Carbon monoxide oxidation on a Au(111) surface modified by spontaneously deposited Ru

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The spontaneous deposition of Ru on Au(111) was performed in 10^{-3} M RuCl$_3$ + 0.5 M H$_2$SO$_4$ solution. The obtained surface was characterized by STM under potential control in 0.5 M H$_2$SO$_4$ solution. The coverage of the Au(111) terraces by deposited Ru was estimated by STM to be 0.02 ML. Step decoration could be noticed in the STM images, which indicates that the steps, as lined defects, are active sites for the nucleation of Ru monolayer islands, while the random distribution of Ru nuclei, observed on the terraces indicates point defects as active sites. The electrocatalytic activity of Au(111) surface modified by spontaneously deposited Ru was studied towards CO oxidation. The significant enhancement in the reaction rate compared to CO oxidation on a pure Au(111) surface, indicated that the edges of the deposited Ru islands were the active sites for the reaction.

Keywords: spontaneous deposition, Ru, Au(111), CO oxidation, STM.

INTRODUCTION

An *in situ* STM (Scanning Tunnelling Microscopy) study of the electrochemical deposition of Ru on reconstructed Au(111) surfaces has been reported by the authors of this paper[1] with emphases on the selectivity of specific surface sites for Ru nucleation. A comprehensive study of the electrochemical deposition of Ru on Au(111) over a wider potential region have shown a variety of surface morphologies depending on the deposition conditions. It was also shown that the coverage of the electrodeposited Ru did not change linearly with deposition time. It appeared that it is extremely difficult to achieve a defined coverage lower than 0.1 ML (monolayer) by electrochemical deposition for a defined deposition time and deposition potential. The activity of the obtained structurally well defined Ru/Au(111) bimetallic surfaces was studied towards CO oxidation.[2,3]

It was noticed that Ru deposition on the Au(111) occurs even when the electrode is only immersed into the Ru containing solution without the application of an external

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potential, *i.e.*, at the open circuit potential (OCP). This so-called spontaneous deposition of Ru on Pt single crystals was also confirmed by both electrochemical[4] and STM methods.[5] The spontaneous deposition of Ru on gold has not been reported so far. Since this observation is new, the morphology of the Ru/Au(111) surface obtained by the spontaneous deposition of Ru and the activity of such a surface towards CO oxidation will be presented in this paper.

Since the spontaneous deposition appeared to be more sensitive to the deposition time than the electrochemical deposition, a lower coverage of Au(111) with Ru was easily achieved. For a particular concentration of the Ru solution, the saturation coverage is achieved relatively quickly, which enables the avoidance of a strict deposition time control. Besides, the preferred nucleation of Ru monolayer islands at the step sites during spontaneous deposition offers the possibility to examine the role of those specific surface sites for CO oxidation on the Au(111) surface. The results on the activity of such a surface towards CO oxidation in 0.5 M H_2SO_4 solution will be presented in this paper.

EXPERIMENTAL

A single crystal, Au(111), 10 mm in diameter (Metal Crystals and Oxides, Cambridge, England), cut and oriented to better than 1°, was used as the substrate. After mechanical and electrochemical polishing,[3] the Au(111) crystal was annealed by a butane flame for several minutes, cooled down in air, and then mounted into the electrochemical cell of the STM, which was used for all the measurements described below.

STM measurements were performed using a self made scanning tunneling microscope described in detail in Ref. 6. The tunneling 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 *versus* Ag/AgCl(KCl saturated) reference electrode. The coverage was estimated exclusively on the terrace areas as the fraction of the substrate surface area covered by over layer structures in the STM images.

Since the Ru-containing solution is not stable, *i.e.*, the RuCl$_3$ is slowly converted into RuO $(H_2O)_4$ $^{2+}$, the solution was freshly prepared from RuCl$_3$·aq (Fluka), suprapure H_2SO_4 (Merck) and Milli-Q water before each measurement.

