Carbon monoxide oxidation on bare and Pt-modified Ru(10\bar{1}0) and Ru(0001) single crystal electrodes

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Received 22 January 2002; received in revised form 14 March 2002; accepted 21 March 2002

Dedicated to Professor Sergio Trasatti on the occasion of his 65th birthday and in recognition of his contribution to electrochemistry

Abstract

Carbon monoxide oxidation on bare and Pt-modified ruthenium surfaces with the (10\bar{1}0) and (0001) orientations was investigated with cyclic voltammetry, scanning-tunneling microscopy and in situ Fourier transform infrared spectroscopy. Facile oxidation kinetics of CO on Ru(10\bar{1}0) are observed, in contrast with a slow reaction on Ru(0001). Scanning tunneling microscopy (STM) measurements confirmed that spontaneous deposition of Pt produces island-like structures on both single crystal Ru surfaces. CO oxidation on a bimetallic Pt/Ru(10\bar{1}0) surface with a Pt coverage of approximately one monolayer occurs at potentials that are 140 mV more negative than those for bare Pt. This potential is, however, more positive than the potential of the onset of the oxidation on Ru(10\bar{1}0). IR spectroscopy shows one peak for linearly adsorbed CO on bare and Pt-modified Ru(10\bar{1}0) surfaces, while two peaks are visible for the Pt-modified Ru(0001) structure. A single broad peak for the bimetallic Pt/Ru(10\bar{1}0) surface may result from addition of the red-shifted peak for Pt and the peak for the Ru(10\bar{1}0) substrate. A large red shift of CO on the Pt/Ru(10\bar{1}0) surface requires further work to be explained. A negative shift of CO oxidation on Pt/Ru(10\bar{1}0) indicates a decrease of the Pt–CO bond strength on that surface compared with the bond with bulk Pt. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Spontaneous Pt deposition; Metal monolayers; In situ infrared spectroscopy; STM

1. Introduction

Carbon monoxide is one of the best-characterized adsorbates in catalysis and electrocatalysis because of its specific much-studied role in various catalytic reactions. Ruthenium is an important co-catalyst material in Pt–Ru fuel cell electrocatalysts for the oxidation of methanol and H\textsubscript{2}+CO mixtures, the latter being obtained by reforming methanol or gasoline [1,2]. It has a critical role in these electrocatalysts because it is believed to provide oxygen-containing species at potentials lower than that of platinum. This helps in the oxidation of trace amounts of CO, which acts as a catalytic poison for Pt [3]. Elucidation of the role of ruthenium and its oxides in Pt–Ru electrocatalysts, as well as the structure–activity relationship for CO oxidation on Ru, could help in further work on fuel cell electrocatalysts.

Oxidation of polycrystalline ruthenium electrodes has been the topic of considerable activity [4,5]. Electrochemical investigations of ruthenium single crystal electrodes, however, have been hindered by the lack of an easy preparation method for clean and well-defined single crystal surfaces. Vacuum-based preparation is apparently satisfactory, albeit time consuming [6–8]. A simpler method has been used recently which involves annealing Ru crystals in a hydrogen stream. This produces a well-ordered surface as verified by scanning tunneling microscopy (STM) [9].

The gas phase CO oxidation on Ru(0001) surfaces has been the subject of several surface analytical and theoretical studies [9–12]. A very slow oxidation of CO on this surface is a consequence of the overall low surface oxidation and practically nonexistent subsurface
oxygen. The latter has been found to play an important role in catalytic activity for CO oxidation [13]. The Ru(0001) surface becomes active for CO to CO₂ conversion only after it has been transformed to an oxygen-rich state, either by dosing O₂ at elevated temperatures in UHV measurements [14], or by electro-chemical surface oxidation [8]. Furthermore, the catalytic activity of Ru(0001) can be altered if the surface morphology has a significant contribution of steps, as reported recently [15,16].

