On the oxidation mechanism of C1-C2 organic molecules on platinum.

A comparative analysis.

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Abstract

The rationale design of better electrocatalysts for the oxidation of C1-C2 organic molecules requires the detailed knowledge of their oxidation mechanism. Pt single crystals are powerful tools to study, in a simple way, the surface structure effect on the different reaction pathways. Here, the oxidation mechanism of these molecules is compared so that the knowledge gained with the simpler mechanism is transferred in the analysis of the more complex ones. The goal is to design strategies so that the platinum electrodes improve their performance in their oxidation by the appropriate modification with other elements by attacking the bottlenecks in the reaction mechanism.

Highlights

- Similarities and differences between the oxidation mechanisms of C1-C2 molecules are highlighted.

- The active pathway of formic acid oxidation through CO_2 requires the adsorption of monodentate formate.

- A surface covered by adsorbed OH is required for methanol and ethanol oxidation reactions.

- Greater reactivity towards the C—C cleavage by partially oxidizing the α carbon of ethanol molecule.

1. Introduction.

Small organic molecules, especially those C1 and C2, have been proposed to be used as combustible in fuel cells to generate electricity from the chemical energy stored in their bonds. Those molecules present the advantage with respect to hydrogen that can be obtained from renewable sources, i.e., biomass and they are liquids that can be distributed using the present network used for the oil products. However, the overpotentials for the oxidation reaction of these molecules on the available electrodes is significantly higher than that measured for the hydrogen oxidation reaction, which diminishes the efficiency of these devices. For this reason, additional research is required in the quest of more efficient electrocatalysts. To reach this goal, a detailed mechanism for the oxidation reaction is required, so that the elemental steps are identified, and the key factors governing the electrocatalysis are known. The oxidation mechanism of these molecules shares many common elements, and the knowledge acquired in one can be transferred to the other and better practical electrocatalysts can be prepared in rational way.

From all the C1-C2 molecules, formic acid is the one that presents the simplest mechanism in the oxidation to CO_2. This process involves the exchange of 2 electron and 2 protons. From a chemical point of view, the oxidation reaction requires the cleavage of a C—H and an O—H bond. Pt and Pd electrodes have been shown to have a good performance for the formic acid oxidation reaction (FAOR) [1,2]. The main characteristic of these metals is their affinity for hydrogen, which is readily adsorbed on these surfaces.

The next molecule in the series is methanol. In this case, the complete oxidation (which involves the exchange of 6 electrons) requires not only the cleavage of several bonds, but also the formation of new ones. Thus, three C—H bonds have to be cleaved

and also an O—H bond in the alcoholic group. On the other hand, a new C—O bond has to be formed so that CO_2 is obtained. The increasing complexity of this reaction is translated to the practical results [3], and thus oxidation currents are smaller and the overpotentials are higher than those measured for formic acid.

The equivalents for formic acid and methanol in C2 molecules are acetic acid and ethanol. The complete oxidation to CO_2, in which 8 and 12 electrons are transferred, respectively, involves an additional step not considered in the previous oxidation mechanisms, the C—C bond cleavage, which appears to be the most difficult step [4–6]. In fact, acetic acid is stable on platinum at room temperature and it is only oxidized at very high potential [7]. On the other hand, when the oxidation of ethanol is considered, a mixture of acetaldehyde, acetic acid and CO_2 is obtained, depending on the operating conditions and the electrode properties. The formation of species different from CO_2 implies the diminution in the efficiency of the reaction, since the formation of acetaldehyde or acetic acid involves the transfer of 2 and 4 electrons, respectively.

All these C1-C2 molecules share common characteristics and therefore the knowledge acquired when studying one of these molecules can be applied to the other molecules. One of the shared features of all the mechanism is the existence of several pathways in the reaction mechanism, which make difficult to identify the key elements in it. In fact, the FAOR, which has the simplest reaction mechanism, already have a dual pathway: the direct path involves an active intermediate whereas the secondary path implies the formation of adsorbed CO as intermediate species, which act as a poison [8]. Despite all these common features, the translation of the knowledge from one to the other is not straightforward and has to be adapted to the specific properties of the studied molecule. In this review, the similarities, and differences between the oxidation of these molecules will be highlighted so that a better understanding of the oxidation

mechanisms can be achieved, with the final aim of synthesizing tailored anode electrocatalysts for fuel cells.