The crystal was contacted with the 0.5 M H_2SO_4 solution at the OCP and the STM images were recorded in order to characterize the initial Au(111) surface. After the electrolyte had been replaced by a Ru containing electrolyte (10^{-3} M RuCl$_3$ + 0.5 M H_2SO_4), the spontaneous deposition of Ru on Au(111) was performed for three minutes. With the replacement of the electrolyte, the OCP value changed from 0.38 V to 0.75 V within 10 s. The electrolyte was again exchanged for 0.5 M H_2SO_4 and the STM images were recorded under potential control. A potential of – 0.1 V was chosen in order to ensure that the deposit was stable on the surface.[2]

The CO oxidation measurements were performed after STM imaging, using the same STM cell. CO was purged over the cell through a reduced space made by a glass cover to avoid contact with air. The potential was kept at – 0.1 V, when CO is expected to be adsorbed on the Ru/Au(111) surface. After several minutes, when the saturation coverage of the Ru/Au(111) surface with CO is expected to be achieved, the CO oxidation was followed by cyclic voltammetry (CV). For comparison, CO oxidation measurements on a pure Au(111) surface were performed under the same conditions.

RESULTS AND DISCUSSION

The initial Au(111) surface was characterized by both STM at the open circuit potential and cyclic voltammetry in 0.5 M H_2SO_4 solution. The standard STM image of
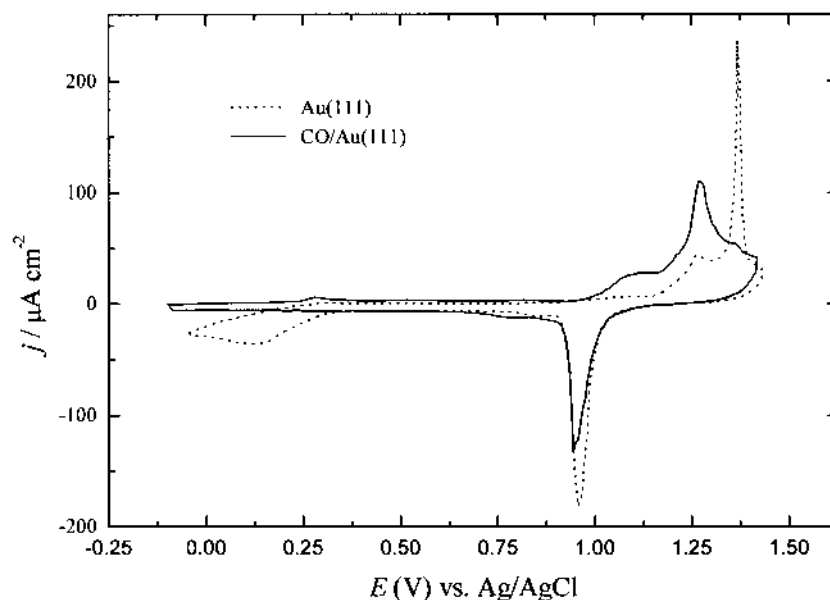
Fig. 1. Cyclic voltammogram for: (···) Au(111); (—) CO oxidation on the Au(111) surface in 0.5 M H₂SO₄ solution. Sweep rate 20 mV/s.
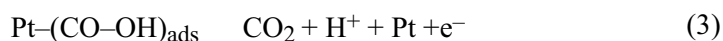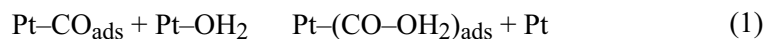
the initial unreconstructed Au(111) surface,[7] exhibited large terraces (ranging from 1000 to 2000 Å in width) and monoatomic steps with no islands of any origin, indicating the good orientation and cleanliness of the electrode.

The CV curve, presented in Fig. 1 by the broken line, shows the typical features of a clean Au(111) surface in sulphuric acid solutions.[8,9] The well known small peak at 0.25 V corresponds to the electrochemical lifting of the reconstruction and sulphate anion adsorption. The shoulder at 1.2 V is ascribed to oxide formation on the steps and the sharp peak at 1.35 V to oxide formation on the terraces of the Au(111) face. Both oxide formation peaks are coupled with the replacement turnover process (RTO).[8] Reduction of O_2 can be noticed at lower potentials, indicating the presence of the traces of O_2 in the solution, which could not be removed successfully from the STM cell by the procedure described above. Therefore, the small peak at 0.25 V is not well pronounced.

