates in the dehydrogenation of ethanol on a Pt$_3$Sn$_1$ catalytic surface: In the simulation of the process of dehydrogenation of ethanol on the Pt$_3$Sn$_1$ catalytic surface, one or two hydrogen cations were released of the ethanol molecule, as it was commented in the previous section. Taking into account this, the different geometries for the stable adsorbed intermediates on the Pt$_3$Sn$_1$ catalytic surface after the dehydrogenation of ethanol are showed in the Figure 16 and in the Table 2. The geometries showed in this figure are only those with a relative energy value below zero. In this section, the geometries of these stable intermediates (ethoxy, 1-hydroxyethyl, 2-hydroxyethyl and acetaldehyde) are described and analyzed, trying to find criteria to gain more understanding of the first step of ethanol decomposition on a Pt$_3$Sn$_1$ catalytic surface.

The Figure 16 shows that ethoxy is a stable compound because it appears adsorbed in quite similar configurations as it is showed in the Figure 16-1, 16-3 and 16-4. These three modes of stable adsorption of ethoxy have similar relative energies. In the Figures 16-1 and 16-3, ethoxy is primarily adsorbed specifically through the bond O – Sn, this bond distance is 2.05 and 2.04 Å respectively. In the Figure 16-4, the only change is the orientation of the ethoxy molecule, but still the bond distance is 2.04 Å. The adsorption of ethoxy in these tree configurations has almost the same distances with respect to the catalyst and quite similar geometries, which demonstrates that ethoxy is definitely a stable intermediate in the ethanol decomposition on this surface.

In the Figure 16-2, acetaldehyde is produced after the dehydrogenation of ethanol. In this case there is a double dehydrogenation in only one step of decomposition. It means that it is possible that the dehydrogenation of ethanol does not only proceed through the release of only one hydrogen cation, but also with the release of two hydrogen cations when the CH$_2$ group (methylene group) in the ethanol molecule is affected by the Pt$_3$Sn$_1$ catalyst. After the release of these two hydrogen cations, the acetaldehyde tends to desorb, this molecule remains at a distance of 2.62 Å (Table 2).

In the Figure 16-5, it is showed 1-hydroxyethyl as a stable intermediate of the ethanol reaction mechanism. This compound remains adsorbed to the surface through the bond

### Table 2. Energetics and geometries of the intermediates of the dehydrogenation of EtOH.

<table>
<thead>
<tr>
<th>Intermediates</th>
<th>Erel (kJ/mol)</th>
<th>Ads. Mode</th>
<th>Ads. Site</th>
<th>BAS</th>
<th>d O-CAS (Å)</th>
<th>d C-CAS (Å)</th>
<th>d C - C (Å)</th>
<th>d C - O (Å)</th>
<th>d C - H (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxy (CH$_3$OH)</td>
<td>-29.9</td>
<td>A</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.05</td>
<td>3.03 (C)</td>
<td>1.52</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-29.1</td>
<td>B</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.04</td>
<td>3.04 (C)</td>
<td>1.52</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>1-Hydroxyethyl (CH$_3$CHOH)</td>
<td>-16.2</td>
<td>C</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.04</td>
<td>3.00 (C)</td>
<td>1.52</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxyethyl (CH$_2$CH$_2$OH)</td>
<td>-23.3</td>
<td>D</td>
<td>atop-mod</td>
<td>Pt</td>
<td>2.39</td>
<td>2.07 (C)</td>
<td>1.51</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde (CH$_3$CHO)</td>
<td>-19.9</td>
<td>E</td>
<td>atop</td>
<td>Pt</td>
<td>2.29</td>
<td>3.16 (C)</td>
<td>1.49</td>
<td>1.24</td>
<td></td>
</tr>
</tbody>
</table>
between the Cβ-Pt of 2.11 Å. It is important to note here that this compound remains quite close of the catalyst, for instance the O-Sn distance is 2.87 Å (Table 2). Despite this, the relative energy is not so high, which seems to indicate that on a Pt3Sn1 catalytic surface, 1-hydroxyethyl is a stable compound but the interaction with the catalyst is not strong. This is analyzed deeper in the calculation of the reaction barriers in the next section.

