CATALYTIC ACTIVITY OF A Pt(111) ELECTRODE MODIFIED BY RUTHENIUM DEPOSITION: A COMBINED STM AND IR-SPECTROSCOPIC STUDY

K.A. Friedrich, K.-P. Geyzers, U. Stimming, J. Stumper and R. Vogel

Institut für Energieverfahrenstechnik (IEV)
Forschungszentrum Jülich GmbH (KFA),
D-52425 Jülich, Germany

The structure of a Pt(111) electrode modified by Ru deposition is studied by STM and the CO electrooxidation on this electrode surface was monitored by IR spectroscopy. The STM images of the Ru-modified Pt(111) electrode in aqueous perchloric acid show islands of monoatomic height and about 3 nm in diameter. In situ IR spectroscopy of the CO stretching vibration shows distinct bands for CO adsorbed on Pt and on Ru. With increasing potential the vibrational bands assigned to CO adsorbed on Ru and on Pt decrease simultaneously at the potential of CO oxidation. A reaction mechanism assuming that the Ru islands act as nucleation centers for CO oxidation is proposed in order to explain the experimental results.

INTRODUCTION

Currently the development of a fuel cell based vehicle propulsion system is considered worldwide by several companies and research facilities using a polymer electrolyte membrane fuel cell (PEMFC) (see e.g. (1)). The fuel gas, a mixture of H2, CO2 and CO, is produced by a heterogeneously catalyzed steam reforming reaction of methanol. A major obstacle in the development of polymer electrolyte membrane fuel cells operated with a hydrogen-rich synthesis gas is the drastic deactivation of the anode electrocatalyst (such as dispersed platinum) caused by adsorption of carbon monoxide (2, 3). Therefore, the realization of this fuel cell system for mobile applications requires either the reduction of the CO content of the fuel gas to levels lower than 100 ppm CO or the development of new CO-tolerant electrocatalyst for the anode. The latter concept has triggered a renewed interest in bimetallic electrocatalyst such as Pt-Sn (4-6), Pt-Rh (7) and Pt-Ru (8, 9) that have been reported in the literature to show an enhanced electrochemical activity in the oxidation of hydrogen in H2/CO fuel gas mixtures.

The promoter effect of these bimetallic electrocatalyst, and in particular that of Pt-Ru, has been explained by a preferential adsorption of water on the Ru surface sites at more negative potentials compared with platinum (the so-called bifunctional mechanism) (10) but a detailed understanding of the enhancement of catalytic activity is still lacking. Therefore, fundamental investigations performed on well-defined Pt-Ru model surfaces should provide a deeper insight into the relationship between surface structure and reactivity that is expected to further the development of better anode electrocatalysts.

Recently, UHV prepared and well characterized Pt-Ru alloys have been studied with respect to their catalytic activity for the electrooxidation of CO and methanol (11-15). A
distinct dependence of the rate of CO electrooxidation upon surface composition of the alloys with an optimum Pt:Ru surface-atom ratio of 1:1 was observed. Our approach to investigate the electrocatalytic activity of structurally defined composite electrodes has been to deposit Ru on a Pt(111) single crystal electrode. The mostly ideal surface of the single crystal facilitates the surface characterization by STM, since structural modifications are readily observed. The characterization with respect to surface structure and composition is a prerequisite for the understanding of the electrochemical behavior of these Ru-modified electrodes. Several studies have used a Pt electrode modified by Ru deposition as a Ru/Pt electrocatalyst for the oxidation of methanol and CO before, but the interpretation of the observed enhancement in catalytic activity has been complicated by the unknown structure of the Ru deposits (8, 16).

In this study, relatively large (2 - 5 nm in diameter) structures are detected in the STM images, which are attributed to deposited ruthenium islands. From the STM measurements we conclude that our electrodes can be considered Ru "nano-electrodes" deposited on a Pt(111) substrate. As will be discussed below, the electrode structure of our electrodes can be regarded as an intermediate surface structure between two limiting cases: pure Pt (e.g. as the (111) surface) and Pt-Ru alloys.

In addition, we use in-situ IR-spectroscopy in order to further elucidate the role of Ru surface atoms in the mechanism of CO electrooxidation on this Ru-modified Pt(111) single-crystal surfaces. IR spectroscopy of the stretch vibration of adsorbed CO and CO2 provides detailed information regarding the bonding configuration and the onset of CO electrooxidation to CO2. As it is well-known, CO adsorbs strongly on Ru and the reported CO-stretch frequency is lower by about 30 - 40 cm⁻¹ compared to CO on Pt (17). This frequency shift is large compared to the line width of the vibrational band and should therefore allow a distinction of Pt and Ru adsorption sites and enable an investigation of their respective functionality for CO electrooxidation.