The oxidation of CO on the Au(111) surface was followed starting from a potential of – 0.1 V, which belongs to the potential region where the initial Au(111) surface was reconstructed, over the double layer and oxide formation, which is presented by the full line in Fig. 1. According to CO stripping measurements, performed in the separate cell by the hanging meniscus method in the double layer potential region,[2] the characteristic peak at 0.25 V, indicative of the formation of an ordered sulphate adlayer, was unchanged, which is incompatible with a high CO adsorbate coverage on the Au terraces. Hence, it was assumed that the Au(111) surface was inactive for CO adsorption at least up to a potential of 1.0 V, where the possible adsorption on the steps occurs ,[2] which is also in agreement with previous spectroscopy results.[10] Consequently, CO oxidation was expected to take place at po-

tentials higher than 1.0 V, which is now confirmed with the CV obtained over a wider potential region as presented in Fig. 1 (full line). CO oxidation on the Au(111) surface begins at approximately 1.0 V, which is 0.15 V negative to the formation of oxide (AuOH) on the steps of the Au(111). It should be noticed that in the beginning of the process, the kinetics of CO oxidation is very low resulting in very low current densities. At higher potentials, CO adsorption takes place at the terraces too and CO oxidation proceeds with much higher current densities. The current for CO oxidation begins to decrease at the potential corresponding to the formation of oxide on the terraces, when CO oxidation is suppressed most likely due to the RTO process, which makes OHAu unavailable for the reaction. Due to the difference in the charge of 140 μC/cm^2 (out of 444 μC/cm^2 for the whole Au(111) surface) corresponding to oxide reduction on the Au(111) surface before and after CO oxidation, we suggest that oxide formation is suppressed on the steps and partly on the terraces by CO adsorption.

According to previous CO oxidation studies on Au single crystal electrodes with several orientations in perchloric acid solutions,[11,12] a plausible formal mechanism involves an adsorption equilibrium of CO on Au before it reacts with OH_{ads} to form CO_2. It was, however, pointed out that apparently OH adsorbs on Au only at potentials more positive than that of the onset of CO oxidation,[12] which is in agreement with the results in sulphuric acid solution, presented above. Hence, the state of the oxygen-containing species participating in the oxidation of CO is still unresolved and alternative pathways, such as the reaction of CO with strongly adsorbed water (activated water) in that potential region is assumed. An attempt to establish an appropriate reaction mechanism involving activated water as a reactant, was made recently by Grgur[13] for CO oxidation on Pt single crystals, where the following mechanism was proposed:

$$Pt–CO_{ads} + Pt–OH_2 \quad\quad Pt–(CO–OH_2)_{ads} + Pt \tag{1}$$

$$Pt–(CO–OH_2)_{ads} \quad\quad Pt–(CO–OH)_{ads} + H^+ + e^- \tag{2}$$

$$Pt–(CO–OH)_{ads} \quad\quad CO_2 + H^+ + Pt + e^- \tag{3}$$

where the activated water, $Pt–OH_2$, was assumed to be formed after the reorientation of adsorbed water molecule Pt–HOH in the potential region of sulphate anion desorption. We suggest that this mechanism might be valid for Au too, where Au-CO_{ads} should correspond to the CO adsorbed on a step site and Au–OH_2 to the neighboring terrace site of the Au(111) surface. The role of steps as active sites for CO oxidation (adsorption) is further verified by the results obtained for CO oxidation on a Au(111) surface modified by spontaneously deposited Ru.

