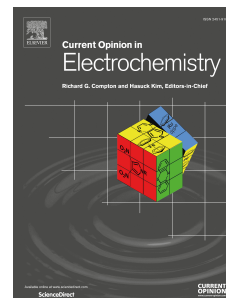


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## The role of adsorbates in electrocatalytic systems: an analysis of model systems with single crystals.

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### SUMMARY

The use of single crystal electrodes as model catalysts has been widely applied for the study of several reactions. The known structure of the surface provides a system with controlled electronic properties that helps in the understanding of the mechanism of reactions. In this model system, any modification, including the adsorption of anions, organic molecules or foreign atoms, generate changes in the electronic properties of the surface and, thus, in the adsorption energy of the species involved in the studied reaction. The adsorbate can hinder the surface and diminish the activity or prevent the oxidation of the surface and improve the catalysis. The changes in electronic properties can modify the adsorption energy and enhance or worsen the catalytic activity. The effect of any adsorbed species will depend on the structure of the surface, the nature of the species and the studied reaction.

### INTRODUCTION

A fundamental question in designing high-active solid catalysts to use industrially is to understand the complex relationship between composition, surface structure and final activity. The strategy of controlling these variables as much as possible and, thus, understanding the role that each one can play in the catalytic system, has been successfully done by the use of well-defined and uniform surface structures: **the single crystals**. Used as model catalysts over the last 40 years, single crystals have been extensively applied to widen our knowledge about many reactions of technological interest, demonstrating their importance to the development of heterogeneous catalysis [1].

Experimentally, single crystals have unique advantages, which ensure the preparation and control the surface structure and, therefore, focusing only in studying the catalytic process: the formation of side products and adsorbates that govern the general reaction mechanism. Studies using single crystals can bring insightful information about the mechanism of the reaction, with some discrimination of the

electronic and geometric effects in the overall behavior, although difficult to evaluate them separately, because there is a mutual influence [2].

In this respect, adsorbates, when specifically adsorbed, can affect the catalytic process in many different ways. For instance, adsorbed ions, metals or molecules can modify the adsorption energy of adjacent sites or act as a poison blocking active sites or promoters of catalytic reactions [3]. Adsorbates can also cause surface restructuring or even changing the work function of the electrode and consequently the potential distribution across the interface [4,5]. Considering that all these effects can simultaneously influence an electrochemical process, the role of ad-species in electrochemical reactions is of fundamental importance if one wants to understand and extend the findings to practical catalysts [1,6,7].

Therefore, we will visit some of the latest works and other important references that deal with the surface modification of platinum single crystal electrodes by ions, organic molecules and metal atoms adsorption and their electroactivity towards some electrocatalytic reactions. We will try to illustrate to which extent such surface modifications on well-ordered surfaces can bring new insights about the intricate relations between the reaction parameters, and how we are using them to make a bridge from surface-science models to the real-world catalysts.

### **Surface modification by anionic species**

In the electrochemical environment, the presence of ions is essential to electron transport. These ions, under the effect of an external potential input, can move towards or away from the surface of the electrode and, aside from taking part of the double layer building up, ions could form chemical bonds with the metal surface, transferring partially their charge and consequently resulting in dramatic changes in the overall electrode/electrolyte interface composition [8].

Such changes are easily observable in the cyclic voltammogram (CV) profiles in the presence of only bulk electrolytes containing anions with different adsorption strengths (Figure 1A). For platinum surfaces, where processes of adsorption/desorption of hydrogen and hydroxyl species can take place, the CVs are strongly affected by the anions. The degree of adsorption strength to transition-metal surfaces was reported by Conway to follow the order:  $F^- < ClO_4^- < SO_4^{2-} < Cl^- < Br^- < I^-$ , which are intimately related to their solvation sphere energy [9].

For non-coordinating anions, as  $ClO_4^-$ , the CV profile is considered just to be the response of the adsorption/desorption processes of  $H^+$  and  $OH^-$  species. In principle, the anion only participates of the water double-layer in the outer Helmholtz plane region (OHP). For halides other than fluoride, however, due to their weak

solvation sphere, these anions are strongly adsorbed onto metal surfaces, particularly at potentials more positive than potential of zero total charge (pztc) [8,10].

In the case of processes that occur through electrocatalytic inner-sphere electron transfer mechanism and at potentials far beyond the pztc, such as oxygen reduction reaction (ORR), organic molecules oxidation, oxygen evolution, among others, the utmost importance of the adsorbed anion on the catalytic surface can be observed [3,11].

