THERMOCHEMICAL STUDY OF GLYCEROL DECOMPOSITION OVER Pt-X BIMETALLIC SURFACES (X=Cu, Ni, Ru)

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Dedicatoria

A Dios.

En memoria de mis padres Emérita y Francisco, que siempre me impulsaron a ser quien soy y confiaron en mí.

A mi hermana y sobrina, mi familia, que son motivación para continuar y seguir luchando por muchos logros más.

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TÍTULO: ESTUDIO TERMOQUÍMICO DE LA DESCOMPOSICIÓN DE GLICEROL SOBRE SUPERFICIES BIMETÁLICAS Pt-X (X= Cu, Ni, Ru)*

AUTOR: JOSÉ MIGUEL BERRÍO SÁNCHEZ**

PALABRAS CLAVES: Termoquímica, Descomposición, Glicerol, Superficie bimetálica, DFT.

DESCRIPCIÓN

Debido al incremento en la demanda de combustible, la producción de biodiesel trajo como consecuencia un exceso de su subproducto, el glicerol. Entre las diferentes rutas catalíticas de transformación de glicerol para obtener productos de valor agregado, pueden ser encontradas deshidratación, reformado, hidrogenólisis y oxidación, las cuales poseen al menos un paso de descomposición en el proceso. Los catalizadores más usados en reacciones de transformación de glicerol están basados en Pt, Cu, Ni, Ru, Pd y Cr, principalmente. Se seleccionó el reformado porque es una reacción representativa de la descomposición de glicerol.

Se realizó un estudio termoquímico de la descomposición de glicerol mediante herramientas computacionales usando la teoría del funcional de densidad (DFT), con el objetivo de contribuir en el diseño de catalizadores más activos y selectivos que los de platino puro. Se identificaron las estructuras y configuraciones más estables de los adsorbatos y superficies bimetálicas para el cálculo de energías de adsorción y energía libre de Gibbs. La superficie de Pt_3Ru fue encontrada como la más afín a compuestos oxigenados y deslumbra una posibilidad para mejorar las propiedades de Pt en algunas etapas del proceso de descomposición de glicerol. Fue confirmado que la superficie de Pt es considerablemente alterada en su geometría y distribución electrónica en presencia de un segundo metal de transición en la superficie, resultando en una débil o fuerte adsorción sobre la superficie de Pt. Debido a un cambio en la estructura electrónica y una redistribución de cargas en las capas más superficiales.

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*Tesis de Maestría

**Facultad de Ingenierías Fisicoquímicas. Escuela de Ingeniería Química, Maestría en Ingeniería Química, Director: PhD. Gustavo Ramírez Caballero. Codirectora: PhD. Sonia Giraldo Duarte

ABSTRACT

TITLE: TERMOCHEMICAL STUDY OF GLYCEROL DECOMPOSITION OVER Pt-x BIMETALLIC SURFACES (X= Cu, Ni, Ru)*

AUTHOR: JOSÉ MIGUEL BERRÍO SÁNCHEZ**

KEYWORDS: Thermochemistry, Decomposition, Glycerol, bimetallic surface, DFT.

DESCRIPTION

Due to increasing of fuel demand, biodiesel production resulted in an excess of its byproduct, glycerol. Between different catalytic routes of transformation of glycerol for value-added products, can be found dehydration, steam reforming, hydrogenolysis and oxidation, which involve at least one step of decomposition in the process of glycerol decomposition. The most used catalysts in transformation reactions of glycerol are based on Pt, Cu, Ni, Ru, Pd and Cr, mainly. It was chosen steam reforming because it is a representative reaction of glycerol decomposition.

A thermochemical study of glycerol decomposition was carried out by computational tools using the density functional theory (DFT), with the aim of contributing to the design of more active and selective catalysts than pure platinum catalysts. more stable structures and configurations adsorbates and bimetallic surfaces to calculate adsorption energy and Gibbs free energy were identified. Pt_3Ru surface was found is more related to oxygenates and dazzles a possibility to improve the properties of Pt in some stages of glycerol decomposition process, where they are. It was confirmed that the surface of Pt is significantly altered in their geometry and electron distribution in presence of a second transition metal on the surface, resulting in a weak or strong adsorption on the surface of Pt. Due to a change in the electronic structure and a redistribution of charges on the surface.

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INTRODUCTION

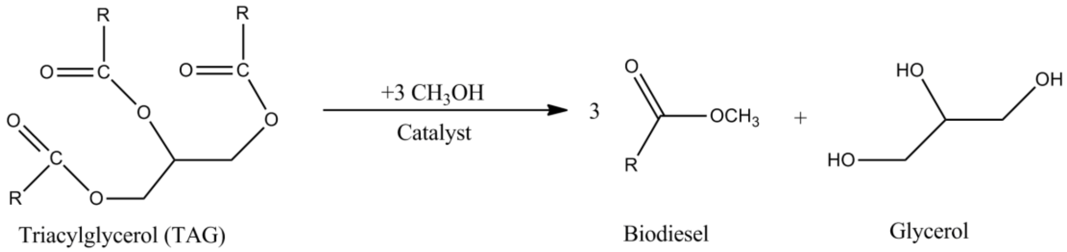
Catalysis contains a wide range of technologies that propose a constant research for the development and study of catalytic processes. In heterogeneous catalysis, chemical transformation takes place on a solid surface. This solid surface is called catalyst whose main characteristic, regardless of the nature of the reaction, is to reduce the activation energy of the process without affecting the thermodynamic of the reaction. A fundamental principle in Catalysis involves the strength of interaction between the reactants and the surface. If adsorption energy is weak, the surface would not have enough capacity to set compounds while it carries out reaction, on the other hand, if the energy is very strong, products could not be free themselves and the product would become a poison for catalyst, which leads inactivation during the process.

The theoretical study of molecular electronic structure is based on numerical solutions of the Schrödinger equation and other approaches, which allow to examine complex models that represent actual systems and at the same time obtain significant results to explain events that take place in chemical processes. Computational methods are a powerful tool for studying these processes. This work shows how theoretical simulation using density functional theory (DFT), can contribute to understand the reaction mechanism and help in the design of new catalysts in the process of decomposition of glycerol.

Glycerol is a byproduct of production of biodiesel, nowadays due to increasing of fuel demand, is produced in large amounts (Figure 1). This situation affects environmental viability and economic activity of biorefineries, therefore, it is necessary to obtain high value compounds from glycerol to achieve better profitability in the process of biodiesel production [1]. Glycerol has three hydroxyl groups which provide an important characteristic as potential starting material for several value-added chemicals [2].

Between different catalytic routes of transformation of glycerol, can be found dehydration [3, 4], steam reforming [1, 5, 6], hydrogenolysis [7-10] and oxidation[2], which involve at least one step of decomposition of glycerol. Among the most used catalysts are transition metals such as Cu, Ru, Pt, Ni and Pd [5, 8, 11-14]. The fundamental study of mechanisms of glycerol decomposition using metallic catalysts allows to determine the best option of catalyst that would favor to obtain the desired product.

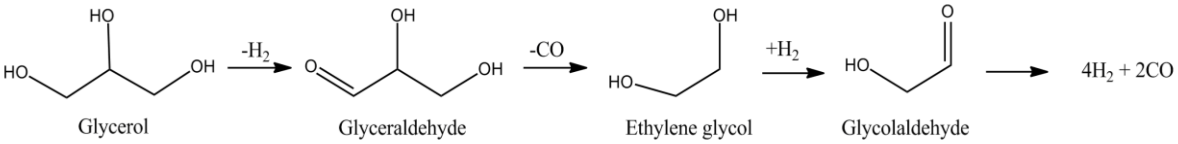
Figure 1. Transesterification of oils yielding biodiesel and glycerol as by-product [2].



Activity and selectivity are highly dependent on catalysts, supports and reaction conditions. This work was about thermochemical study of a glycerol decomposition mechanism over different metallic surfaces conformed by alloys of Pt with Cu, Ru or Ni, to estimate what is the effect of a second transition metal on the surface and achieve a better understanding of decomposition process. Thermochemistry of glycerol decomposition is in order to carry out subsequent investigations about improving activity and selectivity of metallic surfaces in catalytic conversion processes of glycerol [15].

It was chosen steam reforming (Figure 2) because it is a representative reaction of glycerol decomposition, converting it into carbon dioxide and hydrogen. The production of hydrogen or syngas is a promising use of glycerol, hydrogen is widely used to power fuel cell systems; therefore, converting glycerol to hydrogen is considered a renewable alternative [1].

Figure 2. Glycerol steam reforming [1].



A common point in these mechanistic studies is about the dehydrogenation deemed as first step in glycerol steam reforming. The difficulty in this field is that glycerol-derived intermediates are highly reactive, and can be transformed rapidly into stable products. The main investigated topic was adsorption phenomena of glycerol over Pt and Pt-X bimetallic surfaces by studying effect of a second transition metal on the Pt surface through a thermochemical study of these surfaces on decomposition of glycerol. It was used neutral glycerol in gas phase in order to study its decomposition to establish a understanding of the fundamental underlying reaction mechanisms involved in the decomposition of glycerol [16].

There is a competition of scission of C-C, C-H, O-H and C-O in the process of decomposition of oxygenated hydrocarbons, therefore, each scission follows a specific order according to the energy required to break the bond between atoms, thereby creating the sequence of decomposition of the molecule [15]. Preliminary studies with compounds of lower molecular weight and similar characteristics to glycerol, such as ethylenglycol [17] and methanol [18], found that some dehydrogenation steps of the molecule should take place before that scission C-C bond becomes competitive[15]. Computational studies on gas phase can provide useful data about liquid phase process and DFT calculations have reliably predicted studies about production of hydrogen.

Transition metals play an important role in heterogeneous catalysis. The most used catalysts in transformation reactions of glycerol are based on Cu, Cr, Ni, Pt, Pd and Ru, mainly. Pt is the most used because its activity and selectivity to scission C-H, O-H and C-C scissions [19, 20] and it facilitates the dissociation of the intermediates that has been generated after breaking the bond [21]. Platinum has selectivity towards scission of C-C bonds compared with C-O bonds at intermediate temperatures [22].

