Why Methanol Electro-oxidation on Platinum in Water Takes Place Only in the Presence of Adsorbed OH

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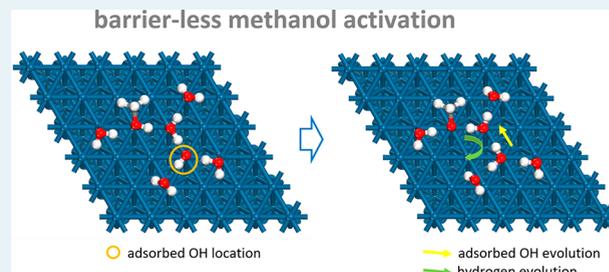
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ABSTRACT: Untangling the mechanism of the methanol electro-oxidation on platinum in water as a model reaction is essential to optimize fuel cells using alcohols as fuel. Recent experiments unexpectedly suggested that this electro-oxidation process would take place only in the presence of adsorbed OH. The here reported results, carefully obtained under low methanol concentrations on the three basal planes of platinum at different scan rates to discriminate between oxidation and adsorption processes, confirm such an unexpected preliminary observation. It is found that adsorbed CO from methanol is only formed when adsorbed OH is already present on the surface. This observation is a clear indication that adsorbed OH is involved in the mechanism beyond providing the oxygen group required to oxidize adsorbed CO, which has never been considered before. Supported by density functional theory calculations, the role played by adsorbed OH in the methanol electro-oxidation to CO on platinum in water and the reason why this reaction is not observed in the absence of adsorbed OH are also here both elucidated. A combination of kinetic and thermodynamic factors, such as the presence of multiple water molecules per methanol molecule, the high adsorbed OH mobility on the surface, the favorable coadsorption of methanol in the presence of adsorbed OH, and the favorable and virtually barrier-less hydrogen transference from the hydroxy group of methanol to adsorbed OH to yield water result in the immediate activation of methanol (as soon as the molecule approaches the surface) through the favorable substitution of adsorbed OH by adsorbed methoxy. This contribution represents a change of paradigm in the understanding of how alcohols are electro-oxidized in reference systems and have crucial implications in the search for better electrocatalysts.

KEYWORDS: electrocatalysis, methanol oxidation, platinum, reaction mechanism, OH adsorption

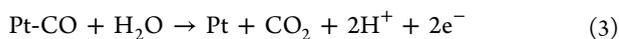Being liquids at room temperature, alcohols are more easily stored than hydrogen to be oxidized in fuel cells.[1−4] As a counterpart, higher oxidation overpotentials are required to oxidize alcohols.[5−8] Thus, untangling the mechanism of the methanol electro-oxidation on platinum in water (the simplest alcohol on the reference anode in the most environmentally friendly solvent) as a model reaction is essential to optimize these processes.[9−18] The complete oxidation of methanol to CO_2 involves six electron transfers and multiple steps,[5−8] according to

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$
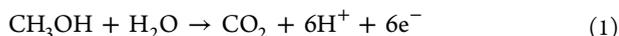
The main path of the reaction probably proceeds through the adsorbed CO intermediate,[19] according to

$$CH_3OH + Pt \rightarrow Pt\text{-}CO + 4H^+ + 4e^- \qquad (2)$$

which is subsequently oxidized to CO_2

$$Pt\text{-}CO + H_2O \rightarrow Pt + CO_2 + 2H^+ + 2e^- \qquad (3)$$

Isotopic labeling unequivocally shows that O−H bond cleavage is the first step in the methanol decomposition on platinum under high vacuum conditions.[20] Also, it is accepted that methanol C−H bond cleavage is the rate-determining step in the methanol electro-oxidation on platinum in water.[20,21] Moreover, it is generally recognized that solvent effects would have a role in the mechanism, though it is not completely understood yet.

