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Electrooxidation Of C1 Organic Molecules On Pt Electrodes

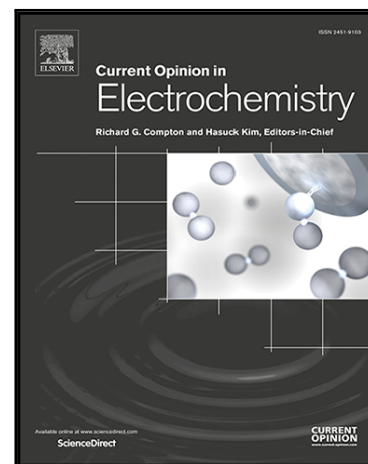
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Highlights

- All C1 molecules follow a dual path mechanism, with adsorbed CO the catalytic poison formed in the indirect path.
- The presence of sites with different reactivity, and the rate of surface diffusion of adsorbed CO, determine the rate and potential range within which CO is oxidised.
- Adsorbed formate appears during the oxidation of all C1 molecules, but its actual role in the reaction mechanism is still unclear.
- The direct and indirect reaction pathways have different site requirements. Three contiguous Pt atoms are required in the indirect path leading to adsorbed CO, while just two adjacent Pt atoms suffice for complete oxidation to CO₂ through the direct path.

ELECTROOXIDATION OF C1 ORGANIC MOLECULES ON Pt ELECTRODES

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Abstract

C1 molecules are potential alternative fuels for fuel cells, with a higher volume-specific energy density than hydrogen, and with higher energy conversion efficiencies than heavier organic molecules like ethanol, because their oxidation does not require the rupture of any C–C bonds. However, the development of economically competitive direct C1 fuel cells is hampered by CO poisoning and by the necessity to employ Pt-based electrocatalysts. Reducing CO poisoning to a tolerable level and developing cheaper and durable electrocatalysts requires a deep knowledge of the reaction mechanism on Pt, the archetypal electrocatalyst. In this brief review we summarise current knowledge in this field.

Introduction

Although hydrogen is the fuel with the highest possible mass-specific energy density, being a gas, it has a very low volume-specific energy density, which poses a problem, particularly if hydrogen-fed PEMFCs are to be deployed in transport applications. This can be alleviated by compressing hydrogen at high pressures, though at the cost of generating a potential safety hazard (and of requiring energy, decreasing the overall efficiency of the energy conversion process).

Alternatively, PEMFCs can be directly fed liquid organic fuels with a higher volume-specific energy density, although in this case emissions will contain CO₂ in addition to water. The energy cycle can still be carbon-neutral, though, if the fuel has been generated via CO₂ reduction using electricity from renewables, or if it is a biofuel. Even if this is not the case, CO₂ emissions might be reduced, as compared with those resulting from combustion engines, due to the inherent higher efficiency of fuel cells.

Although energy density increases with the number of carbons in the molecule, total oxidation of oxygenated C1 molecules (formic acid, formaldehyde and methanol) is more efficient than that of CH₄ or of molecules with a higher number of carbons, because breaking C–C bonds is not necessary, and at least one C–O bond is already present. However, the catalyst is easily deactivated due to CO poisoning, and reactivation of the catalyst requires the electrooxidation of chemisorbed CO (CO_{ad}). Developing new electrocatalysts for the oxidation of C1 molecules with high activity, resistant to CO poisoning, and with high durability requires a detailed knowledge of the mechanism of all the reaction pathways, including the electrooxidation of CO_{ad}. This chapter reviews current knowledge of the mechanism of the electrooxidation of carbon monoxide and C1 molecules on platinum (the archetypal electrocatalyst).

Electrooxidation of carbon monoxide

Significant work on the electrooxidation of CO on Pt electrodes started in the 60's in the Research Laboratories of General Electric in Schenectady, N. Y., with Gilman and Breiter. Gilman was the first to propose that the electrooxidation of CO takes place by what he called a "reactant-pair" mechanism [1], in which CO_{ad} reacts with an adjacent adsorbed water molecule, in what is in effect a Langmuir-Hinshelwood mechanism. This is still at the basis of our current understanding of the reaction mechanism, although the oxygen donor is now assumed to be adsorbed OH (OH_{ad}), generated upon oxidation of interfacial water. The main remaining open question refers to the mobility of CO_{ad} .

