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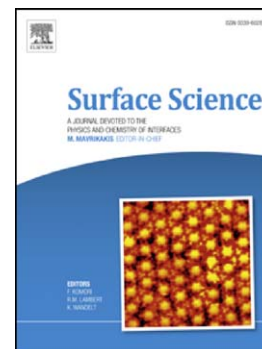
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Influence of beryllium cations on the electrochemical oxidation of methanol on stepped platinum surfaces in alkaline solution

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Abstract

The role of beryllium on the oxidation of methanol on Pt stepped surfaces (Pt[($n-1$)(111)x(110)]) orientation - Pt(553) with $n = 5$, Pt(554) $n = 10$, Pt(151514) $n = 30$), Pt(111) and Pt(110) single crystals in alkaline media was studied by cyclic voltammetry and Fourier transform infrared spectroscopy (FTIRS). The results suggest that under the conditions of the experiment, the methanol oxidation reaction follows a direct pathway with formaldehyde and formate as reaction intermediates. The combination of OH_{ads} and beryllium blocks the adsorption and oxidation of methanol on Pt(111), but appears to promote the complete oxidation of methanol to carbon dioxide/carbonate on Pt(110).

1. Introduction

A fundamental understanding of the influence of the composition of the metal–solution electrochemical interface on the kinetics of electrocatalytic reactions is of great importance for the design of electrochemical energy devices, such as the Direct Methanol Fuel Cell (DMFC). The timeliness and increasing interest in the DMFC as a sustainable energy source has boosted many studies from both fundamental as well as applied perspectives.

From many mechanistic studies¹⁻¹⁰, it is now well accepted that the methanol oxidation reaction follows a dual-pathway mechanism. In the direct pathway of this mechanism, the reactive intermediates are weakly adsorbed on the electrode surface while in the indirect path poisoning intermediates are strongly bonded. Although there is still considerable scientific dispute about the nature of the reactive intermediate species⁴, it is well accepted that that CO is the main poisoning species formed during methanol oxidation at low potentials. CO₂ (as carbonate in alkaline media) is the final product formed at higher potentials³. It is also well accepted that the surface activity strongly depends on its ability to form chemisorbed OH species^{11,12}. In this sense, the catalytic activity towards the CO oxidation on Pt single crystals in alkaline media increases in the following way: Pt(111) < Pt(100) < Pt (110). Moreover, the highest CO tolerance was found at Pt(110) in wide pH range (2-12)¹³. The higher activity of Pt(100) and Pt(110) can be explained by the strong tendency to attract oxygenated species on open surfaces such as Pt(110) and Pt(100) that are necessary to complete the CO oxidation reaction.

Relevant information on the structure sensitivity of methanol oxidation has been obtained by investigating the methanol oxidation on (stepped) single crystal platinum surfaces in both acidic and alkaline media^{1,4}. In acidic media, it has been established that steps enhance the initial dehydrogenation step^{7,8}, and steps are also the active sites

for the oxidation of chemisorbed CO¹⁴⁻¹⁶, due to their higher ability to bind chemisorbed OH. In alkaline media, steps are also the active sites for CO_{ads} oxidation, though the dynamics of CO_{ads} is very different from that in acidic media¹⁷⁻¹⁹. The role of steps in the oxidation of methanol on stepped platinum surfaces in alkaline media has not been studied yet in great detail.