In the Figure 16-6, it is showed that 2-hydroxyethyl is a stable intermediate in the process of ethanol decomposition due to the orientation of the molecule is along of the catalyst, which possibly facilitates the next steps of the dehydrogenation for this intermediate. The adsorption mode of 2-hydroxyethyl is through different atoms of this molecule, the adsorption distance between the Cα and the Pt atom is 2.07 Å, likewise the distance between the O and other Pt atom is 2.39 Å in a modified atop site of adsorption.

In the Figure 16-7, acetaldehyde is showed again as a stable intermediate, but this time the configuration is completely different with respect to the desorbed acetaldehyde of the Figure 16-2 (Table 2). In this case the molecule is weakly adsorbed on the surface through the bond between O and Pt at 2.29 Å, but the compound keeps its trend to desorb, as it is observed in the calculations of the reaction barriers. This shows that acetaldehyde can be present in the decomposition of ethanol through different configurations and on different adsorption points, reason why definitely is a product of the dehydrogenation of ethanol.

In general, this analysis demonstrates that Sn atoms contribute to form two possible pathways of reaction: i) ethoxy pathway and ii) desorbed acetaldehyde pathway. But Sn is important as well as for the destabilization of the intermediates when these are adsorbed on Pt atoms, facilitating other possible reaction pathways as: iii) 1-hydroxyethyl pathway, iv) 2-hydroxyethyl pathway and v) weakly adsorbed acetaldehyde pathway. On the basis of this description and this analysis of the geometries of the adsorbed intermediates, and considering the relative energy values of adsorption of these intermediates, it is important to note that only the following reactions could be taken into account, as suggested the previous analysis:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHOH} + \text{H}^+ + \text{e}^- & \text{Ethoxy formation from A, B or C.} \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHOH} + \text{H}^+ + \text{e}^- & \text{1-Hydroxyethyl formation from C.} \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{CH}_2\text{OH} + \text{H}^+ + \text{e}^- & \text{2-Hydroxyethyl formation from D.} \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^- & \text{Acetaldehyde formation from E.}
\end{align*}
\]

The production of acetaldehyde from the ethanol adsorption mode A is neglected, considering, as it was mentioned previously, that this compound from the decomposition of ethanol in the mode A tends to desorb, as the distances of adsorption in the Table 2 suggest.
In the next section the energy barriers for these proposed reactions are calculated to complete the description and analysis of the decomposition of ethanol on a Pt$_3$Sn$_1$ catalytic surface.

3.4. Reaction barriers and transition states in the dehydrogenation of ethanol on a Pt$_3$Sn$_1$ catalytic surface

3.4.1. Analysis of the activation energy in the dehydrogenation of ethanol: As a consequence of the analysis of the relative energies of the stable intermediates from ethanol and their geometries, it is necessary to determine the energy barriers for the reactions proposed at the end of the previous section to establish the most likely reaction paths and the transition states in the dehydrogenation of ethanol on this specific surface. These energy barriers are calculated using the nudged elastic band method (NEB) to find the minimum energy path (MEP) to form a specific compound with respect to the adsorbed ethanol as reactant. In the Figure 17 are depicted the energy barrier for each one of the former possible reactions in the dehydrogenation of ethanol.

Figure 17. Comparison of energy barriers for the oxidation of ethanol on a Pt$_3$Sn$_1$ catalytic surface: EtOH – Ethoxy reaction in yellow, EtOH – 1-Hydroxyethyl reaction in light blue, EtOH – Acetaldehyde reaction in purple and EtOH – 2-Hydroxyethyl reaction in gray.

