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In situ STM study of nanosized Ru and Os islands spontaneously deposited on Pt(111) and Au(111) electrodes

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Abstract

We provide an overview of structure and reactivity of selected bimetallic single crystal electrodes obtained by the method of spontaneous deposition. The surfaces that are described and compared are the following: Au(111)/Ru, Pt(111)/Ru and Pt(111)/Os. Detailed morphological information is presented and the significance of this work in current and further study of nanoisland covered surfaces in the catalytic and spectroscopic perspective is highlighted. All surfaces were investigated by in situ STM and by electroanalytical techniques. The results confirm our previous data that nanosized Ru islands are formed with specific and distinctive structural features, and that the Ru growth pattern is different for Au(111) and Pt(111). For Au(111), Ru is preferentially deposited on steps, while a random and relatively sparse distribution of Ru islands is observed on terraces. In contrast, for Ru deposited on Pt(111), a homogeneous deposition over all the Pt(111) surface was found. Os is also deposited homogeneously, and at a much higher rate than Ru, and even within a single deposition it forms a large proportion of multilayer islands. On Au(111), the Ru islands on both steps and terraces reach the saturation coverage within a short deposition time, and the Ru islands grow to multilayer heights and assume hexagonal shapes. On Pt(111), the Ru saturation coverage is reached relatively fast, but when a single deposition is applied, Ru nanoislands of mainly monoatomic height are formed, with the Ru coverage not exceeding 0.2 ML. For Ru deposits on Pt(111), we demonstrate that larger and multilayer islands obtained in two consecutive depositions can be reduced in size-both in height and width-by oxidizing the Ru islands and then by reducing them back to a metallic state. A clear increase in the Ru island dispersion is then obtained. However, methanol oxidation chronoamperometry shows that the surface with such a higher dispersion is less active to methanol oxidation than the initial surface. A preliminary interpretation of this effect is provided. Finally, we studied CO stripping reaction on Pt(111)/Ru, Au(111)/Ru and on Pt(111)/Os. We relate CO oxidation differences observed between Pt(111)/Ru and

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Pt(111)/Os to the difference in the oxophilicity of the two admetals. In turn, the difference in the CO stripping reaction on Pt(111)/Ru and Au(111)/Ru with respect to the Ru islands is linked to the effect of the substrate on the bond strength and/or adlayer structure of CO and OH_{ads} species. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Catalysts for many chemical reactions are often composed of two or more noble metals yielding catalytic activity higher than that of the pure components, and this enhancement has been extensively explored for nanoparticle and bulk polycrystalline [1–4], as well as for single crystal [3–5] electrodes. Mixed-metal, single crystal catalytic surfaces of interest to this report can be generated by evaporation of the deposit onto the substrate in UHV [6–9], by electrodeposition [6,10–16], electroless deposition [17], and spontaneous deposition [18–24] (see also Ref. [6]).

Spontaneous deposition procedure involves three major experimental steps. First, the electrode made of a substrate material (Pt and Au in this study) is immersed in an admetal-containing solution (usually, ionic forms of Ru and Os). Second, the electrode is removed from the deposition bath, rinsed (in water) and transferred to an electrochemical cell filled up with supporting electrolyte. Third, while in an electrochemical cell, the electrode is treated by a few negative- and positivegoing scans by cyclic voltammetry or by holding the surface at ca. 50 mV (vs. RHE) in the supporting electrolyte, where the precursor is reduced to metallic ruthenium (or osmium). This procedure leads to formation of the substrate surface "decorated" by metallic nanosized islands of adjustable coverage and height, depending on the details of the deposition, such as the concentration of the electrolytic bath, duration of chemisorption and a follow up electrochemical treatment such as described in Sections 3.2.4 of this report. Notably, holding the potential in the hydrogen adsorption range (near the hydrogen evolution edge) is sufficient to produce the metallic state of the deposit, as was confirmed by XPS measurements [25].

The use of the voltammetry as the preparative component of this method is simply a routine practice of our laboratory, which yields the same surface morphology as obtained by the potentiostatic treatment.

The spontaneous deposition method encodes specific and unique functions to the support material and facilitates preparation of structurally heterogeneous bimetallic electrode catalysts. The method is simple, does not involve electrochemical instrumentation for producing the decorated surface, and is immune to IR drop constrains during deposition, which is of importance for high surface area catalysts [26,27]. Notably, after a few minutes of the first deposition, only Ru coverage at ca. 0.2 ML is achieved, and the deposition stops. Higher deposit coverage can be obtained by using multiple spontaneous depositions; i.e., by repeating the exposure of the electrode obtained after first deposition/reduction cycle to the depositing metal ion containing solution, and again by stabilizing the new deposit by electrochemical reduction [24,27, 28]. The fact that the ruthenium saturation coverage at the first deposition run is low indicates that the Ru-Pt interactions leading to formation of the Ru precursor chemisorbate [29] are no longer operative at the Ru pretreated surface. This may as well be due to the steric reasons: the bulky (oxidized [25,29]) Ru chemisorbate keeps the Ru ions at the interface away from active Pt sites to prevent further chemisorption to continue. Because the repeated deposition yields the Ru coverage above the 0.2 ML level, we conclude that the excess (above 0.2 ML) deposition may begin and/ or continue only on the surface of a metal, either platinum or ruthenium. Since the Ru islands grow mainly in height, the existing Ru islands are preferred sites for Ru deposition in the second (and multiple) exposure to the Ru solution.