To take advantage of properties that some metals have for the reactions mentioned (hydrogenolysis, oxidation, steam reforming, dehydration) such as Cu, which shows higher selectivity to scission of C-O bonds, or Ni and Ru, which produce higher conversion of glycerol in reactions of hydrogenolysis, which presents some steps of glycerol decomposition. In other studies, incorporation of Pd into Pt reduces the charge transfer resistance and activation energy in ethanol oxidation and with high temperatures, ethanol adsorption become increasingly favored [23]. The addition of Cu, Ni, Ru or other element on the surface of Pt, generates geometrical structure changes due to different metallic radius and electronic changes due to charge redistribution which modifies the interaction between the atoms of the surface and adsorbate.

In this work was proposed to conduct a thermochemical study of decomposition of glycerol over Pt-X bimetallic surfaces, where X is a transition metal: Cu, Ni or Ru; in order to establish criteria for further studies that help evaluate the activity and selectivity of catalysts based on Pt. This study focused on finding better catalyst properties through NB method [24]: Determine a reaction mechanism and active sites for each catalyst based on previous studies of the reactions studied and the most probable adsorption sites, developing a microkinetic model for the mechanism intending to reproduce the experimental behavior, based on the adsorbed intermediates and transition states involving each elementary reaction in the reaction mechanism, assume that the same mechanism and active site applies to all surfaces and that the electronic structure allows energy values are representative for other similar materials, determine a linear relation between the energies of adsorbed compounds or transition states and some descriptors as adsorption energy of C, O, N, etc. and Select a new surface and calculate the energies of this descriptors to estimate the energies of adsorption of intermediates or transition states and develop the kinetic model. The evaluation of each step or elementary reaction takes place in the transformation of a reactant to product; therefore, with the energy study of the glycerol decomposition reaction is possible to determine the effect Pt alloys with other transition metal, to obtain a basis for further studies of activity and selectivity of the surfaces.

The hypothesis proposed for this research was “The fundamental study of the mechanisms of glycerol decomposition on bimetallic catalysts Pt-X, where X is a second transition metal, contributes in designing more active and selective catalysts than pure Pt catalysts”.

This work is organized in three sections through which the results of this investigation are shown.

In section 1, *Identification of the most stable structures and configurations of surfaces, reactants and products*, was determined preliminary calculations in order to estimate the most stable geometry of reactants and products, and to established optimal adsorption surfaces.

In section 2, *Evaluation of adsorption energy in decomposition of glycerol over Pt-X bimetallic surfaces,* was studied the most possible adsorption sites and was evaluated adsorption energy of all intermediate products on each surface.

Finally, section 3, S*tudy of thermochemistry of decomposition of glycerol mechanism over Pt-x bimetallic surfaces.* It was studied a reaction pathway of glycerol decomposition, thermochemically, in order to elucidate the effect of other transition metal on the surface of pure Pt.

SECTION 1. IDENTIFICATION OF THE MOST STABLE STRUCTURES AND CONFIGURATIONS OF SURFACES, REACTANTS AND PRODUCTS.

Summary

The decomposition reaction is the formation of two or more compounds from a larger molecule. Except in cases of very small molecules, the decomposition process is generally very complex and not well defined. This work is based on a numerical method, named Density Functional Theory (DFT), to approximate a solution of Schrödinger's equation. The system studied is composed of a surface (Pt, Pt_3Ni, Pt_3Cu or Pt_3Ru) and one molecule (Glycerol or some intermediate reaction product of glycerol decomposition).

The identification of the most stable configurations of adsorption was the first step of the simulation to determine energy adsorption and thermochemical study. For this reason, it was performed the optimization of each molecule (glycerol and intermediates reaction products) and relaxation of surfaces above named. Firstly, the decomposition mechanism for the analysis of intermediate reaction products as well as the composition of the alloy was established to build each Pt-X surface. Secondly, the calculation of key parameters (k-point, lattice constant and encut) was conducted during optimization procedure. Finally, it was defined the most stable configurations of intermediate molecules of reaction mechanism and surfaces to proceed in the next section with calculations of adsorption energy.

1.1 Computational Methods

The Vienna Ab-initio Simulation Package (VASP) [25-28] software was used for *Density Functional Theory* (DFT) calculations. Ionic cores were described by the *Projector Augmented Wave* method (PAW) [29, 30], and Spin polarized DFT calculations were performed with the exchange-correlation functional *Perdew-Burke-Ernzerhof* (PBE) [31, 32].

the number of atoms composing the surface is 64; 48 Pt atoms and 16 atoms of element X. A four-layer, closed packed Pt (111), Pt_3Ru (111), Pt_3Ni (111) and Pt_3Cu (111) surfaces with 10 Å of vacuum between any successive metal slabs were used to model the thermochemistry of elementary reaction intermediates. The DFT-determined lattices constant were found consistent with other studies [33].

A Kohn-Sham electron Valence States were expanded on a basis function of plane wave with a cut of 520 eV energy. For all systems, the surface Brillouin zone was determined using a gang of Monkhorst-Pack of 3 x 3 x 1 [34]. A cell of 4 x 4 with 4 layers with flat-cut (1 1 1) based on the (FCC) face-centered crystal structure was used to shape the metal surface adsorption. The atoms in the two lower layers were fixed to represent the bulk while allowing in the atoms of the upper layers is relaxation during calculations.

1.2 Results and discussion

This section describes a theoretical background followed by optimization calculations performed to determine the position where the adsorbates will be adsorbed on each of the surfaces.

It should be noted that theoretical study follows a mathematical model that represents a real system, then the results shown are approximations using numerical methods to solve the equations of the mathematical model, which in this case is given by the many body Schrödinger equation. DFT describes an approximation solution of this equation applying numerical and computational methods [35].

The Hamiltonian (equation 1) describes a system with i electrons and j nuclei where it contains kinetic energies, interactions between electrons, nuclei and electrons-nuclei. This equation is impossible to solve analytically due to Hamiltonian is an electronic wave function which is a function of each spatial coordinates of each *i* electrons, additionally, the term of interactions between electrons means that wave function of one electron cannot be calculated without considering individual electron wave functions of all others electrons that conform each atom, that is a problem with 3*i* variables.

The Born-Oppenheimer approximation [36] helps to reduce its complexity; thereby obtaining that total energy system is the sum of the energy of the electrons added to the electrostatic energy of the nuclei neglecting its motion.

$$H = \sum_{a=1}^{i} \frac{p_a^2}{2m} + \sum_{b}^{j} \frac{P_b^2}{2M_b} + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{a,b=1;a\neq b}^{i} \frac{e^2}{|r_a - r_b|} - \frac{1}{4\pi\varepsilon_0}\sum_{b=1}^{j}\sum_{a=1}^{i}\frac{Z_b e^2}{|r_a - R_b|} + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{a,b=1;a\neq b}^{j}\frac{Z_a Z_b e^2}{|R_a - R_b|} \qquad (1)$$

Hohenberg-Kohn theorem [37, 38] considers the ground-state energy from Schrödinger equation is a unique functional of the electron density and the electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation. It reduces the problem in four terms: kinetic energy, potential energy, Coulomb repulsion between the electron, the total electron density and the exchange correlation potential.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right]\Psi_i(r) = \varepsilon_i \Psi_i(r) \qquad (2)$$

The exchange-correlation functional is approximated by the generalized gradient approximation using information of the local electron density and local gradient in the electron density. In this work was used the Perdew-Burke-Ernzerhof functional (PBE) [31]. To calculate crystal properties, it was used pseudopotentials. They describe interactions between ions, removing oscillations close to the nuclei and focus in the right description of valence electrons. The Bloch's theorem [39] allows the solution of the Schrödinger equation in a supercell applying boundary conditions that take advantage of the periodicity of the crystal, the so called Bloch boundary conditions. This term is expressed by two others terms: plane wave functions to describe electronic structure and a periodic term.

Among the alternatives of transformation of glycerol there are hydrogenolysis, dehydration, oxidation and steam reforming; reactions which presents at least one glycerol decomposition step. To study decomposition of glycerol, it is necessary to define the most representative reaction that involves decomposition steps, for this reason, glycerol steam reforming was selected. It was proposed a reaction pathway that is shown in Figure 3, based on glycerol decomposition reaction considered by Lin et al. [1] that follows a sequence thermodynamically stable where decomposition of oxygenated hydrocarbons begins with the dehydrogenation [15, 21]. The objective of this reaction mechanism is elucidate differences between the surfaces studied under the same conditions, to study the effect of the alloys of Pt with Cu, Ru or Ni on the adsorption energy and then performing a thermochemical analysis.

Figure 3. Reaction pathway of glycerol steam reforming.

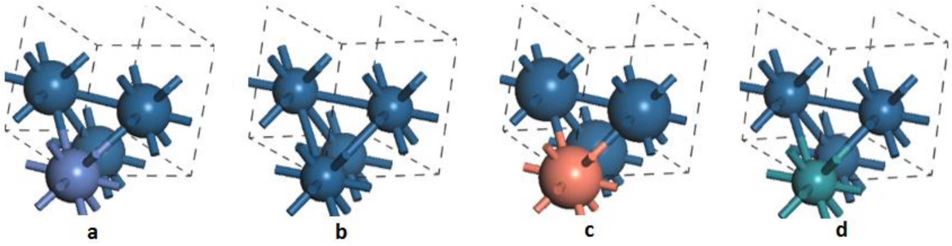
Reaction 1: $CH_2OH - CHOH - CH_2OH \longrightarrow CH_2OH - CHOH - CH_2O + H$
Reaction 2: $CH_2OH - CHOH - CH_2O \longrightarrow CH_2OH - CHOH - CHO + H$
Reaction 3: $CH_2OH - CHOH - CHO \longrightarrow CH_2OH - CH_2OH + CO$
Reaction 4: $CH_2OH - CH_2OH \longrightarrow CHOH - CH_2OH + H$
Reaction 5: $CHOH - CH_2OH \longrightarrow CHO - CH_2OH + H$
Reaction 6: $CHO - CH_2OH \longrightarrow CHO - CHOH + H$
Reaction 7: $CHO - CHOH \longrightarrow CHO - CHO + H$
Reaction 8: $CHO - CHO \longrightarrow CHO - CO + H$
Reaction 9: $CHO - CO \longrightarrow CO - CO + H$
Reaction 10: $CO - CO \longrightarrow 2CO$
Reaction 11: $8H \longrightarrow 4H_2$

Once was defined the reaction pathway, intermediate products were optimized to determine the energy system of each specie, to calculate adsorption. The optimization of each intermediate products was performed separately to set the most stable geometries which would be adsorbed on the surface structure, in figure 4 is shown some optimized intermediate products. Given the location described in similar studies on adsorption and decomposition on Pt metal surfaces as in the case of Liu and Greeley, these optimized structures were located in adsorption sites detailed in Section 2 of this document.