This calculation was made considering in first term, four points in the coordinate reaction and was refined up to achieve the same total energy values for each energy barrier for nine points in the reaction coordinate, after which the total energy does not change with more than nine points. Taking into account this, in the Figure 17, the reaction barrier for ethoxy (orange) has a height of 0.58 eV (55.96 kJ/mol) with respect to the corresponding adsorbed
ethanol configuration. This energy barrier has the lowest total energy value compared with the other energy barriers, so it establishes that this is the most likely reaction of dehydrogenation of ethanol to form ethoxy species and it is a promissory reaction channel to investigate its complete oxidation. This reaction path is also reported in a previous work with a similar system [1] and here it is corroborated. An interesting detail is that the value of the energy of this transition state (E_t) with respect to ethanol gas phase (Around 28.0 kJ/mol – Table 3) is lower than the reported value in the other work for a similar system (56.0 kJ/mol), so these transition states in the formation of ethoxy species have a more negative value than the reported, which means that this reaction channel is more likely than previously thought.

Table 3. Energetics and geometries of the transition states of the EtOH dehydrogenation.

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>E_a (kJ/mol)</th>
<th>E_t (kJ/mol)</th>
<th>Ads. Site</th>
<th>BAS</th>
<th>d-C-CAS (Å)</th>
<th>d-C-O (Å)</th>
<th>d-C-H (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxy (CH₃CH₂OH)</td>
<td>57.8</td>
<td>25.9</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.12</td>
<td>1.52</td>
<td>1.44</td>
</tr>
<tr>
<td>1-Hydroxyethyl (CH₂CHOH)</td>
<td>56.0</td>
<td>27.6</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.12</td>
<td>3.11</td>
<td>1.52</td>
</tr>
<tr>
<td>2-Hydroxyethyl (CH₃CHOH)</td>
<td>59.1</td>
<td>31.4</td>
<td>atop-mod</td>
<td>Sn</td>
<td>2.12</td>
<td>3.08</td>
<td>1.52</td>
</tr>
<tr>
<td>Acetaldehyde (CH₃CHO)</td>
<td>99.1</td>
<td>69.0</td>
<td>atop-mod</td>
<td>Pt</td>
<td>3.01</td>
<td>2.18</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>66.6</td>
<td>53.7</td>
<td>atop-mod</td>
<td>Pt</td>
<td>2.48</td>
<td>2.24</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>107.3</td>
<td>78.7</td>
<td>desorbed</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

The other interesting energy barrier in the dehydrogenation of ethanol is that to produce 2-hydroxyethyl, which has an activation energy of 0.69 eV (66.59 kJ/mol). Although this energy barrier is higher than the ethoxy energy barrier, it is possible the formation of this compound in the dehydrogenation of ethanol, and it is an important product inside the oxidation mechanism of ethanol on this specific surface, because its formation avoid the formation of acetaldehyde which is not a desirable compound in the oxidation of ethanol, due to it is possible that in the successive steps of dehydrogenation of this compound, the methyl group in the C_α could not be formed. It is very important to find this possible reaction channel because it is not proposed in the dehydrogenation of ethanol. It is very important to continue the investigation of this reaction channel, because it could lead to an alternative way to achieve the complete oxidation of ethanol on this specific catalytic surface. This investigation is proposed in this text as a future work.

The third energy barrier under analysis is the corresponding to the formation of 1-hydroxyethyl. This compound is the most important product of the dehydrogenation of ethanol on a pure-Pt catalytic surface [40, 41]. Here it is demonstrated that this is not the privileged product that results of the dehydrogenation of ethanol on a Pt₃Sn₁ catalytic surface. The energy of activation of this barrier is 1.03 eV (99.07 kJ/mol), which is a very high energy barrier, so that it is really difficult that this compound plays an important role in the ethanol dehydrogenation on this specific surface. The relative energy for this
transition state (Eₜ) is 69.0 kJ/mol, which is almost the same value reported in a similar work (68.0 kJ/mol) [1]. Once again, this fact validates the results presented in this work. On the other hand it is also showed in the Figure 17 the energy barrier for the formation of acetaldehyde, which is a remarkable case in this dehydrogenation of ethanol because of the release of two hydrogen cations. Although this energy barrier is calculated from a weakly stable adsorption of acetaldehyde on the surface in the ethanol dehydrogenation, its energy barrier has a quite high value (1.11 eV or equivalently 107.31 kJ/mol), because this compound tends to desorb of the surface, as it is demonstrated in the previous section.