Through exploration of interfacial aspects of this electro-oxidation process, it has been recently and unexpectedly found that the methanol electro-oxidation onset on the Pt(111) surface in water coincides with that of OH adsorption.[22] Preliminary observations suggest that adsorbed OH would be involved in the reaction mechanism beyond providing the oxygen group required to oxidize adsorbed CO. The participation of adsorbed OH in this mechanism has never been considered before.[23−25] In other oxidation mechanisms, such as those related to CO oxidation on gold and copper, the

participation of adsorbed OH explains the unexpected activities found for the reaction.[27,28] Also, it has been shown that preadsorbed oxygen favors the methanol activation in ultrahigh vacuum (UHV).[26] To further explore this issue, new voltammetric experiments performed under low methanol concentrations on single crystal platinum electrodes at different scan rates to discriminate between faradic oxidation and adsorption processes are here discussed. Since methanol oxidation currents on platinum are much lower than diffusion limiting currents, methanol oxidation currents are almost independent of the scan rate on this metal. By contrast, the adsorption currents originated by adsorbed H and OH are proportional to the scan rate. Thus, at low scan rates, the oxidation currents dominate these voltammetric profiles, being the adsorption currents masked by the faradaic current. By contrast, at high scan rates, the adsorption processes dominate the profiles, enabling the comparison of these processes to those registered in the absence of methanol. The here reported results confirm that methanol electro-oxidation on platinum in water takes place only in the presence of adsorbed OH. Supported by density functional theory (DFT) calculations, a complete explanation is provided for that.

In the voltammetric profiles displayed in Figure 1, it can be observed that, at low scan rates, the methanol oxidation onset
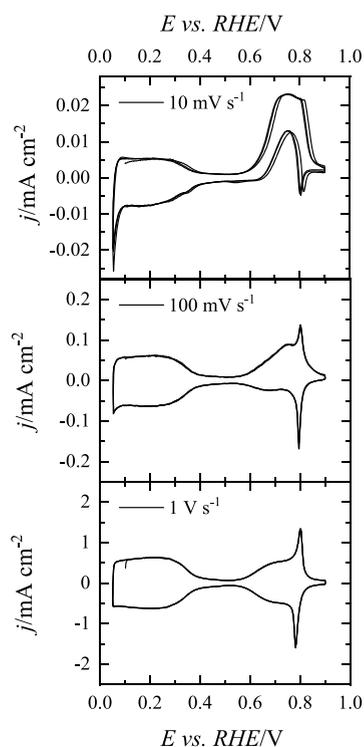

Figure 1. Voltammetric profiles (three full cycles) for the Pt(111) electrode in 0.1 M $HClO_4$ + 0.1 mM MeOH at selected scan rates.

on Pt(111) is 0.6 V. This onset potential coincides with that for OH adsorption on this electrode. At 10 mV s^{-1}, the current reaches a plateau centered at ca. 0.72 V, sharply diminishing for E > 0.8 V. This potential is very close to that for the sharp peak observed in the absence of methanol, which marks the OH adlayer completion in the absence of methanol. In the negative scan direction, oxidation currents increase from 0.8 V, being negligible for E < 0.6 V. The profile is stable upon cycling and no CO accumulation on the surface is detected

since the hydrogen adsorption profile coincides with that obtained in the absence of methanol. As the scan rate increases, the voltammetric profile evolves to that obtained in the absence of methanol (given that oxidation currents are independent of the scan rate and adsorption currents linearly increase with it). This evolution can be more easily appreciated when these profiles are represented in capacitance units by dividing the current density by the scan rate (Supporting Information Figure S1). In fact, the profile obtained at 1 V s^{-1} coincides with that at 50 mV s^{-1} in the absence of methanol, the only difference being the slight displacement of the sharp peaks at 0.8 V (Figure S2). As the scan rate increases, these peaks slightly shift as a result of kinetic effects on the OH adsorption process. It is worth noting that the oxidation profile for methanol at high scan rates on this electrode qualitatively differs from that for formic acid, where a signal related to adsorbed formate can be clearly observed.[29] This difference provides evidence that methanol adsorption on this electrode is weak and does not interfere with those of H and OH.

