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Identity of the Most and Least Active Sites for Activation of the Pathway for CO₂ Formation from the Electro-oxidation of Methanol and Ethanol on Platinum

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Abstract

In the field of the catalysis on solid surfaces, discrimination of the site-specific chemistry taking place on surfaces consisting of multiple types of sites is challenging, especially at electrified solid/liquid interfaces. In this study, site-specific chemical labeling on Pt stepped surfaces was achieved by attaching the ¹³CO species exclusively on the top side of the (110) steps, while maintaining all the (111) sites available. The catalysts were then employed in a spectro-electrochemical study of the electro-oxidation of methanol and ethanol. The onset potentials for the formation of ¹³CO₂ and ¹²CO₂ revealed the existence of two channels of carbon dioxide formation, separated by about 0.22 V, on the same Pt surface. The active sites with lower over-potential requirement (or lower energy input) for activation of the reaction pathway of CO₂ formation resided on the (111) terraces. On the other hand, the active sites with higher over-potential requirement (or higher energy input) for activation of the reaction pathway for electro-oxidation of ¹³CO_{ads} species to ¹³CO₂ were at the top of the (110) steps. The findings revealed the identities of the *most active sites* and *least active sites* involved in the formation of CO₂ during the electro-oxidation of alcohols. On Pt surfaces, the complex interplay involving the steps on the surface favors activation of the pathways for CO_{ads} oxidation on the (111) terraces, rather than promoting reaction steps directly on the steps themselves.

Keywords: Electrocatalysis, platinum, structure sensitivity, step sites, terrace sites, active sites.

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1. Introduction

The concepts of *active sites* and *most active sites* are intriguing in the field of catalysis on solid surfaces. Revealing their identities has proved challenging, but is necessary for understanding the factors underlying the catalysis phenomenon, as well as being of paramount importance for the design of active, selective, and durable catalysts.¹⁻⁴ In this regard, the surfaces of real catalysts are heterogeneous at the molecular scale, with the topmost surface consisting of steps/defects, terraces, holes, and so on,⁵ and these different locations on the surface have different chemical environments.⁶ Historically, a systematic approach concerning the identities of the catalytic active sites on solid surfaces was published by Taylor,⁷ in a review paper in 1925. According to him, low coordination atoms on the surface act, by themselves, as active sites. Today, we know that this affirmation is not entirely correct for any and all reactions on solid surfaces. The concepts of *most active sites* and *less active sites* imply the requirement for lower and higher inputs of energy, respectively, for activation of the pathways and establishment of a reaction. It should be noted that in describing catalytic activity, the concept of active sites is linked to a particular reaction. In the field of electrocatalysis, an especially useful reaction probe that can be used to study the catalytic properties of materials is the electro-oxidation reaction of CO. The reason is that on a Pt catalyst, this reaction is surface structure sensitive,⁸ with CO₂ being the single reaction product. In addition, adsorbed CO (CO_{ads}) can appear as an intermediate species during the pathway of electro-oxidation of alcohols, such as methanol and ethanol, to CO₂.⁹ These two alcohols are potential candidates for use as fuels in direct alcohol fuel cells,¹⁰⁻¹² but the sluggish kinetics of their electro-oxidation on the anode limits the efficiency of these energy conversion devices.^{13,14} One reason for the slow kinetics of alcohol electro-oxidation toward CO₂ is related to the accumulation of CO_{ads} on the surface, which acts as a catalytic poison.¹³ Therefore, study of the nature of the reaction pathway for CO₂ formation is needed in order to be able to understand the origins of the high potentials required for the oxidation of CO_{ads} in the mechanism of electro-oxidation of alcohols. In particular, deciphering the characteristics of the *most active sites* is an outstanding issue in catalysis on solid surfaces and needs to be investigated.

On Pt electrodes, the reactions of electro-oxidation of alcohols are inefficient in terms of CO₂ production. For instance, the electro-oxidation reaction of ethanol, depending on its concentration, yields a fraction of CO₂ that varies from about 0.5 to 7 %.¹⁵ The main reaction

products are acetic acid and acetaldehyde,¹⁶ representing low exploitation of the full Faradaic power of ethanol as a fuel. However, the ethanol electro-oxidation reaction is surface structure sensitive,¹⁷ so one way to selectively tune the reaction consists of changing the structure of the topmost surface (and/or sub-surface). The Pt(111) surface of the basal plane of platinum is less efficient in C-C bond splitting, so there is less conversion of CO_{ads} to CO₂.¹⁸ The introduction of defects in the (111) plane can, to some extent, increase the overall rate of ethanol electro-oxidation.^{19,20} In a computational chemistry study,²¹ the low CO₂ efficiency was interpreted in terms of restricted removal of CO_{ads}, rather than C-C splitting. In the case of methanol, the electro-oxidation reaction on Pt also behaves as being surface structure sensitive.^{22,23} The CO₂ production efficiency was found to vary from ~20 % to ~32 % as the potential was increased from 0.6 V_{RHE} to 0.8 V_{RHE}.²⁴ On the cyanide-Pt(111) modified electrode, it has been reported that at least three contiguous Pt atoms are required for dissociation of the methanol molecule towards CO_{ads}.²⁵ Previous studies employing Pt(111) vicinal surfaces showed that the (110) steps are highly active toward dissociating methanol and yielding CO_{ads},²⁶ but nothing is known about the other step of the forward reaction, which is the conversion of CO_{ads} to CO₂. To further complicate the issue, experiments have shown that the formation of CO₂ from methanol electro-oxidation by the non-CO_{ads} pathway only starts at a potential of about 0.7 V_{RHE}, which is higher than the potential at which CO₂ is formed in the CO_{ads} pathway.²⁵ Due to the heterogeneity of the sites on the catalyst surfaces, it is not plausible that the step and terrace sites present similar catalytic activity, given the structure sensitive nature of the reaction. Therefore, in comparison to non-CO_{ads} pathways, a fundamental issue in heterogeneous electrocatalysis is to investigate the different abilities (meaning energy inputs) that different sites on the catalyst surface present for activation of the pathways of CO₂ formation from the CO_{ads} species derived from alcohols.

Concerning the geometric configuration of the atoms on the topmost surface, the site heterogeneity on catalyst surfaces can, in principle, be spatially resolved by imaging the surface at the atomic level.²⁷⁻²⁹ However, from the chemistry viewpoint, the identification of active sites is not an easy task. In the field of electrocatalysis, it often involves introducing specific types of sites on a basal plane, such as locating crystalline (or even ill-defined) steps over the (111) terraces. In this case, the inhibition or increase of catalytic activity is monitored without distinguishing the chemistry at specific electrocatalytic sites.^{8,19} Another way to probe the site-specific catalytic activity is based on blockage of certain types of sites, such as