Considering these results, it is possible to affirm that the dehydrogenation of ethanol on a Pt₃Sn₁ catalytic surface under the corresponding coverage conditions is carried out mainly through the formation of ethoxy species and with lower relevance, also through the formation of 2-hydroxyethyl.

3.4.2. Analysis of the geometries of the transition states in the dehydrogenation of ethanol: In addition to the analysis of the energy barriers for the previous established reactions, in this section is presented the analysis of the transition state geometries, with respect to this, for the transition state in the formation of ethoxy on this specific surface, the analysis shows that this compound adsorbs primarily through the O-atom on a modified-atop site of Sn (Figure 18a and Table 3). The hydrogen atom is released and goes towards the typical adsorption site for hydrogen on the bridge between Pt atoms. The distance of adsorption for this intermediate is 2.12 Å (Table 3).

The transition state to form 1-hydroxyethyl (Figure 18b) is adsorbed through the C_β of the molecule on a Pt atom, where the distance of adsorption between the C_β and the Pt atom is 2.18 Å. This Pt atom is dragged out of the surface around 0.5Å, which could be the reason for a so high energy barrier in the formation of this compound, because of the energy necessary to pull the Pt atom this distance out of the surface. This is an indicative of a possible trend of desorption of this compound and also an indicative of the formation of a point defect on the Pt₃Sn₁ catalytic surface. Nevertheless from the calculations of this work is not possible to establish if this specific point defect increases or not the catalytic activity, it would be necessary to study specifically this kind of defects separately to establish their influence in the catalytic activity, so this study is also proposed for a future work.

From this work it is found that in the formation of the weakly adsorbed acetaldehyde on the surface through the double dehydrogenation of ethanol, the transition state of this process is 1-hydroxyethyl (Figure 18c). The geometry of this transition state shows that the O remains far of the surface at a distance of 3.12 Å, whereas the hydrogen atom of the hydroxyl group is located at a distance of 2.06 Å, as well as a hydrogen atom of the methyl group that
remains at 2.51 Å, both of them on a Pt atom of the surface. Despite this, when the reaction is completed, the geometry is the described and reported in the Table 2 for weakly adsorbed acetaldehyde (Table 2 – acetaldehyde from mode E). This analysis of the geometry of this transition state indicates that although the transition state is close to the surface, the energy barrier is so high to reach this transition state, furthermore as it is described in the Section 3.3.2, the produced acetaldehyde is adsorbed weakly on the surface, reasons why this reaction is more difficult to occur on this surface than the ethoxy and 2-hydroxyethyl reactions (Table 3).

Figure 18. Geometries of the transition states for: a) Ethoxy, b) 1-Hydroxyethyl, c) Acetaldehyde and d) 2-Hydroxyethyl.

A more detailed description of the process of the production of acetaldehyde shows that ethanol in first place releases one hydrogen cation to form 1-hydroxyethyl, which is the transition state corresponding to the highest peak in the calculation of the energy barrier (Figure 17). After this, the transition state releases the second hydrogen cation to form weakly adsorbed acetaldehyde. The two lower peaks with respect to the highest peak of the transition state correspond respectively to the change of position of ethanol before the formation of the transition state and to the change of position of the formed acetaldehyde
toward the weak adsorption on the surface. So these two lower peaks are formed due to the search of a stable adsorption site and this search process has a relatively high energies that are not found in the calculation of the other barriers, which confirms that the adsorption of acetaldehyde is difficult and that finally, acetaldehyde adsorbs weakly on this specific surface. In consequence at least part of the produced acetaldehyde desorbs of the surface and goes back to the solution, whereas the other part remains weakly adsorbed on the surface.