In this present report, we briefly review our already published STM data on Ru spontaneously deposited on Au(111) [29] and present new data on morphological rearrangements of Ru islands on Pt(111)/Ru induced by an electrochemical treatment. All work reported in this communication was carried out by the use of in situ STM [30]. Cyclic voltammetry and chronoamperometry are used for electrochemical characterization and reactivity measurements. We also present data, both previous [29] and new, which allow us to compare the CO stripping reaction on Pt(111)/Ru and on Pt(111)/ Os, and on Au(111)/Ru [31]. Mechanistic details of CO poison removal process from Pt(111)/Ru are a key topic in present fuel cell catalysis research.

We note that the chemical state of the Ru and Os deposits on Pt(111) obtained spontaneously has recently been studied by electrochemical XPS and synchrotron grazing incidence fluorescence-X-ray absorption spectroscopy (GIF-XAS) (GIF-XAS from Pt(111)/Os) only [25,32]. Immediately after the deposition of Ru on Pt(111) at open circuit, the data show that the deposit contains mainly Ru⁴⁺ and Ru⁶⁺ [18,25]. Such an original (oxidized) Ru precursor is reduced to the predominantly metallic state via the electrochemical treatment described above and reported in Ref. [25]. The work on Pt(111)/Os [32] also included collecting electrochemical data on osmium oxidation/ electrodissolution. Apparently, the Os deposit remains purely metallic up to 500 mV (vs. RHE) while above 500 mV it begins to oxidize to Os(IV). Electrodissolution of osmium oxides to dissolved Os forms begins above 900 mV and occurs simultaneously with platinum oxidation. (Oxidation of metallic ruthenium begins at more negative potential than osmium, approximately at 300 mV.)

It is clear nowadays that there is a need to develop and understand the promoting catalytic effects of nanosized metal islands on selected electrode surfaces for organic molecule oxidation that can be used for fuel cells. Before such catalytic effects are understood, a significant control of the morphology of such bimetallic surfaces needs to be achieved. Also, further work by electrochemical spectroscopies with adisland decorated single crystal electrodes [25,32] requires very detailed structural information about the electrode surface geometry before a spectroscopic assay is performed. The paper we present below responds to these particular needs in fuel cell catalysis science, and provides a comprehensive structural determination of the surfaces selected for the future spectroscopic efforts.

2. Experimental

An Au(111) single crystal, 6 mm in diameter (Metal Crystals and Oxides, Cambridge, England), cut and oriented to better than 0.5°, was used as substrate for the electrochemical measurements reported below. A 10 mm diameter Au(111) single crystal (Accumet Materials, Ossining, New York), cut and oriented to better than 0.5° was used for the in situ STM imaging. After mechanical and electrochemical polishing, the Au crystal was annealed in a hydrogen flame for several minutes, cooled down in air, and either mounted into the electrochemical cell of the STM or in the external electrochemical cell for cyclic voltammetry (CV) characterization. Electrochemical measurements were performed using an EcoChemie Autolab PSTAT100.

Pt(111) single crystals, 10, 6, and 2.2 mm in diameter (Accumet Materials, Ossining, New York), cut and oriented to better than 0.5° were used as substrates for the in situ STM imaging, chronoamperometry, and voltammetry measurements, respectively. After mechanical and electrochemical polishing, the Pt crystal was annealed in hydrogen flame for several minutes, and cooled down in the mixture of H₂ and Ar gases. The crystal, protected by a drop of ultrapure water, was then transferred to an external electrochemical cell for the voltammetric and chronoamperometric measurements. For the in situ STM work, the Pt surface was additionally processed by the I/CO treatment [33] modified in this work, which will be described in detail in Section 3. Multiple depositions were implemented by repeating the deposition and reduction procedures on the Pt(111) substrate containing previously deposited metallic Ru [24,26,27]. In this study, we conducted up to two repetitive depositions of Ru on the Pt(111) substrate.

All potentials in this paper (unless noted otherwise) are reported vs. Ag/AgCl/3M NaCl. Solutions were prepared using $RuCl_3 xH_2O$ and $OsCl_3 xH_2O$ (Alfa Aesar) salts, double distilled H_2SO_4 (GFS chemicals) and $HClO_4$ (GFS chemicals) and Milli-Q water. The spontaneous deposition of ruthenium on Au(111) and Pt(111) electrodes was performed at an open circuit potential (OCP) for the stated deposition time from an aged (over two weeks) 1 mM RuCl_3 + 0.1 M HClO_4 electrolyte. For generating Pt(111)/Os surfaces, a similarly aged 0.1 mM OsCl_3 + 0.1 M H_2SO_4 was used. Before and after the measurements, the electrode potential was kept for a few minutes at 50 mV (vs. RHE) in order to ensure that the Ru or Os deposit was reduced to the metallic phase [25,32,34].

Scanning tunneling microscopy measurements were performed in situ using a Molecular Imaging (MI) Pico STM. Pt–Ir and W tips used were electrochemically etched and insulated with clear nail polish prior to each experiment. STM images were obtained in a constant current mode with the tunneling current between 1 and 27 nA. The coverage on terrace areas was determined as the fraction of the substrate area covered by Ru or Os islands in the respective STM images, while the coverage on steps was calculated as the fraction of the step length covered by the deposited Ru islands. Data analysis was achieved using the Visual SPM software from Molecular Imaging.

