Carbon monoxide oxidation on bimetallic Ru/Au(111) surfaces

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The electrochemical deposition of Ru on Au(111) was performed in 0.5 M H2SO4 + 10⁻⁴ M RuCl3. The obtained bimetallic Ru/Au(111) surfaces were characterised by cyclic voltammetry and in situ STM in 0.5 M H2SO4. The Ru deposit consists of nanoscale islands, which merge with increasing coverage. Two different types of bimetallic Ru/Au(111) surfaces with respect to the distribution of Ru islands over the Au(111) substrate surface were obtained. When the deposition was performed at potentials more positive than the range of Au(111) reconstruction, homogeneous nucleation occurred resulting in a random distribution of Ru islands. When the deposition was performed on reconstructed Au(111) at low overpotentials, selective nucleation occurred resulting in the replication of the Au(111) reconstruction. Only at higher deposition overpotentials, can multilayer deposits be formed, which exhibit a very rough surface morphology. The electrocatalytic activity of such structurally well defined Ru/Au(111) bimetallic surfaces was studied towards CO oxidation with the Ru coverage ranging from submonolayer to several monolayer. CO stripping commences at about 0.2 V and occurs over a broad potential range. The observed influence of the Ru structure on the CO stripping voltammetry is explained by local variations in the CO adsorption energy, caused by differences in the local Ru structure and by effects induced by the Au(111) substrate.

Keywords: Ru deposition, Au(111), bimetallic surfaces, STM, CO-oxidation.

INTRODUCTION

The electrochemical oxidation of CO on platinum based electrodes has been studied intensely for decades with the view of fuel cell application. Ruthenium, tin and rhodium are the elements frequently added to platinum for CO and methanol oxidation. The origin of the high activity of such bimetallic surfaces is not yet clear mainly due to the unknown structure of the deposit. It is now possible using modern microscopic techniques, such as scanning tunnelling or scanning force microscopy (STM/AFM), to monitor the surface morphology in situ in the electrolyte. This may be employed to study the relation between surface structure and electrochemical activity of bimetallic electrodes and in the long run may help to tailor bimetallic surfaces with desired electro-
catalytic properties. As an example, a combined STM, IR spectroscopy, and electrochemical study of Ru/Pt(111) surfaces has recently been reported.\textsuperscript{1}

Here, \textit{in situ} STM results of Ru electrodeposition on a Au(111) surface and the electrochemical behaviour of the resulting electrodes, aimed at gaining an understanding of the dependence of the morphology of the deposit on the potential and its influence on the CO oxidation process, are presented. The study focuses on the submonolayer coverage regime, which is of particular interest for the understanding of bimetallic surfaces.

The Au(111) surfaces were reconstructed in the electrochemical environment at potentials in certain regions. These potentials were chosen to enable the production of bimetallic Ru/Au(111) surfaces exhibiting different distributions of deposited Ru islands for the same coverage. The selectivity of surface sites of reconstructed Au(111) surfaces for the nucleation of Ru islands during electrochemical deposition of Ru has been studied by the authors of this paper.\textsuperscript{2} The obtained results are further exploited and the work extended to the electrodeposition of Ru over a wide potential region with the emphases on the activity of such bimetallic surfaces towards CO oxidation. With respect to the initial potential for CO oxidation, gold is much less active than pure ruthenium\textsuperscript{3} and the Au(111) surface the least active among all other single crystal faces of gold,\textsuperscript{4–6} especially in sulphate containing solution, where the CO oxidation process is possible at very positive potentials, close to oxide formation on gold.\textsuperscript{7,8} Therefore, the choice of the Au(111) surface as substrate offers a unique possibility to extract the contribution of the Ru clusters themselves to the CO oxidation activity of bimetallic surfaces. In order to establish a proper relation between the surface structure and activity, the studies of the CO oxidation were performed in the same STM cell in which the Ru was deposited and the obtained surface characterised by STM under potential control.