On the other hand the geometry of the transition state for the formation of 2-hydroxyethyl in the Figure 18d shows that this compound is adsorbed on a region where there is an ensemble of Pt atoms. The adsorption is through the O atom on a modified-atop Pt-site at a distance of 2.48Å and also the $C_{\alpha}$ of the molecule is adsorbed at a distance of 2.24Å (Table 3). It is important to note that the released hydrogen cation is very close to the molecule of 2-hydroxyethyl at a distance of 1.65Å with respect to the $C_{\alpha}$ of the molecule, though when 2-hydroxyethyl is produced this hydrogen is far of the molecule, which confirms the stable adsorption of this compound on the surface. This geometry of the transition state allows different possibilities of interaction with the catalytic surface due to this position on the catalytic surface (Figure 18d), nevertheless among these possibilities of interaction, the most important is that the molecule is adsorbed through a bond between C and at the same time, the O of the molecule is close to the Sn atom (2.39Å), which could promote a complete oxidation of ethanol. This is the reason why this oxidation channel through 2-hydroxyethyl is very important in the reaction mechanism of ethanol on a $Pt_3Sn_1$ and from this work is proposed to be studied in a future work.

Summarizing, from the analysis of these geometries of the transition states is remarkable the effect caused by Sn atoms in the formation of ethoxy, 1-hydroxyethyl and acetaldehyde. These transition states are induced directly by the presence of Sn (Table 3), only in the formation of 2-hydroxyethyl the Pt atoms are most important that Sn, but still this compound is also affected by the presence of Sn as it is described previously. In the same way, though more relevant for the decomposition of ethanol is that the likely reaction paths are different of the predicted for the oxidation of ethanol on a pure Pt surface and likewise, this work shows a detailed description of the first steps of the dehydrogenation of ethanol on the $Pt_3Sn_1$ catalytic surface, which is not carried out to date and in which is found the interesting result of the formation of 2-hydroxyethyl and its subsequent intermediates, a reaction channel that could change the current understanding of the complete oxidation of ethanol on this catalytic surface due to the complete mechanism depends of these first steps of adsorption and dehydrogenation of ethanol.

As consequence of the previous descriptions and analyses, in the Figure 19 the potential
energy surface (PES) for the first steps (adsorption and dehydrogenation) of the ethanol oxidation on a Pt$_3$Sn$_1$ catalytic surface are depicted. The green line is depicted as point of reference of the behavior of the first steps of the ethanol oxidation with respect to the oxidation of the ethanol for the same steps on pure Pt. It is important to note that the energy variations in this PES of the ethoxy channel and the 2-hydroxyethyl channel are better than the oxidation channel on pure Pt, due to the two channels described in this work have a smoother PES for the first steps of oxidation than the oxidation of ethanol on pure Pt, whereas the rest of channels have a really high energy barrier. This is part of the explanation of why a bimetallic mixture Pt-Sn is a better catalyst (more selective) than pure Pt for the electrooxidation of ethanol.

Likewise, based in the previous analysis it is demonstrated from the Figure 19 that the ethanol reaction mechanism, at least in the first steps of adsorption and dehydrogenation of ethanol, on the Pt$_3$Sn$_1$ catalytic surface is different from the first steps of the ethanol reaction mechanism on a pure Pt surface, which is a well known experimental fact, but in this work this fact is described in detail from a complete theoretical approximation, finding new insights in the ethanol oxidation on this specific surface. Also this PES and the previous analysis of energetics and geometries, also demonstrate that the effect of Sn is crucial to change the PES of the adsorption and dehydrogenation steps in the ethanol reaction mechanism in this surface, altering the likely reaction paths, which are different of the proposed for pure Pt and different, considering the 2-hydroxyethyl reaction channel, of the former proposals for this first dehydrogenation of ethanol on a Pt$_3$Sn$_1$ catalytic surface.