Besides the role of the surface structure, recently special attention has been paid to the role of the cation on the kinetics of oxidation and reduction reactions, particularly in alkaline media²⁰⁻²⁵. The role of non-covalent interactions of the alkali cations with hydroxide groups has been shown to be important in the hydrogen oxidation and the oxygen reduction reaction in alkaline media on Pt(111)^{20,23}, and these results have motivated the study of the role of the cations in other relevant electrochemical reactions. The electrochemical oxidation of chemisorbed carbon monoxide and the interaction of cations with the surface structure on the kinetics of this reaction was studied by our group²¹. From this study, we concluded that small cations such as lithium and beryllium enhance the adsorption of OH on the step sites of the platinum surface, thereby promoting the oxidative stripping of carbon monoxide on stepped platinum electrodes in alkaline solution. A recent study of the effect of cation on the oxidation of glycerol and ethylene glycol on polycrystalline platinum proposed that the increase in the overall rate of ethylene glycol oxidation ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$) is not just related to the favourable adsorption of OH but it is also associated to an increase of the cleavage of the C–C bond²⁴.

In this manuscript, we combine electrochemical measurements on stepped single-crystal platinum surfaces and in-situ electrochemical Fourier Transform Infrared spectroscopy (in-situ FTIR) to study the role of beryllium cations in the electrochemical oxidation of

methanol in alkaline media. Beryllium was chosen as a cation as it was observed to have a strong effect on the oxidation of chemisorbed CO in our previous work.²¹

2. Experimental

For the electrochemistry experiments, bead-type single crystals of Pt[$n(111)x(111)$] (or equivalently Pt[$(n-1)(111)x(110)$]) orientation—Pt(553) with $n = 5$, Pt(554) $n = 10$, Pt(151514) $n = 30$, Pt(111) and Pt(110) orientation prepared according to the method of Clavilier et al.²⁶ were used. For the in-situ infrared experiments, Pt disk electrodes (Mateck[®]) of 1 cm diameter with the corresponding orientation were employed. Before each experiment, the single-crystal electrode was flame annealed and cooled down in an H₂/Ar atmosphere, after which the electrode was transferred to the cell under the protection of a droplet of de-oxygenated MilliQ water.

A Pt foil was used as a counter electrode, and an RHE in the supporting electrolyte was employed as the reference electrode. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT12 potentiostat/galvanostat. The FTIR experiments were carried out with a Bruker Vertex 80V Infrared spectrophotometer. A spectroelectrochemical glass cell with a 60° CaF₂ prism was used, designed for the external reflection mode in a thin layer configuration. FTIR spectra were collected from an average of 20 scans obtained with 6 cm⁻¹ resolution at selected potentials, by applying single potential steps from a reference potential ($E_0=0.05$ V) in the positive-going direction up to 1 V. Spectra are represented as the ratio R/R_0 , where R and R_0 are the reflectance measured at the sample and the reference potential, respectively. Consequently, positive and negative bands correspond to the loss and gain of species at the sample potential, respectively.

All glassware was cleaned by boiling in concentrated sulfuric acid, followed by washing copiously with MilliQ water. Solutions were prepared from high purity reagents

(methanol (Uvasol) from Merck), BeSO_4 (99.99%, Alfa Aesar) and ultrapure water (Millipore MilliQ gradient A10 system, $18.2\text{M}\Omega\text{ cm}^{-1}$, 2 ppb total organic carbon). Argon (N66) was used to deoxygenate all solutions.

Due to the low solubility of the beryllium hydroxide salt, a solution of beryllium sulfate was used to study the effect of beryllium cations. A 0.1 M NaOH solution was used to which a small amount of BeSO_4 solution was added. Only a small molar percentage was added in order to prevent the formation of solid $\text{Be}(\text{OH})_2$, but this was enough to still be able to investigate whether beryllium had any influence on the voltammetry. In this context, voltammetric experiments conducted in 0.1 M NaOH with 0.1 M Na_2SO_4 confirmed that the presence of sulfate anions had no influence on the voltammetric profile in the studied potential region at pH =13 (not shown).