Ru was deposited at the OCP, as described in the Experimental Section since, for CO oxidation measurements, the cycling voltammetry was performed starting from the potential of – 0.1 V, the characterization of the Ru/Au(111) surface by STM was performed at this initial potential. This certainly caused the reduction of the oxidation state of the spontaneously deposited Ru, most likely to metallic Ru,[4] but the coverage of the surface, *i.e.,* the density of the Ru islands should remain the same.
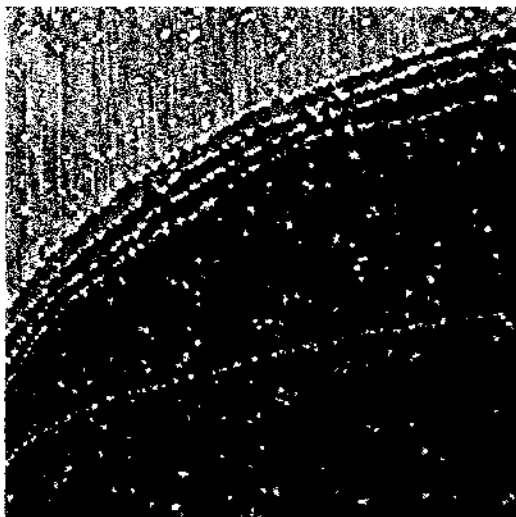
Fig. 2. STM image (210 210) nm recorded in 0.5 M H_2SO_4 at $-$ 0.1 V, after Ru was spontaneously deposited from 10^{-3} M $RuCl_3$ + 0.5 M H_2SO_4 for 3 min. I_t = 1.15 nA; coverage = 0.02 ML.

The STM image of Ru spontaneously deposited on a Au(111) plane from a 10^{-3} M $RuCl_3$ + 0.5 M H_2SO_4 solution after a deposition time of 3 min is presented in Fig 2. The estimated coverage of the Au(111) surface terraces with deposited Ru is about 0.02 ML. The deposited two-dimensional (2D) Ru islands have an average height of 0.22 nm, which is consistent with Ru(111) islands one step high (the Ru(111) step height is 0.219 nm and the Au(111) step height is 0.235 nm) and an average island size of 1.5 nm. The decoration of the step edges by Ru islands is visible. Step decoration during sponta-neous metal deposition is presented here for the first time. A very similar deposit mor-phology is observed for the diffusion-limited galvanic deposition at low Ru-concen-tration and at a potential of 0.0 V (*vs*. Ag/AgCl), where the Au(111) surface exhibits a surface reconstruction, in both sulphuric[14] and hydrochloric acid solutions.[15]

According to Wieckowski *et al.*,[4,5] it was assumed that the Ru spontaneously depos-ited on a Pt(111) surface has no metallic Ru on the surface, but Ru^{6+} and $Ru^{2+.}$ The sponta-neous deposition of Ru was attributed to the presence of RuO $(H_2O)_4$ $^{2+}$ species in the so-lution (its concentration increases with aging, but in this work all the measurements were done with freshly prepared Ru solutions) and to the formation of adsorbed RuO_2. This reac-tion is followed by a disproportionate reaction where $2RuO_2$ gives RuO and RuO_3 on the surface. According to the STM image presented here, we suppose that the steps as lined de-fects and the other defects present on the flat part of the surface (point defects) are active sites for this chemical reaction. This indicates that the concentration of Ru species in the so-lution is not the only factor determining the saturation coverage. The coverage of spontane-ously deposited Ru depends also on the density of the steps and on the density of the point defects present on the flat part of the surface. This means that the better preparation of the Au(111) surface, the lower the coverage of spontaneously deposited Ru is.

The CO oxidation measurements on the Ru/Au(111) surface (presented by the STM image in Fig. 2) is presented in Fig. 3 by the full line, while the CV curve for CO