2. The formic acid oxidation reaction (FAOR).

In principle, any oxidation mechanism that involves the exchange of two electrons, such as that of formic acid, should be simple. However, as will be shown, several complications appear in the formic acid oxidation mechanism. As aforementioned, the oxidation requires the cleavage of two bonds. The first one, the O—H bond breaking is a trivial step because it is involved in the acid base equilibria of the molecule. In fact, formate has been identified as the active species in the reaction [9–12], and thus, the only relevant bond that has to be cleaved is the C—H bond. The knowledge gained in the last years about this reaction has increased significantly using the combination of experimental and theoretical results and has been able to establish the rate determining step in the reaction. These results have been reviewed in previous articles [2,13,14] and here, the most important features will be summarized. First, it is clear that the effective cleavage of the C—H bond requires the adsorption of the molecule in the right configuration, that in which the H atom can interact with the surface. However, the most stable adsorbed configuration of formate, the bidentate form (figure 1A), has been shown to be inactive for the oxidation [11,12,15] because the H atom is far from the surface and thus, the kinetic barrier for the cleavage of the C—H bond is very high (Figure 1A) [2,16].
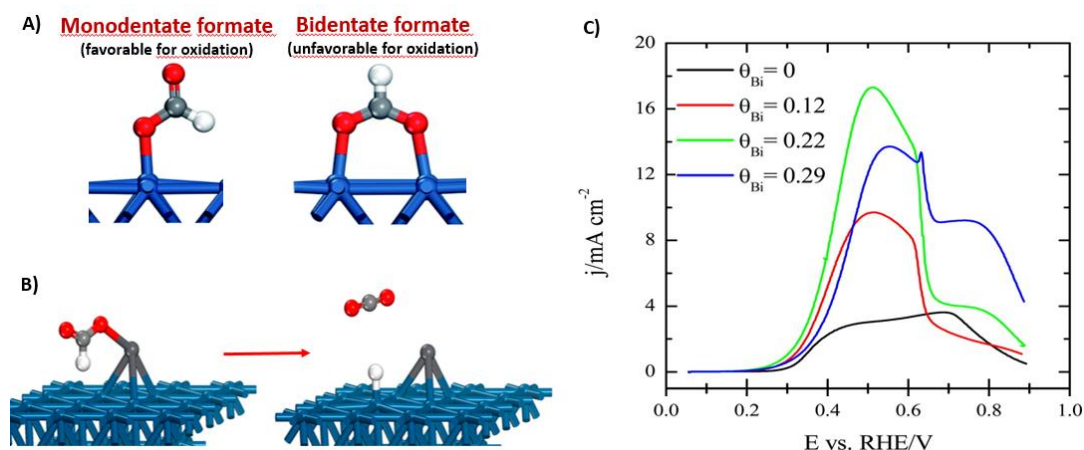
Figure 1. A) Monodentate and bidentate adsorbed formate on a platinum single crystal. Adapted from ref. [2]. B) Geometries of the HCOO fragment chemisorbed on the adatom–Pt(111) surface and the final products yielded from the formic acid oxidation. Adapted from ref [17]. C) Voltammetric profiles for the Bi–Pt(111) electrode for different bismuth coverages in a 0.5 M H_2SO_4 + 0.1 M HCOOH solution at 25 °C. Scan rate: 50 mV s^{-1}. Adapted from ref [17].

The activation of the C—H bond, then requires that formate is adsorbed in a monodentate configuration (Figure 1A) [11]. In this position, the C—H bond can point to the surface so that the interaction of the hydrogen atom with the surface cleaves the bond in a barrierless step, as DFT studies demonstrate [11,16]. To maintain the formate adsorbed in this configuration and preventing the evolution of this adsorption mode to the most stable one, the bidentate formate [2,11], additional adsorbed anions [18–20] or adatoms of the p-block are required [17,21,22] because they prevent the evolution of the monodentate form into the most stable bidentate adsorbed form. If this monodentate form is favored, the reaction rate is very fast and this reaction path is going directly to CO_2 formation, leading to high formic acid oxidation currents (Figure 1B-C) [17]. In fact, under these conditions, the rate is limited by the availability of adsorption sites because is independent of the formate concentration [12].