Breiter was the first to detect, using galvanostatic methods, that both on platinized platinum [2] and smooth Pt [3] electrodes there are two types of chemisorbed CO, one oxidized between 0.2 and 0.4 V vs. RHE (a potential region currently known as the pre-peak or the pre-ignition wave, depending on authors), and another oxidized at higher potentials. The nature of the low-potential pre-peak has been the subject of intensive research [4–13], and will be discussed here in some detail.

It is now firmly established that the potential at which CO is first admitted to the electrolytic cell crucially determines the electrocatalytic properties of Pt for CO electrooxidation: if the admission potential is lower than 0.3 V vs. RHE, a pre-peak appears at potentials between 0.4 and 0.6 V, followed by the main peak at about 0.7 to 0.9 V (the exact peak potential depends strongly on the surface structure, including the presence of defects when working with single-crystal electrodes), while if the Pt electrode is held at higher potentials during CO admission only the main peak appears. In the presence of CO in the solution, diffusion-limited oxidation of bulk CO can occur in the potential region corresponding to the pre-peak.

Fig. 1 shows plots of the CO-coverage, obtained from CO-stripping voltammograms, on Pt(111) [11], Pt(100) [12], and Pt(poly) [9] electrodes in CO-free 0.1 M H_2SO_4 as a function of the dosing potential (E_d). In the case of the Pt(poly) electrode, the coverage as obtained from the integration of the CO_2 -band in FT-IR spectra has also been included. In all cases, the conditions under which the pre-peak appears are also those under which the maximum CO_{ad} coverage can be achieved.

The pre-peak has usually been attributed to the oxidation of CO_{ad} at defect sites [9–12,14–16], although the exact nature of the defects has been a question of debate, proposals ranging from step sites [10] to nanoislands [16]. The pre-peak, and in general the presence of more than one peak in CO-stripping voltammograms, has been often associated to the slow diffusion of CO_{ad} on Pt surfaces [9–12,17,18]. Slow CO_{ad} diffusion would explain the formation of different kinds of CO adlayers on Pt(100) at different E_d , with clearly different CO-stripping voltammograms [12], and would agree with observations based on infrared reflection-absorption experiments (IRRAS) [19], according to which the local CO coverage remains high during CO-stripping even when the total coverage has decreased to 0.06 ML. On the contrary, high diffusion coefficients of $10^{-11} - 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ have been estimated for CO_{ad} on Pt by fitting CO-stripping current transients to a mean-field Langmuir-Hinshelwood model [20]. We have suggested that the rate of diffusion might depend on the CO coverage or even the size of CO domains [11]. A later time-resolved infrared study of the dynamics of CO_{ad} electrooxidation by Samjeské et al. [21] revealed that the mobility of CO_{ad} increases significantly indeed in the main peak, after partial oxidation of the adlayer via a nucleation-and-growth mechanism. They also found that diffusion of CO_{ad} on terraces is much faster than that of CO_{ad} at step edges. Recently, Wang and Abruña [22] have suggested that, even if CO_{ad} diffusion is fast, multiple peaks associated to reaction at different sites may arise due to the competition

between CO_{ad} and OH_{ad} for the most reactive sites once the CO initially on those sites has been stripped.

Electrooxidation of formic acid, formaldehyde and methanol

The dual-path mechanism

A common characteristic in the electrooxidation of methanol, formaldehyde and formic acid is that all three follow a so-called dual-path mechanism. The dual path mechanism is illustrated in Scheme 1. Please note that the sequence methanol \rightarrow formaldehyde \rightarrow formic acid \rightarrow carbon dioxide does not imply a sequential mechanism for the direct path, and is simply intended to illustrate the degree of oxidation of the molecules considered (although HCOOH has indeed been detected as an incompletely oxidised product in the oxidation of methanol and formaldehyde [23], and adsorbed formate has been detected during the electrooxidation of methanol [24] and formaldehyde [25]).

In one of the reaction paths (usually called the indirect path) an undesired catalytic poison, namely, CO_{ad} , is formed en-route to the final reaction product (CO_2), while in the other path (usually called direct) CO_2 is formed through a different set of intermediates which does not include CO_{ad} . Once CO_{ad} is formed, it can only be removed from the Pt surface by oxidative stripping, for which, as discussed above, OH_{ad} is needed. In other words, CO_{ad} can only be stripped at high overpotentials, which in a fuel cell would imply a considerable decrease of the device's power and efficiency.

