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Modeling with DFT and Chemical Descriptors Approach for the Development of Catalytic Alloys for PEMFCs

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Abstract

Material properties and process modeling with density functional theory (DFT) is an accurate method to facilitate the study and the design of materials computationally for the development of different electrochemical technologies such as fuel cells, solar cells, and batteries, among others, mainly to achieve alternative ways for energy conversion and storage. Considering the relevance of DFT in the development of these alternative technologies for energy generation and storage, in this chapter, the application of DFT to study catalytic alloys and their reactivity processes to develop polymer membrane fuel cells (PEMFCs) is presented. In this sense, firstly, a brief review of the application of DFT to develop catalysts for PEMFCs and the relation with the concept of chemical descriptors is presented. Secondly, the main chemical descriptors for this task are presented and discussed. Finally, a summary of the main findings of the modeling with DFT and chemical descriptors approach of catalytic alloys for PEMFCs is presented and analyzed.

Keywords: DFT, chemical descriptors, catalytic alloys, PEMFCs

1. Introduction

The rational design of materials is an important and challenging task, which implies the in-depth understanding of determining factors for the desired properties of the materials. These properties emerge from the material chemistry (atoms involved and its electronic structure) and material structure (organization at nano and microscale) [1, 2], for which the understanding at atomistic level is key and could enable the tailoring of materials that improve the efficiency of almost any technology. Particularly, catalyst development is crucial for efficient

chemical production and clean energy generation and storage technologies such as photoelectrochemical cells, fuel cells, and batteries, which are required for an environmentally responsible economic growth [3].

In the last few decades, density functional theory (DFT) has been successfully used to study heterogeneous catalysis process and the properties of the catalysts, achieving an understanding of reaction mechanisms and the determining factors in the catalytic activity of the materials. For example, it has been found that the electronic structure of the catalytic surface determines its properties [4–6]. Also, some general relations between these factors and the catalytic activity have been developed and used for the search and design of catalytic materials for different applications [7–14].

In the next sections, the application of DFT to study catalytic materials and their reactivity to develop polymer membrane fuel cells (PEMFCs) is presented. The first section is devoted to review briefly and in a general way, the different works, where DFT is applied for studying catalysts for the electrodes of PEMFCs and some determining factors on catalysis found in some of these works are drawn. Secondly, the main factors used for the development of catalysts through the concept of chemical descriptors are presented and discussed. Finally, a summary of the main findings of the modeling with DFT and chemical descriptors approach of catalytic alloys for PEMFCs is presented and analyzed.

2. Using DFT to study heterogeneous catalysis in PEMFCs

Fuel cells are devices that convert chemical energy of supplied fuel and oxidant into electrical energy. Their operation involves two electrodes, an anode and a cathode, separated by an electrolyte. The anode fuel, such as hydrogen, methanol, and ethanol, which have been proposed for PEMFCs, is oxidized and donates electrons. Electrons travel through the extern circuit, where they perform work and reach the cathode, where oxidant, generally oxygen, is reduced combining with electrons. The electrolyte, which in the case of PEMFCs is a conducting polymer, conducts electricity through the movement of ions, completing the circuit. A schematic representation of a unit cell, illustrating the operation principle explained above is shown in **Figure 1**.

The PEMFCs require the improvement of their performance and the decreasing cost. A principal factor for their performance and its cost are the electrodes, where Pt catalysts are commonly used. So, it required the development of low-cost catalysts, mainly for the oxygen reduction reaction (ORR) at the cathode and hydrogen, methanol or ethanol oxidation reaction (EOR) at anode. The catalysts should reduce the Pt content increasing the rates of the corresponding reactions. Looking for better catalysts is an important challenge, which should be addressed with a comprehensive approach that involves the understanding of the reasons for which a material is an efficient catalyst for a given reaction; in this way, materials can be designed with a "scientific" base.

In this sense, the use of simulations to study catalysis is a great tool, particularly, with the use of atomistic models based on DFT and molecular dynamics. DFT is suited to study
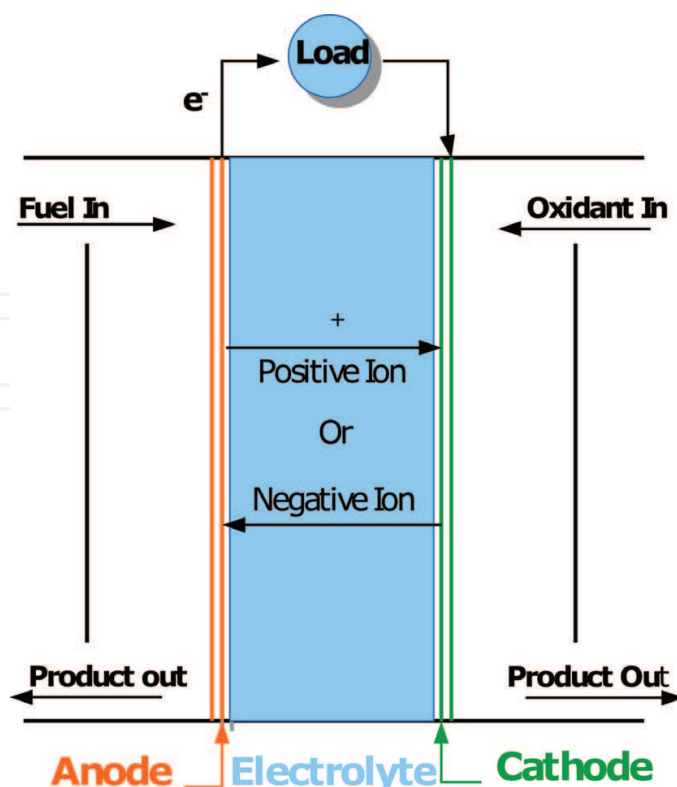
Figure 1. Schematic of a fuel cell.

adsorbate-catalyst interactions, which allow determining the potential energy surface and thus the energy barrier of the chemical transformations, also allows calculating the electronic structure of materials, which can help to understand bond-breaking and bond-making process. Also DFT, through thermodynamics approach, facilitates to describe reaction process and energetics of intermediates, reactants, and products under realistic conditions. Additionally, the information from atomistic scale can be used to compute reaction rates. In the next paragraphs, some works about catalysts for PEMFCs are presented.