EXPERIMENTAL

Surface preparation and electrochemical characterization

The Pt(111) crystal with 10 mm diameter was grown in the Institut für Festkörperforschung (IFF) and was oriented (± 0.1°) and polished in the Institut für Grenzflächen- und Vakuumphysik (IGV), both of the Forschungszentrum Jülich (KFA).

At the beginning of the experiment, the crystal was flame-annealed, cooled in Ar and characterized with cyclic voltammetry using the hanging meniscus method in an electrochemical or in the spectroscopical cell. The cyclic voltammograms in 0.1 M HClO₄ were found to agree satisfactorily with previously published results (18). Ru deposition was performed potentiostatically in 0.1 M H₂SO₄ + 5 mM RuCl₃ at different deposition potentials ranging from 0.6 V to 0.2 V versus RHE. The deposition was performed by a potential step from 0.9 V vs. RHE where no Ru deposition occurs to the deposition potential. Deposition time was always 5 min. In this paper, we show measurements corresponding to deposition of Ru at 0.3 V, 0.4 V and 0.6 V versus RHE. The current transient during deposition was measured with an integrated charge of 15.7, 15.5 and 9.3 mC/cm² for the deposition at 0.3 V, 0.4 V, and 0.6 V, respectively. Different reference electrodes were used in the experiments (Ru deposition: Hg/Hg₂SO₄, STM measurements: Au/AuOₓ, IR measurements: a reversible hydrogen electrode (RHE)) but all potentials are...
reported with respect to RHE. The electrolytes were prepared from suprapure HClO₄ and H₂SO₄ (Merck).

STM

The measurements presented here were performed with a commercial Besocke Delta-Phi STM, which was modified for electrochemical applications and interfaced to a self-built bipotentiostat. The STM was operated in an inert gas atmosphere of argon. Details of the setup are presented elsewhere (19).

The purpose of the STM-investigation was to access information on the morphology of the Ru-modified platinum surface. The most straightforward approach should be to monitor the process of Ru deposition on the platinum surface directly with the in-situ STM. It is known, however, that galvanic reactions can be affected by the tunneling tip. The influence of the tip has been observed to depend strongly on the substrate as well as on the deposition material (20). For ruthenium deposition on platinum, the tip influence is very pronounced (21), thus making this approach unsuitable for the present purpose. To circumvent this problem, another experimental route was followed. The electrodes were pretreated in a separate glass cell, thoroughly rinsed with water, and then transferred to the STM cell with an adhering drop of water protecting them against atmospheric contaminations. Then the STM was purged with Ar and the water was replaced by electrolyte solution. Subsequently the surface was imaged with the STM.

IR spectroscopy

Infrared spectroscopy was performed using a Bruker IFS 66V FTIR Spectrometer with a self-built cell attachment permitting measurements with evacuated IR optics. The spectroscopical cell was made from Duran glass and a CaF₂ window with 60° bevelled edges. IR spectra were accumulated during a continuous positive sweep at a scan rate of 0.5 mV/s. Typically, 400 scans at Δν = 4 cm⁻¹ were taken for each spectrum corresponding to a measurement time of ~90 s. The electrodes were prepared as described above, but then transferred to the spectroscopic cell with the surface protected by a drop of water. Then CO was adsorbed at a constant potential of U = 90 mV up to saturation coverage and subsequently the thin layer configuration for the spectroscopic measurement was established. The CO dissolved in the solution was removed by purging with Ar. For the calculation of the CO₅ₙ₅ signal a reference spectrum R₀ was chosen, which was obtained after complete oxidation of the CO₅ₙ₅ species.