As can be seen in Scheme 1, in the case of formic acid, the indirect path involves breaking one of the C–O bonds, which needs to be formed again upon oxidation of CO_{ad} to reach the final product, CO_2 . In the case of methanol, it can also be deduced from Scheme 1 that in the direct path the additional C–O bond is most likely formed before the oxidation state corresponding to HCOOH and CO_{ad} is reached, while in the indirect path first all the C–H and the O–H are broken, and the new C–O bond is only formed upon oxidation of the resulting CO_{ad} . In the case of formaldehyde, in aqueous solutions 99% will be in its hydrated form, methylene glycol, which already contains the two C–O bonds present in the final product, while formation of CO_{ad} from formaldehyde would only require the rupture of two C–H bonds.

The detailed mechanisms of both the direct and indirect paths are still unknown and debated, because spectroscopic detection of intermediates has proven elusive. Actually, the only species that have been unambiguously detected on the electrode surface during the oxidation of C1 molecules are CO_{ad} and bridge-bonded adsorbed formate (HCOO_{ad}). HCOO_{ad} was initially suggested as an intermediate in the direct path of the oxidation of C1 molecules [24–26], but this role has since been much debated [27,28]. The activation barrier for breaking the C–H bond of HCOO_{ad} is too high [29], and therefore it has been suggested that it cannot be the active intermediate in the direct path of the electrooxidation of formic acid (equivalently, it cannot be the last intermediate in the direct path of the electrooxidation of C1 molecules). However, recent studies analyzing the pH dependence of the electrocatalytic activity towards the formic acid oxidation suggest that some other kind of adsorbed formate is the active species in the oxidation of formic acid/formate [30–35]. The debate does not seem to be over, though [36].

HCOO_{ad} has also been suggested to be the intermediate in the formation of CO_{ad} from formic acid [37,38], in a mechanism that involves an oxidation equilibrium ($\text{HCOOH} \rightleftharpoons \text{HCOO}_{\text{ad}} + \text{H}^+ + e^-$) followed by a reduction ($\text{HCOO}_{\text{ad}} + \text{H}^+ + e^- \rightarrow \text{CO}_{\text{ad}} + \text{H}_2\text{O}$), the latter being the rate-determining step. This mechanism is in agreement with the experimentally observed bell-shaped dependence of

the rate of dehydration of formic acid on potential [39,40]. Very little is known, though regarding the intermediates involved in CO_{ad} formation from methanol or formaldehyde.

Atomic-ensemble effects and site requirements in the electrooxidation of C1 molecules

As in heterogeneous catalysis, in electrocatalysis reactants, products and intermediates need to interact with the surface of the catalytic material, in order to break and form bonds, so that the reactants can be transformed into new chemical species. The availability on the surface of the electrocatalyst of specific atomic groupings that can provide the number of surface atoms necessary for the chemisorption of reactants, intermediates and transition states often plays, hence, a critical role in determining the activity and selectivity of the electrocatalyst.

It is now a well-established fact that the dehydrogenation of methanol [41] and the dehydration of formic acid [42] to CO_{ad} require larger atomic ensembles than their oxidation through the direct path CO_2 . This is summarised in Figure 2, which explains experimental results obtained by applying the so-called site-knockout strategy [43] using cyanide-modified Pt(111) electrodes. The surface structure of cyanide-modified Pt(111) is illustrated in Figure 2A. The six CN_{ad} groups forming the hexagonal rings are not individually resolved in the STM image in Figure 2A and, instead, are observed as a single tunneling spot with a slight depression at its centre. Two translational domains, and the domain boundary separating them, can be observed in the image, which shows some drift, a problem difficult to avoid, particularly in EC-STM. As shown in Figure 2B, the cyclic voltammogram of a cyanide-modified Pt(111) electrode in the presence of methanol in acidic solution shows no hysteresis between the positive- and the negative-going sweeps, which strongly suggests that no CO poisoning is taking place. This is confirmed by the in-situ infrared reflection-absorption spectra (IRRAS) in Figure 2C, where it can be clearly seen that CO_2 is produced during the electrooxidation of methanol on cyanide-modified Pt(111), but no CO_{ad} is generated at all on the surface. Figure 2D shows that modifying Pt(111) with the cyanide adlayer is equivalent to knocking out all the sites containing three contiguous Pt atoms from the Pt(111) surface. These results imply that, although a minimum of three contiguous Pt atoms are required for the dehydrogenation of methanol [41] and the dehydration of HCOOH [42] to form CO_{ad} , two adjacent Pt atoms suffice for their electrooxidation to CO_2 .