Oxygen reduction reaction (ORR) has been widely studied on single crystal electrodes offering an extensive material to evaluate the role of anions in the mechanism. Figure 1B depicts the influence of anions with specific adsorption behavior on the overall reaction. Since the chloride ions bind strongly to Pt surface atoms resulting in a stable adlayer, the onset of ORR shifts to higher overpotentials. Incidentally, the formation of anion adlayers is also structure sensitive, leading to different anion coverages and inducing different changes of reaction mechanisms [3].

In fact, since we are dealing with species that compete for free surface sites, the expected result is the inhibition of the overall reaction rate. However, sometimes, the opposite is observed. Gomez-Marin *et al.* [12] showed a higher ORR activity on Pt(111) modified by a submonolayer of Te adatoms in 0.05M H<sub>2</sub>SO<sub>4</sub> electrolyte when compared to bare Pt(111). The intriguing result is discussed in terms of the chemical nature of the adsorbing anion and not its adsorption strength, since the Te adatoms also inhibit the ORR kinetics. A similar finding was reported by Ciapina *et al.* [13], but changing the electrode surface coverage by cyanide ions.

A behavior different than expected was observed by Souza-Garcia and co-workers for nitrate reduction on Pd modified Pt(110) electrodes [14], in which an increase in activity when H<sub>2</sub>O is replaced by D<sub>2</sub>O. This increase is 10 times higher if H<sub>2</sub>SO<sub>4</sub> is chosen as electrolyte instead of HClO<sub>4</sub>. Changes in hydration energy due to the substitution of water for heavy water lead to a different adsorption energy of sulfate, interfering in the competition with nitrate for active sites on the surface.

One of the most frequently studied poisons in Electrocatalysis is carbon monoxide (CO) and its oxidation reaction is also influenced by the presence of the anions in the electrolyte. CO molecule adsorbs very strongly on Pt surfaces and competes for free surface sites and also inhibits the adsorption anions [11,15,16]. The effect of anion adsorption strength becomes clearer when we examine the cyclic voltammograms profiles of continuous CO oxidation on Pt(111) electrode in different saturated CO electrolytes (see Figure 1C). Note that the ignition peak of CO oxidation reaction shifts to higher potentials following the anion adsorption strength. Once the reaction begins, the competition for free sites is fierce between the anions and the



carbon monoxide; bearing in mind the whole process is occurring at potentials far from the pztc. The presence of  $\text{Cl}^-$  blocks Pt sites hindering CO adsorption and also the formation OH adsorbed species, necessary to CO oxidation, what leads to a low current density after the ignition peak [15].

This behavior is particularly important analyzing the oxidation of small organic molecules on platinum surfaces, which are believed to proceed through CO as intermediate [16]. For methanol electrooxidation Iwasita *et al.* [17] pointed out that the strongly adsorbed anions not only block Pt sites, consequently precluding the methanol adsorption, but also decrease the amount of adjacent sites, disfavoring pathways which involve several free sites, as the complete oxidation to  $\text{CO}_2$  from CO. In line, Fiori *et al.* [18] showed the influence of chloride and bromide in the oscillatory behavior during methanol electrooxidation. Since the reaction parameters are strongly dependent on the system set up, as the nature of anion and CO coverage, the presence of halides changes the reaction pathways, resulting in deep changes in the oscillation behavior.