Heterogeneous catalytic reactions in PEMFCs involve adsorption of reactants, different bond breaking and/or bond making processes and some electron transfer processes, and desorption of products. The reaction follows the path with minimal energy to go from reactants to product configuration, so this path depends, essentially, on the energetics of the possible elementary steps. So, many studies of catalysts applying DFT is focused in considering each possible reaction step to calculate energetics of reactants and products of each step from which energy barrier for each step can be calculated with different methods such as nudged elastic band [15–17], synchronous transit-guided quasi Newton (STQN) methods [18], among others. With this method, a free-energy diagram for different process can be drawn, an example for dissociative mechanism of oxygen on Pt is shown in **Figure 2**.

The above described approach was used to study EOR or the ethanol decomposition in other processes on Pt [19, 20], Rh [21], Pd [22], Au [23], and some Pt alloys as PtRh, PtRe, PtRu, PtSn, and PtPd [24]. In some of these works, only some steps or the complete reaction network was considered. For example, it was calculated by Alcalá et al., the transition states for C-C and C-O
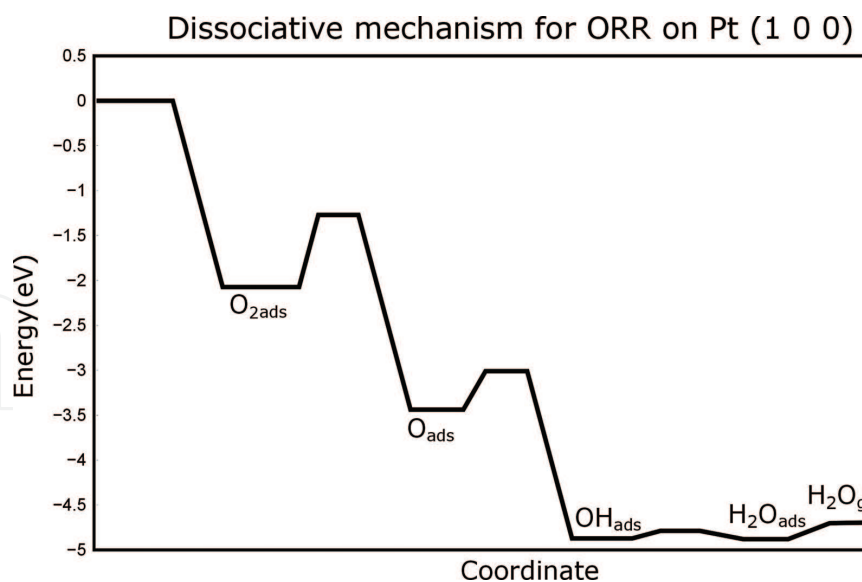
Figure 2. Potential energy surface diagram of dissociative mechanism for oxygen reduction reaction on Pt (1 0 0).

bond cleavage on Pt using constrained optimization, where the length of the bond representing the reaction coordinate is constrained; they identified the steps with lowest activation energy for these bond cleavage reactions. The evaluation of complete reaction network is a formidable task due to the higher quantity of possible intermediate derivatives, but in the ethanol oxidation, reaction network is explored thoroughly identifying key steps for the selectivity on ethanol oxidation and the intermediates, which can lead to C-C bond cleavage in some surfaces.

Also, the mechanistic details of ORR on Pt and Pt-based alloys were investigated using DFT to calculate the intermediate energies and to estimate reaction and barrier energy of each step considered in the reaction pathway [25–33]. Different pathways are considered such as the O_2 dissociation mechanism, and the associative mechanism implying the addition of H to the O_2-containing species. Also, it considered two different ways for hydrogen transfer reaction within each of these pathways: the direct addition of H from the electrolyte (Eley-Rideal type) or the H adsorption and subsequent transfer to O_2-containing species (Langmuir-Hinshelwood type) [27]. For example, in [30], the dissociative mechanism finding that the high stability of oxygen and hydroxyl can imply kinetic limitations in proton/electron transfer to adsorbed oxygen or hydroxyl was studied. In other study, different mechanisms were considered and it is found that under determined conditions, the determining step is the O_2 dissociation, so the associative mechanism is preferred [27].

One of the challenges in the study of electrochemical reactions is considering the effects of the solvation of molecules, the electric field in the interface electrolyte-electrode, and the other adsorbed molecules, nonetheless, some developments have successfully addressed those issues. It is widely accepted that the water layers between the polymer and the catalysts are very important in ORR. It was intended to study the effects of solvation using nine water molecules and one hydronium ion in an ab initio molecular dynamic study [34]. Also, in other studies, adsorption energies of intermediates were calculated adding water adsorbed to the surface or water on top of the adsorbed intermediates [30, 35]. The solvent can be also

described in averaged manner as dielectric continuum characterized by a dielectric constant, which is used to estimate free energy of solute-solvent interactions [36–38]; this approach is named implicit solvation method.

As it is envisioned above, significant progress for the accurate description of electrochemical reactions have been achieved. However, it also can be noted that the complete kinetic description of a given system is quite a demanding task. But, different works show that enough knowledge about catalytic activity could be gained studying some properties of the system at the atomic scale, which can be calculated in a simpler way. These properties are named descriptors, that is, an observable that can be directly linked to a fundamental property [10, 14]; in this case, the catalytic activity. For example, Nørskov et al. show that the oxygen binding energy on metal electrodes is related to the turnover frequency of the oxygen reduction reaction [30].