If STM measurements were made following the electrochemical treatment, e.g. via cyclic voltammetry (see Section 1), the STM image was taken at after the CV run was interrupted and the interruption potential was held constant. A reasonable assumption was made that at such a holding potential, the state of the deposit was "frozen" and available for STM measurements as a genuine signature of the deposit structure.

3. Results and discussion

3.1. Au(111)/Ru surfaces [29]

3.1.1. Cyclic voltammetry

A cyclic voltammogram (CV) of the clean Au(111) surface is shown as a solid line in Fig. 1, and is representative of clean Au(111) surface



Fig. 1. Cyclic voltammograms recorded in 0.1 M H_2SO_4 of the clean Au(111) surface (solid line); after Ru was spontaneously deposited from 1 mM RuCl₃ in 0.1 M HClO₄ for 30 s (dotted line) and 3 min (dashed line) (sweep rate: 50 mV/s).

voltammetric properties in sulfuric acid [35-37]. The peak at 0.35 V is due to lifting Au(111) reconstruction via sulfate adsorption, and the peak at ca. 0.80 V is associated with the formation of an ordered sulfate adlattice [38]. The clean Au(111) electrode was exposed to the Ru-containing solution for 1 min, during which the OCP value rapidly increased from 0.38 to 0.72 V [29]. The electrode potential was then stepped to 0.00 V in order to reduce the high Ru valency deposit species (see Section 1) to a Ru metallic state. Also in Fig. 1, CVs obtained after different Ru deposition times: $t_{dep} = 30$ s (dotted line) and $t_{dep} = 3$ min (dashed line) are shown. The peak at ca. 0.8 V, characteristic of formation of an ordered sulfate adlayer, is increasingly suppressed with the added Ru, indicating that the long-range ordering of the sulfate adlayer is severely inhibited.

3.1.2. In situ STM images

The clean Au(111) surface was first characterized by STM at OCP (Fig. 2). The initial unreconstructed Au(111) surface with large 100–200 nm terraces containing no additional features is shown in Fig. 2A. Also shown in Fig. 2B is a highly stepped area with terrace widths of 2–10 nm (Fig. 2B). STM images were next recorded following different times of the deposition of Ru on Au(111) to display the time effect on the deposit



Fig. 2. STM images of the initial Au(111) surface prior to ruthenium deposition. (A) Smooth area of the Au(111) surface ($285 \times 285 \text{ nm}^2$); (B) Highly stepped surface area ($140 \times 140 \text{ nm}^2$). Images are recorded in 0.5 M H₂SO₄ at an open circuit potential.

morphology (Fig. 3). The in situ images were obtained under electrode potential control after the Ru-containing electrolyte was replaced with the $0.5 \text{ M H}_2\text{SO}_4$ supporting electrolyte. They were recorded and found invariant with electrode potential in the range of -0.1-0.1 V, where metallic Ru is present on the surface [25]. The images reveal a strong step preference for the Ru deposition, indicative of heterogeneous nucleation. The island density on the flat terraces increases at a much slower rate than on the steps, as is demonstrated by the STM images in Fig. 3A and B (obtained



Fig. 3. STM images of Ru modified Au(111) recorded at 0.1 V in 0.5 M H₂SO₄ after Ru was spontaneously deposited from 1 mM RuCl₃ in 0.1 M HClO₄ for (A) 30 s (330×330 nm²); (B) 3 min (360×360 nm²); (C) 3 min (230×230 nm²), obtained on a highly stepped area of Au(111).

after 30 s and 3 min Ru deposition, respectively). The step coverage, $22 \pm 3\%$, is much higher than the terrace coverage, $10 \pm 2\%$, after 30 s deposition. The total coverage is only $12 \pm 2\%$ because of the large size of the terraces. After 3 min depo-

sition, the step coverage is high, $83 \pm 8\%$, so that the Ru islands appear to have coalesced into the strings of multilayer islands. The island density on the terraces increased much less to only $18 \pm 3\%$. Mostly due to the high step activity, the total Ru coverage increases almost threefold to $32 \pm 2\%$.

Given the pronounced role that reconstruction plays in electrochemical deposition of Ru onto Au(111) [13,34], we note that the spontaneous deposition of Ru is performed at high OCP potentials, and on the *unreconstructed* Au(111) surface. Therefore, the surface reconstruction does not play a major role in the nucleation stage of the deposition process. When the electrode potential was reduced to lower values, and the EC-STM measurements were carried out in the region of surface reconstruction, large Ru islands have already been formed, and the diffusion of Ru atoms from such stable islands outward is an unlikely event to consider. On the other hand, there was a clear influence of the deposited islands on the reconstruction process; the reconstruction was clearly inhibited at higher Ru coverage. At a saturation coverage (3 min), no surface reconstruction was found.

To further demonstrate the ability of the surface steps to increase the total Ru coverage, highly stepped areas were chosen for imaging of the Au(111) substrate. After 3 min deposition on a highly stepped surface, shown in Fig. 3C, higher density of islands is observed than on a similarly sized area of Au(111) terraces. Due to the higher coverage along steps than on flat terraces, the total coverage reaches $52 \pm 5\%$ on the highly stepped surface as compared to the $32 \pm 4\%$ obtained on the terraces (see, e.g., Fig. 3B).