oxidation on a Au(111) surface (from Fig. 1) is presented for reference by the broken line. It can be seen that the initial potential for CO oxidation on the Ru/Au(111) surface corresponds to the initial potential for CO oxidation on a pure Au(111) surface. On the other hand, the kinetics of CO oxidation increases substantially, especially in the beginning of the process, showing a peak instead of a shoulder. With increasing potential, the second CO oxidation peak also increases compared to CO oxidation on a Au(111) surface, after which the current decays slowly with increasing potential, as in the previous case.
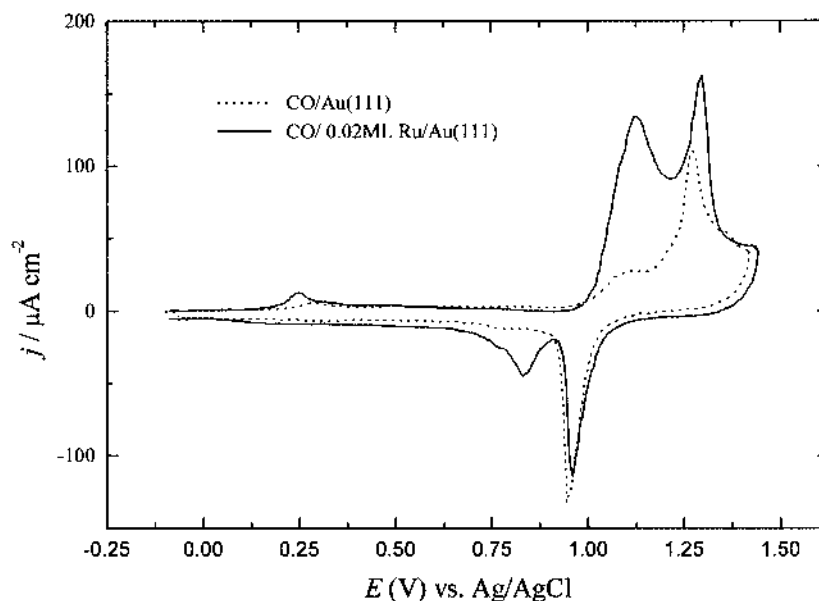

Fig. 3. Cyclic voltammograms for: (···) CO oxidation on the Au(111) surface modified by spontaneously deposited Ru; (—) CO oxidation on the Au(111) surface (taken as a reference from Fig. 1), in 0.5 M H_2SO_4. Sweep rate 20 mV/s.

The effect of the presence of RuO_x islands[2,4] on the surface in the potential region of the first CO oxidation peak can be ascribed to CO adsorption at the edges of the RuO_x islands, *i.e.,* on RuO_x–Au active sites and its reaction with the activated water, similar to that described above. Compared to the pure Au(111) surface, where the steps are the only active sites for CO adsorption, the edges of the deposited RuO_x islands as lined defects contribute significantly to the number of active sites for CO adsorption and thus to the CO oxidation rate.

CONCLUSIONS

The STM results on the spontaneous deposition of Ru on the Au(111) surface showed a preferred nucleation of Ru monolayer islands at the step sites. A random distribution of Ru islands and a very low coverage of 0.02 ML, observed on the terraces, indicate nucleation at point defects.

The investigation of the electrocatalytic activity of the Au(111) surface towards CO oxidation showed that the initial potential for CO oxidation is more negative than the initial potential for OH adsorption on the Au(111) surface. This indicates that activated water rather than OH_{ads} reacts with CO_{ads}. The low reaction rate at the beginning of the process indicates that CO adsorption takes place at the steps only. The presence of a small amount of spontaneously deposited Ru islands on the Au(111) surface causes a significant enhancement of the CO oxidation rate. It is assumed that the edges of the RuO_x islands are active sites for CO adsorption and thus contribute to the CO oxidation rate.

И З В О Д

ОКСИДАЦИЈА CO НА Au(111) ПОВРШИНИ МОДИФИКОВАНОЈ СПОНТАНО ДЕПОНОВАНИМ Ru

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Ru је депонован спонтано на монокристалу Au(111) из раствора 10^{-3} M $RuCl_3$ + 0.5 M H_2SO_4. Карактеризација добијене површине је изведена in situ STM-ом у 0.5 M H_2SO_4. Покривеност Au(111) површине депонованим Ru на терасама је била 0,02 ML. На STM сликама се уочава декорација степеница депозитом, што указује да су степенице, као линијски дефекти, активна места за нукелацију острва Ru, док неравномерна расподела острва Ru на терасама указује на тачкасте дефекте као активна места. Испитивана је електрокаталитичка активност Au(111) површине модификоване спонтано депонованим Ru за оксидацију CO. Значајно повећање брзине реакције на Ru/Au(111) површини у поређењу са реакцијом на чистој Au(111) површини, указује да су ивице депонованих оствра Ru активна места за реакцију.

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