Electrochemical and in-situ infrared spectro-electrochemical measurements on Ru(0001) have been reported recently by this [6,17,18] and by other research groups [7–9]. Voltammetric profiles for vacuum-prepared Ru(0001) in perchloric acid [6,8] and in a variety of other electrolytes [17] have been shown to be quite different from those of polycrystalline surfaces. Indeed, the voltammetric curve for this surface was shown to be insensitive to potential cycling even if the upper limit is extended to 1.2 V, unlike the same symmetry surfaces of other Pt metals [18]. In-situ IR spectroscopy showed another unusual property of Ru(0001), viz. a considerable amount of bisulfate is already adsorbed at potentials slightly positive of the onset of hydrogen evolution [18]. Unlike the polycrystalline surface where only CO₂ is visible [19], CO adsorption on Ru(0001) shows contributions from both on-top or linearly bonded (CO₂) and multiple-bonded carbon monoxide (CO₃) [6,9].

A comparison of the UHV data with electrochemical measurements in the case of Ru, as discussed in the Section 3.1, can be of very limited value. We have shown recently by the in situ surface X-ray scattering (SXS) technique that a strongly adsorbed H₂O (or OH) layer is formed on Ru in contact with water [17]. More recently, on the basis of density functional theory (DFT) calculations, it was concluded that H₂O is partially dissociated on Ru(0001) and forms a hydrogen-bonded hexagonal structure with the hydroxyl fragments [20]. Therefore, the adsorption properties of Ru surfaces in electrolyte solutions may be considerably different from those on bare Ru surface in UHV.

Spontaneous deposition of Pt on Ru has been demonstrated for a Ru(0001) surface [21], as well as with carbon-supported Ru nanoparticles. This phenomenon has been used to design a catalyst with a very small Pt loading, which was shown to have improved tolerance in H₂/CO oxidation as compared to commercial catalysts with considerably larger Pt loadings [22]. In this paper we present for the first time a combined electrochemical, STM and IR study of CO oxidation on bare and Pt-modified Ru(1010) single crystal surfaces. A comparison with the behavior of the Ru(0001) surface is also given. Spontaneous deposition of Ru on Pt(111), involving an irreversible adsorption of RuCl₃ that can be reduced electrochemically to deposit submonolayers of Ru, has been studied in detail by several groups [3,23–25].

2. Experimental

The working electrodes were Ru single crystals 8 mm in diameter (Metal Crystals and Oxides, Cambridge, UK) with the surfaces oriented to better than 0.1° after additional orientation. Crystals were polished with diamond pastes and alumina down to 0.05 μm. Final surface preparation was done by annealing in either UHV, or H₂. The former method is the standard procedure for Ru electrodes [26], consisting of repetitive Ar sputtering at room temperature and oxygen adsorption/desorption at elevated temperature, followed by a single flash annealing at 1400 °C. The cooled electrode was transferred through a glove box filled with ultrapure Ar into the electrolyte solution. Alternatively, the crystal was annealed in a hydrogen stream at 1200 °C, followed by cooling in the same environment and protecting the surface by a drop of ultrapure water before transferring it into the electrochemical cell. Solutions were prepared from Optima H₂SO₄ and Milli-Q UV-plus water (Millipore). Reversible hydrogen electrodes (RHE) or Ag/AgCl|3 M Cl⁻ electrodes were used as the reference, and the potentials were given against the latter electrode.

The cell for in-situ IR spectro-electrochemical measurements, described previously [27], consisted of a CaF₂ hemisphere serving as the ATR window and cell bottom, and a Teflon body. A Mattson RS10000 spectrometer and a PAR273 potentiostat were computer controlled using a custom-made program designed to set the potential of the working electrode to a certain potential prior to data acquisition. One hundred and twenty-eight scans with 4 cm⁻¹ resolution were coadded in a single step. Spectra are given as −ΔR/R using the spectrum at the highest potential as the reference (reference potential is indicated in figures) where no CO oxidation is observed. The positive-going bands therefore represent a gain of a particular species at the sample potential relative to that at the reference. For the CO₂ spectra, the reference potential was 100–300 mV higher than that for CO. Care was taken to purge atmospheric CO₂ and reduce its concentration to a negligible level. STM studies were performed using a Molecular Imaging Pico STM with a 300S scanner and a Molecular Imaging Model 300S Pico bipotentiostat. The cell was made of Teflon with an exposed area of ca. 0.3 cm² and a volume of ca. 1.5 cm³. Prior to each experiment, an STM tip was prepared by etching a 80:20 Pt/Ir wire in a CaCl₂ solution and insulating it with Apiezon wax.
3. Results and discussion