However, the reaction has a second path in which adsorbed CO is formed and then oxidized at high potentials [23]. In this case, the formation of CO is an unwanted

outcome, because it acts as a catalytic poison. The analysis of the kinetics of both paths, the direct one and that going through CO indicates that the rate of the CO path is at least two orders of magnitude lower than that of the main path [11]. Despite this much lower reaction rate, the accumulation of adsorbed CO on the surface eventually controls the reaction rate because it blocks the surface and prevents the adsorption of formate in the monodentate configuration. This effect highlights the importance of side paths in the overall performance of the reaction.

3. Methanol oxidation reaction (MOR).

Following the same scheme as that used for the FAOR, the first step would be to determine whether there is a strong interaction of methanol with the surface, because this interaction is required for an effective catalysis. For formate, the detection of adsorption modes was possible using Fourier-transform infrared spectroscopy (FTIR) in the total attenuated reflection (ATR) mode [10,24,25] or voltammetry at high scan rates [12,26]. In this case, since methanol oxidation currents are significantly smaller, the voltammetric profiles obtained in solutions with low methanol concentration can be used for that. In perchloric acid solutions, the results indicate that methanol does not adsorb on the surface, at least in the low potential region (figure 2A). In fact, the hydrogen adsorption profile in this region is exactly the same as that obtained in its absence during the first scan for platinum single crystals [27].
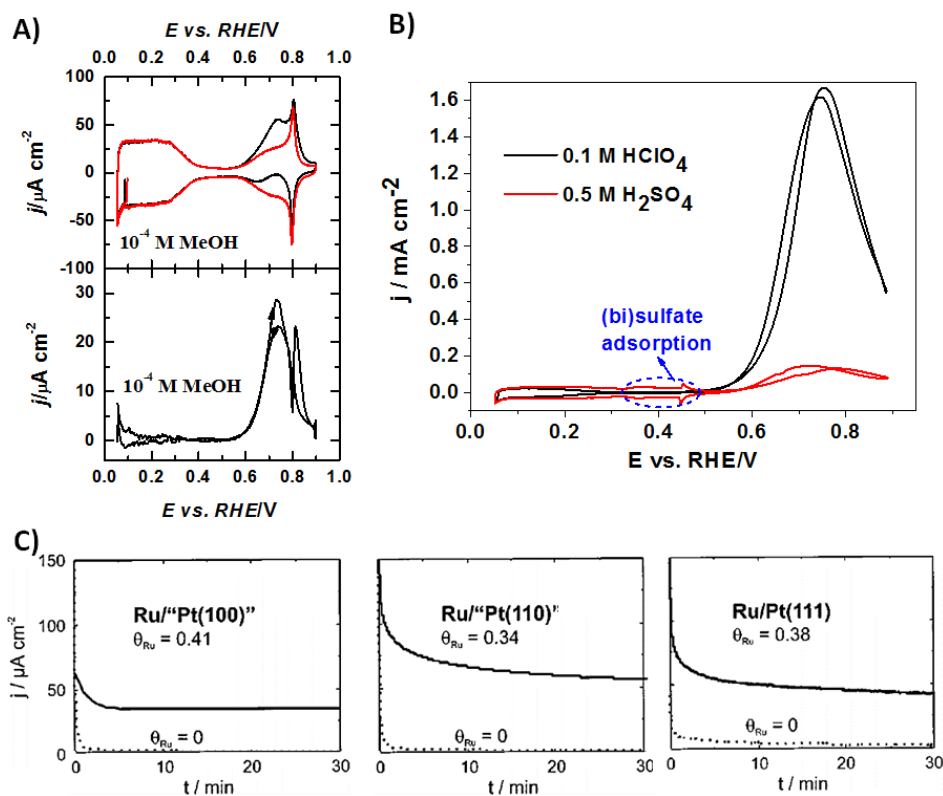
Figure 2. A) Voltammetric profiles of the Pt(111) electrode in 0.1 M HClO$_4$ + 10^{-4} M MeOH. The red trace shows the profile in absence of MeOH. Subtraction of the profiles in bottom panel. Scan rate: 50 mV s^{-1}. Adapted from ref. [27]. B) Voltammetric profiles of the Pt(111) electrode in 0.5 M MeOH + the respective electrolyte. Scan rate: 50 mV s^{-1}. C) Chronoamperometric curves recorded at 0.3 V vs. Ag/AgCl for Pt (100), Pt (110) and Pt(111) in 0.1 M HClO$_4$ + 0.6 M MeOH before and after Ru deposition. Adapted from ref. [28].