Conclusions

Despite decades of intense research, there are still more open questions than answers regarding our understanding of the mechanism of the electrocatalytic oxidation of C1 molecules on Pt electrodes.

We know that the catalytic poison generated along the undesired indirect path is CO_{ad} , and that its oxidation proceeds via a Langmuir Hinshelwood mechanism involving reaction with OH_{ad} generated by the oxidation of H_2O (or via direct electroadsorption of OH^- in alkaline solutions). We also know that sites with different reactivities on the electrode surface are able to oxidise CO_{ad} at different potentials, and that the surface mobility of CO_{ad} might play an important role, with the diffusion coefficient probably depending on both coverage and adsorption site.

Much less is known regarding the intermediates and steps involved in the formation of CO_{ad} or in the direct path. We know that the site requirements for the two paths are different, three contiguous Pt atoms being required for CO_{ad} formation from HCOOH and CH_3OH (and very likely also from H_2CO),

while only two adjacent atoms are necessary in the direct path. The common site requirements of all three C1 molecules for their oxidation through the direct path suggest that the last stages of their oxidation to CO₂ might also be common. This is in accordance with the detection of HCOO_{ad} in all three cases, but it is unlikely that this is the actual last reactive intermediate (HCOO_{ad} and the actual reactive intermediate might be connected through an interconversion equilibrium, though). There exists some solid evidence that HCOO_{ad} is involved in the formation of CO_{ad}, although also in this case it is unlikely that it is the actual intermediate, which might be some other adsorbed formate species in equilibrium with HCOO_{ad}.

Some of the questions that remain open are.

1. What is the real role of HCOO_{ad} in the direct path of the electrooxidation of C1 molecules and in the dehydration of formic acid to CO_{ad}? Is it in equilibrium with the actual reaction intermediates? If yes, what are those intermediates?
2. Do formaldehyde and methanol share the last track of the path to CO_{ad}? If so, what is the intermediate involved?
3. When is the second C–O formed along the direct path of the electrooxidation of methanol and formaldehyde to CO₂? Is this step common for these molecules? If so, is methylene glycol (the majoritary species in aqueous formaldehyde solutions, already containing two O atoms bonded to the C atom) involved?

Solving these questions would considerably deepen our understanding of the electrocatalytic oxidation of C1 molecules, and would provide knowledge critical to the development of more efficient electrocatalysts.

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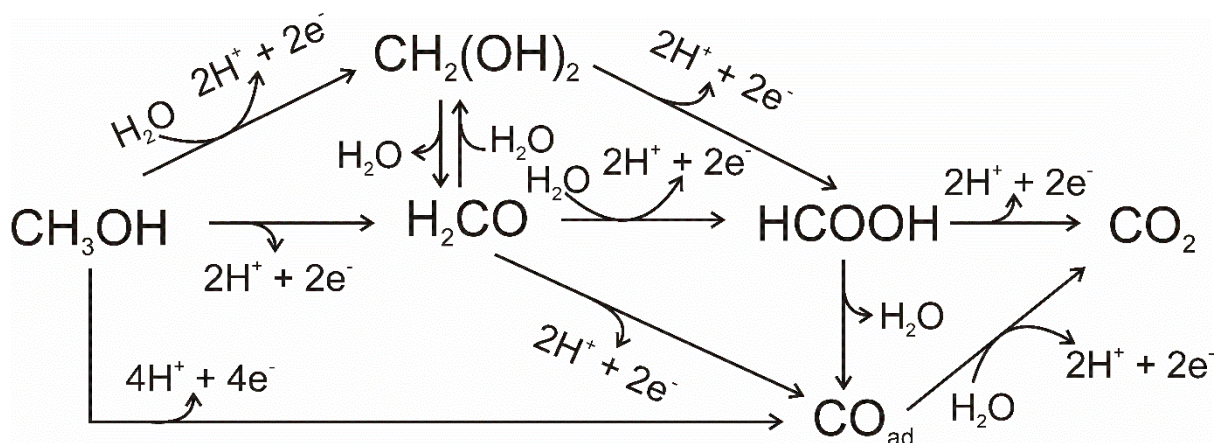
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Probably the Strongest experimental evidence of the site requirements of the two reaction paths of methanol electrooxidation. Similar results were reported for formic acid in [42].
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Scheme 1