For particular deposition conditions, the Ru islands are uniform in size. With increasing deposition time, the size of deposited Ru islands increases up to saturation coverage within 3 min. Namely, the size of islands increases from 5 ± 2 nm width after 30 s to 6 ± 2 nm after 3 min deposition. The same holds true for the island height, which increases from 1.6 layers to ca. 2.5 layers (on the average). The island height distributions are presented in Fig. 4A and B, for the deposition times of 30 s and 3 min, respectively. For the dep-



Fig. 4. The island height distribution for Ru islands spontaneously deposited on Au(111) from 1 mM RuCl₃ in 0.1 M HClO₄ for (A) 30 s; (B) 3 min.

osition time of 30 s, the islands are predominantly one layer high (50%), while 33% are two layers high, 13% are three layers high and 7% consists of four monolayers. With the increase of the deposition time to 3 min, the fraction of the one-layer high islands decreases to 17%, while the fraction of two monolayer high islands increases to 50%, as well as the fraction of three and four monolayer high islands to 25% and 9%, respectively. The appearance of a very small amount of even higher islands was also noticed. The increase in the island width on terraces can be attributed to the activity of the borders between the deposited Ru and substrate Au sites acting as new centers for the Ru nucleation upon the RuO_x reduction process. The limiting factor here is the size of the island; when the top of Ru islands becomes more active

in the deposition than the Ru–Au borders, it leads to further vertical growth of the deposited Ru. Consequently, the transformation of the surface two-dimensional islands to surface clusters is then observed.

A more resolved STM image in Fig. 5A shows the Ru island structure in more detail, including



Fig. 5. Smaller scale STM images taken from Fig. 3B: (A) $(65 \times 65 \text{ nm}^2)$; (B) $(21 \times 21 \text{ nm}^2)$; the cross sectional analysis of the line through the islands.

clear demonstration of the hexagonal shape and uniform size of the islands. The step decoration consists of more than a single string of islands along the step: the islands are arrayed on the steps in strings that are at least two islands wide. The islands are most likely located on both sides of the steps arranged one besides another. Similarly, Ru islands are grouped together also on the terraces. These groupings are attributed to density fluctuations in the nucleation phase, which leads to formation of closely spaced nuclei. Fig. 5B and C demonstrates the multilayer nature of the Ru islands, presenting a large central island (10 nm) and two smaller islands (6 nm) at the bottom. Taking that the height of Ru monolayer is 0.22 nm, the cross section analysis shows (Fig. 5C) that the central island (~1.4 nm high) consists of six monolayers, while the bottom two islands (≈ 0.9 nm high, the cross section not presented) consist of four monolayers.

The data presented above reveal that for a particular concentration of ruthenium in solution, the density of steps is the main factor determining coverage of Ru on Au(111). Using overall highly stepped surfaces of Au results in an increased Ru coverage. For Pt, which does not display high step activity for Ru deposition, further active sites can be generated by multiple spontaneous deposition, as demonstrated below for the case of deposition of Ru on Pt(111).

3.2. Pt(111)/Ru surfaces

3.2.1. Cyclic voltammetry

Cyclic voltammetry (CV) was employed to characterize the electrode surfaces obtained by spontaneous deposition of Ru on Pt(111). A typical CV profile of the clean Pt(111) surface in clean sulfuric acid electrolyte (0.1 M H₂SO₄) is shown in Fig. 6 (solid line). The clean Pt(111) surface was exposed to Ru-containing solution for 3 min, and the OCP was observed to quickly stabilize at ~0.66 V. The curves obtained on the same surface with deposited ruthenium are shown as the dotted (one deposition) and dashed-dotted (two depositions) lines. Notice that the characteristic "butterfly" feature [39] is suppressed after one deposition, indicating that obtaining a long-range



Fig. 6. Cyclic voltammograms recorded in 0.1 M H_2SO_4 of the clean Pt(111) surface (solid line), after 3 min of a single spontaneous Ru deposition (dotted line), and after 2 × 3 min of multiple deposition (dash-dot-dashed) line (2 × 3 min = two spontaneous depositions, 3 min each).

order of the sulfate adlayer, demonstrated on Pt(111) [40,41] is no longer possible on the Pt(111)/Ru surface [42]. Additionally, the surface exhibits a noticeable increase in the double layer capacity.

3.2.2. Preparation of the Pt(111) surface for in situ STM measurements

The integrity of the platinum single crystal order is highly sensitive to oxygen chemisorption and concomitant surface oxidation (Ref. [43] and papers cited therein). Therefore, the use of STM creates an experimental difficulty due to the time it takes to mount the crystal in the STM cell after the flame annealing procedure [44], and the surface may disorder rapidly before the STM images are taken. To prevent such disordering, as well as to eliminate other possible platinum contamination reactions, we have modified in this project a procedure [33] that enables us to mount the crystal in the STM cell while still maintaining the crystallographic longrange order and cleanness of the crystal surface.