ORR involves two key steps, the H transfer to adsorbed O_2 to form adsorbed OOH before the O-O bond breaking and the H transfer to adsorbed OH to form H_2O. The activation energy of each step is related with the energy change in each process, which in turn is related with stability of adsorbed OOH and OH, respectively. These adsorbed species will be more stable if O binding to the surface is stronger; therefore, the O binding energy can be related with the reaction rates of these two key steps. The reasoning for this relation is as follows: If O binding is stronger, it is difficult to destabilize the Pt-OH bond to form H_2O; if it is weak, it is difficult to stabilize the OOH to allow the O-O bond to break, so the O binding energy should be moderated. Precisely, in different works, bimetallic Pt and Pd alloys promising as catalysts for ORR looking for materials with moderated oxygen binding energy were identified [39, 40].

The descriptor approach also was used to search materials for hydrogen oxidation reaction on anode of PEMFC. For this reaction, the binding energy of H atom is a key, and according to Sabatier principle, optimal catalytic activity can be achieved on surfaces with moderated binding energies [9, 41]. Sabatier principle states that the bond between the catalyst and the key adsorbate should not be too weak, such that the reactants do not bind, and are not too strong, since this leads to catalyst poisoning [42]. Similarly, in other work, the CO binding energy is considered along the H binding energy to find active catalysts tolerant to CO poisoning [11].

Other property that can be used as a descriptor of catalytic activity is the d-band center of the transition metal surfaces, that is, the average energy of the d states. As is proposed by the d-band model [6, 43], the d-band center is correlated with the binding energy of adsorbates to the surface. The d-band model is fulfilled for bonding of several atoms and molecules, then, as is shown in several works, tuning the electronic structure of a metal by the addition of alloying atom can lead to a better catalyst for ORR [44–46] or catalysts more tolerant to CO [47]. Also, it identified other electronic structure factors, such as transition metal, e.g., band filling and covalency, that can be used as descriptors for ORR on metal oxide catalysts [13].

It is worth to mention that the review presented is very brief and there are other extensive reviews that should be consulted [48, 49]. Besides, from the works reviewed above, it should be remarked that it seems that one key property for catalytic activity is the adsorption energy of key intermediate molecules, which can be used to search better catalysts for a determined reaction. Next section reviews the principal concepts in catalysis used for the identification of

appropriate descriptor, in this sense scaling relations between activation energies and binding energies, Sabatier principle and d-band model are reviewed.

3. Development of catalysts using chemical descriptors

In the last section, different properties of a material that can be related with its catalytic activity were observed. For instance, binding energies of atoms and molecules can be related with activation energies, so with reaction rates. Sabatier principle shows that a determined value of the adsorption energy of intermediates will lead to higher catalytic activity. Finally, it is mentioned that modification of the electronic structure changes the catalytic activity.

3.1. Correlations between adsorption and activation energies and Sabatier principle

The central issue in catalysis is the effect of the catalyst on the rate of a chemical reaction, the rate constant of an elementary reaction can be calculated using an Arrhenius expression in terms of a pre-factor (v) and an activation energy (E_a) as follows:

$$k = v e^{-E_a/k_B T} \qquad (1)$$

The activation energy is an important quantity, which varies with the change of catalyst, so reviewing the origin of activation energy is useful to understand the effect of catalyst on the reaction rate.

As it is illustrated in **Figure 3**, any chemical reaction can be described as a transition between two local minima on the potential energy surface of the system as a function of the spatial coordinates of all the involved atoms. The reaction path is defined as the minimum energy path, which connects the configuration of the reactants with minimum energy (R) to the
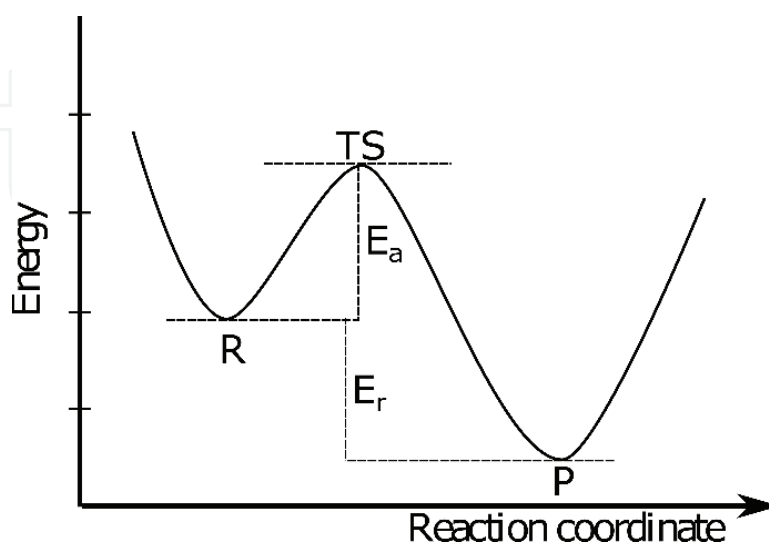
Figure 3. Potential energy surface of a chemical reaction process.

configuration of the products with minimum energy (P) along the reaction path; there is a configuration with the highest energy, which is called transition state (TS). The difference between the TS and R energies is the activation energy (E_a) [50–52]. The configurations of R, P, and TS in a catalytic process involve adsorbed molecules, then the energy of these configurations, and hence activation energy, depends on each surface.

$$E_a = E_{TS} - E_R \qquad (2)$$

Also, it is worth to remark that as transition states have the same basic physics as adsorbed species, then the transition state energy (E_{TS}) is correlated with adsorption energies (E_{ads}). In fact, linear correlations between transition state and adsorption energies have been found [53–56]. This type of relationship is a well-established approach in the understanding of trends in chemical reactions that dates back to Brønsted in 1928, also Evans and Polanyi in 1938 [57], who stated a linear relationship between activation energies and reaction energies, named Brønsted-Evans-Polanyi (BEP) relationship.