3.1. Cyclic voltammetry of Ru(10\bar{1}0) in 0.1 M H$_2$SO$_4$ with and without CO

Voltammetry curves of Ru(10\bar{1}0) in 0.1 M H$_2$SO$_4$ are shown in Fig. 1. Two pairs of peaks are visible between −0.2 and 0.2 V, followed by a much less pronounced pair of peaks at higher positive potentials. In the positive scan, the peaks appear at −0.085, 0.08, and 0.5 V. All three peaks have their respective counterparts in the negative scan, which are shifted by 50 mV towards more negative potentials. The heights of the peaks, as well as the double layer capacitance in the nearly featureless region above 0.2 V are steadily increasing upon opening of the upper limit. This indicates that the surface oxide is growing at the electrode surface. The total charge between the onsets of hydrogen evolution and Ru dissolution is about 360 μC cm$^{-2}$, which amounts to ca. 1.6 electrons per Ru atom. This charge is substantially higher than that observed on the Ru(0001) surface where about one electron/atom is found [17], but is still considerably smaller than that of the polycrystalline Ru electrode. Unlike the behavior of the Ru(0001) surface where the cyclic voltamogram was stable upon potential cycling and/or opening of the potential limit [17], the Ru(10\bar{1}0) surface is sensitive to the electrode potential history.

Identification of adsorbed species associated with the voltammetry peaks in the potential region where usually hydrogen adsorption occurs at platinum metals is often a difficult task. A CO charge displacement method has been used to identify the nature of the species adsorbed at potentials up to 200 mV above the hydrogen evolution potential for Ru(0001) [28]. A negative charge of −117 μC cm$^{-2}$, required for the displacement of the adsorbed species, indicates that H$_{ad}$ cannot be the adsorbed species in that potential region; it is rather an oxygen-containing species, contrary to the conclusion of Lin et al. [7]. In the case of Ru(10\bar{1}0), preliminary data indicate that the negative charge is associated with the peaks in the potential region between −0.18 and 0.12 V (Fig. 1). A plausible reaction to account for the negative charge is

$$\text{RuOH}_{ad} + \text{CO}_{\text{soln}} + e^- \rightarrow \text{RuCO}_{ad} + \text{OH}^-$$

A small positive charge was measured only at −0.20 V, at the onset of the first anodic peak, which may indicate the presence of a small hydrogen coverage at that potential. The lack of appreciable surface and subsurface oxidation of Ru(0001) results in its very poor activity towards CO oxidation. On the other hand, the open-structure surface of Ru(10\bar{1}0) has a sizable activity towards CO oxidation that is not only an order of magnitude higher than that of Ru(0001), but also larger than that of the polycrystalline surface (Fig. 2). It is interesting that no oxidation is visible on Ru(10\bar{1}0) in the CO-saturated solution in the negative scan, if the upper limit is above 0.8 V. Progressive opening of the upper limit shows that the oxidation peak in the negative scan, albeit small, is present as long as the upper limit does not exceed 0.8 V (Fig. 3). This phenomenon has also been observed at polycrystalline Ru electrodes. It could be related to either too high a surface oxide coverage at the electrode surface, or to the different oxidation state of Ru at these potentials. Furthermore, the adsorption rate of CO on an oxide-covered surface produced at high potentials is probably

![Fig. 1. Voltammetric curves of the Ru(10\bar{1}0) surface in 0.1 M H$_2$SO$_4$ solution. The upper limit is progressively opened by 100 mV; sweep rate 20 mV s$^{-1}$. Inset shows the model of one of the two possible terminations of the Ru(10\bar{1}0) single crystal surface.](image1)

![Fig. 2. Voltammetric curves for CO oxidation on the Ru(10\bar{1}0) and Ru(0001) surfaces in CO-saturated 0.1 M H$_2$SO$_4$ solution; sweep rate 20 mV s$^{-1}$.](image2)
different from that at the Ru(OH)-covered surface which exists at low potentials.