steps/defects, by attaching “non-reactive” foreign atoms on them, leaving the rest of the sites free to interact with the reactive species.³⁰⁻³³ In either case, the active site is indirectly identified by means of a notable effect observed in a particular catalytic property, which could be the rate and/or selectivity of a reaction. Although these two procedures described above can be strongly chemically intuitive, they consider that the density of the active sites, or the overall activity, results from a simple linear combination among different facets at the surface. Furthermore, they also consider that the “non-reactive” foreign atoms do not affect the chemistry at neighboring sites. As a matter of fact, the use of foreign atoms to block steps/defects on a substrate originates new steps and neighborhoods that frequently have distinct physical and chemical properties. This principle has been used to explore the active sites in the electro-oxidation of CO on stepped Pt single crystal surfaces selectively modified by foreign atoms.^{34,35} Active sites on solid catalyst surfaces have also been studied by *in situ* electrochemical STM (scanning tunneling microscopy), in which, under operation condition, the relative level of noise of the tunneling current changes as the STM tip passes over highly active sites, in comparison to sites with low activity.³⁶ This innovative *in situ* STM methodology has only been successful for fast reactions or reactions near diffusional control. An additional consideration is that the nanometer scale of resolution of active sites is scattered over the widths of many atoms. This means that the ability to differentiate the activity at the upper sides of the steps and their counterparts has not been achieved. In a general way, the chemistry at different active sites is complex, because the active sites do not correspond exactly to the situation in which there is mere enriching of a geometric configuration of atoms on the surface, as highlighted in studies of catalysis at the solid/gas interface.³⁷ Indeed, the determination of active sites has not considered the influence of steps/defects on their neighbors. Therefore, in order to probe the chemistry at different active sites on a catalyst with heterogeneous sites, an ideal experiment should consist of chemically marking specific electrocatalytic sites, without affecting the chemistry at the neighboring sites, and then monitoring the chemistry at the chemically marked sites, as well as at the rest of the sites. We have developed an experimental strategy that perfectly fulfills this ideal condition and works extremely well at the electrified metal/solution interface, even with sluggish reaction kinetics. The principle concept in this strategy is to use, as a site-specific marking agent, a chemical species that must be naturally formed during the overall mechanism of the reaction in question. This ensures that neighboring sites are not disturbed as a result of the marking of

active sites. For the study of the methanol and ethanol electro-oxidation reactions, a natural species that can be used for marking sites is the CO_{ads} species itself, which arises from the oxidation of alcohols toward CO_2 . We employed stepped Pt surfaces where the top sides of the (110) steps of the Pt(111) terraced surfaces had been previously and selectively marked with $^{13}\text{CO}_{\text{ads}}$ species, after which the catalysts were employed in the electro-oxidation of methanol and ethanol. A similar strategy has previously been shown to be suitable for the study and discrimination of specific electrocatalytic sites.³⁸

In this paper, we investigate the identities of the *most active sites* and the *least active sites* involved in the reaction pathway of CO_2 formation during the electro-oxidation of methanol and ethanol.

2. Experimental Section

2.1. Electrodes and Electrolyte

The Pt single crystals used as working electrodes were two bead-type Pt(332) and Pt(665) electrodes (with oriented areas about 22 mm^2). The nominal structures of the Pt(332) and Pt(665) surfaces corresponded to 5 atoms-wide, and 11 atoms-wide (111) terraces, respectively, which were periodically interrupted by (110) monoatomic steps. According to the Lang-Joyner-Somorjai model,³⁹ these two surfaces belong to the $\text{Pt(s)}-[(n-1)(111)\times(110)]$ series and can be represented individually as follows:

$$\text{Pt(332)} \equiv \text{Pt(s)}-[5(111)\times(110)], n-1=5$$

$$\text{Pt(665)} \equiv \text{Pt(s)}-[11(111)\times(110)], n-1=11$$

The protocol for preparing these electrodes followed the well-known Clavilier procedure.⁴⁰ The counter electrode used was a Pt wire, the reference electrode was a reversible hydrogen electrode (RHE), and all the potentials were referred to the RHE scale. The electrode potentials were controlled using a waveform generator (Model 175, EG&G PARC), a potentiostat (Model 551, Amel), and a digital recorder (Model ED 401, eDAC).

The electrolytic solution was 0.1 M HClO_4 (70%, Aldrich), prepared in ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$). Prior to the experiments, the electrolytic solutions were deoxygenated by bubbling with Ar (N50, Alpha Gaz). The other gases used were CO (N47, Alpha Gaz) and ^{13}CO (99%, Cambridge Isotope Laboratories, Inc.). Absolute methanol and absolute ethanol were used (both 99.9%, Merck).

All the experiments were carried out at room temperature in the laboratory (25 ± 1.0 °C).

2.2. Spectro-Electrochemical Experiments

In situ FTIR spectra were recorded using a Nicolet 8700 spectrometer equipped with an MCT detector cooled with liquid N₂. The spectro-electrochemical cell used has been described elsewhere.⁴¹ The cell configuration included a prismatic CaF₂ window fitted at an angle of 60°. The *in situ* FTIR spectra were recorded as the average of 200 interferograms, with resolution of 8 cm⁻¹, requiring about 2 minutes for the acquisition and storage of each spectrum. The series of spectra for each spectro-electrochemical experiment were recorded from 0.060 to 0.800 V (in intervals of 25 mV). The spectra were presented in terms of absorbance units:

$$A = -\log \left(\frac{R_0 - R_s}{R_0} \right) \text{ versus } \nu/\text{cm}^{-1} \quad (1)$$

where R_0 is the single beam reflectance spectrum at the reference potential and R_s is the single beam reflectance spectrum at the sampling potential. In the spectra, the bands pointing up refer to the species whose concentration grows into a thin layer, while the bands pointing down refer to the species whose concentration diminishes in the thin layer. For the detection of both dissolved species in the thin layer and species on the Pt crystal surface, *p*-polarized radiation was employed, in accordance with the surface selection rule.⁴¹

3. Results

3.1. Fingerprints of Step and Terrace Sites on Pt Surfaces as Probed by Hydrogen Adsorption/Desorption and Adsorption of CO on the Top of the Steps

Figure 1 shows cyclic voltammograms of the Pt(332) and Pt(665) single crystal surfaces in contact with 0.1 M HClO₄ solution. Also shown is a hard sphere model of a stepped surface, indicating the presence of different catalytic sites on the surface. The data shown by the orange line correspond to the condition where the top of the steps at the Pt surfaces were selectively occupied by ¹³CO species. Considering the Pt voltammograms shown by the blue lines in Figure 1, the features of the voltammograms for the Pt(332) and Pt(665) surfaces indicate high quality of the oriented surfaces and solution cleanness. For these two stepped Pt surfaces, at potentials below ~0.25 V_{RHE} (which corresponds approximately to potential of zero total charge⁴²), the interfacial processes were dominated by the adsorption/desorption

of hydrogen, that is the reversible discharge of the proton to form adsorbed hydrogen, together with the reverse reaction, which occurred at all types of available Pt sites.⁴³ Disregarding the adsorption of anions and the participation of the interfacial water in the overall (electro)chemical process, the hydrogen adsorption/desorption reactions can be represented as follows:

This electrochemical reaction is characterized as being fast, surface-limited, and strongly sensitive to the structure of the Pt catalytic sites. These reactions are so surface structure sensitive that a change in the surface of the Pt causes a noticeable change in the voltammetric behavior in the hydrogen region. Reaction (2) occurring at the top side of the steps (see site assignments in Figure 1) is associated with a pair of features at a potential of about $\sim 0.127 \text{ V}_{\text{RHE}}$ for a solution pH about 1⁴⁴, reflecting the reversible character of the reaction. These features result from the reversible discharges of the proton to form adsorbed hydrogen on the top side of the (110) step orientations. The possible presence of (100) steps/defects on the surface would generate a pair of peaks at different (higher) potential,⁴³ which, as can be seen, were not present in the voltammograms shown in Figure 1. If a strongly adsorbing species was to be deposited at the top of the steps (such as the adsorption of CO), the features at $\sim 0.127 \text{ V}_{\text{RHE}}$ would be (partially or completely) suppressed in the voltammogram. It should be noted that the pair of peaks at $\sim 0.127 \text{ V}_{\text{RHE}}$ would be suppressed if the bottom side of the step sites was blocked, as occurs with preferential ad-atom deposition on terraces.⁴⁵ All the features below these peaks in the voltammogram (including those related to the bottom side of the steps) can be attributed to the hydrogen adsorption/desorption reactions involving Pt sites characterized as being (111) terraces. According to reaction (2), the only part of the steps characterized as being steps/defects of (110) step orientation is the top side of the steps. Hence, according to reaction (2), the hydrogen adsorption/desorption reactions at the top side of the (110) steps caused the features at $\sim 0.127 \text{ V}_{\text{RHE}}$, while the counterpart of the steps (the bottom side) behaved electrochemically as (111) terrace sites for hydrogen adsorption/desorption. In this process, the steps on the surface behaved as a dipole. This will be covered in detail in Section 4.2. It is worth noting that the charge density for the feature at $\sim 0.127 \text{ V}_{\text{RHE}}$ increased when passing from the Pt(665) surface to the Pt(332) surface (Figure 1), because the step density ($\rho_{(hkl)}$), defined as the number of monoatomic steps per unit of length with respect to the (111) plane, follows the order $\rho_{(332)} > \rho_{(665)}$.

The data shown in the voltammograms presented using the orange lines in Figure 1 refer to the special condition in which the top of the (110) steps of the Pt(332) and Pt(665) stepped surfaces were selectively blocked by $^{13}\text{C}^{16}\text{O}$ (henceforth denoted ^{13}CO). The voltammetric effects were the same, irrespective of whether the steps were blocked with ^{13}CO or ^{12}CO . The experimental protocol for acquiring ^{13}CO exclusively at the top of the (110) steps consisted of partially oxidizing a ^{13}CO full coverage. For this, at a potential of $0.100\text{ V}_{\text{RHE}}$, full ^{13}CO coverage was obtained by bubbling ^{13}CO gas through the solution for 5 min, after which the solution was bubbled with Ar gas for 25 min to ensure complete removal of the non-adsorbed ^{13}CO . Next, the potential was scanned from $0.100\text{ V}_{\text{RHE}}$ to $0.06\text{ V}_{\text{RHE}}$, at a rate of 0.05 V s^{-1} , after which the potential was switched to an upper limit value ($E_{\text{CO oxid}}$), such that only a small portion of the $^{13}\text{CO}_{\text{ads}}$ adlayer was oxidized, rather than immediate oxidation of the entire ^{13}CO adlayer. When this upper potential ($E_{\text{CO oxid}}$) was reached, the potential was stepped back to $0.100\text{ V}_{\text{RHE}}$. Next, the potential was scanned into the hydrogen region, in order to probe the types of Pt sites that had been regenerated or made available for the hydrogen adsorption/desorption due to partial oxidation of the $^{13}\text{CO}_{\text{ads}}$ adlayer in the previous voltammetric step. On the Pt(111) terraced surfaces, the partial oxidation of a full CO adlayer first involved sites assigned as being the (111) terraces, while at the end, only the sites assigned as being the (110) steps remained occupied by CO_{ads} , such that the top sides of the steps were not available for the hydrogen adsorption/desorption. In the situation in which only CO species at the (110) steps were present on the Pt surface, only the features at $\sim 0.127\text{ V}_{\text{RHE}}$ disappeared from the voltammogram, with the voltammograms shown in Figure 1 (orange line) corresponding to the condition where only the sites at the top of the (110) steps were occupied by $^{13}\text{CO}_{\text{ads}}$. Successive voltammograms collected during the oxidation of a CO adlayer are shown in Supporting Information (Figure SI 1). All the (111) terrace sites (including the bottom sides of the steps) were available for the hydrogen adsorption/desorption. Compared to the top sides of the steps, the (111) terrace sites presented low reactivity for adsorption of carbon monoxide, as reported for studies of solid/gas interfaces.^{46,47} Each Pt single crystal prepared with its (110) steps selectively occupied with $^{13}\text{CO}_{\text{ads}}$ was carefully employed for the electro-oxidation reaction of methanol and ethanol, as will be described in the next section.

In order to further demonstrate the efficiency of the procedure for acquiring adsorbed CO only at the top of the steps, a sample of ^{12}CO (henceforth denoted CO) was used for

decoration of the steps of a Pt(332) surface, using a voltammetric experimental protocol similar to that described above. After the acquisition of CO adsorbed on step sites, the next step was to voltammetrically oxidize these CO_{ads} species at once. The result is shown by the orange line in Figure 2A (together with a blank cyclic voltammogram). The maximum activity of CO oxidation was at ~ 0.72 V_{RHE} (typical of CO electro-oxidation at the top sides of the (110) steps at that potential sweep rate and solution pH⁴⁸). The experiment for the acquisition of CO_{ads} only on the top of the steps was repeated, this time with the CO_{ads} being inspected by *in situ* FTIR spectroscopy. The results are shown in Figure 2B, including an experiment with adsorbed CO at full coverage. In the case of full CO coverage (presumably with all types of Pt active sites occupied by CO), two CO_{ads} bands appeared in the spectra. A band at ~ 2064 cm⁻¹ was due to the stretching frequencies of linearly bonded CO on both (111) terraces and steps, while the band at ~ 1830 cm⁻¹ was attributed to bridging CO only at the (111) terraces. For the coverage condition of CO only on the steps, a single CO_{ads} band was present at ~ 2021 cm⁻¹, attributed to linearly bonded CO on the (110) steps (more precisely, adsorbed CO only on the top of the steps). The spectroscopic inspection of the CO only on the top of the steps was in perfect agreement with the voltammetric results (Figure 1, orange line; Figure 2A, orange line). From inspection of the spectra in Figure 2A, it can be seen that the band corresponding to linearly bonded CO only on the steps presented a redshift of about 43 cm⁻¹, compared to the band for linearly bonded CO at full coverage. Previous studies showed that the intensity of the band for linearly bonded CO on (111) terraces (at higher frequencies) strongly borrowed the band intensity (at lower frequencies) of the adsorbed CO on the step sites.⁴⁹ It could be concluded that our procedure for the acquisition of CO exclusively on the top of the steps was successful. Furthermore, for the condition of CO only on the (110) steps, the *in situ* FTIR spectrum was in agreement with the CO_{ads} occupying the top side of the (110) steps.

3.2. Reactivity of Stepped Pt Surfaces Toward Electro-oxidation of Methanol and Ethanol as Monitored by Cyclic Voltammetry

The voltammetric profiles corresponding to the electro-oxidation of methanol and ethanol are shown in Figure 3. In the experimental procedure, a blank cyclic voltammogram was first recorded, followed by setting the potential of the working electrode at 0.100 V_{RHE} and adding a sufficient volume of 0.1 M methanol or ethanol stock solution into the electrochemical cell to give final a concentration of 5.0 mM (methanol) or 10.0 mM (ethanol).