The linear relationship between E_{TS} of a chemical reaction and a particular E_{ads} relevant for that reaction can be understood thinking that TS is an absorbed specie with a configuration relatively close to the adsorption configuration of the molecule X with which is correlated. Then, it is reasonable to express the E_{TS} as the sum of two contributions, the first is part of adsorption energy of the molecule X (αE_{ads-X}), which accounts, mainly, for the interaction energy between the surface and the molecule. The second is the quantity of energy (β), which accounts for the reorganization of the molecule X to transform into the transition state molecule. So, the general form of linear relationship is:

$$E_{TS} = \alpha E_{ads} + \beta \qquad (3)$$

It is common to use E_{ads} as the energy of products configuration. In this case, parameter α is a value between 0 and 1, which indicates the position of the transition state along the reaction coordinate. If alpha is close to 1, the transition state has a configuration similar to the products (late transition state) [56], whereas β is a part of the energy involved in the reverse reaction (energy to transform products into transition state molecule) [56].

Using DFT calculations to calculate transition state energies and product energies, it has been possible to establish transition state scaling relations with sufficient statistical significance. This linear relationship provides a straightforward way to study the effect of the surface on the activity for a given reaction, as it enables the estimation of activation energies from adsorption energies, which could be calculated in a simpler way using computational calculations.

Transition state scaling relationship implies that the activation energies are lower in surfaces, where the products are more stable (more negative adsorption energies of products) and hence the reaction rate is higher. However, the very strong adsorption of products leads to poison the surface, since the desorption of products is more difficult, hence the rate of desorption is lower. On the other hand, if adsorption of products is very weak, the reaction rate would be lower and the desorption rate higher. Therefore, the adsorption energy of products
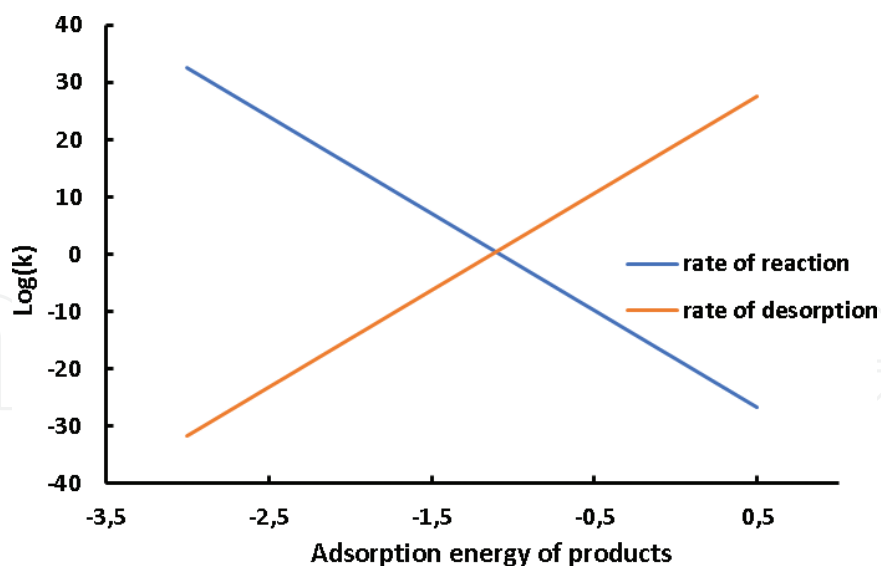
Figure 4. Volcano plot obtained from simple model.

should not be too weak, such that the reaction does not happens, and not too strong since this leads to catalyst poisoning [42]. The above mentioned is precisely the Sabatier principle, a valuable statement for catalyst design.

It allows an explanation of volcano curves, which show the catalytic activity for a given elementary reaction as function of the adsorption energy. As shown in **Figure 4**, at low values of adsorption energy (more positive values), the reaction is slow because the rate of the reaction is rate-limiting, whereas at high values of adsorption energy, desorption becomes the rate-limiting step. Then, the intermediate values of adsorption energies are required in order to obtain the highest activity (top of the volcano) [42, 58–60]. The volcano plot in the figure was obtained from a theoretical calculation, where the rate constants for temperature value of 298 K are obtained from Eq. (1) ($k = v e^{-E_a/k_b T}$), the activation energy for the reaction is obtained from Eqs. (2) and (3) ($E_a = E_{TS} - E_R$, $E_{TS} = \alpha E_{ads} + \beta$) with α and β equal to 1, and E_R equal to −1.2. The activation energy for desorption process is the negative of E_{ads}.

As mentioned above, a key issue in catalysis is chemisorption, the bond formed between surface and adsorbate can be described in terms of electronic structure of the surface. For transition metals, it is described in terms of d-bands of metals, as is proposed in the "d-band model," which is presented in the next subsection.
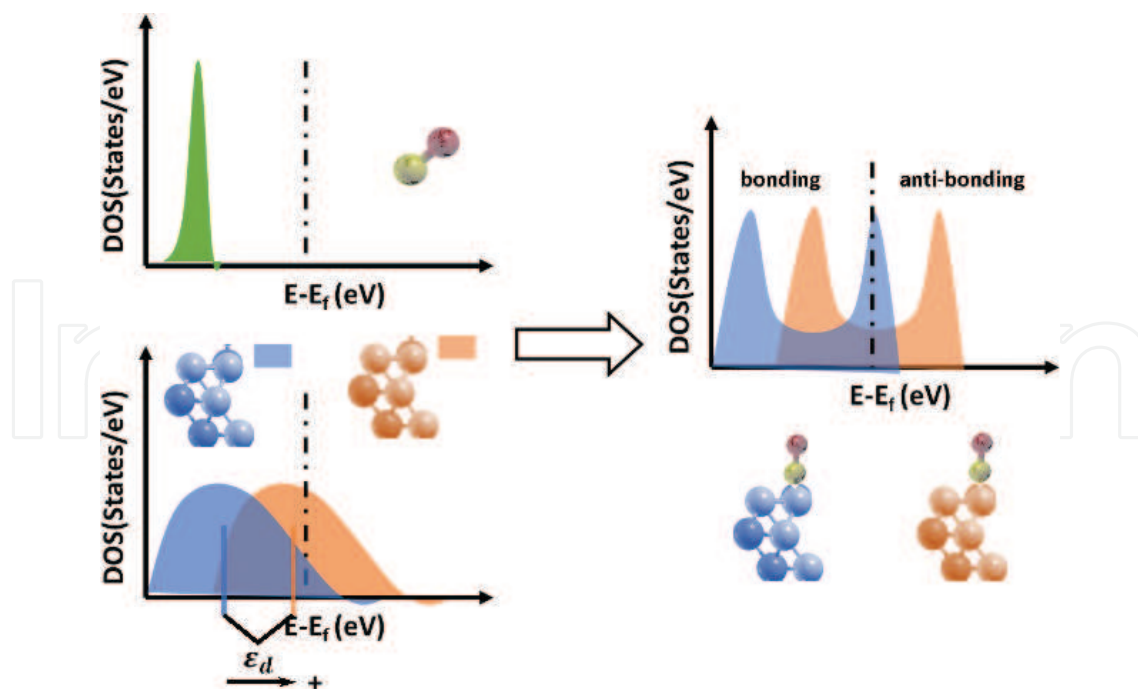
3.2. d-band model