RESULTS AND DISCUSSION

Cyclic voltammetry

Fig. 1 shows the cyclic voltammograms of the clean and two Ru-modified Pt(111) surfaces (dashed line) and of the electrooxidation of a monolayer of CO on these surfaces (solid line). The voltammograms were recorded at 20 mV/s. The electrode surfaces of fig. 1b and fig. 1c correspond to a Ru deposition at 0.6 V and at 0.3 V, respectively. The determination of Ru coverage on platinum electrodes by electrochemical methods is rather difficult, since the deposition process is poorly understood and the decrease of hydrogen adsorption reflects only indirectly the amount of Ru deposited. Watanabe and Motoo (WM) (10) have introduced a determination of Ru coverage on polycrystalline Pt based on the integration of the current wave attributed to OH adsorption on Ru and relating this value to the hydrogen adsorption charge. Since the hydrogen desorption and surface oxidation
(OH adsorption) currents overlap and the OH adsorption current is not prominent in the cyclic voltammograms in Fig. 1, the effective surface area of the Ru deposit cannot be determined accurately. However, if the values of the Ru coverage as determined for polycrystalline Pt-Ru surfaces according to the method suggested by Watanabe et al. are assumed to be valid also for the Pt(111) surface, the Ru coverage of the electrode surface in fig. 1b and fig. 1c would be $\theta_{Ru} = 30\%$ and $\theta_{Ru} = 70\%$, respectively. As shown by STM images below, this somewhat arbitrary Ru coverage determination is qualitatively correct. A more detailed discussion of Ru deposition and the determination of Ru surface concentration will be given elsewhere (22).

We observe a peak potential of CO electrooxidation at $U_{OX} \approx 730$ mV on the uncovered Pt(111) surface which correlates with the onset of the current peak associated with OH adsorption on this surface (23) (dashed line, fig. 1a). On the Ru-modified surfaces (fig. 1b-c), a negative shift of $\approx 130$ mV for the CO electrooxidation potential is observed, but still only a single oxidation current peak is detected. For lower scan rates the CO electrooxidation peak shifts negatively. For a sweep rate of 0.5 mV/s, the recording rate of the potential-dependent IR spectra, a shift by -100 mV compared to the measurements in fig. 1a-c is found.

**STM investigations**

The preparation procedure described in the experimental section does not routinely yield clean, well-defined platinum single crystal surfaces. This is evident from fig. 2a, which shows the as-transferred Pt(111) surface without any Ru deposit. The typical terrace structure of the (111) surface with monoatomic steps can easily be recognized, but a moderate density of islands on the terraces indicates a non-negligible surface disorder, which may either result from insufficient flame annealing or from contamination of the sample during transfer.

Fig. 2b shows a Pt(111) surface with a Ru coverage of 0.3 according to WM and exhibits a striking difference to the unmodified Pt(111) surface. The surface is covered with small islands of 2 to 5 nm in diameter. The height of the islands is predominantly close to the height of monoatomic steps of the substrate. The defect density of the substrate given, it is unclear for an individual island whether it consists of Pt or Ru. From the comparison of fig. 2a and 2b one can, however, derive, that the density of Pt islands is almost negligible compared to the density of islands on the Ru-covered surface. The fraction of the surface which is covered by the islands has been estimated for several images, yielding values between 0.2 and 0.4 with a mean value of 0.25.

A Pt(111) surface with a Ru coverage of 0.7 according to the coverage determination method of WM is shown in fig. 2c. Islands similar to those in fig. 2b dominate the image, but with a considerably higher density. Due to this high density, it is impossible to distinguish the substrate from the deposit, thus one cannot evaluate the images in terms of surface coverage. It is feasible, however, to estimate upper and lower limits for the coverage. From a comparison of fig. 2b and 2c it is obvious, that the respective coverages differ at least by a factor of two. An upper limit can be derived from the fact, that the monoatomic steps of the substrate can still be clearly seen on the Ru-covered surface. This indicates that the coverage is still in the monolayer regime.