3.2. In-situ IR of Ru(10\textbar 10\textbar 0) and Ru(0001) in CO-saturated 0.1 M H\textsubscript{2}SO\textsubscript{4}

FTIR spectra for the oxidation of CO on Ru(10\textbar 10\textbar 0) and Ru(0001) single crystal electrodes are shown in Figs. 4 and 5. The spectra show a peak around 2015 cm\textsuperscript{-1} that shifts to higher frequencies as the potential increases, and another peak at 2346 cm\textsuperscript{-1} that stays at the same frequency, irrespective of the electrode potential. The former peak represents the stretching frequency of C=O that is adsorbed at the Ru surface through a single bond. This linearly bonded CO\textsubscript{L} is present in the spectra obtained for both Ru single crystal surfaces. The other peak at 2346 cm\textsuperscript{-1} is the characteristic IR mode of CO\textsubscript{2} in solution. The spectra for Ru(0001) also show another peak at 1780 cm\textsuperscript{-1}, which corresponds to the triply-bonded CO\textsubscript{H} adsorbed at the threefold symmetry sites of the Ru surface [6,7] (not shown in Fig. 5). In the case of Ru(10\textbar 10\textbar 0) this peak is not visible. Even though the threefold symmetry sites can be found at Ru(10\textbar 10\textbar 0) (see inset of Fig. 1), it is unlikely that CO could adsorb in the hollow site between the three Ru atoms because of the steric effects of the energetically favored CO\textsubscript{L}.

At both single crystal surfaces the CO\textsubscript{L} is visible at the lowest potential of 0.2 V, while the CO\textsubscript{2} peak appears only at a potential equal to, or higher than 0.5 V. Although CO oxidation proceeds on both single crystal electrodes, the kinetics of the reactions are considerably different. The reaction on Ru(0001) is clearly slow since the CO peak remains up to potentials of 1.2 V, while the faster kinetics of CO oxidation at Ru(10\textbar 10\textbar 0) result in disappearance of the CO\textsubscript{L} peak at 0.9 V and above. The slow oxidation kinetics of Ru(0001) precludes the complete removal of CO up to 1.2 V in the thin electrolyte layer between the electrode and the window. In addition, CO was present in solution, which may cause its readsorption at longer times of measurements. These results are in qualitative agreement with the voltammetric curves, where about a 10-fold higher oxidation rate is found for Ru(10\textbar 10\textbar 0) (vide supra). However, the intensity of the CO\textsubscript{2} absorption bands in the IR spectra does not show such a relationship. It should be emphasized that, although the intensities of bands are comparable within a single experiment, they may be quite different in separate experiments due to a
number of factors [29] so that a direct comparison of the band intensities cannot be made.

The peak frequency of the CO L on Ru(1010) is higher than that of CO L on Ru(0001) at any given potential below 0.7 V (see IR spectra shown in Figs. 3 and 4). The plot \( \nu(\text{CO}_L) - E \) reveals major differences in the behavior of the CO adsorption characteristics at the two surfaces. As seen in Fig. 6, the CO L adsorbed at Ru(1010) has the peak frequency of 2028 cm\(^{-1}\) at 0.2 V, which increases linearly in the potential region between 0.3 and 0.8 V with a tuning rate of about 20 cm\(^{-1}\), and finally decreases sharply at 0.9 V. The linear portion of the \( \nu(\text{CO}_L) - E \) plot coincides well with the voltammetry of CO oxidation (see Fig. 2); the higher frequency probably being related to the higher repulsion of adsorbed CO molecules at higher coverages, i.e. at higher potentials.

The sharp decrease of the CO frequency at 0.9 V is therefore related to the decrease of the CO coverage due to the CO oxidation. This phenomenon was also observed on Pt and on Ag-modified Pt [30].

In contrast to the behavior of the Ru(1010) surface, the \( \nu(\text{CO}_L) - E \) plot shows that the CO L frequency at Ru(0001) rises constantly with potential. There is no sign of a sharp decrease at higher potentials. However, a closer inspection of the \( \nu(\text{CO}_L) - E \) plot reveals that there is a change in slope. At potentials below 0.7 V, the CO L tuning rate is about 26 cm\(^{-1}\), while at higher potentials it decreases to 14 cm\(^{-1}\).