EXPERIMENTAL

A single crystal, Au(111), 10 mm in diameter (Metal Crystals and Oxides, Cambridge, England), cut and oriented to better than 0.5°, was used as the substrate. After mechanical and electrochemical polishing described in detail in Ref. 2, the Au(111) crystal was annealed in a butane flame for several minutes, cooled down in air, and then mounted into the electrochemical cell of the STM. The crystal was contacted with the (10\textsuperscript{-4} M RuCl\textsubscript{3} + 0.5 M H\textsubscript{2}SO\textsubscript{4}) solution under potential control at a potential which was chosen for the subsequent Ru deposition. After a chosen deposition time (from several seconds up to several minutes), the electrolyte was exchanged by 0.5 M H\textsubscript{2}SO\textsubscript{4} solution under potential control to avoid a lifting of the surface reconstruction and the spontaneous deposition of Ru,\textsuperscript{9} and STM images and/or cyclic voltammograms of the deposited Ru were recorded.

The Ru containing electrolyte was prepared using RuCl\textsubscript{3}aq (Fluka) and H\textsubscript{2}SO\textsubscript{4} (Merck). Since the electrolyte is not stable and the concentration of RuO\textsubscript{2+} species increases with time, a freshly prepared Ru solution was used for each measurement.

The STM images were recorded using a self-built scanning tunnelling microscope described in detail in Ref. 10. The tunnelling tips were prepared by the electrochemical etching of a W-wire and coated with Apiezon wax. The tip and sample potentials were independently kept under potential control and measured \textit{versus} a Ag/AgCl (KCl saturated) reference electrode, with the tip potential being kept 50 – 100 mV more negative than the sample potential. The STM images were obtained in the constant current mode with tunnelling currents between 1 – 10 nA and are presented as topview images with the darker colours corresponding to lower surface areas.
After characterisation of the bimetallic Ru/Au(111) surface by STM, the same STM cell was used for CO oxidation measurements. CO was purged over the cell through a reduced space made by a glass cover to avoid contact with air. The potential of the electrode was kept at –0.1 V, where CO is adsorbed. After several minutes, when saturation coverage of the Ru/Au(111) surface with CO is expected to have been achieved, the electrolyte was removed and replaced with fresh 0.5 M H$_2$SO$_4$ using a syringe. Ar gas was purged over the STM cell for several minutes in order to remove traces of O$_2$ from the solution and stripping voltammetry was performed. These joint STM-CV measurements should provide a direct insight into the relation between the structure of the bimetallic Ru/Au(111) surface and its reactivity towards CO oxidation.

RESULTS AND DISCUSSION

*Cyclic voltammetry studies of the bimetallic Ru/Au(111) surfaces*

For the STM and CO stripping experiments (see below), Ru was deposited on the Au(111) surface at various, constant deposition potentials and different deposition times. As an example, a CV of Ru/Au(111) in pure 0.5 M H$_2$SO$_4$, obtained after Ru electrodeposition at 0.8 V for 3 min, where a saturation submonolayer coverage is achieved (see below), is presented in Fig. 1 by the dashed line. For comparison, the CV of the initial Au(111) surface exhibiting well known features is presented by the dotted line (for clarity, a part of the double layer, for potentials < 0.6 V, for CVs in Fig. 1 is not presented). An enhanced double layer current, according to Chrzanowski and Wieckowski, corresponds to the RuOH$_{ads}$/RuO$_2$ equilibrium, i.e., to the formation of RuOH on the surface. At more positive potentials, the presence of Ru can be resolved through oxidation and reduction peaks in the potential region before the formation of gold oxide.