The electronic structure of transition metals involves a broad s-band and narrow d-band. The interaction of the adsorbate valence electrons with s-band electrons can be assumed to be similar for all the different transition metals; hence, the principal differences in the interaction emerge from d-band electrons [4, 5, 43]. The interaction between the adsorbate and surface d-electrons can be represented with molecular orbitals theory, as illustrated in **Figure 5**, the interaction causes the formation of new shared states, which can be classified into bonding

and antibonding states; the antibonding states are higher in energy and its filling leads to the weakening of the bond between adsorbate and surface [4, 5, 43, 61].

If more of antibonding states are empty, then the surface bonds strongly the molecule. Since electrons fill up all states located below the Fermi energy, in order to estimate the strength of the bond is enough to know how many antibonding states are higher in energy than Fermi energy (E_F). It has been found that if d-bands of clean surface shifts up in energy, the antibonding states also would shift up in energy and probably would be emptier. In this sense, the "orange surface" of **Figure 5** should bind the adsorbate stronger than blue surface, since it has d-states with higher energy and so the antibonding states would be above Fermi energy (emptier antibonding states).

The average is a representative value for a group the values or a statistical distribution is the average. In this case, energy average of d-states can be used to indicate the energy of all metal d-states, and it is calculated using Eq. (4) [51]. The difference between this value and Fermi energy can be used to compare in an effective way the d-states energy of different metals. This value is named d-band center (ε_d), if it is higher (less negative), then more antibonding states would be above Fermi energy and the bond would be stronger. This is the called d-band model proposed by Hammer and Nørskov [6, 43].

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} n_{d(E)} E dE}{\int_{-\infty}^{+\infty} n_d(E) dE} \qquad (4)$$

Figure 5. Illustration of the d-band model. The interaction of adsorbate states (green) with metal d-states (blue and orange) forms bonding and anti-bonding states. As the d-band center of metal shift down in energy (blue), more antibonding states are below E_F (dotted line) and hence bond is weaker.

The concepts above presented represent the basic theoretical instruments used to investigate catalytic chemical reactions and to provide satisfactory descriptions with a reduced set of properties compared to complete kinetic description.

3.3. Summarizing the descriptors approach

As remarked in the above sections, the descriptor approach is based on the linking of catalytic activity with a limited set of properties, named descriptors. The main step of this approach is to find a suitable reactivity descriptor and the other is to calculate it. As it was remarked, the adsorption energies of key intermediates can be used as descriptors, the identification of particular adsorption energies that are descriptors can be achieved considering the underlying reaction mechanism in order to identify the rate limiting step, also a Sabatier analysis and the known BEP relations can be used to identify the key adsorption energy. Also, an adsorption energy descriptor can be found through an educated guess, resulting in the knowledge on similar reactions [4, 5, 14].

Since adsorbate-surface interaction is a phenomenon originated by electronic interaction, the electronic structure of the systems can be related with adsorption energies, and some characteristics of this electronic structure can be used as descriptor, one of them is the d-band center. But additional research is required to identify more reliable properties, which can be used in other systems different to transition metals. The next section shows the main results of the modeling with chemical descriptors approach of catalytic carbon-carbon bond cleavage in the ethanol oxidation, reaction important for PEMFCs.

4. Analysis of C-C bond cleavage using chemical descriptors

The catalytic cleavage of the C-C bond in ethanol is fundamental for improving the proton exchange membrane fuel cells fueled with ethanol, whose efficiency is still far from obtained with hydrogen fuel cells, which can be partly attributed to the incomplete oxidation of ethanol to CO_2, so energy from ethanol is not totally exploited [62–67]. Catalysts actually used only promotes partial ethanol oxidation to acetic acid, the limiting step for total oxidation to CO_2 is, precisely, the C-C bond cleavage. Some works suggest that addition of metals as Ni [68], Rh [69], Ir [70], and Re [71] to Pt helps in C-C breakage at temperatures below 100°C. So, it is of interest to model this reaction step on Pt-based catalysts in order to clarify the effect of different co-catalysts on the C-C bond cleavage and to understand the conditions under which the C-C bond can be broken. It can be achieved using the descriptor approach above presented.

4.1. Reactivity descriptor for C-C bond cleavage

The C-C cleavage in molecules with more hydrogen atoms attached to the carbon atoms, as ethanol molecule (CH_3CH_2OH) or acetaldehyde (CH_3CHO), has higher activation energies [19, 21, 22]. It is attributed to the high directionality of C-C bond σ-orbital in these molecules, which is constrained along the bond axis, and the several substituents (hydrogen and oxygen atoms) on both carbon atoms constraining sterically this bond, which makes the interaction

of the metal with this bond more difficult than with C-H single bond [72]. Probably, breaking of C-H bonds prior to C-C bond cleavage is required, thus the metal could interact with π-orbitals of double C-C bond, which are oriented sideway and have less steric constrains [72]. In fact, it is found that in hydrocarbon reaction on metal surfaces, molecules dehydrogenate before the cleaving of C-C bond [73].