When the voltammetric profiles for the Pt(111) electrode obtained in the absence and presence of methanol are compared (Figure S3), it is clear that OH is already adsorbed on the surface when CO_2 is produced from methanol. In fact, it can be concluded that methanol oxidation on this electrode takes place only in the presence of adsorbed OH. Oxidation currents appear exclusively in the OH adsorption region, the oxidation being inhibited at 0.9 V after the OH adlayer completion. Upon completion of the OH adlayer, there are not enough contiguous free sites for methanol to adsorb, so that the reaction is inhibited. From the observed behavior, it can be proposed that adsorbed OH takes part in the oxidation mechanism. In the absence of methanol, the OH adlayer completion is signaled by the peaks at 0.8 V. In the presence of methanol and at low scan rates, these peaks overlap with the methanol oxidation current, being displaced to more positive potentials both in the positive and negative scan directions. This behavior clearly indicates that methanol and adsorbed OH are interacting and that adsorbed OH is probably being consumed in the oxidation reaction. The participation of OH in the oxidation mechanism gives rise to lower adsorbed OH coverages at low scan rates (when reaction conditions are close to the OH adsorption equilibrium). At high scan rates, when the OH adsorption rate is much higher than that of oxidation, the adsorbed OH consumption originated by methanol oxidation is negligible.

Unlike the Pt(111) electrode, the H and OH adsorption processes on the Pt(100) electrode overlap. OH adsorption starts at ca. 0.38 V,[30,31] coinciding with the final stage of H desorption, so that, at 0.42 V, H and OH coverages are the same.[32] In the presence of methanol, additional currents between 0.4 and 0.9 V can be observed in the profiles for this electrode (Figure 2). At low scan rates, the profile for the first cycle differs from that for the second and subsequent ones. This observation indicates that CO is being formed and adsorbed on the surface during the oxidation cycles. As before, as the scan rate increases, the profiles evolve toward that obtained in the absence of methanol (Figures S4 and S5), being almost identical at high scan rates. To determine the origin of the observed currents, the profiles obtained in the absence and presence of methanol at low scan rates are compared in Figure S6. The main peak at ca. 0.64 V can be assigned to adsorbed CO oxidation according to reaction 3.[33] The signal appearing at 0.45 V in the first scan, which is not
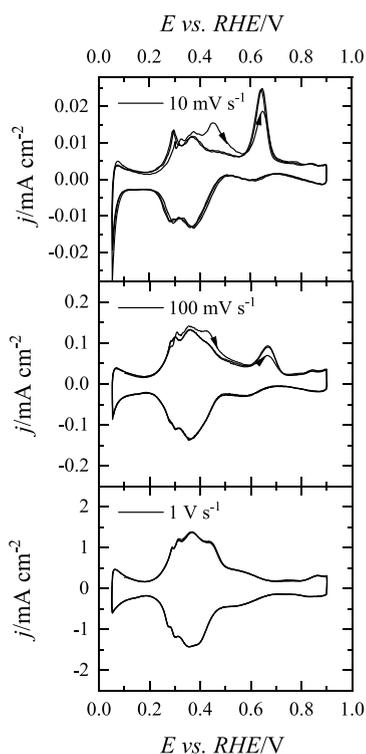
Figure 2. Voltammetric profiles (three full cycles) for the Pt(100) electrode in 0.1 M HClO₄ + 0.1 mM MeOH at selected scan rates. The arrows mark the first positive scan direction of the profile.

present in the profile recorded in the absence of methanol, can be tentatively assigned to CO formation according to reaction 2. Thus, the onset for this signal matches that of OH adsorption on this electrode, providing evidence that OH adsorption and CO formation are linked processes on this surface. In fact, the chronoamperometric curves for methanol oxidation on this electrode indicate that CO formation takes place from 0.4 V.[34,35] This fact explains the differences between the first and subsequent cycles. When the electrode is immersed at 0.1 V, hydrogen readily forms a full adlayer. In the positive scan direction, hydrogen is progressively desorbed, as also happens in the absence of methanol. At the OH adsorption onset, methanol forms adsorbed CO according to reaction 2, giving rise to the signal peaking at 0.45 V. The CO oxidation onset for this electrode is ca. 0.6 V.[36] From this potential, CO oxidation occurs in the peak centered at 0.64 V. At higher potentials, additional methanol molecules are oxidized. In the negative scan direction, at potentials between 0.6 and 0.4 V, adsorbed CO is again accumulated, blocking partially the surface. Thus, in the second scan, at 0.1 V the surface is already partially blocked by adsorbed CO, and the full hydrogen adlayer cannot be formed. In the second scan, when H is desorbed and OH adsorption starts, CO formation according to reaction 2 is hindered by the presence of previously adsorbed CO, explaining the smaller currents obtained in this region during the second and subsequent scans. Despite that, the CO oxidation peak is higher because adsorbed CO has been accumulated during both the negative and positive scan directions. After the second cycle, stationary conditions are attained, and no additional changes are observed upon cycling.