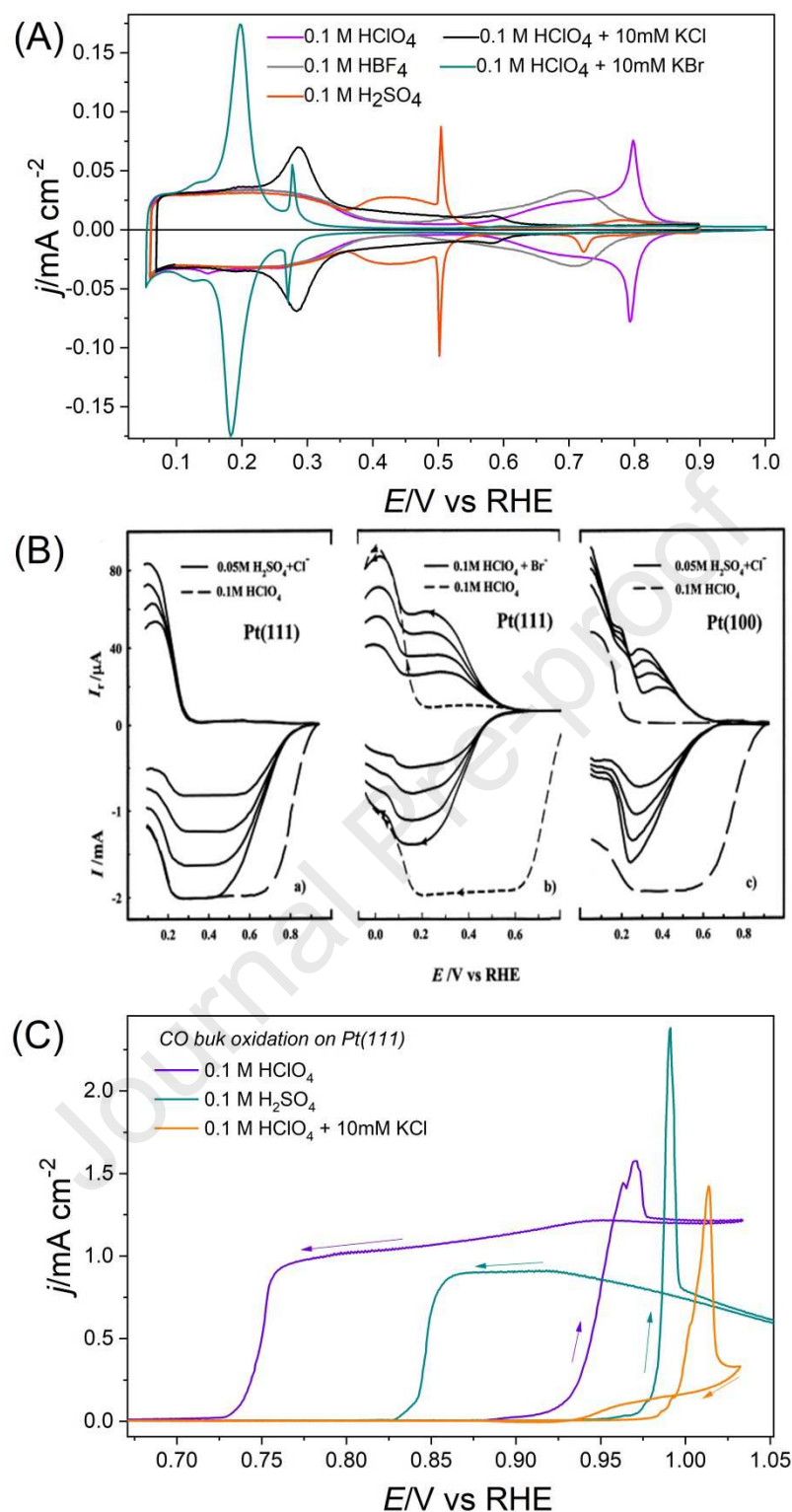


Figure 1: A) Cyclic voltammogram of Pt(111) in the presence of different anions [8]; B) ORR on Pt(111) and Pt(100) (from V. Stamenkovic *et al.*, *J. Electroanal. Chem.*, 500 (2001) 44–51 with permission [19]); C) CO bulk oxidation on Pt(111) in the presence of different anions (adapted from Angelucci *et al.*, *Electrochem. Commun.* 9 (2007) 1113–1119 with permission [15]).

In summary, the complexity of an electrochemical reaction catalyzed by the electrode surface should be evaluated in terms of the co-adsorption of the ionic species intrinsically present in the electrochemical environment and the reactants/intermediates. Although not addressed, the physisorption of water molecules should always be considered in any evaluation of electrochemical processes that take place in aqueous environments [20,21].

### **Surface modification by neutral molecules**

Studies involving the behavior of organic molecules adsorption under potential control is of fundamental importance in electrochemistry. At platinum single crystals, the adsorption of organic molecules can also build up a structured adlayer. The formation of an organic adlayer on electrodes induces severe changes in their interfacial properties. Taking the CO oxidation as the simplest example of a reaction mechanism on transition metals, the literature offers extensive material covering several aspects, spreading from the CO-metal interaction, CO stripping reaction and the generation of CO as intermediate species from other molecules [11,16]. Among them, the formation, stability and behavior under external perturbation is a central subject in many research groups. Figure 2 illustrates the behavior of the adlayer of CO on Pt(111) at different potentials [22]. Wei *et al.*[22], using scanning tunneling microscopy (video-STM), obtained images of CO adlayer at atomic scale on millisecond time scales. The study confirms the general consensus on the CO adlayer structure but, additionally, brings new information about the mobility of CO on the electrode surface [23,24]: the adsorbed CO has high mobility on the electrode surface, which provides an effective mixing between CO and its reaction pair ( $\text{OH}_{\text{ads}}$ ), in accordance with the Langmuir-Hinshelwood type reaction [16] proposed electrochemically [25].