3. Results

3.1. Voltammetric studies

Figure 1 shows the blank voltammetry of a Pt(111) electrode in 0.1 M NaOH in the absence and presence of Be^{2+} in solution (0.001 M BeSO_4 solution) and also the voltammetry of a 0.3 M solution of methanol in the Be^{2+} -containing solution. Note that in the presence of Be^{2+} the peak corresponding to OH_{ads} formation in the blank voltammogram has shifted to lower potential and is much more irreversible than in NaOH. During the positive scan the onset for methanol oxidation starts at ca. 0.4 V, with a shoulder at 0.6 V and peaking at 0.75 V. During the negative scan there is a much lower anodic current between 0.8 and 0.5 V. When methanol is oxidized in a 0.1 M NaOH solution in absence of the beryllium, the negative scan shows an oxidation

peak after the reduction of platinum oxide. Therefore we ascribe the low current for methanol oxidation in the negative-going scan in Fig.1 to the highly irreversible adsorption of Be^{2+} . Another important observation is the similar current at potentials lower than 0.5 V in presence or absence of methanol, which indicates weak methanol adsorption in this potential window.

Figure 2 compares the cyclic voltammograms for methanol oxidation on the five different platinum electrodes in NaOH solution with those obtained in NaOH with 1% beryllium sulphate solution. In general, there is a tendency for the onset for methanol oxidation in NaOH to shift to more negative potentials as density of (110) steps increases. We ascribe this to the lower onset potential of CO_{ads} oxidation with increasing step density.²¹ However, the maximum current density falls on Pt(110). For Pt(111) and Pt(15 15 14), the oxidation current measured in the presence of beryllium is much smaller than in NaOH solution. As more steps are introduced, the oxidation currents gradually become more equal with or without beryllium in solution. These results suggest that methanol oxidation on (111) terraces is restricted in the presence of beryllium, while the (110) steps are the active sites for the oxidation of methanol. In the absence of Be^{2+} , Pt(111) is much more active and its peak current is comparable to the other stepped surfaces. Therefore, the Pt(111) terrace has activity for methanol oxidation, but is strongly blocked in the presence of beryllium. On the other hand, the inhibition by beryllium becomes less important for Pt(110) electrode, which can be associated to the oxophilic nature of this open surface, i.e. the coverage of adsorbed oxygenated species does not change much in absence or presence of beryllium and consequently the methanol adsorption is not significantly inhibited.

3.2. In situ FTIR electrochemical characterization of the methanol oxidation

Figure 3 show sequences of in situ FTIR spectra recorded during methanol electrooxidation on Pt(111) in alkaline media in presence and absence of beryllium in solution, while varying the electrode potential stepwise from 0.1 to 1.0 V ($R_0 = 0.1$ V). From these spectra, similar bands appear in both solutions that however develop with different potential dependence. Six negative-going contributions are apparent at 1630, 1350, 1385, 1576, 1718 and 2343 cm^{-1} . We consider now the assignment of these bands. The small band around 1630 cm^{-1} is due to the O–H bending mode of water, which may disturb the spectral region between 1700 and 1400 cm^{-1} . The bands centred at 1350 (ν_{sCOO}), 1385 (δ_{CH} and/or σ_{COO}), 1576 (ν_{asCOO}) cm^{-1} are characteristic of the presence of formate^{3,27,28}. At a potential higher than ca. 0.3 V in absence of beryllium, another band located at around 1715 cm^{-1} is observed that is assigned to the ν_{CO} stretching mode of a carbonyl group. It is difficult to distinguish between the carbonyl groups in formaldehyde and formic acid, since the bands in these compounds are very close, at 1713 and 1715 cm^{-1} , respectively^{2,3,5,27}. However, in alkaline media the band at 1715 cm^{-1} may be attributed to formaldehyde since formic acid exists as formate in alkaline media. The observation of formaldehyde and formate is in agreement with a recent study of methanol oxidation on Pt in alkaline media by using a HPLC system, in which formate and formaldehyde were detected²⁹.