ACCEPTED MANUSCRIPT

Figures

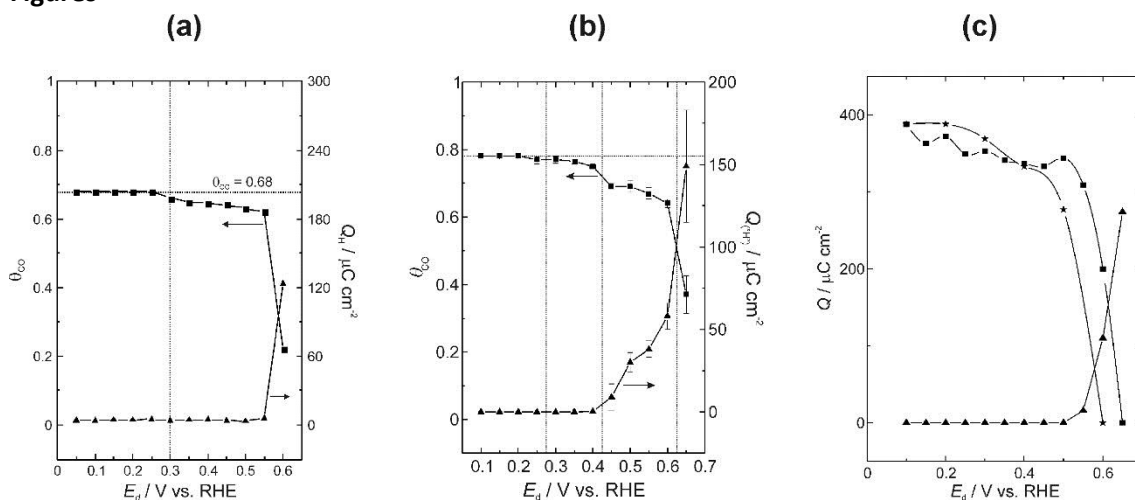


Figure 1. Plot of the CO coverage in CO-free 0.1 M H_2SO_4 as a function of the dosing potential on the Pt(111) **(a)**, Pt(100) **(b)** and Pt(poly) **(c)** surfaces. The total charge, without double layer correction, in the hydrogen region of the cyclic voltammograms (triangles) is also included in the figures. The horizontal lines in **(a)** and **(b)** correspond to the maximum CO coverage in CO-free solutions. The vertical line in **(a)** indicates the dosing potential at which a decrease in the CO coverage is detected. The vertical lines in **(b)** separate the regions giving rise to different types of CO-stripping voltammograms. The star symbols in **(c)** correspond to CO-coverage data obtained from the integration of the CO_2 band in FT-IR spectra after stripping of the CO adlayer. (Adapted from Refs. [9,11,12]).