Experimental works on ethanol oxidation reaction [62, 74–76] shows that ethanol oxidation involves dehydrogenation reactions, forming acetyl CH_3CO; this molecule could be further dehydrogenated forming CH_2CO and $CHCO$. In all the molecules, the C-C bond cleavage is more feasible, so it is worth to focus on them. The reaction for C-C bond cleavage in these CH_xCO molecules is written as follows

$$CH_xCO_{(ads)} \rightarrow CH_{x(ads)} + CO_{(ads)} \tag{5}$$

Linear relationship between products energy and transition state energy has been previously developed for this reaction [19, 22, 53, 77]. So, the activation energy would be related with the interaction of the surface with CH_x and CO molecules. It is expected that the trends in the reactivity do not changes with the molecule CH_xCO chosen, since the adsorption energy of the CH_x molecules is expected to be similar [53], that is, if rhodium has higher adsorption of CH than Ru, it would have higher adsorption energy of CH_2 and CH_3 than Ru. So, in this work, to study the C-C bond cleavage in the simplest molecule CHCO, also this step, according to previous works [19, 22], has the lowest activation energy for the C-C bond cleavage on different transition metals. The linear relationship [77], which will be used, is shown in Eq. (6).

$$E_{TS} = \alpha E_P + \beta \ with \ \alpha = 0.88 \ \beta = 1.07 \tag{6}$$

E_{TS} and E_P are, respectively, the transition state and product energies respect to the energy of reactants in gas phase and the clean slab. So, E_P is the energy involved to go from CHCO and the surface far apart to the CH and CO adsorbed on the surface that is expressed in Eq. (7)

$$E_P = E_{ads-CO} + E_{ads-CH} + E_{diss-CHCO} \tag{7}$$

Activation energy is expressed as in Eq. (2), in this case, E_R is the energy of *CHCO* adsorbed respect to the energy of reactants (CHCO) in gas phase and the clean slab, that is, the adsorption energy of CHCO. So, the final expression for activation energy, which states the relationship between catalytic activity and adsorption energy, is:

$$E_a = \alpha \left(E_{ads-CO} + E_{ads-CH} + E_{diss-CHCO} \right) + \beta - E_{ads-CHCO} \tag{8}$$

Considering that CO_2, which desorbs from surface easily, can be readily obtained from CO oxidation by OH, which is available in alkaline media and in acidic media can be obtained from water activation facilitated by oxyphilic atoms as Sn, Ru, and Mo [20, 75, 78, 79]. So, it seems reasonable to expect that in the appropriated conditions (alkaline media or oxyphilic metal as co-catalyst), the surfaces with higher CO formation also have higher CO_2 formation.

Therefore, the study of the C-C bond cleavage step can give enough information about which catalysts can helps to obtain higher CO_2. The reactivity of the surfaces for C-C bond cleavage is studied through DFT modeling of adsorption of CH, CO, and CHCO.

The adsorption energies of these molecules were calculated for different Pt_3M alloys (M = Sn, Re, Ru, Rh, and Ni). Since the alloys with this composition or lower content of M are commonly proposed as a convenient composition to improve the catalytic activity to ethanol oxidation in experimental studies [68, 69, 71, 80–82].

4.2. Calculation of reactivity descriptors

The adsorption energies of CH, CO, and CHCO are calculated using the slab model to represent the (111) facet of the face-centered cubic metals (Pt_3M) and DFT as is implemented in Quantum Espresso [83]. It used plane waves, exchange correlation energy described by Perdew and Wang (PW91) [84], and ultra-soft pseudopotentials [85]. Convergence was tested with respect to total energy for the Brillouin sampling and for the kinetic energy cut-off in the plane wave expansion, so 3 × 3 × 1 Monkhorst-Pack k-mesh [86] and the kinetic energy cut-off for the plane waves of 544 eV was used.

For slab construction, the lattice parameters obtained from geometric optimization with DFT was used. The effect of the size of the supercell has also been carefully tested for the adsorption energy. Increasing the supercell size from 2 × 2, which we have used, to 4 × 4 changes the adsorption energy by only 0.008 eV, so the description with 2 × 2 is considered good enough considering the computational cost of the simulation of large systems. Five layers of atoms were employed for representing the portion of solid and empty space of 9.00 Å was left above of the atomic surface to avoid self-interaction of the slab. With this empty space, the adsorption energies changed just 0.02 eV compared to the adsorption energies obtained using an empty space of 15.00 Å, indicating that the top of one slab has essentially no effect on the bottom of the next.

The adsorption energy was calculated as total energy of the slab with the i-species adsorbed $E_{i/s}$ minus the total energy of clean slab E_s and the i-species in gas phase E_i.

$$E_{ads-i} = E_{i/s} - E_s - E_i \qquad (9)$$

Adsorption of *CH*, *CO*, and *CHCO* were tested on several sites, atop sites (A-Pt and A-M), bridge sites (B-Pt and B-M), and hollow sites with and without an atom directly below in the subsequent layer, which are called HCP and FCC hollow sites (HCP-Pt, HCP-M, FCC-Pt, and FCC-M).

The most stable adsorption configuration for CO adsorption on Pt_3M is at atop site with molecular axis of CO normal to the surface and C atom bonded to the surface in agreement with the experimental findings for Pt-based catalysts [87]. The CO adsorption energies on A-Pt and A-M for the different surfaces are shown in **Figure 6**. It is found that CO adsorption energy on A-Pt sites in the alloys is reduced respect to pure Pt (dotted line) and it is more reduced when the metal atom adsorbs more strongly the CO molecule. Also it is remarkable that adsorption energy on tin atom is only −0.08 eV. It is in agreement with other works, which points out that Pt-CO binding is weakened in the PtM alloy [88–90], whereas the M-CO bond is strengthened with the presence of Pt and CO adsorption on tin is not stable [91–93].