This procedure, based upon previous work [33], is executed as follows. First, the crystal is annealed in a hydrogen flame and cooled in hydrogen–argon atmosphere [44]. The crystal is subsequently protected by a drop of deaerated water and transferred to a 1 mM KI solution, where I^- adsorbs on Pt forming a protective iodine adlayer against platinum oxidation and contamination. Subsequently, the I-protected crystal is safely mounted in the STM cell, all operations (air transfer and mounting in STM) carried out in air. A CO saturated sulfuric acid solution is then admitted to the electrochemical STM cell and the potential is held at -0.1 V for 10 min to displace the iodide with carbon monoxide [33]. The CO saturated solution is replaced with clean sulfuric acid while still under electrode potential control, and subsequently the surface is scanned to 0.75 V in order to strip the surface of CO without causing surface disorder. A cyclic voltammetric (CV) curve is demonstrated in Fig. 7A, where a regular CO stripping peak from the Pt(111) electrode is observed [45-47]. The CV obtained after the CO stripping (Fig. 7B) depicts the character of a clean, well-ordered Pt(111) substrate, with the relatively "flat" hydrogen adsorption/desorption regions, a well-defined and sharp peak at ca. 0.22 V corresponding to sulfate adsorption on the (111) surface sites, and a small oxidation and reduction peak at 0.48 and 0.44 V, respectively. All these voltammetric features indicate that the Pt surface maintains the proper purity and crystallographic order. After mounting the Pt(111) crystal in the STM cell, the surface was characterized by STM at 0.1 V in 0.1 M H₂SO₄ (Fig. 7C). A typical STM image of the Pt(111) surface, exhibits large terraces (ranging from 50 to 150 nm width) and monoatomic steps. These images demonstrate the absence of surface islands, which are later observable with Ru covered surfaces (see below), which is characteristic of the lack of detectable contaminations and oxide(s).

We notice that the modification involved replacement of the gas phase iodine [33] as the surface protecting factor with solution iodide, which resulted in a major facilitation of the experiment. However, the original idea to keep the protective film of iodine on the surface as long as needed, and then replace it by CO easily removable by electrochemistry (without surface disorder) remains the same [33].

3.2.3. A single spontaneous deposition

Following the clean Pt(111) examination by in situ STM, ruthenium was spontaneously



Fig. 7. (A) CO stripping after replacement of surface iodine by CO on Pt(111) in 0.1 M H₂SO₄ at 50 mV/s (see text); (B) the Pt(111) cyclic voltammogram in 0.1 M H₂SO₄ at 50 mV/s obtained after the CO stripping (the next scan after the stripping); (C) STM image (100×100) nm² of the initial flat Pt(111) surface prior to ruthenium deposition; the image recorded in 0.1 M H₂SO₄ at 0.1 V.

deposited as described before [24] and in Section 1 to this report. One or two depositions were per-



Fig. 8. STM image (40×40) nm² of Pt(111) in 0.1 M H₂SO₄ after Ru was spontaneously deposited for (A) 3 min, recorded at 0.1 V, coverage = $18 \pm 3\%$; (B) the corresponding island height distribution.

formed (the latter consecutively) for 3 min each, and STM images from such Pt(111)/Ru surfaces were obtained in 0.1 M H₂SO₄ and under the electrode potential control. A representative in situ STM image obtained after the first deposition at saturation coverage of $18 \pm 3\%$ reveals that ruthenium islands nucleate homogeneously over the Pt(111) surface (Fig. 8A). This is in agreement with the results of previous ex situ STM investigations of the iodine protected Pt(111)/Ru surfaces [24,42]. The average diameter of the mainly twodimensional Ru islands is in the range of 1–3 nm. As shown in Fig. 8B, most of the islands have monolayer height (76 \pm 5%), but a clearly detectable amount of the multilayer growth appears as well. Note that only the apex height is considered in the counting process, and the islands are not necessarily of homogeneous height across the whole island. In contrast to spontaneous deposition of ruthenium on Au(111), no preferential deposition along the Pt(111) steps is found (Fig. 8A). It therefore seems that the diffusion of Ru adatoms over the Au(111) surface is much faster than on Pt(111), enabling adatoms to diffuse towards and along the steps forming the observed step decoration morphology. The hexagonal shape of growing islands in both cases indicates that adatoms diffuse along atomic rows as well as along the edges of the growing Ru island i.e. there is no preferential direction of diffusion.

3.2.4. Two spontaneous depositions

After imaging the deposit obtained from the first deposition, the crystal was held at -0.1 V in H_2SO_4 for a short time to ensure that metallic Ru was present. H₂SO₄ solution was then replaced by the ruthenium-containing solution (1 mM RuCl₃ in 0.1 M HClO₄) at OCP and the second deposition was performed for another 3 min. The STM image of the resulting surface recorded at 0.1 V is presented in Fig. 9A. The coverage now obtained is $22 \pm 3\%$, and the size of the islands increased vs. data obtained during a single deposition (Fig. 8), with most islands having widths between 2 and 5 nm. However, a significant increase in the average island height is observed (cf. Figs. 8B and 10A). Only $50 \pm 5\%$ of the islands are now of monolayer height, while the remaining islands are made of two to four monolayers. The data show high preference for ruthenium islands to predominantly form on top of the previously adsorbed islands, indicating the capability of ruthenium to spontaneously deposit on the ruthenium surface. Notice that the border sites of the formerly deposited Ru islands of ruthenium also act as nucleation centers for the subsequent depositions, as some increase in the island size is observed (see above for Au(111)).