There are different parameters that affect the energy system and the unit cell that is defined as structural unit of atoms that conform a crystal structure. It was considered the effect of the unit cell on the total energy system because it can change the distribution of electrons in the molecule due to the arrangement of atoms according to the change of lattice parameter. To evaluate this effect, it was performed a convergence study of lattice constant in order to determine the optimal value of lattice parameter where the surface is relaxed without periodic boundary conditions problems.

The initial structures are Bulk of Pt and all its alloys Pt_3Ni, Pt_3Cu and Pt_3Ru shown in Figure 5. Determining bulk structures, it seeks to establish the most stable crystal structure for a material, and it can be addressed by finding shape and atomic positions that minimize the total energy of the system involved.

Figure 5. Bulk structures of a) Pt_3Ni, b) Pt, c) Pt_3Cu and d) Pt_3Ru.



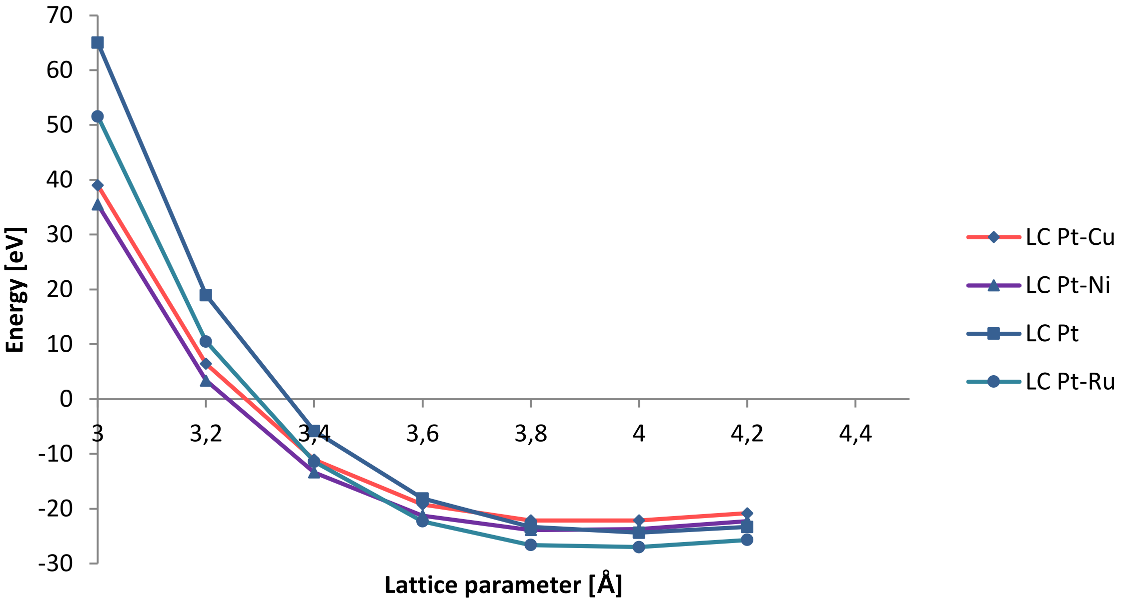
The equilibrium bond length of a molecule is approximately the bond length that minimizes the total energy of the system. In the same way, it was computed the total energy of the surface as a function of lattice constant. Figure 6 shows the results of convergence of lattice constants, where the minimal value of each line corresponds to optimal lattice parameter for each surface. The lattice constant for Pt (111), Pt_3Ru (111), Pt_3Ni (111) and Pt_3Cu (111) were listed in Table 1.

Table 1. Lattice constant.

Surface	**Lattice constant (Å)**		
	This work	**Theoretical[33]**	**Experimental**
Pt	3.97	3.970	3.916 [40]
Pt_3Cu	3.88	3.903	3.788~3.856 [41, 42]
Pt_3Ni	3.86	3.880	3.812 [43]
Pt_3Ru	3.92	3.932	3.917 [44]

In all simulations, it is to expect that the solutions of Schrödinger equation with lower energies are more physically important than solutions with very high energies; in order to define a significance level and truncate calculations to kinetic energies, is used one parameter that must be defined whenever a DFT calculation is performed; the energy cutoff, it represents the range in which the interactions of an atom will be evaluated with their neighboring atoms.

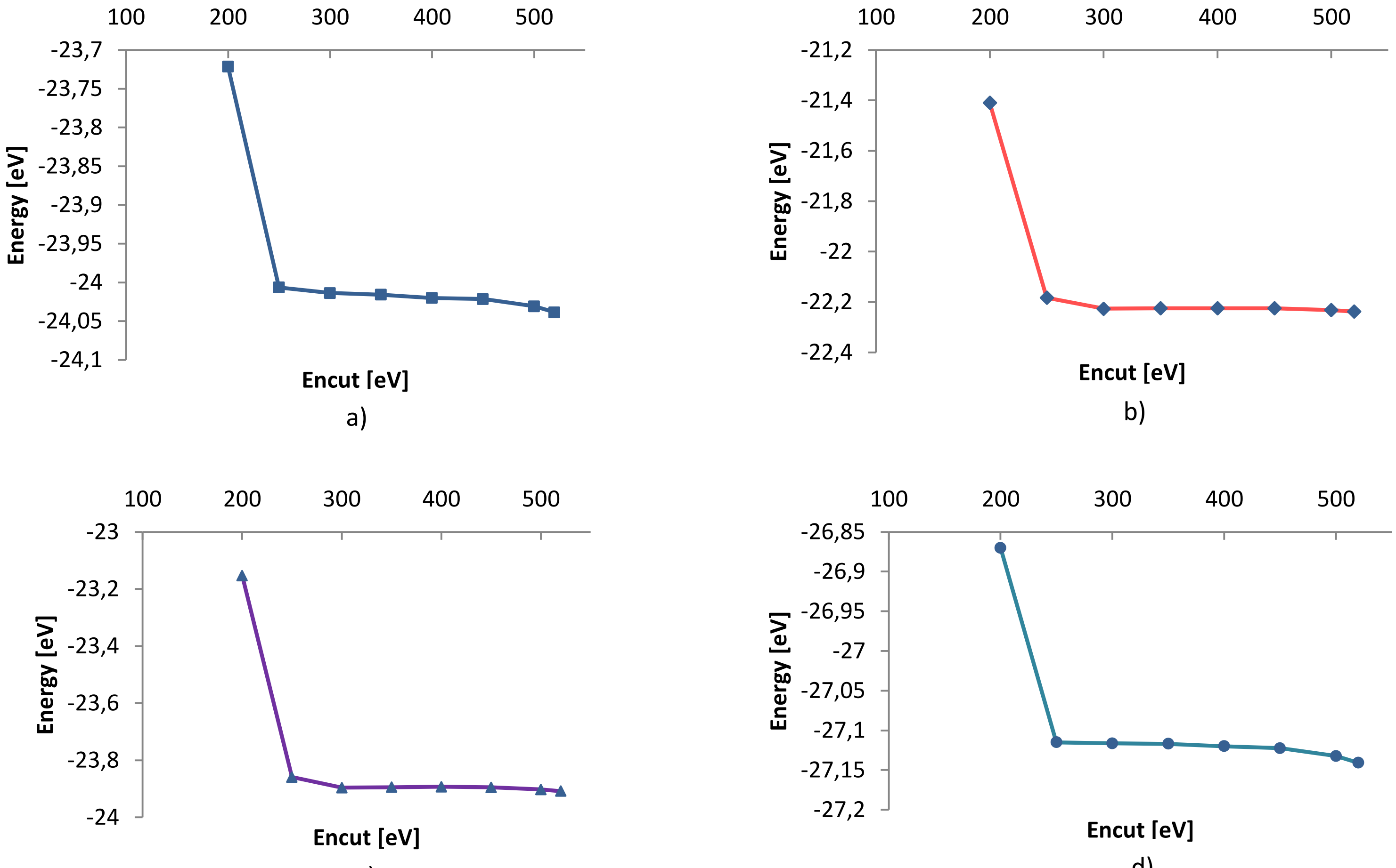
Figure 6. Convergence of Lattice constant.



In VASP, this parameter is represented as encut. For consistency reasons is recommended to define a value of encut for all surfaces, considering the chemical species studied and thereby obtain comparative results between different metallic surfaces, thus value was set in 520 eV that corresponds to 1.3 times the maximum value of ENMAX reported among all the elements of the complex surface-adsorbate being studied, this is equivalent to high precision calculations on VASP. The convergence study was performed to confirm that it was a valid value for this study, results in Figure 7 show. The selected value was 520 eV, to cover all the chemical species present in the adsorbate as both the surface. According to calculations convergence value of 350 eV, it would be an acceptable value, but it is necessary to take into account the maximum value of encut of each species, so the value of 520, selected by heuristics, meets this requirement and criterion convergence confirms that it is a valid value.

A primitive cell is the supercell that contains the minimum number of atoms necessary to fully define a periodic material with infinite extent. It is possible to define a primitive cell in reciprocal space, called the Brillouin zone. During the calculations on crystal systems, several integrals inside the Brillouin zone of the system covering possible values of *k* are performed. The solution of a wave function in a periodic potential can be fully characterized based on their behavior in this volume of reciprocal space. K values are based on method developed by Monkhorst and Pack in 1976 [34]. Figure 8 shows when k-point number is greater than 11, the total energy is seen to be independent of the number of k-points, for that reason to perform calculations on bulk structure it was selected 11 as k-point value [45].

Figure 7. Encut convergence. a) Pt, b) Pt_3Cu, c) Pt_3Ni and d) Pt_3Ru.