The value of 26 cm\(^{-1}\) is at the low-end of the tuning rates reported for CO L at Pt-group metals [31]. Such a low tuning rate was usually related to the high coverage of CO. Indeed, the fact that the CO H is observed together with CO L at all potentials supports this premise. On the other hand, theoretical calculations [31,32] as well as experimental data for CO/Ru(0001) in UHV [33] show that CO is adsorbed almost exclusively at on-top sites. The electrochemical environment is obviously different, as the CO molecules compete for available Ru sites with sulfuric acid anions and water molecules. It is possible that coadsorption of ions at the Ru surface in aqueous environment facilitates the adsorption of CO in the threefold sites by lowering the repulsion between CO atoms.

The tuning rate of 14 cm\(^{-1}\) at potentials higher than 0.7 V is lower than any other reported value. At this potential, the surface of the Ru(0001) electrode is covered by oxygen-containing species, which could be the reason for such a low tuning rate.
3.3. CO oxidation on Pt-modified Ru(10\overline{1}0) and Ru(0001) surfaces

STM images of the Ru(10\overline{1}0) and Ru(0001) surfaces after spontaneous deposition of Pt are shown in Fig. 7. Spontaneous deposition of Pt on a UHV-prepared Ru (0001) has been reported recently [34] indicating the possibility of formation of monolayer-to-multilayer deposits depending on the experimental conditions. Different morphologies of the Pt deposit were found depending on the concentration of the Pt solution. Pt clusters of ca. 10,000 atoms were found for diluted (0.1 mM) Pt solutions, while interconnected one- or two-atom high 2D Pt clusters were obtained from a 10 mM Pt solution [34]. A deposition on Ru single crystals annealed in H\textsubscript{2} at 1100 °C from 1 mM Pt solution produced predominantly uniform deposits of 1–2 atom high clusters. No preferential nucleation and growth at the step edges is observed with either one of the two surfaces. This is quite different from what is usually observed in electrochemical metal deposition on low-index single crystal surfaces where step edges are preferred sites for nucleation.

The voltammetric curve of the Pt-modified Ru(10\overline{1}0) surface in 0.1 M H\textsubscript{2}SO\textsubscript{4} is given in Fig. 8, along with the curve for bare Ru(10\overline{1}0) which is given for comparison. The peaks of the Ru surface are still visible, although considerably reduced and shifted on the potential scale. The larger, more cathodic peak is shifted further negatively, while the smaller peak is shifted positively. Their relative spacing is increased by about 100 mV. This indicates that some Ru sites may still be in contact with the electrolyte solutions and apparently have modified adsorption, i.e. electronic properties. It is, however, quite possible that hydrogen adsorption on Pt sites can account for a fraction of the current associated with these two peaks. Therefore, these peaks cannot be used to identify the area of the Pt-free Ru surface. A new peak, which can be clearly related to hydrogen adsorption on Pt, occurs at ca. −0.2 V with a charge of ca. 40 μC cm\textsuperscript{−2}. This charge would correspond to the coverage of θ\textsubscript{Pt} = 0.17 for bare Pt(111), and it may be associated with the Pt atoms in the clusters that have a small number of atoms in the second layer. These are seen in the STM image as the brightest spots on the surface (Fig. 7). As expected, for the Pt-covered Ru surface, the double layer capacity charging current is decreased. The Ru oxidation is suppressed and a smaller pseudocapacitance of Pt oxidation is determining the observed current.

Fig. 9 shows the CO oxidation at bare and Pt-modified Ru(10\overline{1}0) surfaces. The CO oxidation on a polycrystalline Pt surface is shown for comparison. The onset of the CO oxidation at the modified surface is shifted towards more negative potentials by over 140 mV indicating a considerably higher activity of the bimetallic surface as compared with the activity of bare Pt. The peak current, however, is smaller than for polycrystalline Pt, which can be explained by the considerably less positive potential at which it occurs. The activity of this bimetallic surface is somewhat smaller than that of Ru(10\overline{1}0). The origin of the larger activity of the bimetallic surface, as compared to bare Pt, appears to be a weaker adsorption of CO on the Pt monolayer on Ru(10\overline{1}0) than on bare Pt. This may be a
consequence of the electronic effects caused by the Pt–Ru interaction that reduce the Pt–CO binding energy. Since the Pt monolayer is not pseudomorphic, the question arises about a possible contribution of Ru atoms to the overall activity. This contribution appears to be small; otherwise the current from Ru sites would be seen in the corresponding potential region, which would produce at least a tail preceding the peak at 0.53 V. Since this is not observed (cf. Fig. 9) it appears that the current of CO oxidation on Ru sites is not significant, i.e. most of the active Ru sites appear covered by Pt. It should be noted, however, that the CO oxidation peak at the Pt/Ru(10Î0) surface appears in the potential region where a shoulder is observed for the bare Pt electrode. The latter is usually explained as the oxidation of weakly bonded CO at Pt. This is another indication that the overall CO binding energy is lowered at the modified surface.