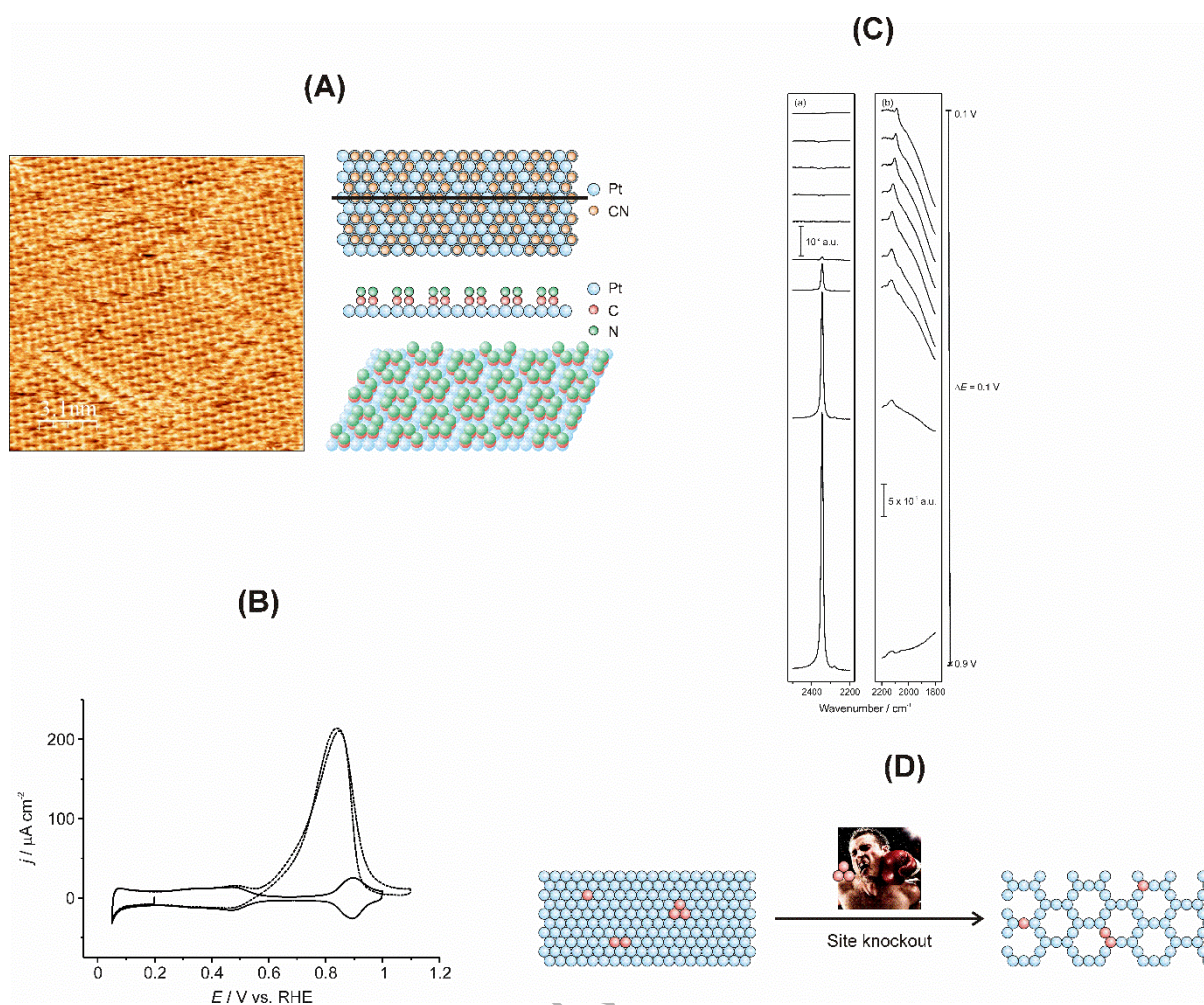


Figure 2. (A) STM image (left, $16 \times 16 \text{ nm}^2$) of a cyanide-modified Pt(111) electrode in $0.1 \text{ M HClO}_4 + 0.05 \text{ M KClO}_4$ at $E = 0.65 \text{ V vs. RHE}$ showing the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure adopted by the adsorbed cyanide ($U_T = 0.37 \text{ V}$ (tip negative); $I_T = 2 \text{ nA}$), and ball model (top right, top view) of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure adopted by the cyanide adlayer on Pt(111). Blue balls correspond to Pt atoms and orange balls to irreversibly adsorbed CN groups. The middle and bottom schemes in the right panel are a cross section of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure along the black line in the top view model, and a perspective of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure adopted by the cyanide adlayer on Pt(111), respectively. From Ref. [43]. (B) Cyclic voltammograms at 50 mV s^{-1} of a cyanide-modified Pt(111) electrode in 0.1 M HClO_4 (solid line) and $0.1 \text{ M HClO}_4 + 0.2 \text{ M CH}_3\text{OH}$ (dashed line). The scan starts at 0.20 V in the negative direction. From Ref. [41]. (C) FT-IRRAS spectra at increasing potentials of a cyanide-modified Pt(111) electrode in $0.1 \text{ M HClO}_4 + 0.2 \text{ M CH}_3\text{OH}$. The spectra in the frequency region between 2500 and 2200 cm^{-1} were calculated using the spectrum at 0.05 V vs. RHE as a reference, while the spectra in the frequency region between 2200 and 1800 cm^{-1} were calculated using the spectrum at 1.30 V vs. RHE as a reference. From Ref. [41]. (D) Chemical modification of Pt(111) with adsorbed cyanide results in knocking out from the surface all the sites with three contiguous atoms, leaving a surface where the largest atomic ensemble corresponds to two adjacent Pt atoms. From Ref. [43].