Successive cyclic voltammograms were then recorded. The two first cycles are shown in Figure 3. The measurements include a blank cyclic voltammogram for comparison. As a general feature, the voltammetric profiles for the electro-oxidation of both alcohols indicated that in the first potentiodynamic cycle, only a fraction of the (110) steps was blocked by fragments originating from the dissociation of methanol or ethanol (see the Figure 3 insert, highlighting the hydrogen region). In the first two potentiodynamic cycles, in the presence of the low concentration of alcohol in solution, the (111) terrace sites remained available for the hydrogen adsorption/desorption, indicating the low reactivity of the (111) terraces. Importantly, this did not mean a lack of catalytic activity of the (111) terrace sites, because reactivity and catalytic activity do not mean the same thing in catalysis. For methanol, in particular, the current density only started at potentials above $\sim 0.5 V_{\text{RHE}}$. No hysteresis between positive and negative scan directions observed. From the voltammetric perspective, at low potentials (or $E < \sim 0.3 V_{\text{RHE}}$), the reactivity behaviors of the Pt(332) surface toward adsorption/dissociation of methanol and ethanol are quite similar, with the adsorption essentially occurring at the (110) step sites. High reactivity of low coordinated atoms for alcohols dissociation has been expected from Density Functional Theory (DFT) calculations.^{50,51}

The voltammetric profiles for the electro-oxidation of methanol and ethanol on the Pt(665) single crystal surface (see Supporting Information) were qualitatively similar to those for Pt(332). *In situ* FTIR spectroscopy experiments were performed employing stepped Pt surfaces where the steps were selectively blocked by ^{13}CO .

3.3. Control of the Band of $^{13}\text{CO}_2$ from the Electro-oxidation of a Common Methanol Sample

Unlike the electro-oxidation of ethanol, the electro-oxidation of methanol on a Pt catalyst at high potentials (above $\sim 0.7 V_{\text{RHE}}$) results in massive production of carbon dioxide. At high concentrations of methanol, two carbon dioxide bands appear in the FTIR spectra. Since one of the goals in this work was to detect the small band of the $^{13}\text{CO}_2$ derived from electro-oxidation of the $^{13}\text{CO}_{\text{ads}}$ species previously deposited on the (110) steps of the Pt surface, it was necessary to eliminate the contribution of the $^{13}\text{CO}_2$ band that appears naturally in the spectrum for the electro-oxidation of common methanol. Common methanol refers to a methanol sample that contains the natural abundance of the stable carbon isotopes (^{12}C and ^{13}C).

After preparing the Pt(332) electrode in the electrochemical cell, the potential was set at 0.100 V and a sufficient volume of 0.1 M methanol stock solution was added to the cell to give a final methanol concentration of 50.0 mM. After homogenization of the solution, the surface of the Pt crystal was positioned against the optical window and spectra were recorded at potentials ranging from 0.05 to 0.80 V, in intervals of 25 mV. Selected spectra from this experiment are shown in Figure 4A. The electro-oxidation of methanol was also performed at lower concentrations (10.0, 5.0, 1.0, and 0.5 mM). The result for a 5.0 mM methanol solution is shown in Figure 4B.

For 50.0 mM methanol, the spectra showed two bands corresponding to the asymmetric stretching mode of carbon dioxide. A dominant band at 2343 cm^{-1} , starting at $\sim 0.4\text{ V}_{\text{RHE}}$, was attributed to $^{12}\text{CO}_2$, while another small band at 2277 cm^{-1} , starting at about $0.6\text{ V}_{\text{RHE}}$, was attributed to $^{13}\text{CO}_2$. The band at 2277 cm^{-1} ($^{13}\text{CO}_2$) became more intense when the potential was set above $0.7\text{ V}_{\text{RHE}}$, associated with an increasing rate of methanol electro-oxidation. At concentrations of around 5 mM and below, the $^{13}\text{CO}_2$ band no longer appeared in the spectra, even at higher potentials such as $0.7\text{ V}_{\text{RHE}}$. The bipolar band ($2021\text{ cm}^{-1} - 2043\text{ cm}^{-1}$) indicated the presence of adsorbed CO on the electrode surface at the potential of the reference spectrum ($0.100\text{ V}_{\text{RHE}}$). In the series of spectra shown in Figure 4, all the bands at around 1600 cm^{-1} were affected by the broad and dominant band of the uncompensated water bending mode at 1650 cm^{-1} ; these bands were not considered, since they had no analytical purpose in this work. The series of spectra showed no bands due to the presence of formic acid, at $\sim 1712\text{ cm}^{-1}$ (due to carboxylic acid C=O stretching vibration).⁵² This suggested that for the thin layer configuration, carbon dioxide was the single soluble final product from the electro-oxidation of methanol. It was not possible to know whether any small amount of formic acid (and even formaldehyde) produced was rapidly oxidized to carbon dioxide.

For a series of experiments using 50.0 mM methanol, the magnitudes of the bands (A_i) for both $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ were integrated for spectra acquired at 0.7 and 0.8 V_{RHE} . A ratio of $\sim 1/102$ (within experimental error) was obtained for the $A(^{13}\text{CO}_2)/A(^{12}\text{CO}_2)$ bands, in agreement with the natural ^{13}C abundance of $\sim 1.06\%$.⁵³ For methanol concentrations of around 5 mM (see Figure 4B) and below, the contribution of the $^{13}\text{CO}_2$ band did not exceed the level of the spectral noise, which was the desired experimental condition.

It should be noted that the band at 2277 cm^{-1} appears clearly in spectra for the electro-oxidation of common glycerol (50 mM)⁵⁴ and common formic acid (1 M)⁵⁵ on Pt electrodes,

at potentials at which massive production of carbon dioxide occurs. For the electro-oxidation of ethanol on a Pt electrode, the carbon dioxide production is so low, even at 75 mM ethanol, that a single carbon dioxide band (corresponding to $^{12}\text{CO}_2$) appears in the spectra.⁵⁴

3.4. Electro-oxidation of Alcohols on Stepped Pt Single Crystal Surfaces with the (110) Steps Marked with $^{13}\text{CO}_{\text{ads}}$ as Monitored by in situ FTIR Spectroscopy

3.4.1. Electro-oxidation of Methanol on $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$ and $\text{Pt}(665)_{\text{steps}}/^{13}\text{CO}$ Surfaces