In line with the previous works, Fang *et al.*[26] have applied successfully a method which combine computational tools of vibrational spectroscopy with electrochemical models of eletroodic interfaces to elucidate the CO oxidation mechanism by predicting IR and Raman spectra of CO adlayer on Pt(111) surfaces system. In consonance, but using in-situ electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) Su *et al.* [27] found direct evidence of adsorbed intermediate species as OH and COOH during CO electrooxidation, elucidating the mechanism as well as the role of the surface orientation on intermediation formation.

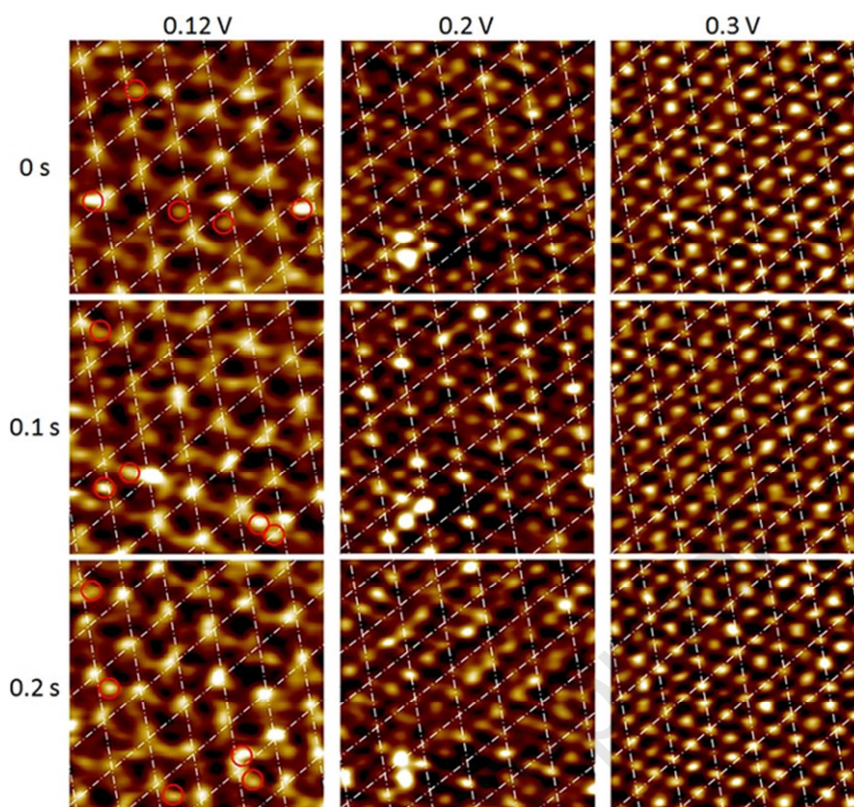


Figure 2: Subsequent images of CO adlayer on Pt(111) in CO-saturated 0.1M H<sub>2</sub>SO<sub>4</sub> at different potentials (from Wei *et al.*, *Angew. Chem. – Int. Ed.*, 59 (2020) 6182-6186 with permission [22])

The adsorption of more complex organic molecules on well-ordered surfaces have shown that they can alter the adsorbed water structure on the surface and also the vacancy density of the d-band of the metal catalyst. It influences the adsorption of concurrent species for free sites, for instance O<sub>2</sub> molecule in the ORR mechanism or CO during small organic molecules oxidation.

The interaction of acetonitrile with platinum surfaces is one example of how an organic molecule can influence the electrocatalytic process. The surface modification by its adsorption was studied for ORR on platinum electrodes [28,29]. In general, by combining the results obtained from DFT calculations with the results of cyclic voltammetry, it has been shown that the adsorption of acetonitrile inhibits significantly the ORR kinetics by hindering hydrogen adsorption and surface oxidation on Pt. On the other hand, for formic acid oxidation, the irreversible adsorption of acetonitrile increases the activity of Pt electrodes, with a shift of the onset potential to less positive potentials and an increment of current. This behavior was attributed to the inhibition of CO formation due to the blockage of Pt sites by acetonitrile[30]. Also, acetonitrile

seems to act as adatoms, changing formic acid adsorption mode and facilitating C-H cleavage to yield CO<sub>2</sub>.