Using the Pt(111) electrode covered by Ru via two spontaneous depositions, we found that a major factor determining the size of the ruthenium



Fig. 9. STM images (40×40) nm² of Pt(111) in 0.1 M H₂SO₄ after Ru was spontaneously deposited for 2×3 min (2×3 min = two spontaneous depositions, 3 min each): (A) recorded at 0.1 V, coverage = 22 ± 3%; (B) recorded at 0.35 V (partially oxidized); (C) upon decreasing of the electrode potential back to 0.1 V after surface oxidation at 0.7 V (see Fig. 11C). The coverage = 25 ± 3%.

islands was the ruthenium oxidation state, as it depends on the electrode potential at which STM



Fig. 10. The island height distribution for Ru islands spontaneously deposited on Pt(111) from 1 mM $RuCl_3$ in 0.1 M $HClO_4$ for 2×3 min deposition (see Fig. 9): (A) at 0.1 V, initial surface before oxidation; (B) after oxidation at 0.7 V and subsequent reduction at 0.1 V (Fig. 9C and text).

imaging was performed. As shown in Fig. 9B, increasing the electrode potential to 0.35 V leads to an increase in the island lateral size and height. These new features may be attributed to the transformation of metallic Ru to Ru oxides, which already takes place at 0.35 V [25]. Notably, after lowering the potential back to 0.10 V (Fig. 9C), a new surface morphology was obtained which is very much different from those shown in Fig. 9A and B, but shows some resemblance the surface presented in Fig. 8A, that is to the one obtained by a single deposition, although at a higher Ru coverage. Detailed comments on this image will be provided in subsection below.

In Fig. 11A, an STM image obtained while scanning over a small (20×20) nm² surface area

is given to illustrate the hexagonal shape of the deposited islands. The island height can be envisaged from the cross-section analysis. With a further increase in the electrode potential, a more pronounced oxidation of the deposited Ru islands takes place and, consequently, the morphology of the deposited Ru changes. This is illustrated by the STM image and the corresponding cross section analysis obtained at the electrode potentials of 0.50 and 0.70 V, Fig. 11B and C, respectively. It can also be seen that upon applying the potential of 0.50 V, the disintegration of the Ru islands into smaller islands begins. Breaking of the Ru islands becomes even more pronounced with increasing the potential to 0.70 V. Here, either one island is close to another (like twin islands), or the islands are fully separated.

3.2.5. The increase in Ru adisland dispersion; consequences for methanol oxidation

Data in Figs. 9 and 11 show that when the oxidized Pt(111)/Ru electrode at 0.7 V (Figs. 9B and 11) is polarized to 0.1 V a new STM image is obtained (Fig. 9C). The inspection of these images indicates that, upon reduction, the originally oxidized and partially disintegrated islands (Fig. 11) become smaller in size and more dispersed than those at 0.7 V. They are also smaller than would be expected if the surface were simply returning to the original metallic state from before the oxidation (compare Fig. 9A and C). Namely, while the island width before the oxidation was 2-5 nm, it is now reduced to 1-2 nm (Fig. 9C). At the same time: (i) the island density is higher, (ii) the island height decreases with $79 \pm 5\%$ of the islands displaving only monolayer height, Figs. 9C and 10B, and (iii) the Ru surface coverage increases to $25 \pm 3\%$. We therefore conclude that a significant change in surface morphology and an increase in the adisland dispersion were obtained after the redox sequence: 0.1-0.7 V and back to 0.1 V.

The increase in the island dispersion, as it increases the ruthenium coverage, removes platinum sites that were present on the bimetallic surface before the experiment reported above was executed. In other words, the number of "ensembles" of Pt sites [48,49] available, e.g., for chemisorption on



Fig. 11. STM images (20×20) nm² in 0.1 M H₂SO₄, and corresponding cross sectional analysis of Pt(111) after Ru was spontaneously deposited for 2 × 3 min (2 × 3 min = 2 spontaneous depositions, 3 min each), recorded: (A) at 0.35 V; (B) upon increasing the electrode potential to 0.5 V; (C) upon increasing the electrode potential to 0.7 V.

the Pt sites of the Pt(111)/Ru surface is reduced. A typical case where this development is important is the process of dissociative chemisorption of methanol, as it requires as many as three adjacent sites for methanol dissociation (dehydrogenation) to the chemisorbed CO [2,48,49]. Because methanol oxidation to CO₂ predominantly occurs via CO formation process [2,5], the overall rate of methanol oxidation may be affected by the increase in ruthenium coverage at the expense of the number of the collective Pt sites needed for methanol decomposition to CO [48,49].

We also performed chronoamperometric measurements in a methanol containing solution (0.6 M CH₃OH + 0.1 M H₂SO₄ solution) at a constant electrode potential after using several Pt(111)/Ru surfaces prepared as described above. The electrode was immersed in the solution at -0.1 V for 1 min to ensure that the Ru deposit was initially metallic, and a very slow methanol decomposition [19]. Current-time decays were then collected at 0.16 V, which are representative of the methanol oxidations kinetics at this electrode potential [19].