A weaker adsorption of CO on Pt monolayer on Ru(0001) has been shown by thermal desorption spectroscopy at a metal/gas interface [35], and recent density functional analysis calculation showed that the lowest CO–Pt binding energy can be expected for a monolayer of Pt on Ru(0001) [36]. The reduction in CO binding energies on Pt-modified metals has been well documented [37], based on significant core level shifts in the deposited atoms. The model of Hammer and Nørskov [38] for the binding trends of CO on modified transition-metal surfaces and alloys shows that an effective transfer of d electrons from Pt to Ru takes place and the Pt d-band shifts down in order to maintain the pure d-band filling and charge neutrality. The lowering of the d-band causes a weaker CO adsorption because of decreased back donation from Pt to antibonding CO orbitals. Therefore, both experimental and theoretical data suggest a favorable electronic effect that reduces CO adsorption energy on the Pt submonolayer on a Ru catalyst in comparison to pure Pt and Pt–Ru bulk alloy.

The enhanced activity, compared with bare Pt(111), of the bimetallic Ru/Pt(111) surface with a small Ru coverage for methanol and CO oxidation has been ascribed to the oxidation of CO at Ru sites according to the bifunctional mechanism [3,24]. This is supported by a recent study of the Ru/Pt(110) bimetallic surface, which concluded that a small electronic effect and a predominant bifunctional mechanism are the origin of its activity for CO oxidation [39]. There are two major differences between the Ru/Pt(111) and Pt/Ru(0001) bimetallic surfaces. First, Pt and Ru have opposite roles in these two bimetallic systems. Second, the Pt coverage in Pt/Ru(0001) is high (cf. Fig. 7), while the Ru coverage in Ru/Pt(111) is low. Therefore, the role of the bifunctional mechanism for the former surface is expected to be small.

In situ IR spectroelectrochemistry of Pt-modified Ru(10Î0) and Ru(0001) surfaces immersed in CO-saturated 0.1 M H2SO4 solution are presented in Figs. 10 and 11. The conditions for the IR collection are identical to those of bare Ru surfaces (Figs. 3 and 4). The spectra show a single COL peak at Pt/Ru(10Î0), with its frequency shifted by ca. 7 cm⁻¹ towards higher values with respect to that of the bare surface. Interestingly, the adsorbed CO disappears from the spectra at a less positive potential at the Pt-modified surface than for the bare Ru(10Î0) surface (0.8 vs. 1.0 V, respectively). However, CO oxidation is not completely removed at 0.8 V, as can be clearly seen from the CO2 peak at 2346 cm⁻¹. In fact, the CO-oxidation rate seems to be at a maximum at that potential, judging by the intensity of the CO2 peak. In contrast to these data, the IR spectra for the Pt-modified Ru(0001) surface show two peaks for CO adsorbed in a linear configuration. At the lowest potential investigated (0.2 V), the two peak frequencies are observed at 2053 and 2002 cm⁻¹. Since the CO2 at the bare Ru(0001) surface at the same potential has a peak at 2011 cm⁻¹ (see Fig. 4), the peak at the lower frequency is assigned to the COL at the unoccupied Ru clusters of the Pt-modified Ru surface. The higher-frequency peak appears to be associated with CO adsorbed at Pt clusters. It is interesting that the stretching frequency of the COL band at Pt(111) appears at much higher values. The frequency usually reported for the lowest CO coverages, or at low potentials, is 2070 cm⁻¹ [30,40]. Therefore, the CO stretching frequencies of the molecule adsorbed on-top on both metal clusters are lowered with respect to those of the bare metals.