As discussed in Section 3.1, the top side of the (110) steps of the surfaces of the Pt(332) and Pt(665) single crystals was selectively occupied with $^{13}\text{CO}_{\text{ads}}$. Here, these “chemically modified” catalyst surfaces are denoted as $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$ and $\text{Pt}(665)_{\text{steps}}/^{13}\text{CO}$ for Pt(332) and Pt(665), respectively. The experiments corresponding to these two chemically marked electrodes are shown in Figure 1 (orange line). The acquisition of the *in situ* FTIR spectra was according to the following experimental protocols. After acquisition of $^{13}\text{CO}_{\text{ads}}$ on the (110) steps (Figure 1, orange line), the electrode was kept at 0.100 V_{RHE} and a sufficient volume of 0.1 M methanol stock solution was added to the spectro-electrochemical cell to give a final methanol concentration of 1.0 mM. The solution was briefly homogenized, after which the crystal was pressed against the optical window. It is important to note that the electrode was not depolarized at any stage of the experiments. A series of spectra was then recorded at different potentials. The results for the electro-oxidation of 1.0 mM methanol on the $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$ electrode are shown in Figure 5. Then, the series of spectra shown in Figure 5 were recorded employing the Pt(332) surface with the top side of the (110) steps decorated with $^{13}\text{CO}_{\text{ads}}$ shown in Figure 1 in the orange line. Since the electro-oxidation of methanol at very low concentration, under the thin layer configuration, results in carbon dioxide as the only reaction product (see Figure 4), only the wavenumber regions containing signals for the carbon dioxide ($^{13}\text{CO}_2$ and $^{12}\text{CO}_2$) and CO_{ads} bands will be shown (full spectra in Supporting Information). For $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO} + 1.0$ mM methanol (Figure 5), the spectra exhibited two carbon dioxide bands. A band centered at 2343 cm^{-1} appeared at a potential of 0.45 V_{RHE}, while another band centered at 2277 cm^{-1} appeared at ~0.62 V_{RHE}. The band at 2343 cm^{-1} was due to carbon dioxide produced from electro-oxidation of the methanol. The band at 2277 cm^{-1} was due to electro-oxidation of the $^{13}\text{CO}_{\text{ads}}$ previously deposited at the top of the steps of the Pt(332) surface. As expected, the band at 2277 cm^{-1} was small, compared to the band at 2343 cm^{-1} . At potentials above 0.77 V_{RHE}, the band at 2277 cm^{-1} completely disappeared, probably

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3 due to the following reasons: (i) all the $^{13}\text{CO}_{\text{ads}}$ species had already been oxidized at 0.77 V_{RHE};
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5 (ii) there was no external source of $^{13}\text{CO}_{\text{ads}}$ species, that is, there was no $^{13}\text{CO}_{\text{ads}}$ other than
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7 that previously adsorbed on the electrode surface; (iii) the molecules of $^{13}\text{CO}_2$ diffused from
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9 the thin layer. Once the top of the steps were released during the electro-oxidation of the
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11 previously attached $^{13}\text{CO}_{\text{ads}}$, these Pt sites probably became available for the
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13 dissociation/oxidation of methanol molecules, with CO_{ads} species being among the fragments.
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15 However, at potentials above ~ 0.7 V_{RHE}, the band at 2343 cm⁻¹ decreased slightly, probably
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17 due to depletion of methanol (initially 1.0 mM) in the thin layer.

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19 Considering the band for adsorbed CO, there was no evidence of a signal for the $^{13}\text{CO}_{\text{ads}}$
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21 species. This was because coupling between dipoles caused the transfer of intensity to the
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23 band at higher frequency (such as for linearly bonded CO on the terraces), at the expense of
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25 the intensity of the band at lower frequency (such as for linearly bonded CO at the steps).^{49,56}
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27 Hence, in the presence of both $^{12}\text{CO}_{\text{ads}}$ and $^{13}\text{CO}_{\text{ads}}$, the phenomenon of band intensity transfer
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29 may result in the band for $^{13}\text{CO}_{\text{ads}}$ being undetected or invisible in the spectra. Previous work
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31 has shown that for $^{13}\text{CO}/^{12}\text{CO}$ mixtures, the $^{13}\text{CO}_{\text{ads}}$ band becomes visible in the spectrum
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33 when the amount of ^{13}CO present in the mixture is around 80 %.⁵⁷ In the present case, the
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35 amount of $^{13}\text{CO}_{\text{ads}}$ was very low (and restricted only to the (110) steps), which probably
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37 explained why no bands for $^{13}\text{CO}_{\text{ads}}$ were observed in the spectra.

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39 Other considerations should be highlighted regarding the experimental procedures for
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41 recording of the experiment shown in Figure 5. The electrode potential remained at 0.10 V
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43 for a longer time in the experiment shown in Figure 5, compared to the experiment shown in
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45 Figure 3. In the case of the purely electrochemical experiment (Figure 3), methanol was added
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47 to the electrochemical cell and the potential then remained at 0.100 V_{RHE} for only a few
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49 seconds, followed by recording the voltammetric scans. On the other hand, in the spectro-
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51 electrochemical experiments, after the addition of the alcohol to the electro-chemical cell and
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53 pressing the electrode against the optical window, sufficient time was always allowed for
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55 stabilization of the thin layer, and only after that were the spectra recorded. This procedure
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57 could take up to 2 minutes or more. Furthermore, the time required for acquisition and storage
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59 of one spectrum was around 2 minutes. Consequently, in the case of the spectro-
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electrochemical experiments, due to the long waiting time at 0.100 V_{RHE}, there was probably
the accumulation of alcohol fragments on the electrode surface. This was why the (bipolar)
band of CO_{ads} at 2043 cm⁻¹, likely due to $^{12}\text{CO}_{\text{ads}}$ formation on the (111) terraces, appeared in

the spectra shown in Figure 4. Consequently, the intense band for $^{12}\text{CO}_{\text{ads}}$ on the (111) terraces masked the band for the $^{13}\text{CO}_{\text{ads}}$ species on the top of the steps. Different to the spectro-electrochemical experiment, the voltammetry results for the electro-oxidation of methanol (Figure 3) suggested that there was no formation of CO_{ads} on the terraces. This difference is intrinsic to *in situ* FTIR spectroscopy experiments.

Data for the electro-oxidation of 1.0 mM methanol on a $\text{Pt}(665)_{\text{steps}}/^{13}\text{CO}$ electrode are shown in Figure 6. The spectra were recorded employing the $\text{Pt}(665)$ with the top of the steps decorated with $^{13}\text{CO}_{\text{ads}}$ (Figure 1, orange line). For simplicity, only the regions of the spectra containing the carbon dioxide bands are shown. The same features described for the $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$ electrode were valid for the $\text{Pt}(665)_{\text{steps}}/^{13}\text{CO}$ electrode. As expected²⁶, step sites are highly active for splitting of C-H bond and forming CO_{ads} . Another general observation was that for the two stepped Pt surfaces, a higher potential was required for the formation of carbon dioxide from the electro-oxidation of carbon monoxide at the top side of the steps, compared to the formation of carbon dioxide from the CO_{ads} on the rest of the Pt sites, which were assigned as being the (111) terrace sites. In this sense, the experiment carried out with $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO} + 1.0 \text{ mM methanol}$ and $\text{Pt}(665)_{\text{steps}}/^{13}\text{CO} + 1.0 \text{ mM methanol}$ revealed the existence of two routes of carbon dioxide formation, whose activation involved the top side of the steps and the (111) terraces on the same Pt surface. This experiment also enabled the chemistry at different points on the surface to be molecularly monitored.