Fig. 12 displays four chronoamperometric methanol oxidation curves. Curve A was obtained with clean Pt(111), i.e. with no ruthenium on the



Fig. 12. Current-time transients for curve (A) clean Pt(111); curve (B) modified by 3 min of Ru deposition (to produce the STM image shown in Fig. 8A); curve (C) 2×3 min Ru deposition before methanol oxidation, (see caption to Fig. 9, and Fig. 9A); curve (D) also 2×3 min Ru deposition but the potential was increased to 0.7 V, and subsequently returned to 0.1 V (see Fig. 9C and text). The current-time transient was recorded at 0.16 V in 0.6 M CH₃OH + 0.1 M H₂SO₄.

surface. The low current at the end of the decay (after 30 min [19]) is due to Pt site-blocking by adsorbed CO from methanol dehydrogenation [2]. For the Pt(111)/Ru surface obtained after the first Ru deposition with $18 \pm 3\%$ coverage of ruthenium (see Fig. 8A), there is a much higher methanol oxidation current (curve B), showing the high catalytic enhancement of the Pt(111)/Ru electrode versus clean Pt(111). The current measured for the Pt(111)/Ru surface obtained after two consecutive Ru depositions (Fig. 9A) is 1.6 times that obtained after the single spontaneous deposition (curve C of Fig. 12). However, after the surface has been perturbed by oxidizing the Ru islands at 0.70 V and subsequently reducing them again at 0.1 V (see Fig. 9C), the methanol oxidation current drops to 1.3 times of that measured after the first Ru deposition, as shown in curve D. This conforms well to the expectations presented above, which are in agreement with the bifunctional methanol oxidation mechanism [50] that, to become optimized, requires the appropriate balance of the Pt and Ru sites on the surface [2,19,48,49].

3.3. Pt(111)/*Os surface*

3.3.1. Cyclic voltammetry

The CV obtained after exposing a Pt(111) electrode to a 0.1 mM $OsCl_3 + 0.1$ M H_2SO_4 solution for 1 min is shown in Fig. 13. The feature at -75 mV going in the negative direction we attribute to the reduction of Os oxides/hydroxides obtained during spontaneous deposition [32]. After several sweeps, a stable voltammogram is obtained; four cycles are shown in Fig. 13. The characteristic "butterfly" peak at 0.24 V is only slightly suppressed by Os deposition, although complete suppression can be obtained with deposition from 1 mM Os solution for 5 min [32].

3.3.2. STM images

A single deposition was performed for 1 min from the 0.1 mM $OsCl_3 + 0.1$ M H_2SO_4 solution at the open circuit potential, after which the solution was exchanged for 0.1 M H_2SO_4 . Nine potential cycles from -0.2 to 0.6 V at 50 mV/s were then used to stabilize the Os deposit, attaining a complete reduction of the osmium precursor to the



Fig. 13. Cyclic voltammograms recorded in 0.1 M H_2SO_4 of the clean Pt(111) surface (solid line), and after exposing the electrode to 0.1 mM $OsCl_3 + 0.1$ M H_2SO_4 solution for 1 min (dotted lines, four cycles).

metallic Os. The STM image was obtained at 0.1 V, that is, at a potential at which Os on Pt(111)is metallic, as determined by XPS [32] (Fig. 14A). The total coverage obtained from the STM image is $22 \pm 3\%$. In these measurements, we have found a significant multilayer growth of the Os islands, in contrast to the images presented in the previous study [32], undoubtedly because of the I^{-/}CO method of surface preparation used in this work. As shown in Fig. 14B, for 1 min deposition from 0.1 mM Os solution, only $39 \pm 5\%$ of the islands are one Os layer high (0.22 nm), and there is a significant multilayer growth even up to five monolayers height. To determine the height distribution, zoomed portions of images were analyzed by counting the apex height of each island. In general, the tallest islands are the widest islands as well, and they seem to be composed of several smaller islands fused together. One layer high islands typically are of only 1.5–2.5 nm width, whereas islands 2-4 layers high were 2.0-3.5 nm wide. The tallest islands (five monolayers or higher) are even larger at 3.0-5.5 nm wide.

The deposition of Os on Pt(111) occurs much faster than Ru. Comparing the surfaces obtained under the deposition conditions of 1 min/0.1 mM Os solution and 3 min/1 mM Ru solution, a similar Os coverage vs. the Ru coverage limit is reached by the Os coverage even when the concentration of Os



Fig. 14. (A) STM image $(185 \times 185 \text{ nm}^2)$ of Pt(111) after exposing the electrode to 0.1 mM OsCl₃ + 0.1 M H₂SO₄ solution for 1 min and performing nine potential cycles from -0.2 to 0.6 V to reduce the deposited Os (see text). Surface potential was 0.1 V, and Os coverage = $22 \pm 3\%$; (B) the island height distribution for the Os islands.

in the depositing solution is 10 times lower than the Ru one and the deposition time is shorter, irrespective of the electrolyte composition (from perchloric to sulfuric acid medium). Multilayer growth appears more significantly with Os, with $61 \pm 5\%$ multilayer growth after only 1 min/0.1 mM deposition versus only $24 \pm 3\%$ multilayer growth on Pt(111)/Ru after 1 min/1 mM deposition. There is a wider distribution of the island width and height for a single deposition of Os versus a single deposition of Ru on Pt(111), and the islands are on average wider and taller. The islands are in fact more comparable to those obtained from two Ru depositions. Many of the larger Os islands are composed of smaller, rounded units of 1–2 nm width, whereas segmented growth was not pronounced for Ru. When measuring the height of the Os units defined in this way (counting each segment), the number of Os units present with multilayer height was still found to be $43 \pm 4\%$, which is still much greater than for Pt(111)/Ru. Like with all Pt(111)/Ru surfaces studied here, osmium is deposited homogeneously without any preference for steps (see above).

3.4. Oxidation of surface CO on Au(111)/Ruand Pt(111)/Me surfaces (Me = Ru and Os)

3.4.1. CO on Au(111)/Ru

We will next use CO chemisorption as a probe of surface state of the studied electrodes in the CO stripping voltammetry experiment. The first characterized electrode is Au(111)/Ru. Because CO desorbs from Au(111) to CO-free H_2SO_4 electrolyte upon argon purging in the electrode potential range of interest (with possible exception of adsorption on step sites), the observed CO stripping voltammetry profiles can be attributed to the catalytic properties (chemisorption/oxidative desorption) of the Ru islands on the surface of gold.