![Cyclic voltammograms of bimetallic Ru/Au(111) surface in 0.05 M H$_2$SO$_4$ with: (---) Ru coverage of 0.35 ML, showing the peaks for RuOx formation. The Ru was deposited for 3 min from a 10$^{-4}$ M RuCl$_3$ + 0.5 M H$_2$SO$_4$ solution at $E_{dep}$ = 0.8 V. (—) Ru coverage higher than a monolayer showing the hydrogen UPD region characteristic for metallic Ru. The Ru was deposited for 5 min at – 0.1 V. (—) CV of the initial Au(111) surface in 0.05 M H$_2$SO$_4$. Sweep rate 50 mV/s.](image-url)
The few overlapping but clearly distinct oxidation peaks at 1.1 V and 1.25 V indicate the presence of various oxides of Ru. According to recent XPS studies of Crown et al.\(^\text{13}\) the amount of Ru oxides (RuO\(_2\) and RuO\(_3\)) increases with increasing potential, in particular the high-valence ruthenium (VI) oxide (RuO\(_3\)). The deposited Ru is irreversibly bound to the Au surface and can be dissolved only at potentials in the Au oxidation range. The current associated with the removal of Ru does not correspond to the amount of dissolved Ru as it overlaps with O\(_2\) evolution. It is not sensitive to the potential of Ru deposition or the manner of Ru deposition,\(^\text{9}\) which indicates that cyclic voltammetry is not sensitive enough to enable a proper characterisation of Ru/Au(111) surfaces. Besides, in the STM cell, there are always traces of O\(_2\) and its reduction makes the quantitative detection of the deposited Ru on the surface at lower potentials almost impossible.

For Ru coverage higher than a monolayer, obtained by deposition of Ru at potentials below the Nernst potential, the subsequent CVs (presented in Fig.1 by the solid line) are similar to the CV for polycrystalline bulk Ru samples, measured under identical conditions.\(^\text{14}\) In particular, a slowly increasing anodic current at potentials > 0.7 V and broad cathodic peaks at about 0.0 V and 0.2 V are found, which are also observed for Ru submonolayer deposits in a separate electrochemical cell.\(^\text{15}\) Based on the results of the STM experiments, these features are attributed to the irreversible formation and reduction\(^\text{15}\) of oxide/hydroxide species.

Since the deposited Ru exist in various oxidation states, as well as due to the presence of different Ru species in the solution, the Ru coverage cannot be estimated correctly from the electrochemical data. The Ru coverage was, therefore, determined in this work from the STM images and is, due to the unknown structure of the Ru deposit, defined as the fraction of the Au surface covered.

**In-situ STM observations of bimetallic Ru/Au(111) surfaces**

STM images of the Ru/Au(111) surfaces used for the subsequent CO oxidation measurements are presented in Figs. 2 and 3. Two different types of bimetallic Ru/Au(111) surfaces with respect to the distribution of the deposited Ru islands over the surface were examined.

The first type of bimetallic Ru/Au(111) surfaces were obtained when Ru was deposited on unreconstructed Au(111) surface, Figs. 2a and c. Ru deposition at potentials positive of the range of surface reconstruction (lifting of the reconstruction occurs at about 0.25 V in 0.5 M H\(_2\)SO\(_4\)) proceeds via homogeneous nucleation of Ru monolayer islands. A random distribution of Ru islands of approximately the same size (1–2 nm) over the substrate surface is observed (see Figs. 2a and c). It should be pointed out that the coverage obtained after a deposition time of 3 min corresponds to the saturation coverage for a given deposition potential, since with a prolonged deposition time (up to half an hour) the coverage did not change.

The second type of bimetallic Ru/Au(111) surfaces were obtained when Ru was deposited on a reconstructed Au(111) substrate, Figs. 2b and d and Fig. 3a. Ru deposition on a reconstructed Au(111) surface results in similar islands to those found on unreconstructed surfaces. The position of these islands, however, is affected by the presence of the reconstruction and depends on the overpotential. At low overpotentials, Ru is
preferentially deposited in the fcc areas of the Au surface reconstruction, replicating the Au(111) reconstruction pattern with a high perfection, an effect which has been described in detail elsewhere. At higher coverage, the Ru islands apparently merge into larger ramified aggregates. The maximum Ru coverage is a highly defective monolayer (0.8 ML Ru coverage). Characteristic STM images obtained under these conditions for various Ru coverage are shown in Figs. 2b and d and Fig. 3a. Only at higher overpotentials (< −0.1 V), can multilayer deposits be formed, which exhibit a very rough surface morphology, Fig. 3b.