To corroborate that the peaks at 0.45 V in Figures 2 and S6 are linked to CO formation on Pt(100), a charge analysis can

be performed. The ratio between the CO formation charge according to reaction 2 and the CO stripping according to reaction 3 should be 2. However, this charge ratio cannot be easily estimated since additional processes are involved in these peaks. The CO oxidation peak at 0.64 V, whose charge stands for 69 μC cm⁻², includes the charge exchanged in the OH re-adsorption process on the sites previously occupied by adsorbed CO. The peak at 0.45 V contains the charge for the CO formation process and the charge involved in the OH adsorption on the free sites non-occupied by CO. To eliminate the adsorbed OH contribution, the profile obtained in the absence of methanol can be used as baseline, resulting in 86 μC cm⁻². However, this baseline overestimates OH adsorption because, in the presence of adsorbed CO, lower OH coverages will be attained. Under these conditions, the estimated charge ratio (86/69 = 1.25) is lower than expected. However, the CO oxidation charge and the CO formation charge have been overestimated and underestimated, respectively, almost in the same amount. The correction due to the OH coverages can be estimated from the maximum OH coverages, which is estimated to be close to 0.5.[30] Thus, every two adsorbed CO molecules displace an adsorbed OH species, and when two CO molecules are oxidized, an OH species is re-adsorbed. Therefore, from the measured CO oxidation charge (69 μC cm⁻²), 55 μC cm⁻² would correspond to CO oxidation and 14 μC cm⁻² to OH adsorption. With this correction, the ratio would be (86 + 14)/(69 − 14) = 1.8, which is close to the expected value (within the errors of the measurements).

In the voltammetric profiles for methanol oxidation on Pt(110) displayed in Figures 3 and S7, oxidation currents are observed above 0.5 V in the positive scan direction. CO displacement experiments indicate that OH adsorption takes place below 0.2 V on this electrode.[37] Thus, adsorbed OH is
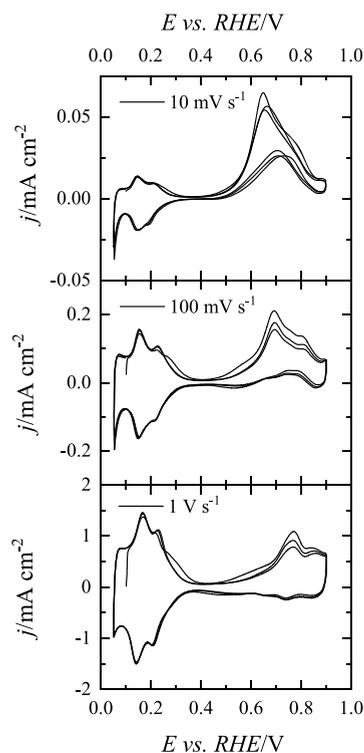