The CO stretching frequency depends on the surface composition and state, and this frequency has been often used as an indication of the binding strength of CO to metal surfaces. For Pt–Ru alloys there are several reports [41,42] on a downshift of the frequency for the CO adsorbed in an on-top configuration as compared with CO adsorbed on Pt. This shift has been ascribed to a stronger binding of CO to Pt–Ru than to Pt. Iwasita et
al. [43], however, reported a small increase in frequency and interpreted the shift as a weaker adsorption of CO. While it appears that the frequency shift upon CO adsorption on metal surfaces can be attributed to the weakening of the C–O bond in the Blyholder donation-backbonding model, the frequency shifts observed for modified surfaces cannot be explained by this model. Several effects have been identified as factors determining the metal-dependent vibrational shifts [31,32,44–47]. One is the ‘wall’ effect caused by the Pauli repulsion between the electronic densities approaching each other. This repulsion is compensated by the substrate polarization contribution and contributions related to the donation-backbonding mechanism. These analyses indicate that no simple relationship between the field-dependent binding energies and adsorbed CO frequencies is evident. The calculated [48] and experimental [42] data for CO adsorbed on Pt–M generally show a small decrease in the CO stretching frequency despite the weaker Pt–C bond on these surfaces compared with bare Pt. The DMT calculations of Liao et al. [48] for mixed PtM cluster surfaces found that the CO frequency is sensitive to neither the surface composition nor the strength of the Pt–C bond.

If one assumes that the frequency of the peak at 2035 cm$^{-1}$ at the Pt/Ru(1010) surface corresponds to CO adsorbed on-top of unmodified Ru atoms at the surface, then it would be difficult to explain the absence of IR bands corresponding to the Pt-covered parts. In contrast, if the above peak corresponds to CO adsorption on Pt clusters, that would mean that all active Ru sites of the single crystal surface are covered with Pt and consequently no Ru atoms are available for CO adsorption. Alternatively, the very broad peak at 2035 cm$^{-1}$...
cm⁻¹ can result from the contribution of the peak for a bare Ru(10\(\overline{1}0\)) at 2028 cm⁻¹ and the red-shifted peak for Pt. This seems a more viable explanation than the first two, considering the large and uniform Pt coverage seen in the STM image and the down-shifts of the CO L₃ frequency for Pt in bimetallic systems [41,42,48]. Although a decrease in CO L₃ frequency is in agreement with literature data, a large red shift of ca. 35 cm⁻¹ is surprising. This shift occurs despite the weaker binding of CO to the Pt monolayer on Ru(10\(\overline{1}0\)) than on bare Pt, which can be inferred from the shift for CO oxidation to less positive potentials on the bimetallic surface as compared with bare Pt (Fig. 9). Further analysis is needed to clarify such a shift, as well as the frequency for CO on the Ru sites.

4. Conclusions

The oxidation of CO on Ru surfaces is a highly structure-sensitive reaction, as inferred from the considerably different reaction rates observed for the Ru(10\(\overline{1}0\)) and Ru(0001) surfaces. Infrared spectra of CO adsorbed on Ru(10\(\overline{1}0\)) show a single peak that is associated with the CO bonded in a on-top configuration in contrast to on-top CO and triply-coordinated CO on Ru(0001) [6,7]. STM images show that spontaneous deposition of Pt on Ru also occurs on the H₂- annealed Ru single crystals, which yields a more uniform deposit on Ru(10\(\overline{1}0\)) than on Ru(0001). CO oxidation on a bimetallic Pt/Ru(10\(\overline{1}0\)) surface, with the Pt coverage of approximately one monolayer, occurs at potentials 140 mV more negative than those for bare Pt. This shift appears to be due to a weaker bonding of CO to the Pt monolayer on Ru than on bulk Pt. The contribution of the bifunctional mechanism to the activity of this surface is probably small because of the small area of Ru not covered by Pt. Infrared spectra for CO adsorbed on bimetallic Pt/Ru surfaces show a single broad peak at 2035 cm⁻¹ on the Pt/Ru(10\(\overline{1}0\)) surface that may result from the addition of the red-shifted peak for Pt and the peak for the Ru(10\(\overline{1}0\)) substrate. The explanation of a large red shift of CO₂ on the Pt/Ru(10\(\overline{1}0\)) surface requires additional work.

Acknowledgements

This research was performed under the auspices of the U.S. Department of Energy, Chemical Sciences and Material Sciences Division, under Laboratory Energy Research Program DE-AC 02-98CH10886.

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