The influence of adsorbed neutral molecules with high molecular weight on ORR was explored by Hoshi and co-workers. The authors studied the effect of the irreversible adsorption of aromatic organic molecules [31], melanine [32] and alkyl amines [33,34] on Pt single crystal electrodes. The presence of those molecules, in general, leads for the increase in ORR activity after modification. The adlayer formation is structure sensitive and dependent on the width of terrace sites and also the orientation of the step sites.

All in all, it is clear that the electrocatalytic effect depends on the nature of the adsorbed organic molecule and on the desired surface reaction that would be electrocatalyzed.

### **Surface modification by admetals**

The modification of platinum surfaces by foreign atoms is generally applied to increase surface selectivity towards the desired reaction. As in the case of anion and organic molecules, the adsorption of foreign atoms on the surface of metal electrodes will generate changes in the electronic properties of the surface, with modification of the d-band vacancy density leading to different adsorption energies [2]. Due to the new properties, the modified surface may change the reaction mechanism. Furthermore, the electrocatalytic properties are dependent on the extension of the adlayer: while the atoms from the first layer have the electronic properties influenced by the substrate, atoms from the second or third layers will be less and less impacted [6].

Usually, the goal is to investigate if substrate and adatom participate in a bifunctional mechanism, e.g. with one atom being responsible to provide oxygenated species and the other adsorbing the studied molecule. This mechanism can only be observed if the modification is below monolayer, allowing sites of both metals to be available in neighbor positions on the surface. Atoms in the middle of an island would not participate in this mechanism. In this respect, discussing the activity of modified electrodes only in terms of bifunctional mechanism may be an oversimplification of the observed phenomena.

The decoration of the surface with metal adatoms can take place in different ways, depending on the surface structure of the substrate and nature of the adsorbed species. The modification usually starts with the formation of islands of atoms and can evolve to 3D islands or to the formation of a complete monolayer [6,35,36]. The construction of the subsequent layer can occur before the first one is complete. Also,



the presence of defects facilitates deposition. Each deposition site leads to different modifications in electronic properties and structure of the surface, impacting the overall electrocatalytic activity [37]. This situation generates surfaces with different electronic properties. In Figure 3 some typical adsorption configurations are shown [37].