Figure 3. Voltammetric profiles (three full cycles) for the Pt(110) electrode in 0.1 M HClO₄ + 0.1 mM MeOH at selected scan rates.
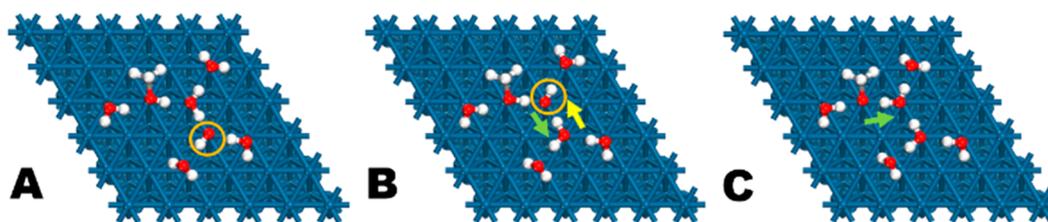
Figure 4. Adsorption configurations on the Pt(111) surface in water involving methanol, adsorbed OH, and their recombination to yield water. (A) Adsorbed methanol in the presence of nonadjacent adsorbed OH. (B) Coadsorbed OH and methanol on adjacent locations. (C) Adsorbed methoxy formed with the aid of adsorbed OH to yield water. Orange circles highlight adsorbed OH locations and yellow and green arrows emphasize adsorbed OH and hydrogen evolutions with respect to the previous state, respectively.
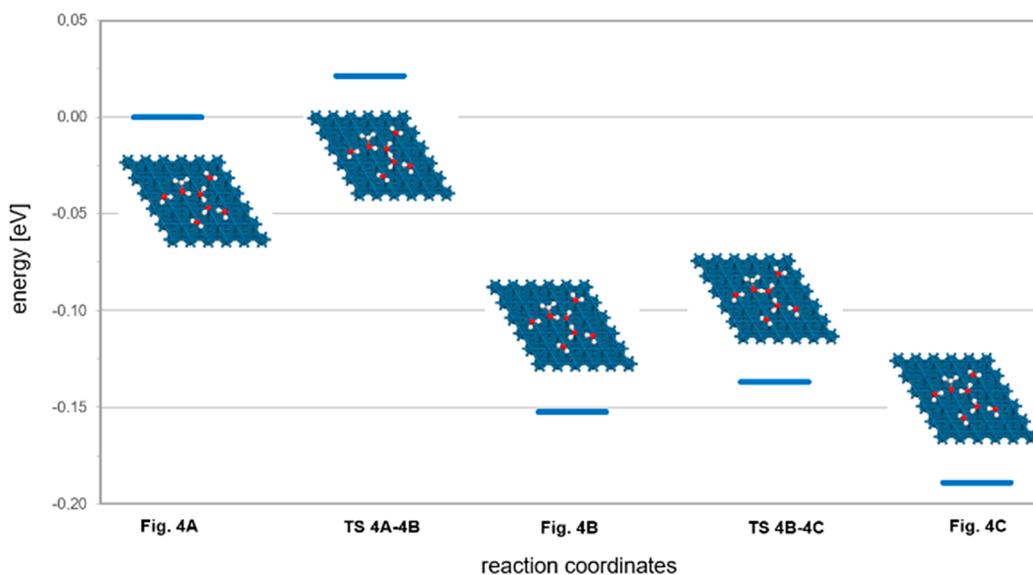

Figure 5. Energy profiles for the virtually barrier-less methanol activation on the Pt(111) surface in the presence of adsorbed OH (using the adsorption configurations from Figure 4A−C and the corresponding transition states).

already present on the surface at the immersion potential and CO can be formed, although a specific CO oxidation peak is not observed. Currents are significantly smaller in the negative scan direction, since surface oxidation, which is an irreversible process for $E > 0.8$ V, hinders methanol oxidation. A small evolution can be appreciated in the profiles upon cycling. This is probably due to surface oxidation/reduction processes, which induce the presence of surface defects. Unlike the other two electrodes, oxidation is here still noticeable at 1 V s^{-1} (Figures S7 and S8). At this scan rate and low potentials, the voltammograms show some differences from that obtained in the absence of methanol, which can be also observed at lower scan rates (Figure S9). These differences are likely due to the presence of adsorbed CO, which blocks the surface and reduces the charge for hydrogen adsorption. The differences between the first and successive scans are minimal, indicating that CO is already formed at the immersion potential.

To elucidate the role played by adsorbed OH in the methanol electro-oxidation to CO on platinum in water, DFT calculations on periodic models of the Pt(111) surface were carried out. Different configurations involving methanol, adsorbed OH, and their recombination (to yield water) were considered (Figure 4). In these configurations, the OH coverage (0.05) corresponds to that observed just after the onset potentials. In Figure 5, the energies for adsorbed methanol in the presence of nonadjacent adsorbed OH (Figure 4A), coadsorbed OH and methanol on adjacent locations

(Figure 4B), and adsorbed methoxy formed with the aid of adsorbed OH to yield water (Figure 4C) are compared. Transition states were also considered.