The asymmetric stretch vibration of CO_2 at 2343 cm^{-1} suggests a pH lower than 6.37 ($\text{pK}_{\text{a},1}$ of carbonic acid) in the thin layer at $E > 0.6$ V. Additionally, carbonate and bicarbonate can be produced and their contributions appear as broad bands centred at 1400 and 1360 cm^{-1} . The latter distort the band intensities at 1350 and 1380 cm^{-1} of formate.

At $E > 0.3$ V, simultaneously with the increase of the faradaic current, only bands associated to the formation of formate are observed with beryllium in solution (together to low-intensity bands at 2343 cm^{-1} at higher potentials), whereas formate, formaldehyde and CO_2 are observed in absence of beryllium. The formate and CO_2 band intensities are higher in absence of beryllium in agreement with the higher faradaic current observed in the voltammogram in Figure 2. Intriguing is the absence of a CO signal in the infrared spectra under the present conditions. The absence of this signal indicates that CO is not a high-coverage intermediate during the methanol oxidation in alkaline media, and the formate route appears to be the main operating path⁴.

The infrared spectra corresponding to methanol oxidation on Pt(110) are depicted in Figure 4. Significant differences are observed with respect to Pt(111). In absence of beryllium, at low potentials only carbonate (1400 cm^{-1}) is formed on Pt(110), whereas at higher potentials also formate and CO_2 are observed. On the other hand, in the presence of beryllium, at $E < 0.5$ V beryllium promotes the formation of carbonate as well as formate. At $E > 0.6$ V bicarbonate is produced, while carbon dioxide seems to be formed from the oxidation of formate.

Figure 5 compares the intensities of the band associated to carbon dioxide formation for Pt(111) and Pt(110) in presence and absence of beryllium. A clear correlation between the carbon dioxide formation and the faradaic current (Figure 2) is observed. Remarkably, the effect of beryllium strongly depends on the surface structure. While beryllium inhibits carbon dioxide formation at Pt(111), on Pt(110) the presence of beryllium appears to promote the formation of carbon dioxide.

4. General discussion

From the results presented above, a more general picture of methanol oxidation on stepped Pt single crystals in alkaline media and the effect of beryllium can be extracted. Adsorption of methanol is the rate determining step and strongly depends on the surface structure of Pt³. The complete oxidation requires Pt-(OH)_{ads} as a reactant, however the nature and the coverage of the oxide on the surface is important. The OH_{ads}/oxide acts as a reactant in the oxidation of CO_{ads}, but high-coverage strongly bonded oxide layers on the surface will inhibit the adsorption of methanol, thereby acting as a poison. The coverage of OH absorbed on the Pt surface is promoted by the presence of bivalent cations²¹. This appears to lead to a poisoning of terraces with (111) orientation, on which methanol adsorption and consequently its oxidation is highly inhibited in presence of beryllium in solution. On surface with a higher step density and on Pt(110), this poisoning effect is much reduced, which suggest small changes in the surface oxide coverage in presence of beryllium. Formaldehyde and formate species are the main reaction intermediates produced on surfaces with (111) orientation, while carbonate is formed on sites with (110) orientation. It is important to highlight that the indirect path (formation of strongly adsorbed CO) was not observed under the present conditions, and consequently CO poisoning does not appear to be very relevant for the methanol oxidation under this conditions.

5. Conclusions

Methanol oxidation on Pt stepped single-crystal electrodes in alkaline media and the effect of dissolved beryllium have been studied using Fourier transform infrared spectroscopy. It was observed that methanol oxidation reaction strongly depends on the surface structure and the presence of beryllium. The activity towards methanol

oxidation reaction increases with the density of steps with (110) orientation. It was found that the specific non-covalent interaction of beryllium with hydroxide groups strongly inhibits the methanol adsorption on Pt(111), but the inhibition becomes much less in the presence of (110) sites. The FTIR results show that methanol oxidation on Pt stepped single-crystals in alkaline media mainly follows a direct pathway with formaldehyde and formate as reaction intermediates.