The most stable adsorption configuration for CH adsorption on Pt$_3$M is at hollow site (both hollow sites have similar adsorption energy) with molecular axis of CH normal to the surface and C atom bonded to an atom on the surface in agreement with other theoretical studies [94–96]. It is noted in **Figure 6**, a trend similar to CO adsorption, adsorption on sites with only Pt in the alloy is weaker than pure Pt, whereas the sites with metal atoms have higher or similar adsorption energy than pure Pt with the exception of Pt$_3$Sn, which is significantly lower.

The most stable adsorption configuration for CHCO on the alloys (except for Pt$_3$Sn) and pure Pt is shown in **Figure 7**. In this geometry, the CH part is located at bridge position between M and Pt atom (B-M), whereas the CO part is located close to a Pt atom in a Pt-atop-like position (A-Pt). For both groups, the C atom is closer to the surface. This configuration is like other found in theoretical studies for transition metals [77, 97]. Other adsorption configuration is found when CHCO is close to hollow-Pt sites, except for Pt$_3$Rh, whose Pt sites have an adsorption configuration as the above described. In this configuration, the carbon atom linked to the hydrogen atom is bound to the surface in a bridge position between two Pt atoms (B-Pt), whereas the carbon atom linked to oxygen is far from the surface as is shown in **Figure 7**. This configuration was found in other work for metals considered inactive [97].

Adsorption energies of former configuration with CH and CO parts bonded to the surface ranges from −3.66 to −3.98 and C-C bond length is stretched by 0.20 ± 0.01 Å, whereas adsorption energies of last configuration ranges from −2.68 to −3.24 eV and C-C bond length is only
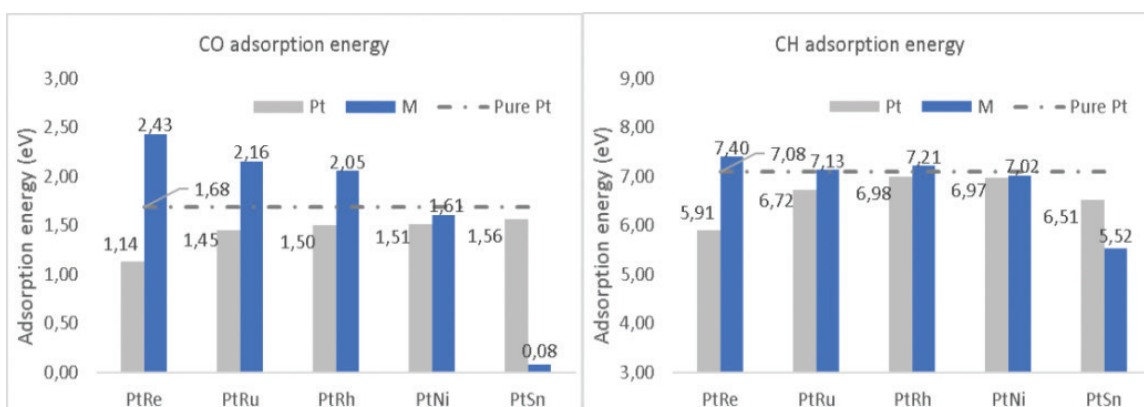
Figure 6. CO and CH and CHCO adsorption energies on Pt(111) and Pt$_3$M(111) surfaces.
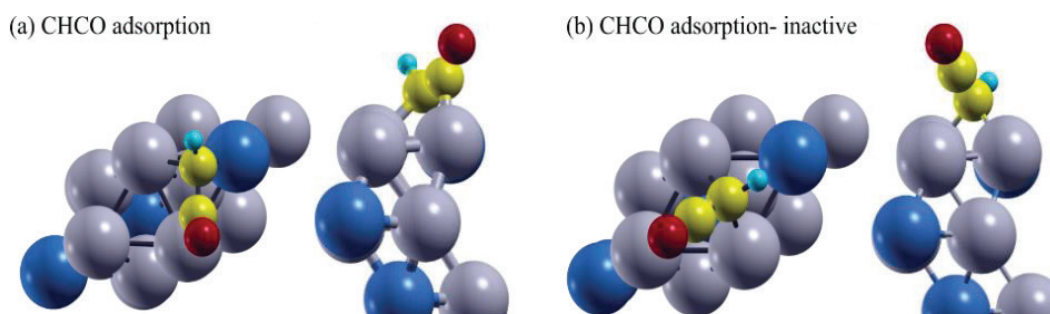
**Figure 7.** Geometric configurations found for CHCO adsorption on Pt$_3$M(111) surfaces.

stretched slightly by 0.08 ± 0.01 Å. So, the ensembles with only Pt atoms in Pt$_3$M (with exception of Pt$_3$Rh) have adsorption energies significantly lower than pure Pt and do not stretch significantly the C-C bond, whereas the ensembles with M atom have adsorption energies similar to Pt and stretch significantly the C-C bond. Indicating that the addition of M to Pt decreases the ability of Pt for interacting with CHCO and hence part of the alloy is inactive, except for Pt$_3$Rh.

Summarizing, the adsorption of CH, CO, and CHCO shows that the addition of M (M = Re, Rh, Ni, Ru, or Sn) to Pt leads to obtain two active sites with different reactivities. The Pt atoms in all these alloys form bonds with the described molecules weaker than Pt atoms in pure Pt, whereas the Re, Rh, and Ru atoms in the alloys have a stronger interaction with CH, CO, and CHCO than pure Pt. This difference explains that adsorption energies of CO on metal atoms in Pt$_3$M (M = Rh, Re, and Ru) are higher than Pt (111), whereas the adsorption energies of CH on sites with M atoms in Pt$_3$M (M = Rh, Re, and Ru) are similar to Pt (111), since CH interacts with two Pt and one M atom at hollow site. Then, the stronger interaction of mentioned M atoms should compensate the weaker interaction of Pt in these alloys.