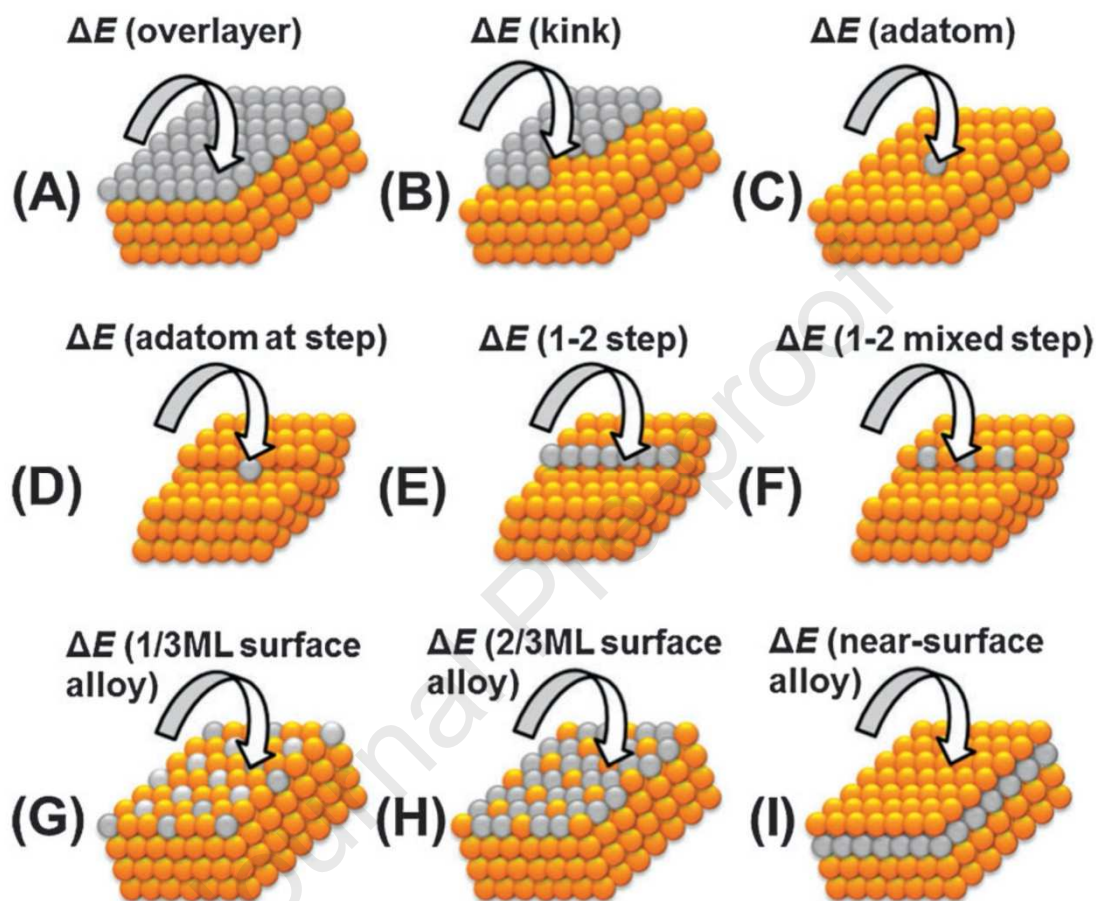


Figure 3: Schematic drawing of typical adsorption configuration of adatoms (From Calle-Vallejo *et al.*, *Chem. Soc. Rev.*, 42 (2013) 5210-5230, with permission [37])

Different adatoms have been used to decorate platinum single crystal electrodes for several reactions, e.g. nitrate reduction reaction [14,38–45], ORR [12,46], organic molecules oxidation [47–55], among others. The influence of adatoms depends on the substrate, the adatom and the studied reaction and no straightforward conclusion can be made from the available results. Some results of CO oxidation on Pt(hkl) modified with ruthenium atoms can be cited as an example. Ruthenium is one of the most studied metals to decorate platinum electrodes, including single crystals [47,51,56]. The effect of Ru atoms in the activity of Pt electrodes towards the oxidation of small organic molecules has been known since the 70s [57] and still today experiments are designed to understand its contribution in electrocatalytic

mechanisms. Farias *et al.* [49] observed that Ru and Sn increase the activity of Pt(111) sites towards CO oxidation, but no improvement in the catalytic behavior of Pt(110) was observed, even a slight decrease for Sn on Pt(110) sites [49]. Since the authors were able to identify the sites where CO oxidation was taking place, they suggested that the bifunctional mechanism could not be used to explain the observed effect. The bifunctional mechanism for the oxidation of CO molecules was demonstrated by Zhuang *et al.* [56] using a STM configuration, physically separating the Pt(111) surface from Ru atoms (tip), but the authors did not discard the presence of other oxidation mechanisms in this system. Either way, the improvement of CO oxidation on some surfaces gives Ru the ability to facilitate the oxidation of small organic molecules on Pt, avoiding CO poisoning [47,49], but the bifunctional mechanism cannot be used universally.

Several combinations of platinum electrodes and adatoms have been proposed as catalysts to many reactions. This is a common approach to determine ideal electrocatalyst composition to a specific reaction. However, the discussion of the results not always addresses the electronic changes and its influence in the adsorption energies of the reactant species and the improvement in catalytic activity is usually attributed to the bifunctional mechanism. The use of single crystals as substrates to investigate the electronic properties of the surface in the presence of these adatoms is necessary for understanding the mechanism under well-defined conditions, to extrapolate the results to more commercial catalysts.

## Conclusion

We have reviewed some recent studies using single-crystal electrodes that have been used to rationalize experimental results and have contributed to understand electrocatalytic reactivity. We have addressed our attention to analyze the main results involving one of the fundamental processes that occurs on the catalytic surface: the adsorption. The formation of a stable adlayer on well-ordered surfaces formed by charged electrolyte species, metal adatoms or neutral organic molecules encompassed the majority of the examples that inherently take place in heterogeneous catalysis. The structural and electronic changes that these species can provoke on the surface are reflected in the electrodic reactivity. In summary, although the strategy of using single crystal electrodes goes back to the 1980s, we have shown that in the course of the following decades their use in experimental and theoretical approach have helped us to understand the variables present in complex heterogeneous electrocatalysis processes appearing in solid/liquid interfaces.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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As corresponding author I state that all authors have contributed equally in the conceptualization, CAA and JSG have contributed equally in the, writing – original draft, and JMF have contributed in writing – review & editing and supervision.

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