Acknowledgements

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Figure Caption

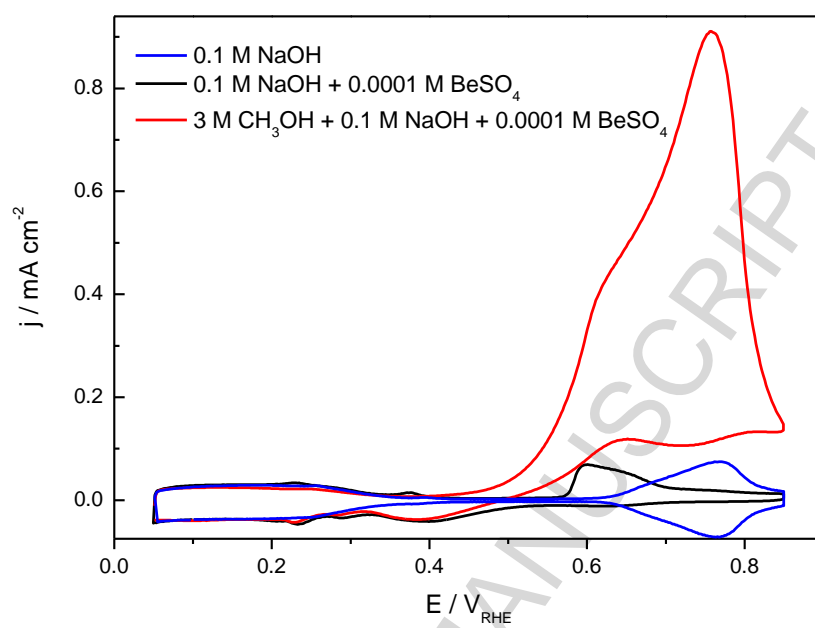
Figure 1. Cyclic voltammograms of Pt(111) (black curve) and of methanol (0.3 M) oxidation on Pt(111) (red curve) in 0.1 M NaOH + 0.001 M BeSO₄ solution. Scan rate: $\nu = 50 \text{ mV s}^{-1}$. Blank voltammetry of Pt(111) in 0.1 M NaOH (blue curve) also shown for comparison.