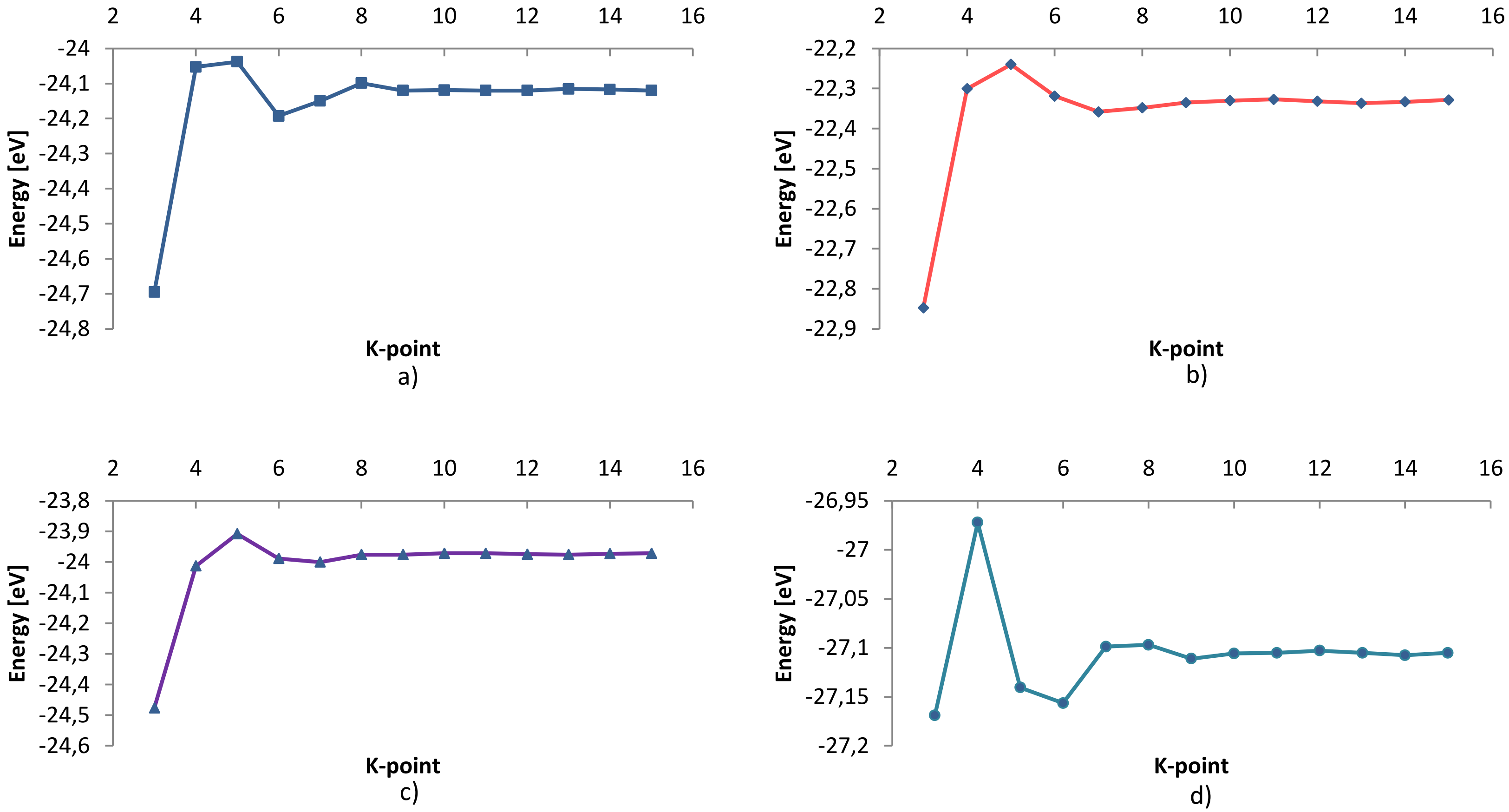
a)

b)

c)

d)

Figure 8. K-point convergence. a) Pt, b) Pt_3Cu, c) Pt_3Ni and d) Pt_3Ru.



a)

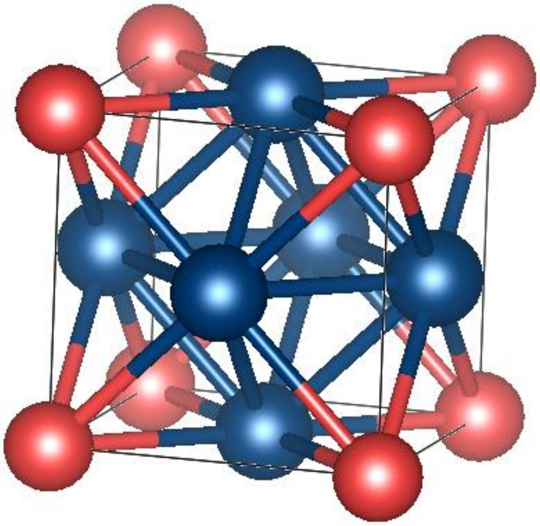
b)

c)

d)

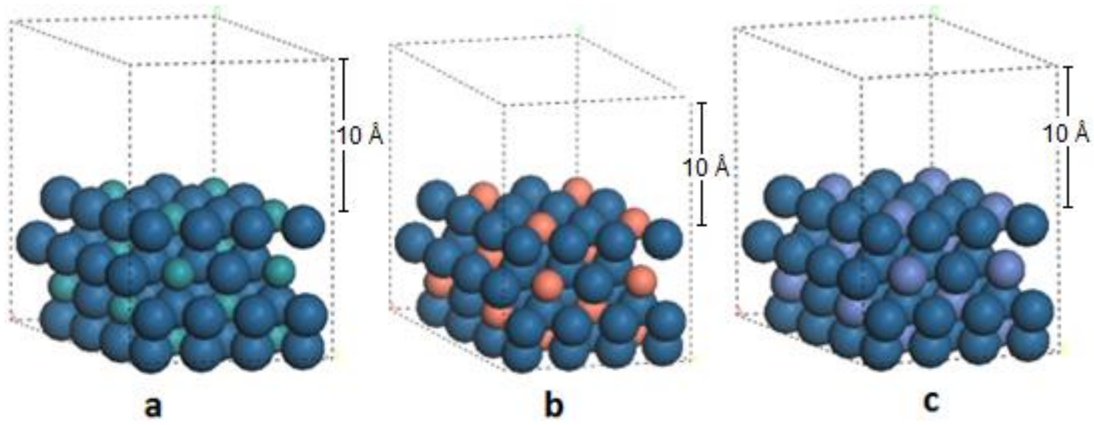
Once the bulk parameters were defined, the next step was to build slab models for each alloy. Most metals adopt a packing arrangement which maximizes the occupation of space. FCC structures have been widely used to model various Pt_3X crystalline alloys [46-48]. Pt_3X alloys possess close-packed FCC structures, in which the Pt atoms occupy the face-centered positions and the X atoms (X=Cu, Ni or Ru) are located at the corners in the unit cell, as shown in Figure 9.

Figure 9. Pt_3X structure. Blue = Pt atoms, Pink = X atoms.



The supercell consists of a 4-layer building the slab, and a vacuum of 10 Å, thereby ensuring that there is no interaction between the adsorbed molecules and surfaces replicated by periodic boundary conditions. In the 4 x 4 unit cell, each slab layer contains 12 Pt atoms and 4 X atoms (Cu, Ru or Ni), thereby obtaining a Pt_3X alloy, where the surface has a plane (1 1 1). This plane has the highest possible density of atoms in the surface of an FCC material. Surfaces with the highest surface atom densities are typically the most stable, and thus they play an important role in real crystals at equilibrium (Figure 10).

Figure 10. Slab models: a) PT$_3$Ru, b) Pt$_3$Cu and c) Pt$_3$Ni.



Atoms closer to top surface do not follow the same behavior that has the bulk structure, therefore, it is necessary to relax the upper layers in order to simulate the real system, for this purpose calculations of surface relaxation were performed. In each calculation, the bottom two layers were constrained in their bulk positions and all other layers were allowed to relax. When optimization was completed, atoms on top layers are closer than bottom layers, the slight contraction in the lattice parameters with respect to that of elemental Pt is consistent due to the incorporation of Cu, Ru or Ni into the Pt lattice. Table 2 gives the corresponding displacement of atoms on top two interlayers, to compare the geometrical effect of alloys in Pt surface.

Table 2. Displacement of atoms at the topmost surface.

Surface	**d_{12}* (Å)**	**d_{23}** (Å)**	**Pt-Pt bond (Å)**	**Pt-X bond (Å) X= Cu, Ni or Ru**
Pt	2,304	2,286	2,807	-
Pt$_3$Cu	2,262	2,227	2,759	2,744
Pt$_3$Ni	2,253	2,215	2,718	2,744
Pt$_3$Ru	2,300	2,248	2,745	2,773

*d_{12} denotes the distance between the first and the second layer.
**d_{23} denotes the distance between the second and the third layer.

Pt surface is considerably altered in presence of a second transition metal, thus creating a more compact structure associated with metallic radius given that Cu, Ru and Ni possess smaller radius than Pt [33]. This geometric changes involve a new electronic structure with a reduction of distance on Pt bonds and an alteration of the surface electronic properties caused by charge redistribution on the surface that modifies interaction between adsorbate and surface, Pt bond lengths are shown in Table 2 [49, 50].

In this section the more stable configurations intermediates refer to optimization of molecules in order to obtain structures which are adsorbed on the surfaces to calculate adsorption energy. After performing the optimization of the surfaces it was possible to confirm that the second metal present in the structure will modify its interaction with the adsorbate due to the change of space between the atoms of Pt and other metal, and between the layers of each surface because a charge redistribution occurs between the electrons present in the upper layer by effect of interactions with other atoms of the lower layers remain fixed.

SECTION 2. EVALUATION OF ADSORPTION ENERGY IN DECOMPOSITION OF GLYCEROL OVER Pt-X METALLIC SURFACES.

Summary

In order to achieve a fundamental knowledge of a reaction mechanism involved in the decomposition of glycerol on Pt surface and the effect of alloying Pt surface with transition metals such as Cu, Ni and Ru on the decomposition mechanism, it was studied adsorption energy of reformed glycerol over Pt, Pt_3Ru, Pt_3Cu and Pt_3Ni surfaces. The catalytic properties are primarily determined by the geometry and electronic structure of the surface. This structure can be modified by the surface composition of the alloys, allowing an atomic redistribution to improve interaction between atoms on the surface and atoms from adsorbate [51].

In this section were evaluated different adsorption sites for each intermediate specie on glycerol decomposition mechanism proposed in the previous section, similar behavior among alloy surfaces was established and it was confirmed that Pt surface is considerably altered in the presence of a second 3d metal in the surface, thus determining a relationship between adsorption energy and geometric structure of surfaces. It was found that Pt alloy surfaces with 3d metals exhibit higher affinity to oxygenated compounds than surfaces that only have Pt, therefore, present stronger adsorption energy.