Probably, the best example is the Pt(111) electrode, which displays very small currents for low methanol concentrations (figure 2A) [27]. Under these conditions, only small currents are observed above 0.6 V when OH is adsorbed on the surface, whereas the rest of the voltammetric profile during the first scan coincides with that obtained in the absence of methanol. A similar situation is observed for the Pt(100) electrode for potentials below 0.4 V [27]. The absence of changes in the profile in the presence of methanol indicates that the interaction of methanol with the surface is weak. Indeed, when strongly adsorbed anions are present in the electrolyte, such as sulfate or phosphate [29], currents diminish significantly, even for relatively high methanol

concentrations and the typical profile observed in the absence of methanol is superimposed to the small methanol oxidation currents. Thus, the typical phase transition in the adsorbed sulfate layer on the Pt(111) electrode can be still observed in the presence of methanol (figure 2B), implying that the presence of methanol has not disturbed the adsorption of sulfate [30–32]. The large decrease in the currents in the presence of specifically adsorbed anions and the observation of the typical features of the supporting electrolyte clearly implies that the interaction with the surface is very weak, which makes the electrocatalysis more difficult.

The second important consequence of the previous results is that the oxidation of methanol requires a surface covered by adsorbed OH. Having this result in mind, and considering the dehydrogenation capabilities of platinum shown with the FAOR, it can be proposed that the oxidation mechanism starts with three dehydrogenation steps to form adsorbed CO. Moreover, it has been shown on a cyanide-Pt(111)-modified electrode that the indirect pathway through adsorbed CO is a site-demanding process that requires wide atomic arrangements with at least three contiguous atoms of platinum [33]. Then, this adsorbed CO is oxidized through the well-known Langmuir-Hinselwood mechanism with the aid of adsorbed OH. This would explain the necessity of adsorbed OH. However, the results indicate that adsorbed OH not only is required for the oxidation of CO but also for additional steps. First, the kinetic analysis of transients shows that CO is only formed on Pt(111) and Pt(100) at $E > 0.6$ V and $E > 0.35$ V, respectively [31]. Both potentials coincide with the onset of OH adsorption. Second, the observed kinetic isotopic effects using CD_3OH imply that the cleavage of a C—H bond is involved in the rate determining step [29]. All these results point out the importance of adsorbed OH on the surface for the dehydrogenation steps, which are a bottleneck in the reaction rate. This will also explain the significant diminution of the oxidation

currents in the presence of adsorbed anions, such as sulfate or phosphate [29], because these anions hinder the adsorption of OH.

The previous discussion implies a change in the paradigm in the methanol oxidation mechanism. When trying to identify the mechanism by DFT modeling, the model surface for the calculation of the different elemental steps have been always a clean surface in the absence of any adsorbate [34,35]. However, these results point out to the necessity of adsorbed OH in the platinum surface. Thus, any reliable model should contain some adsorbed OH species on the interface, so that the interaction of these species with the incoming methanol molecules can be analyzed and considered on the mechanism. In fact, the presence of adsorbed OH can explain the differences between the behavior of methanol in UHV and water environments [36,37]. Previously, the origin of these differences was assigned to the presence of water that may alter the interaction of the methanol molecules with the platinum surface [37]. However, the main difference is the surface state, whereas a clean surface is used in UHV studies, in electrochemistry, the surface state when methanol oxidation takes place is different, because it is covered by OH. In this sense, the bimetallic combination PtRu has been shown to be a promising anode catalyst material owing its greater performance for MOR and the electrooxidation of CO (Figure 2C) [28]. The improved electrocatalysis has been explained by a bifunctional mechanism, in which the higher affinity of Ru for OH promotes the oxidation of CO [28,38,39]. From the above results, Ru atoms will not only help in the oxidation of CO, but also may play an important role in the dehydrogenation steps, since OH is required.

4. Ethanol and ethylenglicol oxidation reactions (EOR and EGOR).

The EOR at low temperatures have two possible final products. The first one is CO_2, which implies that the C—C bond has been cleaved. The second one is acetic acid, which maintains the C—C bond intact. To obtain the maximum energy from the reaction, that is, the 12 electrons that can be finally exchanged, the cleavage of the C—C bond is required. However, this step is the most difficult one, because the main products of the oxidation at room temperature are acetic acid or acetaldehyde (the previous step in the formation of acetic acid).