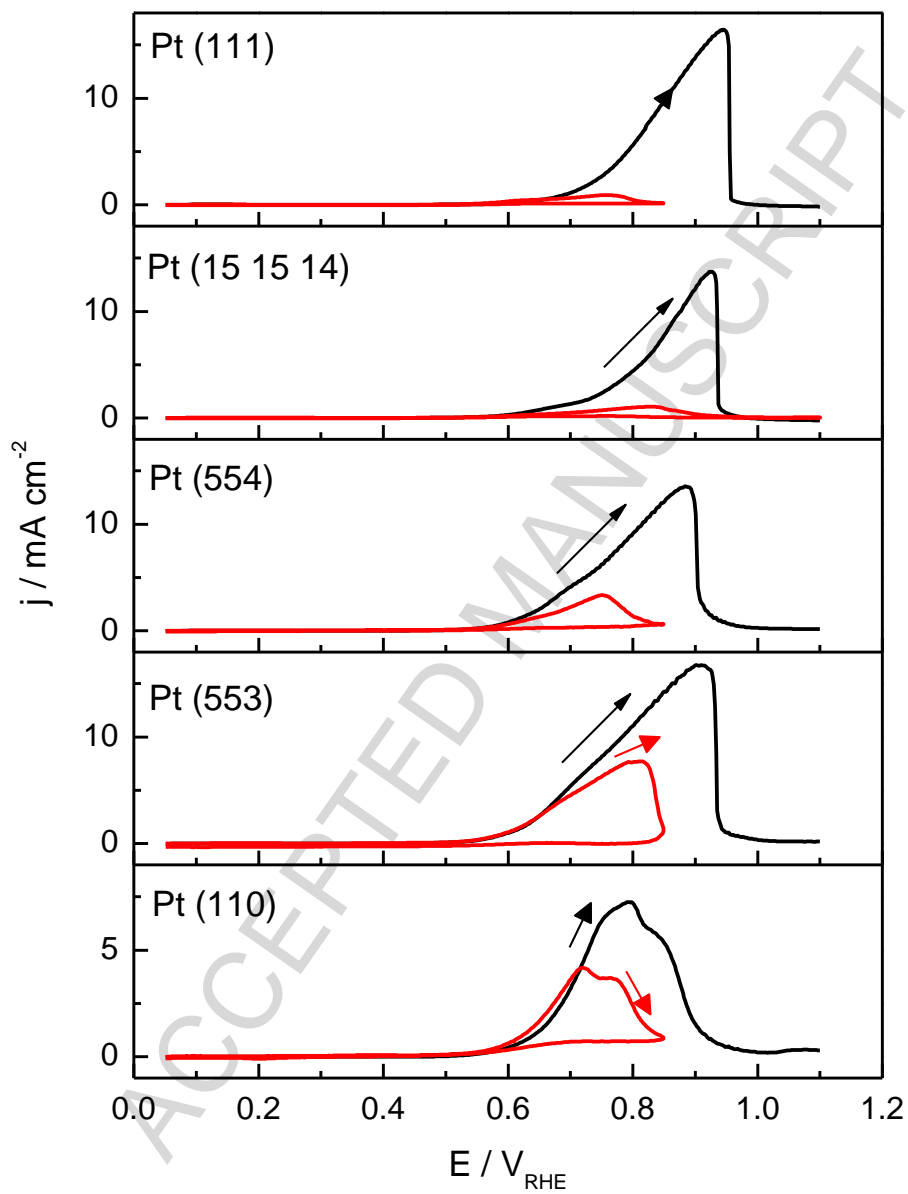
Figure 2. Cyclic voltammograms of methanol (0.3 M) oxidation for Pt(*hkl*), as indicated in the figure, in 0.1 M NaOH (black curves) and 0.1 M NaOH + 0.001 M BeSO₄ (red curves) solutions. Scan rate: $v = 50 \text{ mV s}^{-1}$.

Figure 3. In situ FTIR spectra for the oxidation of 0.3 M methanol on Pt(111) in (left panels) 0.1 M NaOH and (right panels) 0.1 M NaOH+BeSO₄. The potential was stepped positively from 0.1V up to 1 V. Reference potential: 0.1 V. The sample potentials are indicated in each panel at the corresponding spectra.

Figure 4. In situ FTIR spectra for the oxidation of 0.3 M methanol on Pt(110) in (left panels) 0.1 M NaOH and (right panels) 0.1 M NaOH+BeSO₄. The potential was stepped positively from 0.1V up to 1 V. Reference potential: 0.1 V. The sample potentials are indicated in each panel at the corresponding spectra.

Figure 5. Potential dependence of the integrated band intensity of the band associated to CO₂ formation for Pt(111) and Pt(110) in presence and absence of beryllium.