3.4.2. Electro-oxidation of Ethanol on $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$

Similar experiments were performed employing the $\text{Pt}(332)_{\text{steps}}/^{13}\text{CO}$ electrode in the presence of 10.0 mM ethanol. In the case of ethanol, the study to determine the best ethanol concentration (which was performed for methanol) was not necessary, because the electro-oxidation of ethanol on Pt electrodes produces little carbon dioxide. The experimental protocol employed for the electro-oxidation of ethanol was similar to that used for methanol. The results are shown in Figure 7. In the case of the electro-oxidation of ethanol, other reaction products are formed, besides carbon dioxide. Hence, the spectra shown include the spectral region for acetic acid and acetaldehyde. A band at 2343 cm^{-1} , starting at $\sim 0.47 \text{ V}_{\text{RHE}}$, was due to the $^{12}\text{CO}_2$ originated from the electro-oxidation of ethanol on the (111) terraces. A band at 2277 cm^{-1} , appearing at a potential of $\sim 0.62 \text{ V}_{\text{RHE}}$, was due to the electro-oxidation of $^{13}\text{CO}_{\text{ads}}$ previously deposited at the top side of the steps of the $\text{Pt}(332)$ surface. The band at

~2051 cm⁻¹ refers to the stretching frequencies of adsorbed CO, dominantly on the (111) terraces. Because of the band intensity transfer (explained above) the band of ¹³CO_{ads} on step sites is not observed.^{49,56,57} Generally, the *in situ* FTIR data confirm that steps on surfaces are high active toward splitting of C-C and C-H bonds.⁵⁰ At lower wavenumber, the dominant uncompensated water bending mode band was present at 1650 cm⁻¹. A band at 1413 cm⁻¹, which shifted toward higher wavenumber as the potential was increased, could be attributed to symmetric OCO stretching of the -COO⁻ group (adsorbed acetate). This band appeared in the spectra at a potential of ~0.62 V_{RHE}, the same potential as for initiation of the pathway of electro-oxidation of adsorbed CO present on the top side of the steps. A band at 1282 cm⁻¹ was due to the combined C-O stretching and OH deformation of the COOH group of acetic acid.⁴¹ It should be noted that the intense water band at around 1650 cm⁻¹ (corresponding to the water bending mode) obscured the possible acetaldehyde band that should appear at 1717 cm⁻¹,⁴¹ corresponding to the stretching of C=O of acetaldehyde or acetic acid (CHO or COOH groups, respectively).

4. Discussion

This paper reports a direct spectroscopic disentangling of the set of specific electrocatalytic active sites involved in different reaction pathways of carbon dioxide formation during the electro-oxidation of methanol and ethanol on Pt electrodes in an acid solution. The set of experiments allows a more complete characterization of the complex interplay involving steps/defects on Pt surfaces during the electrocatalytic oxidation of alcohols.

4.1. Identity of the Active Sites Involved in the Formation of CO₂ and the Formation of Acetic Acid

The mechanisms of the electrochemical oxidation of methanol and ethanol involve a series of proton-coupled electron transfer steps. Based on thermodynamic considerations,⁵⁸ the standard potentials (at pH = 0) characteristic of the electro-oxidation of each of these alcohols to CO₂ are as follows:

Taking CO₂ as the reaction product from electro-oxidation of the alcohol, the *most active sites* are those able to activate the reaction pathway of CO₂ formation at lower over-potentials, that is, the active sites which require lower energy input during the electro-oxidation of methanol or ethanol toward carbon dioxide, under specified conditions. According to the *in situ* FTIR spectroscopic data (shown in Figures 5, 6, and 7), the onset potential at which the band for ¹³CO₂ appeared in the spectra was ~0.62 V_{RHE}. The carbon monoxide whose electro-oxidation originated the ¹³CO₂ was the ¹³CO_{ads} species selectively adsorbed on the top side of the (110) steps. Therefore, for the condition under which the ¹³CO_{ads} exclusively occupied the top of the (110) steps, the only set of sites available for interaction with the alcohol molecules and their oxidation were the sites assigned as being the (111) terraces. In the experiments shown in Figures 5, 6, and 7, the band for CO₂ formed from the electro-oxidation of the alcohols appeared at a potential of ~0.45 V_{RHE}, which was lower than the potential at which the oxidation of ¹³CO_{ads} on the top of the (110) steps occurred. It could therefore be concluded that the set of *most active sites* involved in the formation of CO₂ from the alcohols undoubtedly resided at the (111) terraces of the stepped Pt surfaces. However, in order to find the lowest potential for activation of the pathway for formation of CO₂ on the (111) terraces, it was necessary to consider that the potential for initiation of CO₂ formation depended on the concentration of the alcohol (Figure 4). Furthermore, it is reasonable to assume that the ¹³CO_{ads} species (previously adsorbed on specific sites) behaves chemically in a similar way to the ¹²CO_{ads} originated from the dissociation of the alcohols. Thus, both ¹²CO_{ads} and ¹³CO_{ads} behave electrochemically as if they were species (or reaction intermediates) derived from dissociation of the alcohol. It is then reasonable to suppose that in the absence of ¹³CO_{ads} species marking the top of the (110) step sites, the initiation of the electro-oxidation reactions of the alcohols also involves the same set of most active sites that manifested in the presence of ¹³CO_{ads} marking step sites. Considering all this, the electro-oxidation reaction of methanol towards CO₂ started at about ~0.40 V_{RHE} for 50.0 mM methanol (Figure 4A). Therefore, based on the spectroscopic experiments, it can be concluded that the *most active sites*, which require lower over-potentials (or lower energy input) for activation of the pathway for carbon dioxide formation, reside at the (111) terraces of the stepped surfaces, probably closer to the bottom side of the (110) steps, which are the (111) terrace sites. On the other hand, the sites requiring higher over-potential (or higher energy input) for the initiation of CO₂ formation were at the top

side of the steps. Under the condition where all the steps were chemically marked with $^{13}\text{CO}_{\text{ads}}$ species, the difference of potential for activation of the pathways for CO_2 formation on the (111) terraces (the location of the most active sites) and on the top side of the steps (which behaved as the least active sites) was of the order of $\Delta E \simeq 0.22 \text{ V}$ ($\equiv 0.62 \text{ V} - 0.40 \text{ V}$). Hence, the *most active sites* and *least active sites* were energetically separated by about $\sim 0.22 \text{ V}$, which is a substantial difference. The experimental strategy of site-specific marking using isotope-labeled species was successful and allowed direct disentanglement of the catalytic activities related to the terraces and the steps on the same catalyst surface. Although the tops of the step sites were highly active for the dissociation of alcohols (see Figures 3-7), these sites were not able to act in the CO oxidation step at low potentials, including the incorporation of any type of oxygen-containing species originating from the interfacial water molecules: $\text{CO}_{\text{ads}} + (\text{H}_2\text{O})_{\text{species}} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- + *_{\text{free Pt sites}}$. Since there was a large difference ($\Delta E \simeq 0.22 \text{ V}$) between the potential for activation of the pathway of CO_2 formation on the (111) terraces and the potential for electro-oxidation of CO_{ads} on the top side of the steps, the results (shown in Figures 4-7) suggested that at potentials less than $\sim 0.62 \text{ V}_{\text{RHE}}$, all the sites characterized as being at the top side of the steps remained entirely poisoned with CO_{ads} species. Therefore, CO_{ads} at the top side of the steps behaved chemically as a catalytic poison, whereas CO_{ads} on the (111) terrace sites along the stepped surface behaved chemically more like an active reaction intermediate. The controversial question about the role played by the CO_{ads} species in catalysis of the electro-oxidation of small organic molecules is now better understood. This question was addressed by Weaver *et al.*⁵⁹ in the 1980s, according to whom the CO_{ads} species obtained from the dissociation of alcohols acts as a catalytic poison. In contrast, Iwasita and Camara⁶⁰ considered that the CO_{ads} species behaves chemically purely as a reaction intermediate. Neither possibility is entirely accurate. As we have shown above, the action of CO_{ads} as a poison or as a reaction intermediate depends on the type of site at which the CO_{ads} resides, as well as on the potential. Our results provides further information about the chemistry intrinsic to the top side of the step sites, compared to the chemical properties of the (111) terraces on the same surface.