Besides, Ni and Pt atoms in Pt$_3$Ni have slightly weaker interaction than pure Pt (111), so the adsorption energies at different sites in this alloy are slightly lower than pure Pt. On the other hand, Sn and Pt atoms in Pt$_3$Sn have a weaker interaction with the molecules than pure Pt (111), suggesting that Pt$_3$Sn has low catalytic activity toward C-C bond cleavage, confirming previous experimental and theoretical works that affirms that PtSn alloys have lower catalytic activity for C-C bond cleavage, but they increase the catalytic activity for EOR by promoting bifunctional mechanism and the pathway toward acetic acid [70, 98]. Other remarkable finding is the two configurations for CHCO adsorption, one of them destabilizes the molecule binding it strongly and stretching significantly the C-C bond (around to 0.20 Å) and the other is found in metals inactive, it suggests that part of alloy is inactive, except for Pt$_3$Rh.

The adsorption energies obtained can be related with activation energy for C-C bond cleavage through Eq. (8), only the active sites are considered since the linear relationship between ETS and Eads only have sense for them. As is can be expected from Eq. (8), the surfaces with higher adsorption energies of CH and CO have lower activation energy, that is the sites with Re, Rh, and Ru atoms, it can be observed in **Figure 8**, which shows the product energies E$_p$ (see Eq. (7)) and activation energies for the different active sites.

These results indicate that Pt$_3$Sn is the catalyst with the lowest activity for C-C bond cleavage, since in this alloy Sn has a weak interaction with all molecules studied and Pt atoms have a weaker interaction than Pt atoms in pure Pt (111). Also, it is expected that Pt$_3$Rh alloy has higher reactivity for C-C bond cleavage since all sites, sites with only Pt, and sites with Rh atoms have similar or higher reactivity than pure Pt. Whereas Pt$_3$Re and Pt$_3$Ru have a nonsignificant improvement of the reactivity with respect to pure Pt, since they have one site with higher reactivity (site with M atom) and other with lesser reactivity (site with only Pt atoms); between these ones, Pt$_3$Re has the most reactive site. Pt$_3$Ni has slightly weaker interaction with molecules than Pt. Consequently, the ranking from high to low reactivity for C-C bond cleavage is Pt$_3$Rh, Pt$_3$Re, Pt$_3$Ru, Pt, Pt$_3$Ni, and Pt$_3$Sn.
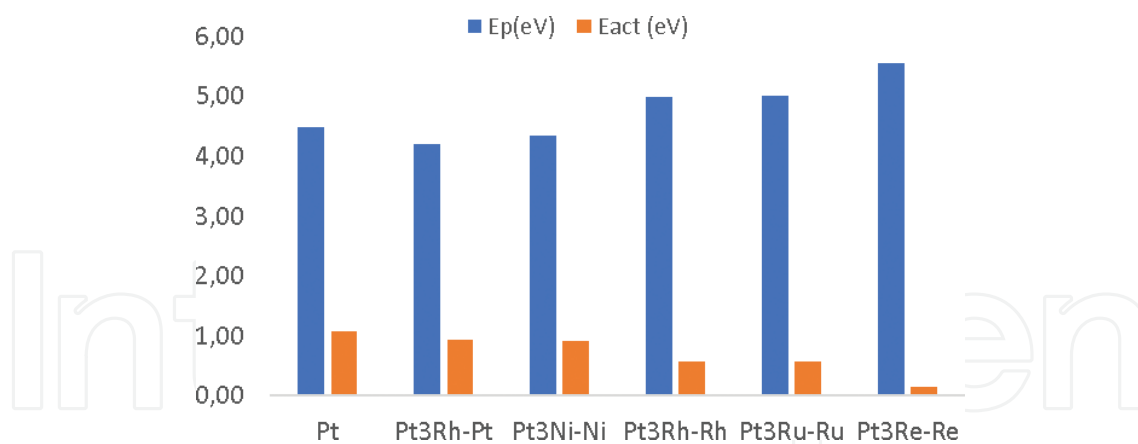
Figure 8. Final state energy (E_p) relative to reactants (CHCO) in gas phase and clean slab and activation energy on the different surfaces sites found active.

This trend agrees with previous experimental results, where it is reported that Pt-based alloys with rhodium (PtRh and PtSnRh) show a production of CO_2 higher than Pt and Pt alloys [69, 99]. In contrast, addition of Rhenium to Pt improves performance for C-C cleavage, but this improvement is not much higher, it is reported that Re addition to Pt improves the acetaldehyde decomposition, increasing the produced CO (product of C-C bond cleavage) from 10 to 18% [100]. On the contrary, it is reported that Sn addition to Pt decreases the CO_2 product respect to Pt [70, 98]. But the PtSn alloys are recognized as the better catalyst for EOR, where the enhancement of the activity with this alloy is attributed to the promotion of bifunctional mechanism promoting the acetic acid production.

Due to mentioned issues, different authors propose materials with Pt, Sn, and Rh as effective catalysts in splitting the C-C bond and oxidizing intermediates molecules of EOR via bifunctional mechanism. This mix in the appropriate composition will provide high overall conversion of ethanol and higher selectivity to CO_2 than Pt. However, the selectivity can be considered low and the total conversion to CO_2 remains elusive. It can be attributed to the presence of oxidants as OH, which should promote the oxidation of intermediates to acetic acid and decreases the C-C bond cleavage rate [101]. But the unavailability of oxidants limits the conversion of CO to CO_2, poisoning the surface. Finding a better catalyst for EOR requires considering, in addition of C-C cleavage, the step of oxidation to produce acetic acid and the dehydrogenation step.

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