**Figure 1.**

**Figure 2.**

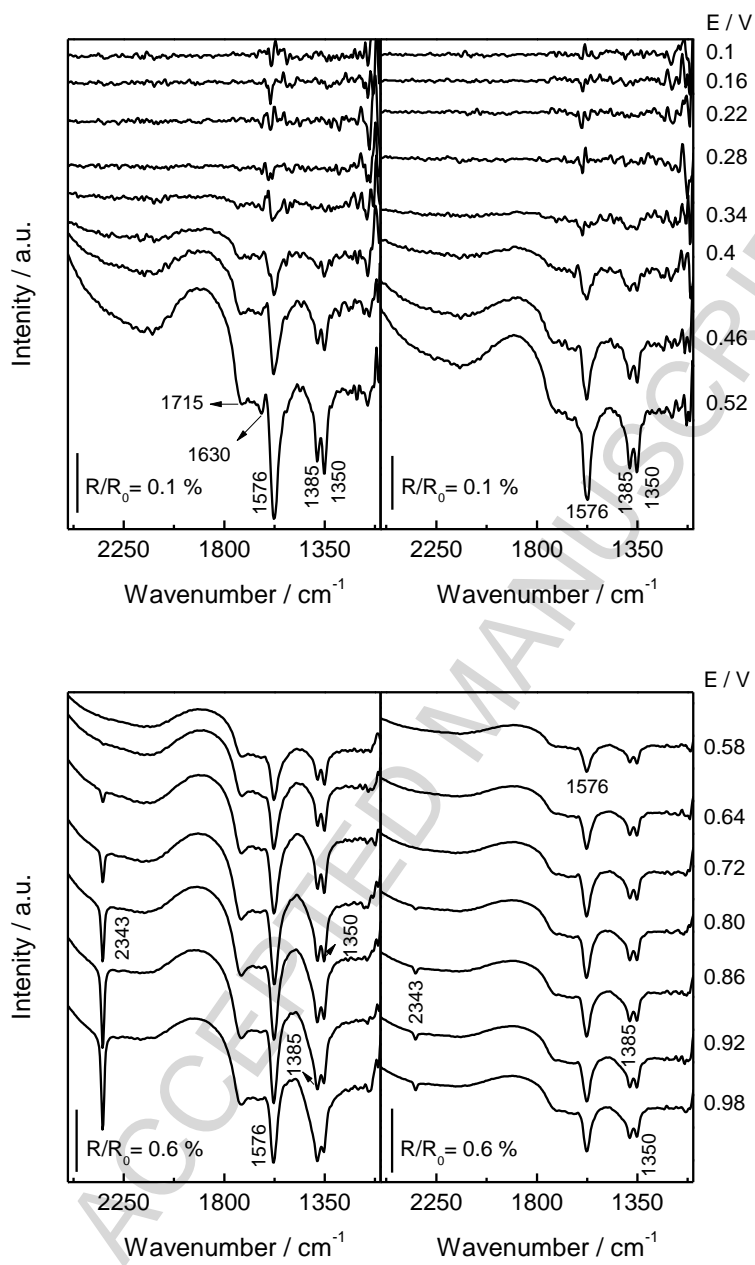


Figure 3

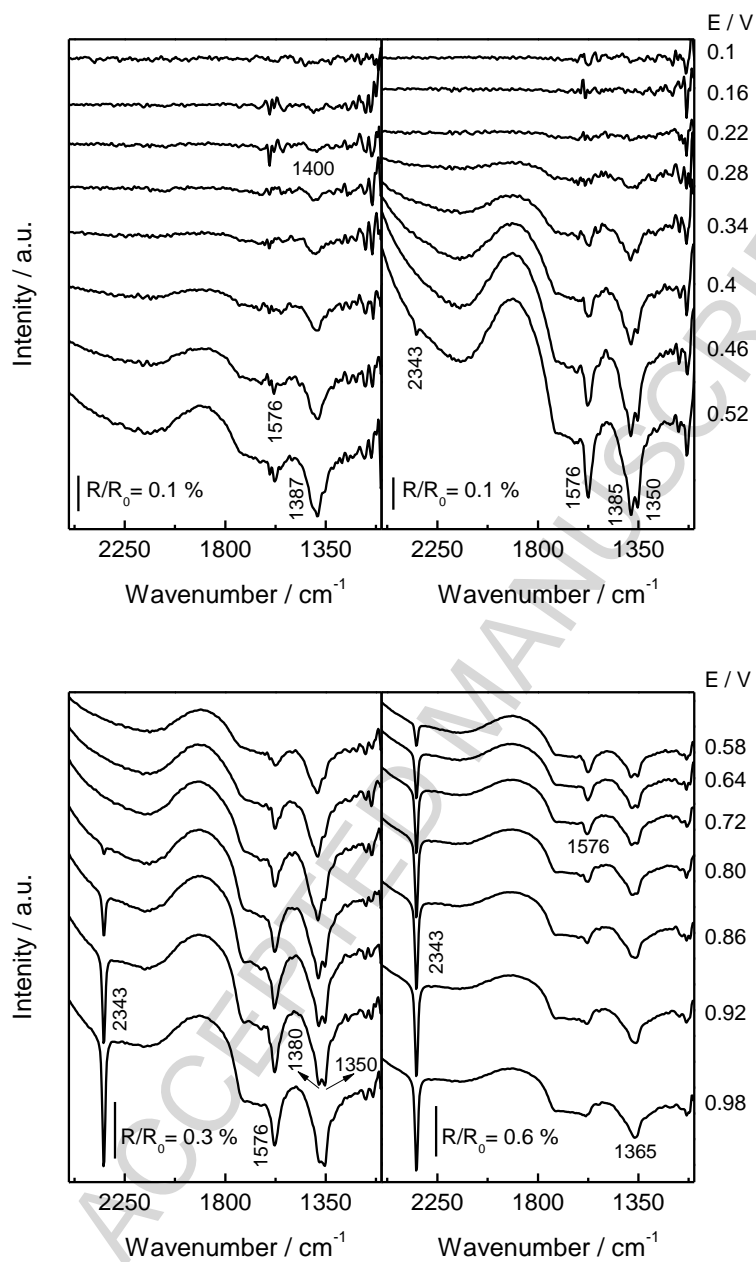


Figure 4

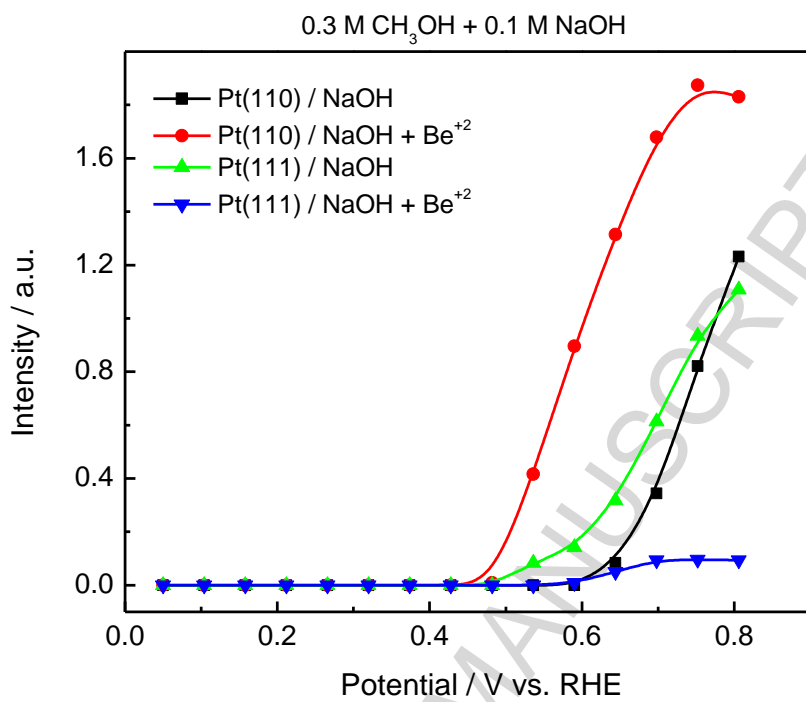


Figure 5.

Highlights

Steps enhance the oxidation of methanol on platinum single crystal electrodes in alkaline media

The presence of beryllium blocks methanol oxidation on (111) terraces

The presence of steps much reduces the blocking effect of beryllium

Methanol follows the direct pathway on Pt(111) and Pt(110) through the formation of formaldehyde and formate; no adsorbed CO is observed

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