Fig. 2. STM images (150 Å) of the defined bimetallic Ru/Au(111) surfaces used for CO oxidation measurements: a) $E_{dep} = 0.5 \text{ V}; t_{dep} = 3 \text{ min}; I = 11 \text{ nA}$; image recorded at 0.15 V; coverage = 0.25 ML; b) $E_{dep} = 0.0 \text{ V}; t_{dep} = 30 \text{ s}; I = 11 \text{ nA}$; image recorded at 0.0 V; coverage = 0.45 ML; c) $E_{dep} = 0.15 \text{ V}; t_{dep} = 3 \text{ min}; I = 33 \text{ nA}$; image recorded at 0.15 V; coverage = 0.65 ML; d) $E_{dep} = 0.0 \text{ V}; t_{dep} = 60 \text{ s}; I = 11 \text{ nA}$; image recorded at 0.0 V; coverage = 0.65 ML.
STM images of the deposits studied above were also recorded at higher potentials, with the aim of clarifying the structure and stability of the Ru/Au(111) electrodes over the whole potential range where CO oxidation was later to be studied. The results of the experiment in which Ru was first deposited on reconstructed Au(111) at 0.0 V and then the potential increased stepwise up to 0.9 V, where Ru oxidation commences according to the CVs (see Fig. 1, dashed line), are shown in Fig. 4. It is important to note that up to 0.9 V, the Au(111) substrate surface is still in its metallic form (see Fig. 1, dotted line). As illustrated by the image in Fig. 4a, which was recorded at 0.3 V, the Au(111) surface in this potential regime is predominantly covered by a ramified structure of condensed 2D Ru islands of well-defined height with only a few islands with apparently larger heights. According to the CVs in Fig. 1 and the discussion given above, in this potential region, a mixture of metallic Ru and RuOH and RuO is assumed. The first morphological changes were observed at 0.6 V (Fig. 4b), when new islands of a second type start to form on top of the Ru islands. As seen in the images recorded at 0.8 V and 0.9 V, (Fig. 4c and d, respectively), the number of these islands continuously increases. In addition, the underlaying flat islands increase in size, resulting in the filling of the trenches and holes between these islands. According to Fig. 1, at these potentials, the fraction of RuO increases further and high-valence RuOx, with larger lattice parameters are formed. This is accompanied by a significant rearrangement of the islands on the surface, which can be ascribed to the increased size of the RuOx islands and to the lifting of the reconstruction of the underlying Au(111) substrate surface. The effect of the oxidation and rearrangement of the Ru islands on the course of CO oxidation will be discussed below.

CO oxidation on bimetallic Ru/Au(111) surfaces: STM and CV measurements

The activity of the bimetallic Ru/Au(111) surfaces towards CO oxidation was evaluated as a function of Ru coverage by CO stripping in 0.5 M H2SO4 solution. As a
prerequisite, these experiments were first performed on a freshly annealed Au(111) surface. Here the CVs obtained in the double layer regime are identical to those recorded prior to CO-exposure. Hence, the Au(111) surface is inactive for CO adsorption at least up to a potential of 1.0 V, when adsorption on the step sites possibly takes place, which is in agreement with previous infrared spectroscopy results. Consequently, CO oxidation occurs at potentials higher than 1.0 V, as shown in Fig. 5 (dotted line). On the other hand, CO stripping voltammetry on sputter-cleaned pure Ru electrode in 0.5 M H₂SO₄ showed that CO oxidation begins at approximately 0.2 V, and has a peak at 0.4 V, which is presented, for comparison, in Fig. 5b by the dotted line. Therefore, the data obtained on the Ru/Au(111) electrodes reflect the electrochemical behaviour of ultrathin Ru films and Ru submonolayer islands on an inert substrate.