**IR spectroscopy**

Fig. 3 compares IR reflection absorption spectra of clean Pt(111) (fig. 3a), Ru-modified Pt(111) with a nominal Ru coverage of 0.3 (fig. 3b) and with a nominal Ru
coverage of 0.7 (fig. 3c) at about 400 mV. The spectra shown in Fig. 3 were obtained during a slow positive potential scan (0.5 mV/s) in a thin film configuration. The vibrational bands shown in this figure all exhibited a strong potential dependence and are therefore associated with CO adsorbates. For each spectrum the collection time was \( \approx 100 \) s, therefore the potentials given in Fig. 3 refer to the mean values of the potential interval \( (\Delta U = 50 \) mV). On the clean Pt(111) surface, the bands around 2070 and 1790 cm\(^{-1}\) have been reported before and are assigned to CO\(_{\text{ads}}\) in a linear-bonded (on-top) and threefold hollow coordination (24). A 2:1 ratio for the integrated intensities of the 2070 cm\(^{-1}\) to the 1790 cm\(^{-1}\) band has been attributed to a \((2\times2)-3\)CO adsorbate structure as shown by a combination of STM and IRAS studies (25). In fig. 3b, apart from the absorption bands around 2070 cm\(^{-1}\) and 1790 cm\(^{-1}\), a new vibrational feature around 2010 cm\(^{-1}\) is present. This third band has not been observed on the unmodified Pt(111) surface. For the surface with a high Ru coverage (fig. 3c), this band is very pronounced (its integrated band intensity is higher than that of the 2070 cm\(^{-1}\) band). Therefore, this band is most likely associated with a Ru-CO species. CO adsorbs readily on polycrystalline Ru electrodes and a CO vibrational band, assigned to linear-bonded CO, is observed around 2040 cm\(^{-1}\) at saturation coverage (17). Coverage dependent lateral interactions between the adsorbed CO molecules lead to a lowering of \( \nu_{\text{CO}} \) with decreasing coverage and this effect has been observed very dramatically in UHV studies of CO adsorption on Ru(001) (26), where a coverage dependent variation of \( \nu_{\text{CO}} \) between 1984 and 2061 cm\(^{-1}\) was found. Since multiple-bonded CO has not been detected in UHV studies (26, 27) and since the typical frequency ranges for linear-bonded CO lie above 2000 cm\(^{-1}\) we propose to assign the vibrational band around 2010 cm\(^{-1}\) to CO linear-bonded to Ru surface atoms. In the spectrum with the high ruthenium coverage (fig. 3c) the band around 1850 cm\(^{-1}\) can be assigned to bridge-bonded CO adsorbed on platinum (24). Interestingly, no CO in a threefold coordination is present for this surface. As far as we know of, a ratio of integrated band intensity of 1:1 for the bridge band to the on-top band has not been reported before and we assume that the high density of Ru islands has disrupted completely the ordered \((2\times2)-3\)CO adsorbate structure. Likewise, the ratio of integrated intensities of the threefold hollow band to the on-top band diminishes from 1:2 on the clean Pt(111) crystal to 1:5 on the Ru-modified Pt(111) electrode with 0.3 coverage in fig. 3b. This preferential removal of the threefold hollow band in the spectra of the Ru-covered Pt(111) crystals suggests the existence of a boundary region along the circumference of the Ru islands, where threefold-bonded CO is affected with higher probability than CO adsorbed in a linear or a bridge configuration.

Fig. 4 shows IR spectra measured during a positive sweep after adsorption of CO at 90 mV on a Ru-modified Pt(111) electrode with a coverage of 50 % according to WM. Again, the spectra show three potential-dependent bands; the bands around 2070 and 1790 cm\(^{-1}\) are due to linearly bonded CO and triply bonded CO, respectively. The band around 2010 cm\(^{-1}\) is assigned to linearly bonded CO on Ru. The band frequency of CO/Ru shifts at a rate of \( d \nu_{\text{CO(Ru)}}/dU = 48 \) cm\(^{-1}\)/V which is considerably higher than the tuning rate of the vibration of CO adsorbed on Pt \( (d \nu_{\text{CO(Pt)}}/dU = 27 \) cm\(^{-1}\)/V in this study for linearly bonded CO). Nevertheless, this shift is similar to the value reported for the frequency shift of CO on a Ru electrode by Gutiérrez et al. (41 cm\(^{-1}\)/V) (17). Small differences in the tuning rate may be explained by coverage effects. CO\(_{\text{ads}}\) is oxidized to CO\(_2\) at a potential of \( \approx 550 \) mV and within the resolution of our experiments \( (\Delta U = 50 \) mV) the intensities of the vibrational bands of CO/Ru and CO/Pt decrease at the same potential. The simultaneous electrooxidation of CO/Pt and CO/Ru is in agreement with a single current peak in the cyclic voltammograms in Fig. 1.

Electrochemical Society Proceedings Volume 95-23

303
The STM images in fig. 2 and the observation of two separate vibrational bands for CO bonded to Pt and to Ru both clearly demonstrate that relatively large Ru and platinum areas with their respective chemical properties are present. However, the cyclic voltammograms of the investigated electrodes are not a superposition of Pt and Ru, but reveal a pronounced promoter effect for CO electrooxidation with a single sharp current peak (fig. 1). The bifunctional mechanism of CO electrooxidation postulates a coadsorbed oxygen-containing species such as -OH. OH adsorption on pure Pt(111) is evident in the current peak at \(\approx 580\) mV (23) (fig. 1a) and therefore the uncovered Pt(111) surface area is considered free of adsorbed OH at the onset of CO oxidation on the Ru-modified surfaces. Consequently, CO electrooxidation has to start on the Ru islands and along their periphery; the adjacent Pt sites can be considered active sites for CO electrooxidation (denoted Pt*). Furthermore, we have to assume a high mobility of the CO adsorbates on Pt in order to explain the single current peak. This way, the Ru islands act as nucleation centers for CO oxidation according to the following reaction scheme (1a-d):