When the total energy for adsorbed methanol in the presence of nonadjacent adsorbed OH (Figure 4A) is compared to that for coadsorbed OH and methanol in adjacent locations (Figure 4B), it can be concluded that methanol adsorption on the Pt(111) surface in water is significantly favored in the presence of adsorbed OH (Figure 5). The negligible barrier between these states additionally ensures that adsorbed OH on a nonadjacent location will evolve quickly toward the most favorable coadsorption location. Thus, this effect contributes to a better methanol fixation on the surface. Moreover, when the total energy for coadsorbed OH and methanol (Figure 4B) is compared to that for dehydrogenated methanol (Figure 4C), it is observed that hydrogen from the hydroxy group of methanol can be favorably transferred to adsorbed OH to yield water during the methanol electro-oxidation on the Pt(111) surface in water in the presence of adsorbed OH (Figure 5). The negligible barrier between these states additionally assures the high probability of this step. Then, both combined mechanisms give rise to the immediate activation of methanol on the Pt(111) surface in water in the presence of adsorbed OH as soon as the molecule approaches the surface. With the methanol C−H bond being much less polarized, adsorbed OH and methanol coadsorption is not favored through this bond. Thus, the

presence of adsorbed OH has a crucial effect on the methanol electro-oxidation on platinum in water, as it has been experimentally evidenced. These mechanisms explain how the methanol OH bond cleavage is favored under solvation conditions in water. However, these effects do not explain the reason why methanol electro-oxidation on platinum in water is not observed in the absence of adsorbed OH

To further understand the methanol electro-oxidation mechanism on platinum in water, the direct methanol dehydrogenation on platinum in the absence of adsorbed OH was also investigated using DFT. In agreement with previous DFT calculations,[17,18] it has been found that the methanol C−H bond can be more easily cleaved on the Pt(111) surface than the methanol O−H bond, both under high vacuum conditions and in water, which seems to disagree with the experiments (Table S1). However, before these bond cleavages can occur, the C−H (and the O−H) bond have to be unfavorably elongated by a non-insignificant amount, so that each atom can simultaneously interact with each one of a pair of adjacent platinum atoms of the surface, respectively. This requirement determines that these direct dehydrogenation processes on platinum, both in the vacuum and under solvation conditions, are only accessible after surmounting significant barriers (between ca. 0.70 and 1 eV) during the short time interval in which the methanol molecule is in close contact with the surface (methanol weakly interacts with platinum). In any case, large overpotentials are required for that (greater than 0.7 V, as the barriers would suggest). But, well before reaching such potential values, the surface is already covered by adsorbed OH, formed by the direct adsorption of OH⁻ from solution, which is rapidly regenerated by the multiple water molecules that are in a much more continuous close contact with the surface. This mechanism explains how the methanol OH bond cleavage is favored under solvation conditions in water, and why significant methanol electro-oxidation on platinum in water is not observed in the absence of adsorbed OH. The experimental evidence that methoxy formation is the first step in vacuum can be explained by the preferred adsorption geometry of the methanol molecule with the surface, which favors the interaction through the hydroxy group.[20] Under electrochemical conditions, the presence of adsorbed OH favors the methanol O−H bond scission, so that it is no longer the rate-determining step, as observed in UHV, but the C−H bond cleavage, as found experimentally. Moreover, from the different paths proposed for the oxidation of methanol,[17,18] the activation of the O−H bond of methanol favors the path in which the scission of this bond to form adsorbed CH_3O is followed by sequential dehydrogenation to adsorbed CO.[17,18]

In summary, it has been here confidently established that methanol electro-oxidation on platinum in water takes place only in the presence of adsorbed OH. Although the results were obtained for very low methanol concentrations, the onset potentials do not depend on the concentration, and the only change observed when increasing concentration is higher currents.[22] Weak surface interaction and significant barriers hinder the direct methanol activation on platinum at low overpotentials in the absence of adsorbed OH. Before these direct dehydrogenation barriers begin to be surmountable favored as an effect of the potential, the surface is partially covered by adsorbed OH from the media. In the presence of adsorbed OH, high adsorbed OH mobility on the surface, favorable methanol and adsorbed OH coadsorption, and favorable and virtually barrier-less hydrogen transference from the hydroxy group of methanol to adsorbed OH result in the immediate activation of methanol. As soon as the molecule approaches the surface, the favorable reaction of adsorbed OH yields adsorbed methoxy. These mechanisms would operate on the three basal planes of platinum. The present work stands in for a paradigm shift in the understanding of how alcohols are electrochemically oxidized in model systems, demonstrating the key role that species from the media play in the reaction mechanisms and evidencing that engineering different adsorption scenarios can profoundly impact the electrocatalysis of these processes.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c05122.

Experimental and computational methods, additional voltammograms for methanol oxidation on different single crystal electrodes, and methanol dehydrogenation energy profiles (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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