Fig. 4. STM images (700 × 700) Å recorded on a Au(111) surface in 0.5 M H₂SO₄, showing the rearrangement and oxidation of the Ru islands with increasing electrode potential. The Ru was deposited from a 10⁻⁴ M RuCl₃ + 0.5 M H₂SO₄ solution on a reconstructed Au(111) surface. E_{dep} = 0.0 V; t_{dep} = 120 s; I_t = 11 nA; coverage = 0.55 ML; Image taken at the electrode potential of: a) 0.3 V (the same as for 0.0 V); b) 0.6 V; c) 0.8 V; d) 0.9 V.
For a direct correlation of surface structure and electrochemical behaviour, CO stripping experiments were performed in the STM cell directly after the structural characterization of the deposit by *in situ* STM. The CVs and the corresponding STM images are shown in Fig. 5 and Figs. 2 and 3, respectively.

On all the Ru/Au(111) electrodes studied in these experiments, CO stripping commences at about 0.2 V and reaches a current plateau at about 0.6 V, independent of the Ru coverage, morphology and deposition potential. Interestingly, the CVs for 0.25 and 0.45 ML Ru (Fig. 5a) are almost identical, suggesting a similar average CO coverage on both electrodes despite the pronounced differences in the Ru coverage. This might indicate that the very uniformly distributed Ru islands found at 0.25 ML Ru (Fig. 2a) can adsorb a higher amount of CO, e.g., due to adsorption of additional CO molecules at the island edges, than the islands at 0.45 ML, which tend to aggregate. At a Ru coverage of 0.65 ML, the activity is the same regardless of the distribution of Ru islands, which only differ from those at the lower coverage by a factor of two higher plateau current densities, Fig. 5b, solid line. Increasing the coverage further up to 0.8 ML,
which corresponds to a monolayer formation, does not change the activity of the bimetallic Ru/Au(111) significantly. Moreover, the activity remains the same even for a coverage of 3–4 ML (see Fig. 3). Therefore, it seems that a kind of limiting activity of the bimetallic surfaces is achieved at a coverage of about 0.65 ML. For all the Ru/Au(111) surfaces examined, at potentials >1.0 V a pronounced increase in the current is found, which is related to the oxidation of CO on the fraction of the Au(111) substrate surface not covered with Ru, coupled with the reactions of O₂ evolution and oxide formation.

It should be noted that CO oxidation commences at about 0.2 V on a bimetallic Ru/Au(111) surface, which is in very good agreement with the CO stripping experiments on bulk Ru, Fig. 5b, dotted line. A significant CO oxidation current, however, still exists at potentials more positive than 0.6 V, where CO oxidation ceases on pure Ru. The wider potential range of CO oxidation on the bimetallic surface can be explained by the variety of Ru oxidation states in the deposited islands and the variety of their distribution over the substrate surface. Consequently, such a surface offers a variety of CO adsorption sites with different binding energies. Besides, if the rearrangement and oxidation of the deposited Ru islands with increasing potential are taken into account (see Fig. 4), it can be assumed that even if an ordered deposit was obtained at certain potentials the orderliness would be lost in the course of the CO oxidation and the coverage of deposited Ru remains the only parameter which affects the kinetics of the process at more positive potentials.

The second fact which has to be taken into account is that there is no CO adsorption on the Au(111) surface (except in a limited amount on the steps), which means that its adsorption is limited to adsorption on the Ru islands. Some indication of the possible adsorption sites for CO on the different Ru/Au(111) electrodes can be derived from the STM data. For Ru coverage < 0.3 ML, the deposit usually consists of well-separated Ru islands with diameters in the nm-range. Here sites within the Ru islands and at the edges of the islands (i.e., on Ru step atoms) have to be considered, which should exist at approximately equal amounts due to the small diameter of the islands. At higher coverage, the Ru islands start to merge, resulting in a highly defective Ru adlayer, which may also exhibit other types of adsorption sites (e.g., Ru vacancies). Furthermore, the STM images indicate a small amount of higher Ru islands (multilayer islands or Ru oxide/hydroxide species). Hence, a larger variety of different adsorption sites exists on these surfaces, which could account for the observation of a broad plateau rather than well-resolved peaks in the CVs.