\[
\begin{align*}
a) & \quad \text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru-OH} + \text{H}^+ + e^- \\
b) & \quad \text{CO} - \text{Ru} + \text{OH} - \text{Ru} \rightarrow 2\text{Ru} + \text{CO}_2 + \text{H}^+ + e^- \\
c) & \quad \text{CO} - \text{Pt}^* + \text{OH} - \text{Ru} \rightarrow \text{Pt}^* + \text{Ru} + \text{CO}_2 + \text{H}^+ + e^- \\
d) & \quad \text{CO} - \text{Pt} \rightarrow \text{CO} - \text{Pt}^* \\
\end{align*}
\]

[1]

Water adsorption takes place on the Ru island at low potentials [1a]. CO adsorbed on Ru and at Pt* is oxidized at sites in close proximity to a Ru-OH surface species [1b,c]. After initiation of the CO electrooxidation, CO adsorbed on Pt migrates to an active site Pt* (step [1d]) in close proximity to Ru (the adsorption site of the oxygen-containing species) and, subsequently, CO-Pt* is oxidized to CO\(_2\) (step [1c]).

For polycrystalline Pt-Ru alloys, only one vibrational band has been reported, shifted to lower frequencies by about 15-30 cm\(^{-1}\) as compared to polycrystalline Pt (28). This disparity to the results presented here is rationalized in terms of a homogeneous distribution of Ru and Pt atoms at the surface of the alloys. CO is either adsorbed only on platinum sites on the alloy surface with a low coverage or, more likely, the local binding configuration are averaged out by lateral interactions (dipole-dipole coupling). In this case, an intensity transfer from the low (CO/Ru) to the high frequency band (CO/Pt) occurs as well as a shift towards higher wavenumbers of the lower frequency band. This would also explain the observed asymmetry of the CO absorption band on Pt-Ru alloys.

In conclusion, the STM investigation showed that Ru on Pt(111), electrodeposited from 5 mM solution of RuCl\(_3\) in H\(_2\)SO\(_4\) at submonolayer coverages, forms islands of monoatomic height with diameters from approximately 2 to 5 nm. A variation of the Ru coverage results in a variation of the density of Ru islands, but does not affect their shape. Rough estimates of the coverage have been derived from the STM images and, for medium coverage, gave values slightly smaller than the evaluation according to the method of WM. Since STM is, however, not the most suitable technique for the detection of average surface properties, we consider this small deviation not significant.

Electrochemical Society Proceedings Volume 95-23
IR spectroscopic studies of the CO stretching vibration exhibit distinct bands for CO adsorbed on Pt and on Ru. A band around 2010 cm\(^{-1}\) is assigned to CO adsorbed on Ru in an on-top configuration. The vibrational bands assigned to CO adsorbed on Ru and on Pt persist in the potential range negative of the oxidation potential and diminish simultaneously upon oxidation. This shows that although CO adsorbs both on Ru and Pt, a promoting effect is operative which gives rise to a single oxidation process. These findings are consistent with the bifunctional mechanism if we postulate an initiation of CO oxidation on/or around the Ru islands in combination with a sufficient high mobility of the CO adsorbate on platinum. Therefore, these surfaces modified by Ru deposition may be considered an intermediate surface structure between pure Pt and Pt-Ru alloys.