2.1 Computational methods

Calculations were performed within the DFT framework using VASP, which is a DFT code based on plane wave basis sets. Electron-ion interaction WAS described using the projector-augmented wave (PAW) method, which was expanded within a plane wave basis setting up a cutoff energy of 520 eV. Electron exchange and correlation effects were described by the Perdew-Burke-Ernzerhof (PBE), generalized gradient approximation (GGA) type exchange correlation functional. Spin polarization was included in every simulation. The system is a slab model, infinite in the x and y directions and finite in z direction. It consists of a periodically repeated FCC Pt slab composed by four-layers modeled using 4×4 supercells.

The top two layers were allowed to relax, and the bottom two layers were fixed. In order to represent a surface, a vacuum space was used to build the system separating the slabs of the upper and lower cells. Because of the periodic boundary conditions used in the three spatial directions, the top (111) surface is separated a distance 10 Å from another (111) surface (Figure 10).

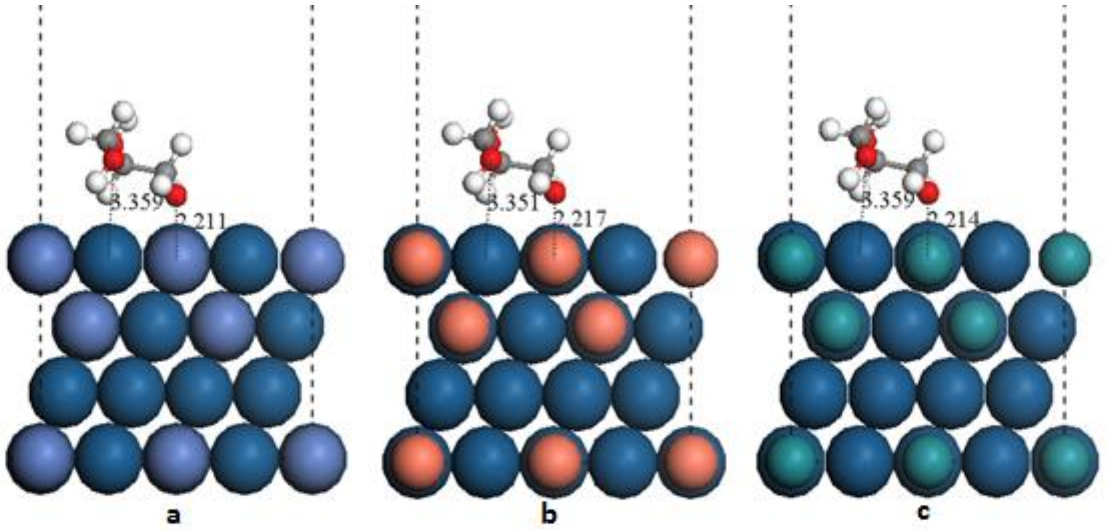
The simulation conditions were established in the previous section. As Pt_3X (X = Cu, Ru and Ni), slab models were constructed based on the ordered FCC structure, with the lattice constants studied previously.

2.2 Results and discussion

The structures of metals selected are equivalent in their crystal structure (FCC) and surface (111) plane was selected as the adsorption surface. The system was modeled without impurities to focus on the effect of alloys in the phenomenon of adsorption over Pt_3X surfaces. Adsorption energy is one of major factor that determine the thermodynamic and dynamic of dissociation processes [52]; understanding the geometry and electronic structure of surfaces is important to establish if exists a correlation between the structure of a surface and its catalytic activity [53]. Many characterization techniques have been used to determine surface structure of metals in order to study their effect over molecules being adsorbed [45]. For this reason, the adsorption study is a useful tool to analyze the mechanism of glycerol decomposition, thus allowing further studies to evaluate activity and selectivity of the surfaces that act as catalysts in this reaction.

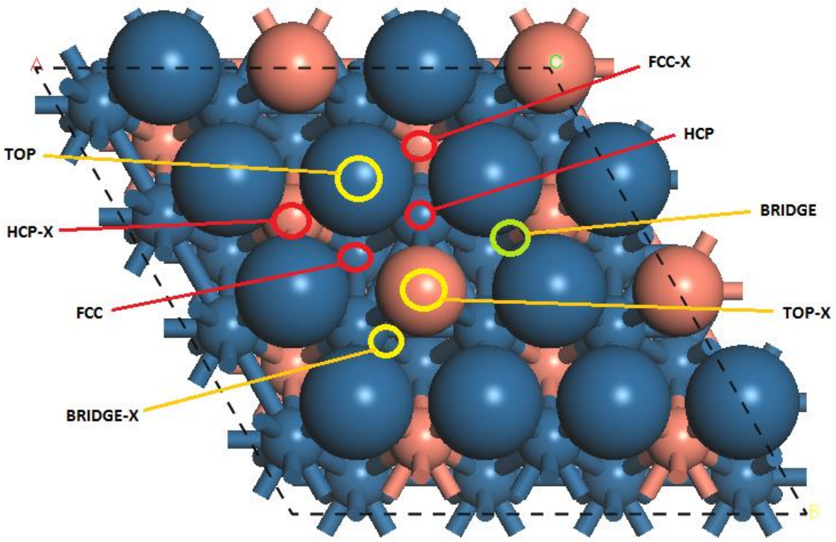
The initial geometry of glycerol adsorption was taken from study by Liu and B. J. Greeley (Figure 11); they established the initial position of glycerol depending on the oxygen atoms at the ends of the molecule. Thus having an oxygen atom at 2.21 Å from the surface, and another oxygen at 3.36 Å, approximately [15]. Each intermediate specie was located in the same way.

Figure 11. Glycerol adsorption over each surface. a) Pt-Ni, b) Pt-Cu and c) Pt-Ru.



To locate the adsorbate on the surface, adsorption sites were studied. For Pt surface, four types of adsorption sites: top, bridge, HCP, and FCC, were examined. Furthermore, for Pt alloys, other sites were included: top-X, HCP-X, bridge-X and FCC-X, corresponding to interactions with the second 3d metal. Figure 12 shows all adsorption sites. The relevance of selected sites is to evaluate most stable adsorption position of each intermediate product and determine the effect of transition metal on Pt surface by calculating the adsorption energy.

Figure 12. Adsorption sites.



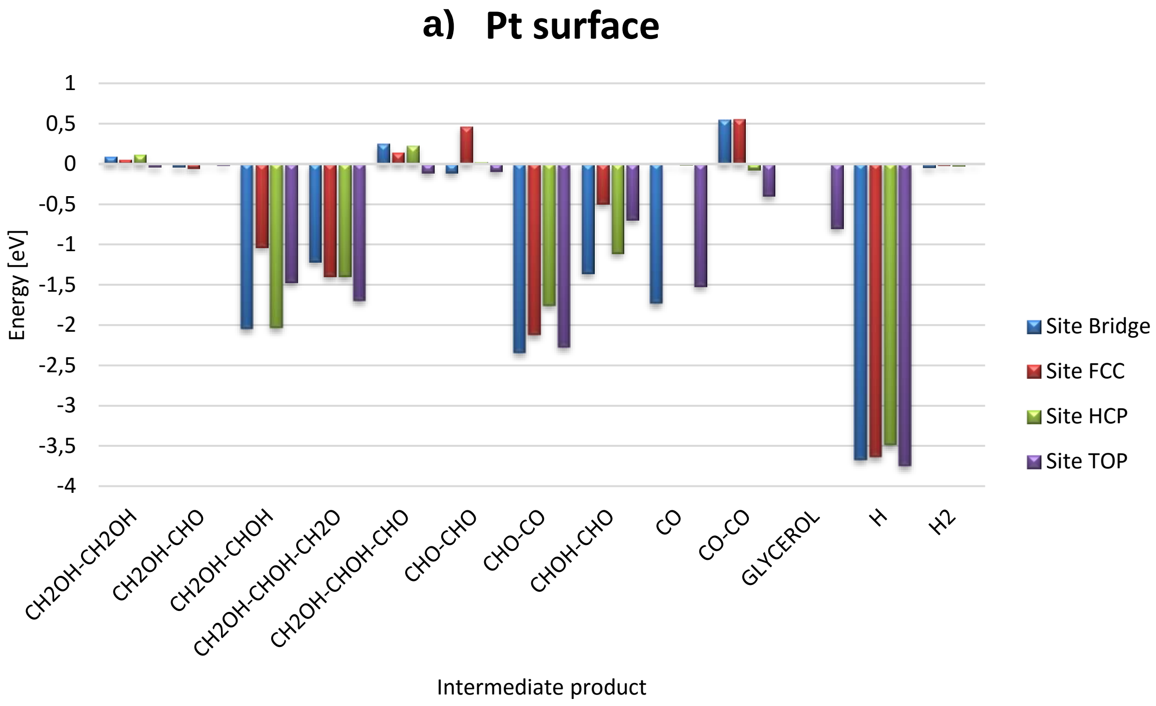
Once defined all total energy of complex adsorbate-surface in each sites through optimization calculations, it was proceeded to calculate the adsorption energy to find the most probable sites of adsorption.