According to the CO stripping measurements, performed in a separate cell by the hanging meniscus method, the charged data indicate that 0.7 ML of CO is adsorbed on ML Ru films exhibiting a flat surface morphology, while practically a monolayer of CO is adsorbed on 10 ML Ru films or pure Ru, as expected from the higher surface roughness. This perfectly matches the results presented above, where the Ru/Au(111) surface with a Ru coverage of (0.65 ± 0.05) ML, showed the maximum activity with nonsignificant changes up to a coverage of 3–4 ML. As shown in Ref. 15, the maximum activity of metallic Ru was achieved for a coverage of 10 ML. A similar result was obtained for CO oxidation on Rh/Au(111). In contrast to the case of a Ru/Pt(111) surface, where due to an electronic effect, the activity of a Ru/Pt(111) surface is enhanced compared to pure Ru or Pt, the activity of a Ru/Pt(111) surface is not enhanced compared to pure Ru or Pt.
Ru/Au(111) surface shows an inhibiting effect of the underlying Au(111) substrate. TPD data have shown lower CO adsorption energy on the Ru areas of the Ru/Pt(111) surface than on the pure Ru surface.\textsuperscript{17} The same was obtained by \textit{in situ} FTIR measurements of CO oxidation on the Ru/Pt(111) surface in the electrochemical environment.\textsuperscript{18} The lower activity of the Ru/Au(111) surface can be explained by the opposite effect, \textit{i.e.}, by an enhanced CO adsorption energy on the Ru islands of the Ru/Au(111) electrode compared to pure Ru. This effect is caused by an electronic modification of the Ru surface atoms due to interaction with neighbouring Au atoms.

**CONCLUSIONS**

The results on CO stripping voltammetry on bimetallic Ru/Au(111) surfaces, showed that CO oxidation on deposited Ru islands commences at the same potential as on pure Ru, although it continues to more positive potentials. The initial potential is the same for all the faces investigated, while the current density increases with increasing coverage, reaching a maximum value for app. 0.65 ML. For lower coverage, the Ru/Au(111) bimetallic surface with a random distribution of Ru islands showed a higher activity. The observed influences of the Ru structure on the CO stripping voltammetry were explained by an electronic modification of the Ru surface atoms due to interaction with neighbouring Au atoms and by the formation of a mixed Ru adlayer, regarding the oxidation state of the deposited Ru, causing local variations in the CO adsorption energy.

**ИЗВОД**

ОКСИДАЦИЈА СО НА БИМЕТАЛНИМ Ru/Au(111) ПОВРШИНАМА

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Ru je депонован електрохемијски на монокристалу Au(111) из раствора 0,5 M H\textsubscript{2}SO\textsubscript{4}+10\textsuperscript{-4} M RuCl\textsubscript{3}. Карарактеризација добијених биметалних Ru/Au(111) површина је изведена цикличном волтаметријом и \textit{in situ} STM-ом у 0,5 M H\textsubscript{2}SO\textsubscript{4} раствору. Депозит Ru се састоји од нанометарских острова, која се стапају са повећањем покривености. У односу на расподелу острова Ru по површини Au(111) субстрата, добијена су два различитих типа биметалних површина. Ако је депозиција изведена на потенцијалима позитивнијим од област који се реонструкцијом, тј. на нереконструкцираној Au(111) површини, добија се неуређена распода острова Ru. Ако је депозиција изведена на реконструкцираној Au(111) површини на малој препанетости, добија се селективни раст острова Ru, чиме се резултат утискує у среплечкој реонструкцији. Само на већим препанетостима, формира се вишеосложени депозит, на који се веома једноструком морфолошком. Испитиван је електрокатализативни активност за оксидацију CO оваквих структурним дефинисаних биметалних Ru/Au(111) површина, са покривености до неколико моноложева. Окислачко CO почиње на око 0,2 V и одграва се у широкоме области потенцијала. Утицај структуре депозита Ru на оксидацију CO се објашњава варијацијама у енергији адсорпције CO због различитих локалних структурних депонованих острова Ru.

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