The complexity of the catalytic behavior of the step sites on the Pt(111) terraced surfaces is further increased considering the route for the electro-oxidation of ethanol toward acetic acid. As shown in Figure 7, activation of the pathway for acetic acid formation occurred at $\sim 0.62 \text{ V}_{\text{RHE}}$, which was the same as the potential for oxidation of CO on the top of the steps.

This evidenced that the pathway for acetic acid formation was not activated on the (111) terraces of the stepped Pt surface, at least at potentials below $\sim 0.62 V_{\text{RHE}}$. This was in direct contrast to the catalytic behavior of the Pt(111) basal plane, which is active in the electro-oxidation of ethanol toward acetic acid, whose formation on Pt(111) basal plane occurs at a potential of $\sim 0.4 V_{\text{RHE}}$.¹⁸ Therefore, since acetic acid is not formed until the top side of the step sites are released due to the electro-oxidation of CO_{ads} , the reaction pathway for acetic acid formation is kinetically hindered by the presence of the CO_{ads} on the top side of the steps, in accordance with previous results.³⁸ Our results shed light to the understand information of the reasons why acetic acid formation on stepped Pt surfaces always takes place at potentials greater than the onset potential of CO_2 formation (as we can see in *in situ* FTIR spectra of ethanol electro-oxidation on stepped Pt surfaces in acid media elsewhere^{50,61}). Moreover, our results explain why the activation pathway of acetic acid formation is favored in defected surfaces at potentials above $\sim 0.7 V_{\text{RHE}}$, as reported by Colmati *et al.*¹⁹ for a series of stepped Pt surfaces. Then, in contrast to the formation of CO_2 (which requires the incorporation of any sort of oxygen-containing species into CO), in the case of acetic acid formation, the incorporation of oxygen-containing species into the ethanol intermediate preferentially occurs on the top side of the steps. Therefore, since acetic acid is formed on the “infinitely wide” (111) terraces of the platinum at low potentials (about $0.4 V_{\text{RHE}}$),¹⁸ but is not formed on terraces of the stepped surfaces at similar potentials, this suggests that the chemical or catalytic properties of the (111) terraces of the quasi-perfect Pt(111) surfaces differ from the (111) terraces of the stepped surfaces. The structural difference between these two surfaces is related to the presence of steps/defects on the latter type of surface.

4.2. Interplay of Steps/Defects in the “Creation” of the Most Active Sites on the (111) Terraces of the Pt Surfaces

On the basis of the discussion in Section 4.1, it is clear that the *most active sites* at which the carbon dioxide is preferentially formed reside at the (111) terraces of the stepped surfaces. However, it is true that the quasi-perfect Pt(111) or “infinitely wide” (111) terraces have low activity in activation of the pathway for carbon dioxide formation from the electro-oxidation of alcohols,^{18,23} with almost no carbon dioxide formed from the electro-oxidation of ethanol on a quasi-perfect Pt(111) surface.¹⁸ Therefore, the preferential activation of the pathway for carbon dioxide formation on the (111) terraces of stepped surfaces suggests that the presence

of the steps changes the catalytic properties of the (111) terraces. Another example concerns the “inhibition” of the reaction pathway for acetic acid formation from the electro-oxidation of ethanol on (111) terraces of stepped surfaces (highlighted above), while the (111) terraces of the Pt(111) basal plane are very active toward acetic acid formation.¹⁸ These two examples suggest that the catalytic properties of the (111) terraces on stepped surfaces arise due to the presence of the steps. Steps on surfaces may be understood as a dipole on the surface (as depicted in Figure 1), where there is a charge redistribution involving a lack of charge (+) at the top side of the step and charge accumulation (-) in the counter-part (or bottom side) of the step. For a metallic surface, this is known as the Smoluchowski effect.⁶² From the chemical (or catalytic) perspective, the interplay of the steps/defects on the surface gives rise to a new reaction pathway favoring CO₂ formation on the (111) terraces during the electro-oxidation of alcohols. At the same time, the pathway of another reaction (acetic acid formation) may be inhibited at these same (111)-type terrace sites, due to the action of the steps. Therefore, the steps/defects on the surfaces have multi-functionality and these attributes can change the chemical properties of the neighboring (111) terrace sites. Hence, the steps on the surface alter the chemistry on the (111) terraces, making them active for a reaction pathway that is completely inactive on the “infinitely wide” (111) planes, or inhibiting a reaction pathway that is favorable on the “infinitely wide” (111) planes.

The sites on which the sources of oxygen-containing species (from water) were formed could be inferred from the spectra for the electro-oxidation of methanol and ethanol on Pt surfaces where the top sides of the steps were chemically marked with ¹³CO_{ads}, together with the knowledge that the CO₂ formation pathway was activated on the (111) terraces before the top of the (110) steps were released. Given that the top of the (110) steps was blocked by ¹³CO_{ads} and that the reaction pathway for CO₂ formation was preferentially activated on the (111) terraces (Figures 5, 6 and 7), it is likely that the oxygenated species from water were also formed on the terraces (and not on the steps). Hence, at potentials below ~0.62 V_{RHE}, the (111) terraces participated in activation of the pathway for CO₂ formation when the tops of the step sites were entirely blocked (poisoned) with ¹³CO_{ads} (see Figures 5, 6, and 7). Consequently, all the electrochemical events that resulted in the formation of CO₂ occurred on the domains of the (111) terraces of the stepped Pt surfaces. This suggests that for activation of the pathway for CO₂ formation on the (111) terraces, at low potentials, the role played by steps/defects on the surface was physical in nature (since no elementary step of the catalyzed

reaction occurred at these sites), rather than chemical, as previously thought. This enables information to be obtained about the role of the structure in the catalytic phenomena. From the surface structure point of view, the nature of an active site includes a local part of the set of atoms on the surface of the catalytic substrate. However, it must also be taken into account the influence coming from the surrounding environment, where it is probable that there was no direct contribution to the elementary steps of the catalyzed reaction, although this surrounding environment is fundamental for configuring the “ideal” condition for the catalytic phenomenon. Considering that the entire (111) terraces of stepped Pt surfaces are more catalytically active for CO₂ formation, compared to the top side of the steps, it is reasonable that the concept of *most active sites* on Pt(111) terraced surfaces must include the influence of the steps toward the terraces. At least in the case of stepped Pt surfaces and the two reactions considered in this study, the concept of the *most active site* does not seem to be something confined locally to the place where the reaction (elementary) steps are developed.

The present article does not discuss the importance of the extrinsic surface part (the electrolyte^{63,64}) in the configuration of the active sites. In this sense, we make the concept of active site more general in 2-dimension. It can be concluded that the steps act in modifying their neighboring environments, which results in favoring activation of the pathway for CO₂ formation at the (111) terraces (while other reaction pathways are inhibited in this places). At the limit of the terraces of the stepped surfaces, the *most active sites* for CO₂ formation reside at the bottom side of the (110) steps or the locally concave structure (see Figure 1), which for the reaction of hydrogen adsorption/desorption ($H_{ads} \rightleftharpoons H^+ + e^- + *_{available\ Pt\ sites}$) behave as being the (111) terrace sites. In this regard, it should be highlighted that optimizing the population of the most active sites on the surfaces requires the employment of Pt surfaces with shorter terraces. Account must be taken of the three-dimensional electrochemical environment in which the site resides, considering the structural characteristics of the interface, nature of the electrolyte and mass transport.