When studying the reaction in acidic solutions on Pt(111) electrodes, no CO_2 can be detected on defect-free electrodes [4,40], implying that defects are involved in the cleavage of the C—C bond. On the other hand, in perchloric acid, the initial currents in the transients for the oxidation of ethanol are very high for E > 0.6 V [4], where OH is adsorbed on the electrode surface. This fact indicates that the oxidation of ethanol to yield acetic acid is very active in this potential region. The reaction to form acetic acid requires the transfer of an oxygen group, which is facilitated by the presence of adsorbed OH through a Langmuir-Hinselwood mechanism. Thus, ethanol molecules interact with the Pt surface covered by OH and acetic acid is formed. Although the initial current in the transients is very high, the transients show a fast decay. In fact, the current after 1 second can be ten times smaller than the initial current. The decay is due to the adsorption of acetate from acetic acid, which is detected by FTIR [4]. Acetate is adsorbed in the bidentate configuration, the typical adsorption configuration for the carboxylic groups on metals [41]. Two consequences can be extracted from this behavior: i) OH is required in the oxidation of ethanol to acetaldehyde/acetic acid, ii) the interaction of ethanol with the surface is weak, because other adsorbed species significantly diminishes the oxidation currents. Moreover, as happens with formic acid,

the adsorption of acetate in bidentate configuration is inactive for the further oxidation of this species because none of the atoms in the adsorbed species can interact readily with the surface. In alkaline solutions, where acetate is not adsorbed, voltammetric currents are significantly larger and the decay in the currents is much slower, which support these conclusions [42]. In this case, the observed decay is due to the polymerization of acetaldehyde, which is produced also with acetic acid in alkaline solutions, leading to the blockage of the electrode surface.

Regarding the cleavage of the C—C bond, the studies indicate that it requires special conditions. FTIR experiments carried out on Pt basal planes demonstrated that the C—C cleavage is strongly influenced by the electrode surface structure. Thus, the Pt(110) electrode displays the highest activity for the C—C bond splitting, whereas this step is very unfavorable on Pt(111) electrodes, producing mostly acetic acid during the reaction [4]. DFT calculations demonstrated that the reason of the poor ability of Pt(111) to oxidize ethanol to CO_2 is related with its higher activation barrier for C—C bond breaking (1.36 eV) when compared to Pt(100) (0.65 eV) and that the bond cleavage occurs through strongly chemisorbed precursors, such as CH_2CO or $CHCO$, only at low-coordinated surface sites [43] or (110) steps on (111) terraces [41], corroborating the experimental results [44].

Studies with isotopically labelled ethanol ($^{12}CH_3^{13}CH_2OH$) have been also able to produce very valuable information on how this bond cleavage takes place on the step sites [45]. The cleavage takes place at low potentials (E < 0.2 V) and produce two fragments. The $\cdot^{13}CH_2OH$ fragment evolves immediately to adsorbed ^{13}CO, which is eventually oxidized to $^{13}CO_2$ above 0.6 V. On polycrystalline Pt surfaces, it have stablished that the other fragment, $\cdot^{12}CH_3$ reduces to CH_4 at low potentials during the

first positive scan, with the aid of H_{ad} on (100) sites, present during the first scan (Figure 3A) [46]:

$$H_{ad}\,(100)+\ CHOHCH_{3,ad} \longrightarrow CO_{ad} + CH_4 + 2H^+ + 2e^-$$
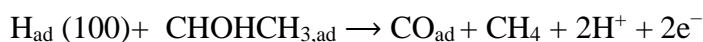
In parallel to the production of methane, the coverage of adsorbed carbon monoxide increases. The formation of CH_4 explains why in the isotopically labelled ethanol experiments the amount of $^{13}CO_2$ is always higher than that of $^{12}CO_2$, during the first scan. Only when the C—C bond cleavage takes place above 0.5 V, the $^{12}CH_3$ fragment yields adsorbed ^{12}CO. This step requires the presence of adsorbed OH on the surface, highlight the importance of adsorbed OH in the oxidation of the molecule.
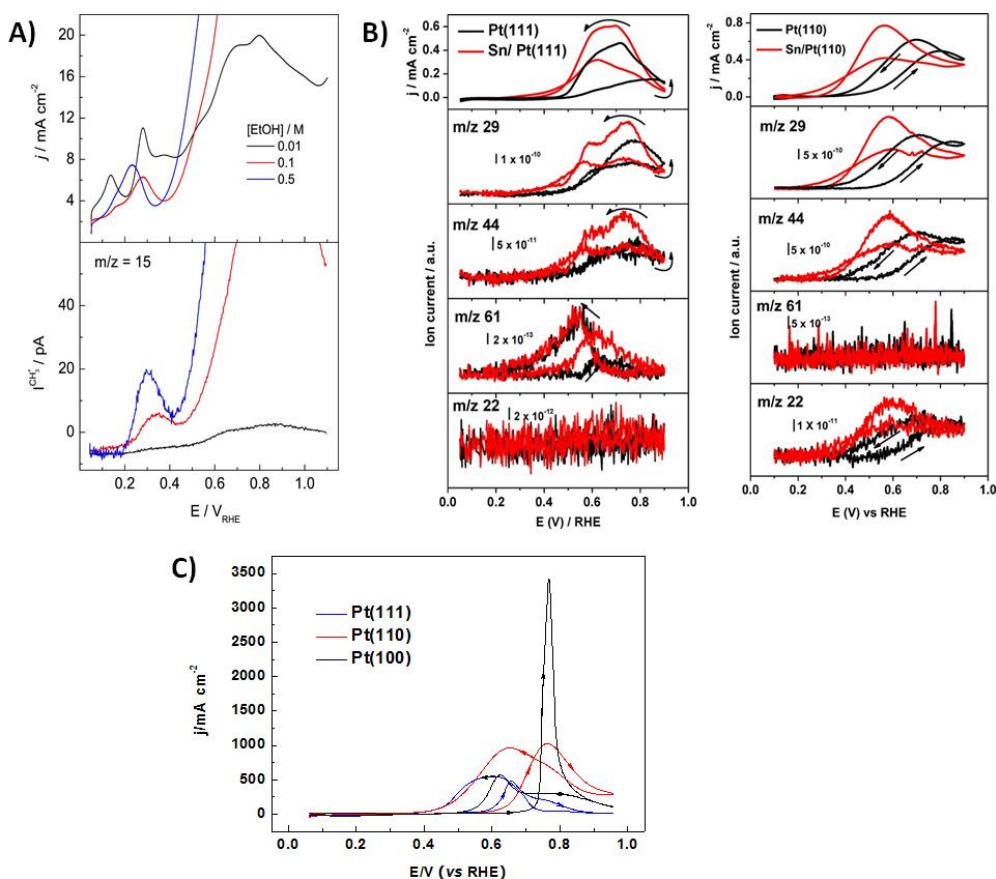

Figure 3. A) Cyclic Voltammetries (top panel) and mass spectrometer cyclic voltammetries (bottom panel, $m/z = 15$ corresponds to CH_3^+ fragment and denotes methane formation) for EOR on mesoporous Pt in 0.01, 0.1 and 0.5 M ethanol in 0.5 M H_2SO_4 solution. Scan rate: 2 mV s^{-1}. Adapted from ref [46]. B) Cyclic Voltammetries (top panels) and mass spectrometer cyclic voltammetries (bottom panels) for $m/z = 29$ (CHO^+, acetaldehyde formation), $m/z = 61$ ($C_2H_5O_2^+$, acetic acid formation) and $m/z =$

22 (CO_2^{++}, carbon dioxide formation) for EOR on Pt(110) and Pt(111) (black lines) and Sn/Pt(110) and Sn/Pt(111) (red lines) in 1 M EtOH + 0.1 M $HClO_4$; Scan rate:1 mV s^{-1}. Adapted from ref. [40]. C) Stationary voltammetric profiles for the oxidation of 0.1 M EG in 0.1 M $HClO_4$ solution on the Pt basal planes. Scan rate: 50 mV s^{-1}. Adapted from ref. [47]