REFERENCES

1. V.M. Schmidt, P. Bröckerhoff, B. Höhlein, R. Menzer and U. Stimming, J. Power Sources, 49, 299 (1994).
2. H.P. Dhar, L.G. Christner and A.K. Kush, J. Electrochem. Soc., 134, 3021 (1987).
3. W. Vogel, J.G. Lundquist, P. Ross and P. Stonehart, Electroch. Acta, 20, 79 (1975).
4. K.J. Cathro, J. Electrochem. Soc., 116, 1608 (1969).
5. M.M. Jansen and J. Moolhuyzen, Electrochim. Acta, 21, 861 (1976).
6. S.R. Wang and P.S. Fedkiw, J. Electrochem. Soc., 139, 3151 (1992).
7. P.N. Ross, K. Kinoshita, A.J. Scarpellino and P. Stonehart, J. Electroanal. Chem., 59, 177 (1975).
8. M. Watanabe and S. Motoo, J. Electroanal. Chem. Interfacial Electrochem, 60, 275 (1975).
9. P.N. Ross, K. Kinoshita, A.J. Scarpellino and P. Stonehart, J. Electroanal. Chem., 63, 97 (1975).
10. M. Watanabe and S. Motoo, J. Electroanal. Chem., 60, 267 (1975).
11. H.A. Gasteiger, N. Markovic, P.N.J. Ross and E.J. Cairns, J. Phys. Chem., 98, 617 (1994).
12. H.A. Gasteiger, N. Markovic, P.N.J. Ross and E.J. Cairns, J. Electrochem. Soc, 141, 1795 (1994).
13. H.A. Gasteiger, N. Markovic, P.N.J. Ross and E.J. Cairns, Electrochim. Acta, 39, 1825 (1994).
14. H.A. Gasteiger, Electrochem. Soc. Interface, 3, 49 (1994).
15. H.A. Gasteiger, N. Markovic, P.N.J. Ross and E.J. Cairns, J. Phys. Chem, 97, 12020 (1993).
16. K. Franaszek and J. Sobkowski, J. Electroanal. Chem., 327, 235 (1992).
17. C. Gutiérrez, J.A. Caram and B. Beden, J. Electroanal. Chem., 305, 289 (1991).
18. J. Clavilier, R. Albaiat, R. Gomez, J.M. Orts, J.M. Feliu and A. Aldaz, J. Electroanal. Chem., 330, 489 (1992).
19. N. Breuer, U. Stimming and R. Vogel, in Nanoscale Probes of the Solid/liquid Interface, A. G. Gewirth and H. Siegenthalers, Eds., NATO ASI Series E: Applied Sciences, vol. 288, Kluwer Academic Publishers, (1995).
20. N. Breuer, U. Stimming and R. Vogel, Electrochim. Acta, 40, 1401 (1995).
21. K.-P. Geyzers, U. Stimming and R. Vogel, in preparation.
22. K.A. Friedrich, K.-G. Geyzers, J. Stumper and U. Stimming, in preparation.
23. K.A. Jaaf-Golze, D.M. Kolb and D. Scherson, J. Electroanal. Chem., 200, 353 (1986).
24. F. Kitamura, M. Takahashi and M. Ito, Surf. Sci., 223, 493 (1989).
25. I. Villegas and M.J. Weaver, J. Chem. Phys., 101, 1648 (1994).
26. H. Pfnür, D. Menzel, F.M. Hoffmann, A. Örtega and A.M. Bradshaw, Surf. Sci., 93, 431 (1980).
27. G.E. Thomas and W.H. Weinberg, J. Chem. Phys., 70, 954 (1979).
28. R. Ianniello, V.M. Schmidt, U. Stimming, J. Stumper and A. Wallau, Electrochim. Acta, 39, 1863 (1994).
Fig. 1. Cyclic voltammograms of Pt(111) electrodes (dashed line) and for electrooxidation of a CO adsorbate layer (solid line) in 0.1 M HClO₄ at a sweep rate of 20 mV/s. Adsorption was performed at 90 mV for 5 min. in CO-saturated electrolyte.
(a) Pt(111) without predeposited ruthenium.
(b) With predeposited ruthenium at a coverage of 0.3.
(c) With predeposited ruthenium at a coverage of 0.7.
Fig 2. In-situ STM images of Pt(111) electrodes after transfer to the STM cell, measured in 0.1 M HClO₄ at a sample potential of 0.5 V vs. RHE with a tip potential of 0.8 V and a tunneling current of 0.4 nA.
A) Blank experiment without predeposited ruthenium.
B) With predeposited ruthenium at a coverage of 0.3.
C) With predeposited ruthenium at a coverage of 0.7.
Fig. 3 In situ IR spectra of Ru-modified Pt(111) with different Ru coverages, measured in 0.1 M HClO₄ after CO adsorption at 90 mV; signal averaging of 400 scans at a resolution of 4 cm⁻¹. (a) Pt(111) without predeposited ruthenium. (b) With predeposited Ru at a coverage of 0.3. (c) With predeposited Ru at a coverage of 0.7.
Fig. 4. In situ IR spectra of a Ru-modified Pt(111) with a Ru coverage of about 0.5 in 0.1 M HClO$_4$ during a slow anodic scan (scan rate: 0.5 mV/s) after adsorption of CO at 90 mV; parameters as in Fig. 3.