4.3. The Chemical Reactions Concerning CO₂ Formation

In this paper, we analyze the pathway of CO₂ formation during the electro-oxidation of methanol (and ethanol) involving CO_{ads}. The specificity of the experiments precluded a more accurate elucidation of the CO_{ads} pathway. Based on the experimental results shown in Figures 5, 6, and 7, from the surface structure viewpoint, there were two channels of CO₂

formation from the electro-oxidation of methanol and ethanol. One channel involves the electro-oxidation of the CO_{ads} species on the (111) terraces, as summarized in Equation 5. The other channel involves the CO_{ads} on the top of the steps, with the oxygen-containing species being formed on any type of active site, which could be terraces or steps, as summarized in Equation 6.

In these equations, $\text{Pt}_x^{\text{terr}}-(\text{H}_2\text{O})_{\text{activ}}$ and $\text{Pt}_b^*-(\text{H}_2\text{O})_{\text{activ}}$ represent active sites occupied by oxygen-containing species at the (111) terraces and any type of Pt site, whether terrace or step ($\text{Pt}_b^{\text{terr}}-(\text{H}_2\text{O})_{\text{activ}}$ and $\text{Pt}_b^{\text{step}}-(\text{H}_2\text{O})_{\text{activ}}$). $\text{Pt}_y^{\text{terr}}-(\text{CO})$ and $\text{Pt}_a^{\text{step}}-(\text{CO})$ represent CO adsorbed on sites assigned as being (111) terraces and the top side of the steps, respectively. The onset potentials for Reactions 5 and 6 were ~ 0.40 and ~ 0.62 V_{RHE} , respectively, giving $\Delta E \simeq 0.22$ V. It should be noted that the two proposed reactions behave as being competitive if the CO_{ads} on terraces and CO_{ads} on steps are oxidized by oxygen-containing species on terraces (see Equations 5 and 6). We think that this is especially likely to occur at larger overpotentials. These general ideas are depicted in the Graphical Abstract, which illustrates that the preferential reaction pathway for CO_2 formation from the alcohols takes place on the terraces of the Pt surfaces, with the least active sites being the top side of the steps.

5. Main Conclusions

This paper reports specific experiments designed to decipher the nature of the active sites involved in the electro-oxidation of methanol and ethanol at Pt electrodes, from which the following main conclusions can be drawn:

- i. The electro-oxidation reactions of methanol and ethanol present the same types of surface structures behaving as the *most active sites* for activation of the pathway for CO_2 formation. On Pt(111) terraced surfaces, the *most active sites* reside on the (111) terraces, while the *least active sites* reside on the top of the steps. The reaction pathways related to the *most active sites* and *least active sites* are separated by about ~ 0.22 V.
- ii. In the electro-oxidation of methanol and ethanol toward CO_2 by means of the CO_{ads} pathway, the lowest catalytic activity at the top of the steps implied that at that location, the CO_{ads} acted mainly as a catalytic poison, while CO_{ads} on the (111) terraces behaved as an active reaction intermediate.

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3 *iii.* The existence of the *most active sites* residing on the (111) terraces is linked to the
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5 influence of the physical nature of the steps toward the terrace domains. In comparison
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7 to the “infinitely wide” (111) terraces, the existence of the steps/defects on the surface
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9 changes the chemical properties of the (111) terraces of the stepped surfaces, favoring
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11 activation of the reaction pathway for CO₂ formation. Additionally, in the case of
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13 ethanol, the presence of steps on the surface inhibits the pathway of acetic acid formation
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15 on the (111) terraces. The pathway of acetic acid formation is only activated when the
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17 top of the steps starts to be released due to CO_{ads} electro-oxidation at these sites. The role
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19 played by steps/defects in the creation of *most active sites* for the formation of CO₂ on
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21 terraces was physical in nature, rather than chemical, since no elementary step of the
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23 catalyzed reaction occurred at them. Therefore, the concept of active site was made more
24
25 general, involving two dimensions.

26 Associated Content

27 Supporting Information

28 Additional experimental results, including the cyclic voltammetry and *in situ* FTIR data
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30 (PDF).
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Figures

Figure 1. Cyclic voltammograms of the Pt(332) and Pt(665) crystals in the presence of 0.1 M HClO₄, at 50 mV s⁻¹. Black line: blank voltammogram; orange line: ¹³CO exclusively on the top of the (110) steps. The data include a hard model (drawn here: <http://surfexp.fhi-berlin.mpg.de/>) of a crystal surface. The row of atoms at the bottom of the steps is part of the steps.

Figure 2. (A): Cyclic voltammetry for oxidation of CO only on the top of the (110) steps of Pt(332) in 0.1 M HClO₄ electrolyte solution (orange line). The data shown by the black line refer to the blank cyclic voltammogram. Data recorded at a potential scan rate of 50 mV s⁻¹. (B): *In situ* FTIR spectra at 0.200 V_{RHE} of adsorbed ¹²CO on a Pt(332) surface in 0.1 M HClO₄, for CO at full coverage (blue line) and CO only on the top of the steps (olive line). The reference spectra were acquired at 0.800 V_{RHE}.

Figure 3. Two consecutive voltammetric cycles for the electro-oxidation of methanol (5.0 mM) and ethanol (10.0 mM) on a stepped Pt(332) single crystal in 0.1 M HClO₄ electrolyte. Orange line: first potentiodynamic cycle; blue line: second potentiodynamic cycle; black line: blank voltammogram. Data recorded at a scan rate of 50 mV s⁻¹.

Figure 4. Spectra for electro-oxidation of methanol on a Pt(332) stepped single crystal in 0.1 M HClO₄. (A) 50.0 mM methanol; (B) 5.0 mM methanol. The data show the influence of the concentration of common methanol on the magnitude of the band for ¹³CO₂. The series of spectra (200 interferograms at resolution of 8 cm⁻¹) was acquired from 0.050 to 0.800 V_{RHE}, in intervals of 25 mV (only some selected spectra are shown). The reference spectrum was acquired at 0.100 V_{RHE}.

Figure 5. Spectra for the electro-oxidation of methanol (1.0 mM) on a Pt(332) stepped surface with the (110) steps previously and selectively decorated with ¹³CO_{ads}. The series of spectra (200 interferograms at resolution of 8 cm^{-1}) was acquired from 0.050 to 0.800 V_{RHE} , in intervals of 25 mV (only some selected spectra are shown). The reference spectrum was acquired at 0.100 V_{RHE} .

Figure 6. Spectra for the electro-oxidation of methanol (1.0 mM) on a Pt(665) stepped surface with the (110) steps previously and selectively decorated with ¹³CO_{ads}. The series of spectra (200 interferograms at resolution of 8 cm^{-1}) was acquired from 0.050 to 0.800 V_{RHE} , in intervals of 25 mV (only some selected spectra are shown). The reference spectrum was acquired at 0.100 V_{RHE} .

Figure 7. Spectra for the electro-oxidation of ethanol (10.0 mM) on a Pt(332) stepped surface with the (110) steps previously and selectively decorated with ¹³CO_{ads}. The series of spectra (200 interferograms at resolution of 8 cm⁻¹) was acquired from 0.050 to 0.800 V_{RHE}, in intervals of 25 mV (only some selected spectra are shown). The reference spectrum was acquired at 0.400 V_{RHE}.

Graphical Abstract