Metallic adatoms have also been extensively employed to decorate the Pt single crystal surface with the aim to tune the C—C bond cleavage and the mechanism toward EOR. Ru or Sn have been found to increase the oxidation currents [40,48]. In particular, the decoration of Pt(111) and Pt(110) with Sn appears to enhance the oxidation of ethanol to acetaldehyde although the further oxidation of acetaldehyde is sensitive to the Pt surface structure. On the Pt (110) surface there are sites able to break the C—C bond and the oxidation of acetaldehyde to CO_2 is promoted, whereas on Pt(111) such sites are not available taking place the oxidation of acetaldehyde to acetic acid (Figure 3B) [40]. Similarly, the decoration of (110) steps by Sn or Ru on (111) terraces also increases the activity for the oxidation behavior that is associated with an increase in the formation of acetic acid [48]. Both metals, Ru and Sn are oxophilic, and OH adsorption takes place at low potentials promoting the incomplete oxidation of ethanol by bifunctional mechanism with any catalytic effect of the C—C bond splitting. On the contrary, the breaking of the C—C bond can be favored by the modification of the Pt surface with Os [49]. FTIR experiments showed an increase of the CO and CO_2 bands by the modification of Pt basal planes with low coverage of Os, which suggest a better capability of the Pt–Os system to cleave the C—C bond of ethanol, in comparison with the non-modified platinum electrodes. On the other hand, other metals such as Rh and Ir have been explored as secondary metals in Pt-based nanoparticles for EOR [43,50]. These studies demonstrated that the presence of both noble metals favors the cleavage

of the C—C when compared to the Pt pure formulation. However, as far as we know, no works on Rh and Ir modified Pt single crystals can be found in literature.

Alternatively, the C—C bond can be destabilized when the methyl group of the EtOH molecule is partially oxidized [51–54]. In this sense, the oxidation of ethylene glycol (EG) in acid media occurs via the spontaneous and extensive C—C bond breaking in contact with Pt to produce adsorbed CO as major surface residue [47,51,55]. Therefore, the introduction of a second OH group at the α carbon confers greater reactivity towards the C—C cleavage although producing the partial blockage of the surface at lower potentials. However, the EG can also react in other reaction pathways where the C—C bond is not altered and the OH groups of the molecule are sequentially oxidized. Moreover, each intermediate product can react to produce C1 products different from CO, leading to an even more complex reaction mechanism that involves different reaction intermediates and products [52,56]. *In situ* spectro-electrochemical studies have provided fundamental understanding of the reaction steps during interaction of EG with Pt, showing that adsorbed 2-hydroxyacetyl is the precursor for CO_{ad} at low overpotentials, and that adsorbed glycolate (in equilibrium with glycolic acid under acidic conditions) results as a reaction side product/intermediate at potentials above 0.6 V [51,52]. On the other hand, structure-related studies have shown that within the basal planes, and similarly to EOR [4,48], the Pt(111) electrode exhibits the best electrocatalytic properties in terms of the lowest onset potential for the oxidation of EG and little hysteresis between the positive and the negative direction scans, also pointing out the lowest poisoning rate by CO_{ad} (Figure 3C) [47,55]. Moreover, the inclusion of steps on the (111) terrace catalyzes the EG oxidation to CO_2, being the {110} steps the most catalytic for the C—C cleavage. Also, FTIR results showed that the incomplete oxidation towards glycolic acid and oxalic acid are produced principally at the close-

packed terraces [51]. The selective decoration of Pt surfaces with adatoms or other adsorbed species, in combination with the higher reactivity of the C—C bond of the EG molecule, could lead to a site-selective electrocatalysis and the exploit of the 10 electrons per EG molecule that can be extracted from its complete oxidation to CO_2.

5. Conclusions.

The ideal electrocatalyst for the oxidation of these molecules should comply several properties. Platinum is one of the best electrocatalysts for the dehydrogenation, which is a required step in all the oxidation. However, the dehydrogenation requires that the molecule is adsorbed in the right configuration. For the carboxylic acid, the most stable configuration, the bidentate adsorption, is not favorable for this purpose. In the case of alcohols, the interaction of these species is very weak and only when OH is adsorbed on the surface, the molecule can interact with the surface and dehydrogenation can occur. For this reason, oxophylic atoms, such as Ru or Sn, may help in the catalysis of these steps. These adatoms also catalyze the oxidation of CO, which appear an intermediate after the dehydrogenation. For the cleavage of the C-C bond, which is the most difficult step and platinum is not very active, other adatoms, such Os, Rh or Ir may be required.

Authors contribution.

All authors have contributed equally.

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