Figure 19. PES of the adsorption and dehydrogenation of ethanol on a Pt$_3$Sn$_1$ catalytic surface. IS: CH$_3$CH$_2$OH. On pure Pt: TS:1-Hydroxyethyl, MS1: 1-Hydroxyethyl.
4. CONCLUSIONS

As a summary of the findings of this work, it is relevant to remark the following points, which are arranged in the order of the themes of this text:

- The method of calculation of physical parameters as the lattice constant is enough accurate to work this kind of problems. On the basis of these calculations, it is possible to affirm that this theory and its inherent level of calculation gives results that represent with high precision the systems calculated in this research and other to continue researching this kind of selectivity problems on catalysts.

- The preferential configuration of adsorption of the ethanol molecule is through the hydroxyl group of the molecule, it is not possible an adsorption through the methyl group of the molecule because this group is quite stable chemically.

- In this work also is demonstrated that three layers are not enough to describe properly the PES of this specific system. In the case of this $\text{Pt}_3\text{Sn}_1$ catalytic surface, the minimum necessary number of layers is five to avoid the strong reconstruction of the surface. Three layers simulating this catalyst are not enough, consequently it changes the description of the PES for the adsorption and dehydrogenation steps of the ethanol.

- Small changes in the composition of the surface, or extrapolating this result, changes in the composition of the slab originates a different PES for the oxidation mechanism.

- Through ELF is demonstrated that there is chemical bonding between ethanol and the catalyst, with an important localization of electrons in the hybridization region, which is a sign of specific adsorption. This specific adsorption is stronger in terms of localization, when EtOH is adorbed in Sn sites or on a close sites of Sn.

- The most important details of this PES for the adsorption and dehydrogenation of ethanol consist in the finding of the different modes of adsorption of ethanol. These modes of adsorption of ethanol are competitive modes of adsorption, which allows to have different possibilities of reactions, and consequently there is not a preferential mode of adsorption of ethanol.

- The dehydrogenation of ethanol not only proceed with the release of only one cation of hydrogen in each step, it could have also a double dehydrogenation, depending of the mode of adsorption from which the molecule comes.
From the results of this work it is possible to affirm that the dehydrogenation of ethanol on a Pt\textsubscript{3}Sn\textsubscript{1} catalytic surface under the corresponding coverage conditions is mainly through the formation of ethoxy species and also it is relevant the formation of 2-hydroxyethyl. Acetaldehyde has a high probability of desorption or of a weak adsorption as it is demonstrated from this study.

The analysis of the energy barriers and the geometries of the transition states demonstrates that Sn causes a remarkable effect in the formation of ethoxy, 1-hydroxyethyl, 2-hydroxyethyl and acetaldehyde, changing the potential energy surface for the adsorption and dehydrogenation of EtOH on a Pt\textsubscript{3}Sn\textsubscript{1} catalytic surface, compared with the oxidation of ethanol on a pure Pt surface.

It is possible to use this kind of simulations to predict in detail the behavior of a catalyst, allowing the identification of adsorption modes, formation of chemically stable and unstable compounds, calculating and proposing the possible reaction paths and describing whole mechanisms of reaction, crucial information to design selective catalyst, complementing the experimental information and optimizing the research process.

**Future Work**

From this work it is possible in the near future to make contributions in the design of selective catalysts for fuel cells as: i) understanding of the role of the different species under several conditions, ii) to simulate coverage effects, iii) to simulate electrode potential effects, iv) to understand the influence of aqueous environments in the design of catalysts, v) to describe in detail the different alloy effects on the ethanol electrooxidation, vi) the identification of complete reaction mechanisms, vii) the understanding of the surface composition effects over the activity and selectivity, viii) even the reaction kinetic of the systems could be studied from this work.
REFERENCES

51. Errol Lewars