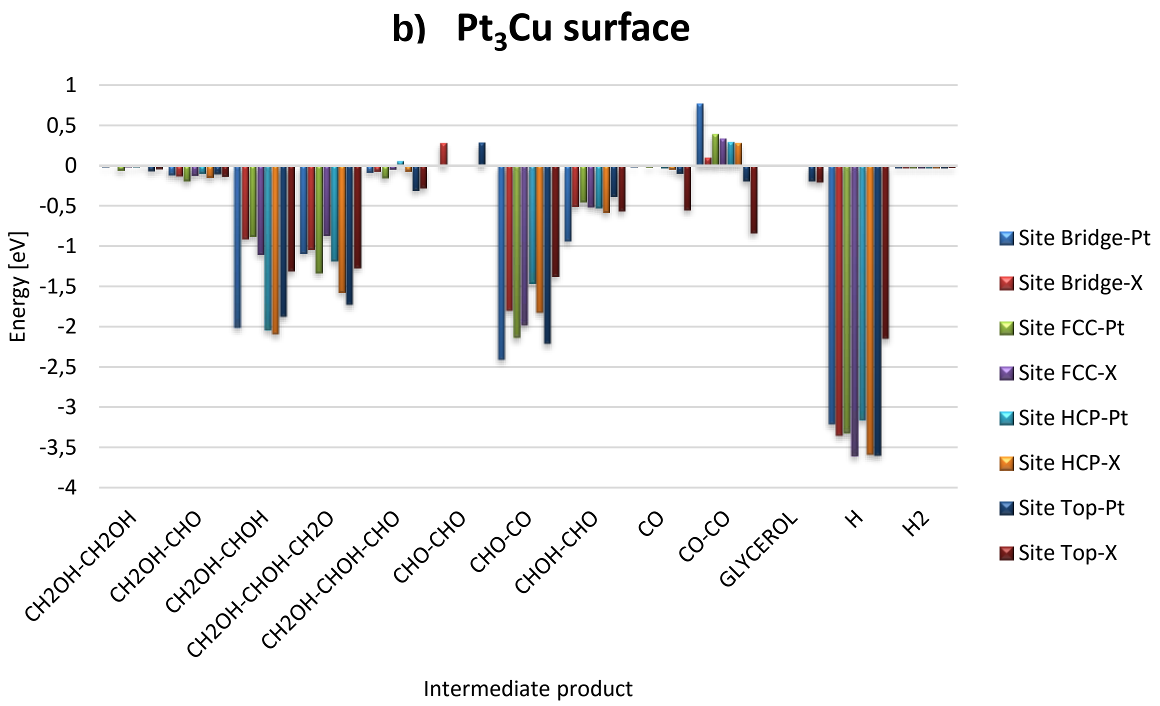
The adsorption energy for each molecule is given by the equation

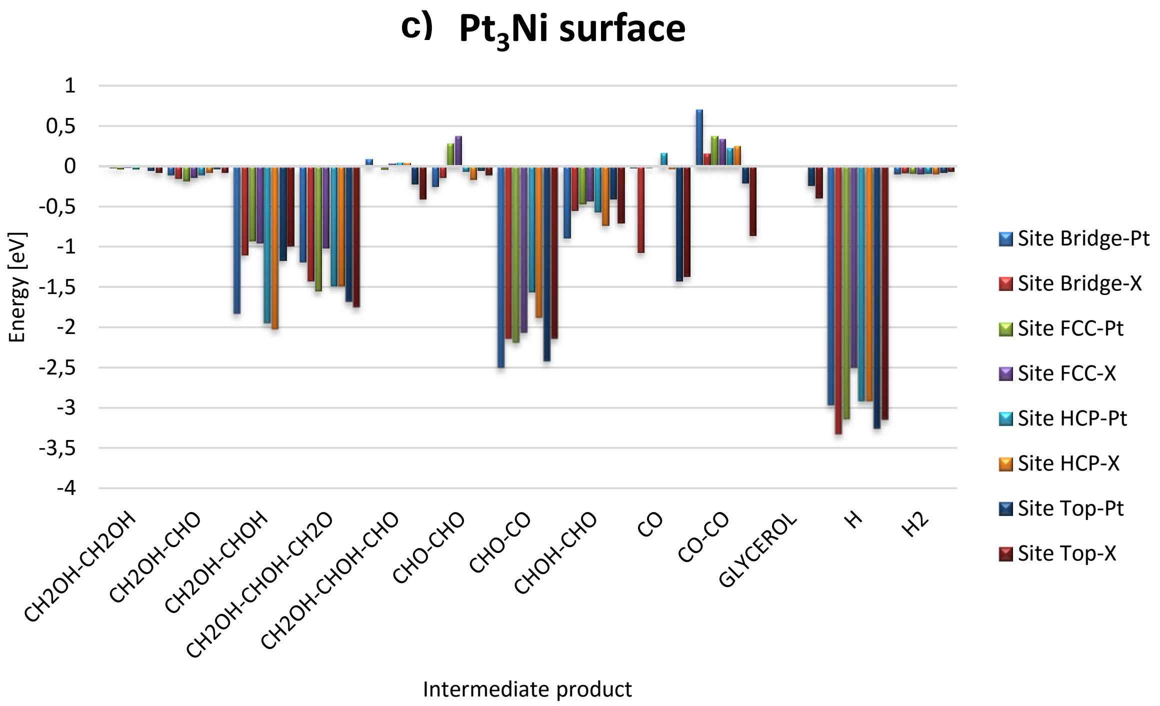
$$E_{ads} = E_{slab/m} - E_{slab} - E_m \tag{3}$$

Where $E_{slab/m}$ is the total energy of the slab with adsorbed molecule, E_{slab} is the energy of the slab, and E_m is the energy of gas phase molecule [51]. The most probable site of adsorption is determined by the lowest adsorption energy on each Pt_3X surface for each molecule (reactants and products), through equation 3.

Figure 13. Adsorption energy in all sites. a) Pt surface, b) Pt3Cu surface, c) Pt3Ni, d) Pt3Ru.






c) Pt_3Ni surface

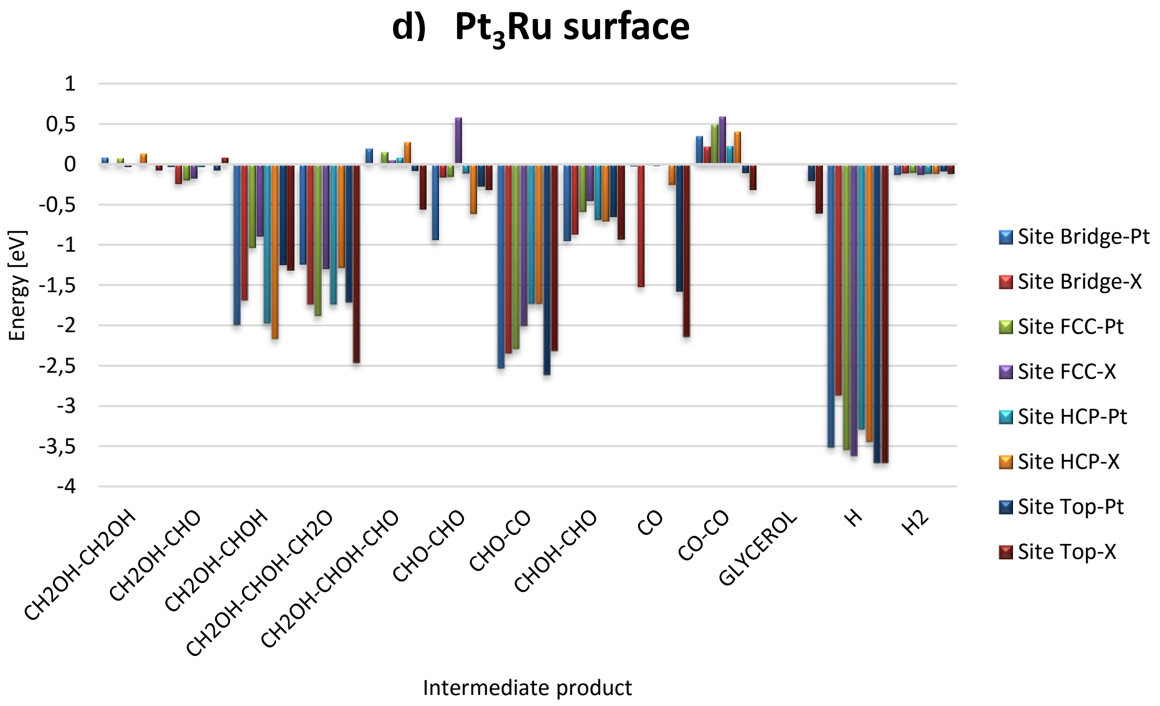

d) Pt_3Ru surface

Figure 13 shows adsorption energy taking into account all the adsorption sites. On the surface of Pt-Ru they are observed higher adsorption energy values due to its electronegative character. Top and Bridge are the most likely sites for the adsorption phenomenon. Separately analyzing each surface is observed that the most stable compounds in the mechanism proposed have higher adsorption energy value. Each surface has a very similar behavior in each reaction step, therefore, it is possible to determine a linear relationship between descriptors adsorption energy of constituent elements, as well as the Gibbs free energy, to establish parameters that define the properties of each surface to design catalysts. The study of each adsorption site was performed to identify the most likely sites and contributes the calculation of adsorption energy, which is important to establish the model of behavior that each surface has, in order to improve foreclosing on catalytic activity and selectivity of pure Pt. In Table 3 is shown the chosen adsorption site by each intermediate molecule on each surface.

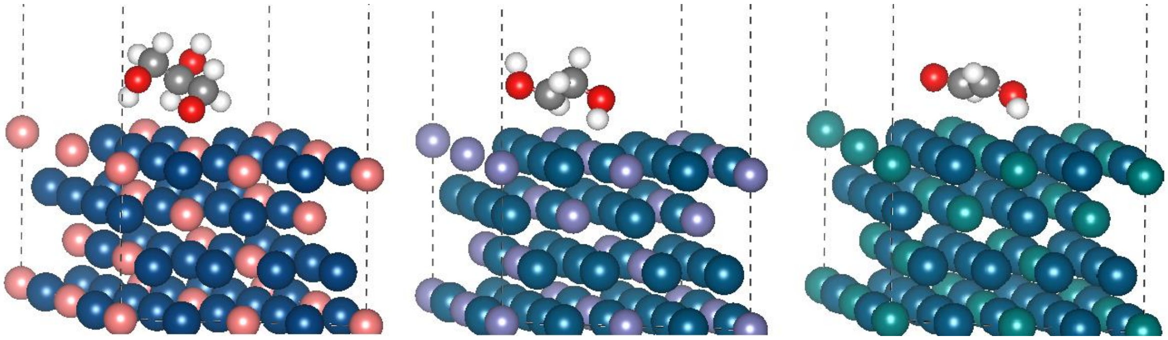
Table 3. The most probable sites of adsorption on each Pt3X surface.

Number	Intermediate	Pt	Pt_3Cu	Pt_3Ni	Pt_3Ru
1	CH2OH-CHOH-CH2O	Top	Top	Top-x	Top-x
2	CH2OH-CHOH-CHO	Top	Top	Top-x	Top-x
3	CH2OH-CH2OH	Top	Top	Top-x	Top-x
4	CH2OH-CHOH	Bridge	HCP-x	HCP-x	HCP-x
5	CH2OH-CHO	FCC	FCC	FCC	Bridge-x
6	CHOH-CHO	Bridge	Bridge	Bridge	Bridge
7	CHO-CHO	Bridge	Bridge-x	Bridge	Bridge
8	CHO-CO	Bridge	Bridge	Bridge	Top
9	CO-CO	Top	Top-x	Top-x	Top-x
10	CO	Bridge	Top-x	Top	Top-x
11	H	Top	FCC-x	Bridge-x	Top
12	H2	Bridge	FCC-x	FCC-x	Bridge
13	GLYCEROL	Top	Top-x	Top-x	Top-x

3d metals generally exhibit higher affinity to oxygen; the variation on interaction between oxygenated species and Pt pure or Pt_3X surfaces is attributable to the effect of lattice parameter compression. Stronger adsorption is expected when oxygen atoms are bound to 3d-metal-enriched surfaces [47]. The Pt_3X surfaces possess stronger adsorption energies than Pt surface because 3d metal atoms are engaged into the interactions with oxygen due to charge density generated by geometrical changes, thus modifying the adsorption on the surface.

The binding energy of an adsorbate to a metal surface is largely dependent on the electronic structure of the surface itself. The metal d-band hybridizes with the bonding (σ) orbital of the adsorbate to form bonding (d-σ) and antibonding (d-σ)* states; the extent of filling of the (d-σ)* state depends on the local electronic structure of the metal at the surface. An increased filling of the antibonding (d-σ)* state corresponds to a destabilization of the metal-adsorbate interaction.

Figure 14. Adsorption of intermediate products. a) CH2OH-CHOH-CH2O over Pt_3Cu, b) CH2OH-CHOH over Pt_3Ni and c) CHOH-CHO over Pt_3Ru.



Chemisorption of molecules to a metal surface, a higher d-band center results in stronger bonding. On the other hand, a lower d-band center means weaker bonding [54]. Alloying platinum with other 3d metal could decrease or increase the d-band center which in turn causes the resulting alloy to bind adsorbate more weakly or strongly than Pt surface.

The oxygenate hydrocarbons reforming yield displays a correlation and increases as the surface d-band center is shifted closer to the Fermi level. On the basis of the comparison of the activity and reaction intermediates of ethylene glycol and glycolaldehyde, the presence of the C=O functionality enhances the activity on the Pt surface. Adsorption energy of glycolaldehyde is found to increase as the surface d-band center moves closer to the Fermi level [55].

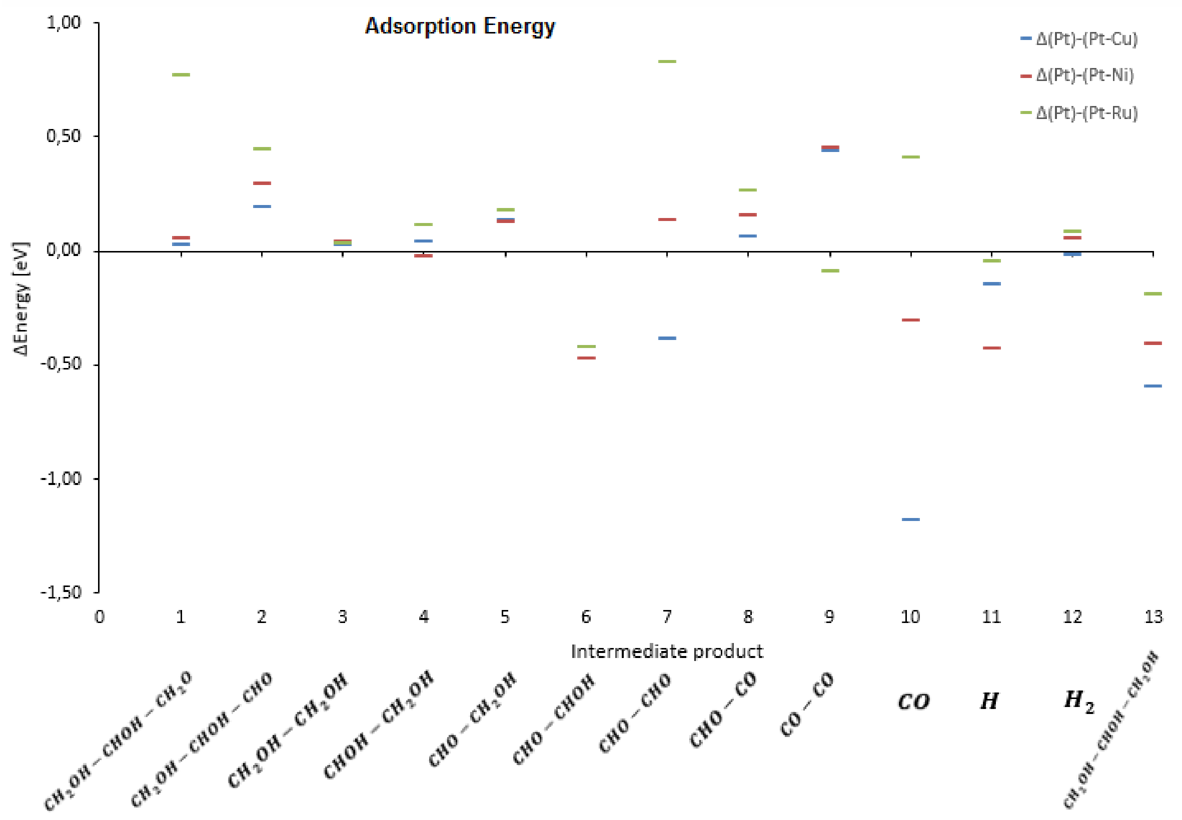
The desirable reaction pathway is selective C−C bond scission, to produce H2 and CO, selective reforming of oxygenated hydrocarbons is a promising way to produce hydrogen for use as fuel and syngas for production of chemicals and fuels. DFT calculations were carried out to study the trend in the adsorption energies of these oxygenates on bimetallic surfaces as is shown in Figure 14.

A danger to solid catalysts is their poisoning, that is, when a molecule binds strongly to adsorption positions, ceasing to be available for the catalytic reaction, for this reason, study of adsorption strength over Pt_3X surfaces is important in adsorption-desorption phenomena [56].

A comparison of energy adsorption values is shown in Figure 15, a value above zero point on X-axis indicates a higher adsorption energy therefore, it is expected greater interaction between the adsorbate and the surface. In the case of oxygenated hydrocarbons, it is reflected behavior with a stronger interaction in Pt_3X surfaces than surface of pure platinum. Furthermore, the high affinity having platinum with hydrogen is observed, confirming why platinum is an important element on dehydrogenation processes.

The Pt and Pt_3Ru surfaces have similar behavior with respect to the adsorption sites, and Pt_3Ru surface shows higher adsorption energy implying a higher resistance in the process of transformation and desorption of products, within all surfaces. Pt_3Ni surface has a smaller standard deviation value of alloys, following a similar behavior to the surface of pure Pt.

Figure 15. Comparison of adsorption energy between all surfaces.



*zero point on X-axis refers to adsorption energy on Pt surface.

The comparison indicates that surfaces that bind adsorbates more strongly, such as Pt_3Ru, promote reforming reactions. One would also predict that at sufficiently high binding energies oxygenates would undergo complete decomposition instead of reforming. Pt-Ru catalysts have been found to be more active for alcohol steam reforming than either parent metal [55]. Cu and Ni promote the overall rate of glycerol reforming by reducing the adsorption energy of CO to Pt, which makes surface sites more available to participate in reforming.

The electronegativity of Ni = 1.91, Cu = 1.9, Ru = 2.2 and Pt = 2.2; which leads to expect that in addition to having a more compact structure between the alloy of Pt-Ru, also there is a greater adsorption force of this surface with the adsorbate, which can be seen in Figure 15, which shows the comparison of adsorption energies. This result would correlate the adsorption values calculated for constituent species of the molecule of adsorbate and adsorption energies of the surface to be studied, in order to contribute to the design of catalysts with improved catalytic properties of activity and selectivity than Pt surfaces. Given that the Ru has a higher affinity for oxygenates, is a good choice for the first steps of decomposition of glycerol, as would greater stability adsorption of molecules of intermediates, ensuring that they carry out the reaction compared to adsorption energy values of Pt-Ni and Pt-Cu.

In order to achieve a fundamental knowledge about a reaction mechanism involved in the decomposition of glycerol over Pt and the effect of alloys with transition metal on this process, it was studied the adsorption energy on steam reforming of glycerol over Pt, Pt_3Ru, Pt_3Cu and Pt_3Ni surfaces. It was evaluated different sites of adsorption for each intermediate product in a proposed reaction pathway of steam reforming. With data of adsorption energy is concluded that Pt_3X surfaces offer better phenomenon of adsorption of intermediate hydrocarbons in the glycerol decomposition reaction in comparison with Pt surface.

SECTION 3. STUDY OF THERMOCHEMISTRY OF GLYCEROL DECOMPOSITION MECHANISM OVER Pt-X BIMETALLIC SURFACES.

Summary

Electronic structure calculations based on Density Functional Theory (DFT) are increasingly used to probe reaction mechanisms on catalyst surfaces. These calculations provide information about geometry, stability, and reactivity of adsorbed species on various surfaces. Results from DFT calculations alone cannot be used to evaluate the relative rates of various pathways, because these rates depend on reaction conditions.

Thermochemical studies energy changes during chemical reactions. Quantum mechanical approaches, such as DFT, can be used to estimate thermochemical parameters like enthalpies and entropies and kinetic parameters like activation energies and frequency factors of chemical reactions. It has been noted that although for some catalytic systems the support may play a significant role; many times the active sites are on the metal surface. Such studies can be used for generating useful correlations for predicting the binding energies of reaction intermediates on a variety of surfaces. In this section, it was performed a thermochemical calculation of glycerol decomposition over Pt and Pt_3X surfaces, to contribute to understanding of the reaction mechanism and generating a starting point for subsequent investigations about improving activity and selectivity of metallic surfaces.

3.1 Mathematical models

Standard DFT total energy calculations give access to the total electronic ground state energy at 0K, $E_{tot} \approx U$.

The heat of the reaction, ΔH, is an important parameter in kinetic modeling, since it has a strong influence on the reaction equilibrium. DFT calculations provide an efficient way to calculate the total electronic energy of a system. For the case of adsorption of a species on a surface, ΔH is approximated by the binding energy of the species [57].

Knowledge of the total energies of the adsorbed complex, the metallic surface and the isolated gas phase molecule can be used to calculate the Binding Energy, BE, as:

$$BE = Et_{sur-ads} - Et_{sur} - Et_{ads} \qquad (4)$$

The binding energies thus calculated, can be used for determining ΔH as follows:

$$\Delta H \approx \sum BE_{productos} - \sum BE_{reactivos} \qquad (5)$$

3.2 Results and discussion

The need for discovery of new heterogeneous catalytic processes is of vital importance in view of the growing need to expand the applications of catalytic technologies and reaction engineering into areas beyond the current chemical and petrochemical industries. Theoretical studies are useful in the research and development process to supplement these experimental studies with quantitative analyses of the reaction kinetics to compare the performance of different catalytic materials at various reaction conditions.

It is presented a free energy analysis of a decomposition reaction pathway. Such free energy analysis is well suited to obtaining the general insights into the reaction kinetics and thermochemistry, such as comparisons of the kinetics of glycerol steam reforming.

For each intermediate product, all surfaces were evaluated by free energy changes, in order to evaluate stability of surfaces on decomposition mechanism that was studied above.

It was reported the most stable intermediate products in the evaluated reaction at each metallic surface and it allowed to elucidate some conclusions about glycerol decomposition; although this approach does not provide significant predictive values, it is useful to establish a behavior and effect of adding other 3d metal to the bare Pt surface.

The energy change of a closed system is equal to the heat supplied less work done;

$$\Delta E = Q - W \qquad (6)$$

For a system where the pressure is constant and the kinetic and potential energies are not significant, the total energy of the system is given by $E_{tot} \approx U$; getting this:

$$\Delta U = Q - W \qquad (7); \qquad W = P\Delta V \qquad (8)$$

The enthalpy is expressed as:

$$H = U + PV \qquad (9)$$

For a closed system at constant pressure $\Delta H = Q$, in terms of chemical reactions would be the heat of reaction, whose expression is in Equation 5.

Gibbs free energy is relevant because the chemical reactions are typically developed at constant temperature and pressure.

$$G = H - TS \qquad (10)$$

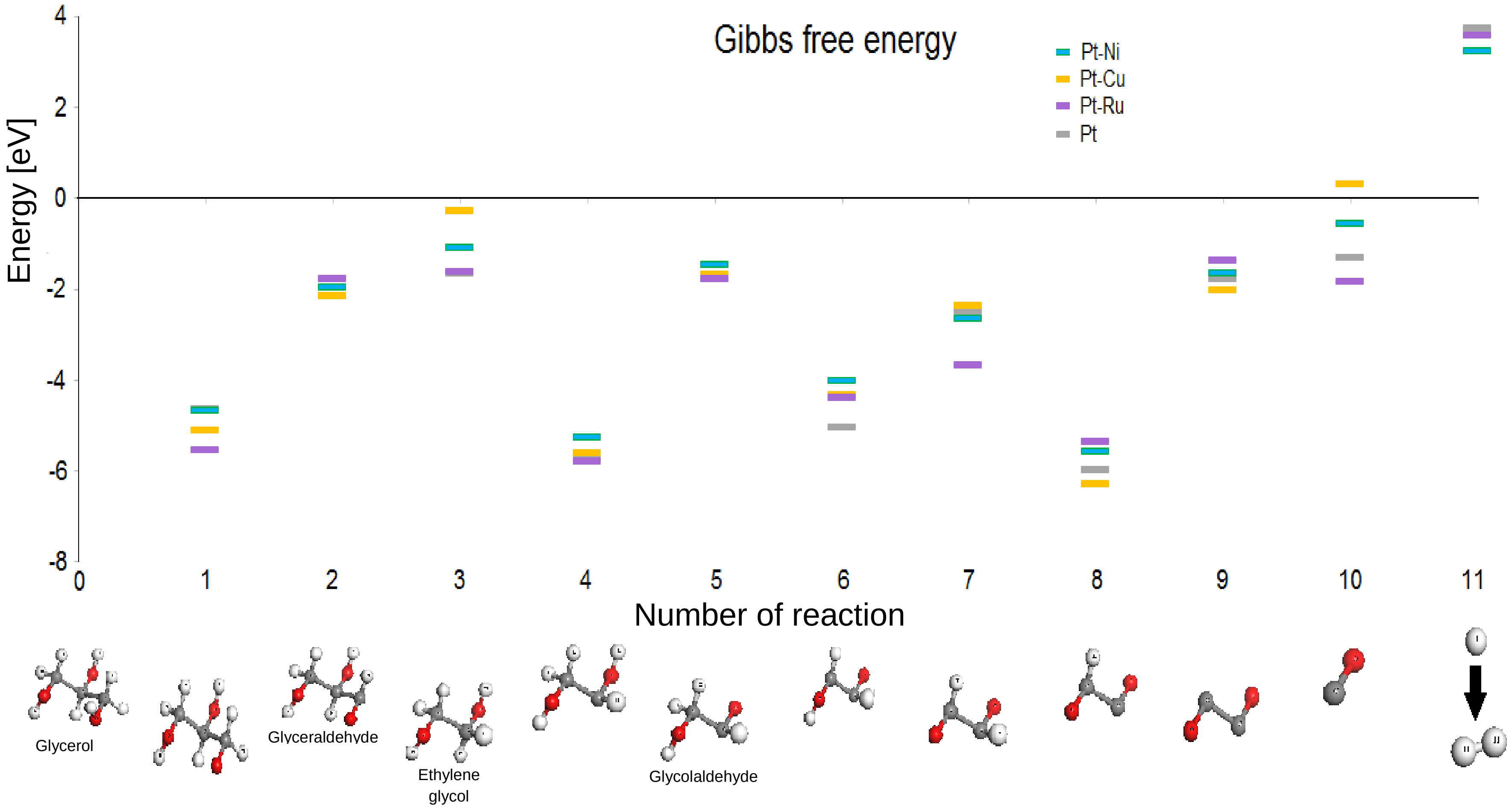
$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

In the absence of mechanical work of expansion, the energy consumed in the chemical reaction is given by the chemical work. Assuming that a reaction occurs reversibly and isentropic then $\Delta G = \Delta H$, meaning that equals the heat of reaction. If $\Delta G < 0$, the reaction is spontaneous and it does not need energy to convert reactants to products.

Table 4. Heat of the reaction.

# Reaction	ΔH [eV]			
	Pt	Pt_3Cu	Pt_3Ni	Pt_3Ru
Reaction 1	-4,65	-5,13	-4,69	-5,57
Reaction 2	-2,17	-2,18	-1,97	-1,80
Reaction 3	-1,66	-0,31	-1,10	-1,65
Reaction 4	-5,77	-5,64	-5,27	-5,81
Reaction 5	-1,76	-1,70	-1,48	-1,78
Reaction 6	-5,06	-4,36	-4,03	-4,41
Reaction 7	-2,50	-2,39	-2,68	-3,70
Reaction 8	-5,99	-6,30	-5,58	-5,39
Reaction 9	-1,80	-2,03	-1,67	-1,40
Reaction 10	-1,34	0,28	-0,57	-1,84
Reaction 11	3,71	3,58	3,23	3,58

Figure 16. Gibbs free energy



The calculation of Heat of reaction (Table 4) is determined by binding energy that it was calculated above by adsorption energy. In the table is shown the heat of reaction for each reaction step, on each surface. Negative values indicate exothermic processes where energy is released.

After obtaining the heat of reaction, taking into account the above assumptions where $\Delta G = \Delta H$, values of Gibbs free energy for each reaction in each surface, in order to compare the stability of the surfaces were plotted in Figure 16. With low values of Gibbs free energy, the surface is more stable. It is observed that reactions of decomposition are spontaneous and bimetallic surfaces follow no definite trend in their behavior with respect to the surface of pure platinum. Pt_3Ni alloy, has a less stable behavior in most reactions in comparison with Pt. It is not possible to define a trend in order to evaluate if a surface is better than other for glycerol decomposition reaction.

values Gibbs free energy calculated from the adsorption energy, these data raised the possibility that the reaction occurs is studied, and the surface stability of occurrence are shown in Figure 16. According to the method Nørskov, Bligaard et al, it is assumed that the same mechanism and active site applies to all surfaces and that the electronic structure enables the energy values are representative of other similar materials, so it is possible to determine a linear relationship between the energies of adsorbed compounds or Gibbs free energy of each adsorbate and some descriptors such as adsorption energy of C, O, N, among others; in order to have predictive performance criteria of other metal surfaces, based on the study of these bimetallic surfaces. The establishment of this correlation between variables, allows to optimize the procedure for calculating of adsorption energies, in order to contribute to the design of new catalysts with improved catalytic properties than pure Pt.

It is necessary to study other possible reaction pathways to verify adsorption values and behavior regarding the transition metals in addition to a kinetic study to elucidate the advantages of a second metal on the surface of Pt.

Within observations and taking into account the results obtained, it is possible to identify the assumptions and simplifications that were made, and the capacity of computational resource, affected research so although relevant data were obtained to establish that the transition metals selected alter the interaction of the metal surface with each adsorbate in the decomposition process of glycerol and allows to obtain basis for further studies of activity and selectivity of the surfaces; it is required a kinetic study on transition states and activation energy for the design of catalysts based on the studied surfaces.

CONCLUSIONS

It was confirmed that the surface of Pt is significantly altered geometry and electron distribution in presence of a second transition metal on the surface, resulting in a weak or strong adsorption on the surface of Pt. This condition is due to a change in the electronic distribution of charges on the surface.

The calculation of the adsorption energy and Gibbs free energy of each the Pt3X surfaces allows establishing descriptors behavior considering adsorption energies of constituent elements of each molecule intermediate, in order to have a predictive judgment when to study other similar metal structures in the same reaction mechanism and studying the same active sites.

Pt_3Ru surface is more related to oxygenates and dazzles a possibility to improve the properties of Pt in some stages of glycerol decomposition process, where they are.

The thermochemical study of glycerol decomposition mechanism on Pt_3X surfaces, contributes to the design of more active and selective catalysts than pure platinum catalysts, although it is necessary to supplement the information with kinetic studies.

RECOMMENDATIONS FOR FUTURE WORKS

It is recommended the study of segregation effects of all adsorbed intermediate compounds over the metallic surfaces.

To continue thermochemical study including analysis of transition states and further research on selectivity and activity of Pt_3X surfaces in glycerol decomposition reactions.

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