Fig. 15 depicts the CO stripping voltammetry for Au(111)/Ru prepared by a 30 s spontaneous deposition of Ru (Fig. 3A) and by 3 min deposition (Fig. 3B). Two main peaks associated with CO stripping (solid line) are observed at 0.36 and 0.51 V for the 30 s case ($\sim 12\%$ coverage), and at 0.37 and 0.56 V for the 3 min case (\sim 32% coverage). The peak positions are significantly more positive than the single peak at 0.30 V for CO oxidation on bulk Ru or thick electrodeposited Ru layers on Au(111) [34,51]. The peak is also more positive than the CO stripping peak from Ru(0001) at ca. 0.28 V, although for Ru(0001) several sweeps are required to completely remove CO, perhaps due to the formation of compact, CO islands that are only reactive at the edges as inferred from in situ FTIR studies [52]. The stripping was complete in a single sweep here, indicat-



Fig. 15. CO-stripping voltammograms recorded in 0.1 M H_2SO_4 of Au(111)/Ru in 0.1 M H_2SO_4 (A) after Ru was spontaneously deposited from 1 mM RuCl₃ in 0.1 M HClO₄ for 30 s and (B) after Ru was deposited for 3 min. The solid lines show the CO-stripping and the dotted lines show the following sweep depicting a CO-free surface. In A and B, CO was dosed for 5 min at -0.1 V in the CO saturated solution, followed by 20 min Ar purging to remove CO gas from solution. Scan rate was 10 mV/s.

ing a different CO adlayer structure in this case that should be investigated by spectroscopic techniques. As previously noted by Strbac et al. [34] using electrodeposited Ru adatoms (15% coverage), the shift of the CO stripping peak to more positive potential reflects the stronger bond between CO and Ru due to the pseudomorphic expansion of the Ru lattice relative to bulk Ru(0001), based on DFT calculations of lattice strain effects on CO bond strength on Ru(0001) by Mavrikakis et al. [53].

As before [34], we attribute the appearance of the two peaks to the existence of two different types of Ru sites, in the island centers and at the island edge. However, the position of the second peak for 30 s deposition ($\sim 12\%$ coverage) is not as positive as that obtained from electrodeposited Ru (15% coverage), 0.51 V versus 0.60 V [34]. The Ru islands obtained by electrodeposition were smaller, with monolayer height and ca. 1.5 nm size. The peak shift is likely due to the larger, multilayer islands obtained by spontaneous deposition behaving more similarly to bulk Ru. For this case, however, there is also a broad region of significant CO oxidation occurring after the second peak up to 0.9 V. This region is due to the heterogeneous morphology of surfaces prepared by spontaneous deposition (Fig. 3A). In contrast, electrodeposition resulted in a homogeneous distribution of deposits with no preferential step decoration. Because the coverage values are similar, the differences in CO stripping profiles are clearly related to the specific surface morphologies.

3.4.2. CO on Pt(111)/Ru (comparison with Au(111)/Ru), and Pt(111)/Os

CO stripping voltammetric measurements were next carried out using the Pt(111)/Ru and Pt(111)/Os electrodes prepared as described above in this report. Fig. 16A shows a typical CV curve for the CO stripping on Pt(111)/Ru, and the CO stripping from Pt(111)/Os is shown in Fig. 16B. While in both cases a clear split in the CO stripping profile was observed, the separation is markedly different, and the threshold for the CO oxidation changes by 70 mV in the positive potential direction upon the Ru by Os replacement. While it is well known that on Pt(111)/Ru the first CO oxidation peak originates from the CO oxidation on the Ru adisland [31], an equivalent evidence for the CO oxidation on the Pt(111)/Os surface has been missing, although it is very likely to be the case. The shift in the CO oxidation threshold is then indicative of the Pt(111)/Os-CO phase being less active to CO oxidation and overall to organic molecule oxidation (at low potentials, see below) that undergoes oxidation via the surface CO intermediate path. This can be linked to the difference in oxophilicity of the two metals and



Fig. 16. (A) CO stripping from the Pt(111)/Ru electrode in 0.1 M H₂SO₄. The Pt(111) crystal was covered by Ru via two spontaneous depositions in 1 mM RuCl₃ + 0.1 M HClO₄ for 2 min, and stabilized with three voltammetric cycles. (B) CO stripping from Pt(111)/Os surface in 0.1 M H₂SO₄. The Os deposit obtained in 0.5 mM OsCl₃ + 0.1 M HClO₄ for 30 s. In A and B, CO was dosed for 5 min at 0.0 V in the CO saturated solution, followed by 20 min Ar purging to remove CO gas from solution. Scan rate was 50 mV/s.

their relative ability to provide oxygen-containing species for CO oxidation.

Indeed, our previous XPS results demonstrate that Os is less oxophilic than Ru on Pt(111): Os is entirely metallic at potentials lower than 0.31 V whereas Ru shows oxide formation already at 0.12 V [25]. This is in accordance with the expectation based on the work function or electronegativity difference between Os and Ru. The oxophilicity difference between Ru and Os may also account for the observed better performance of Pt(111)/ Ru for methanol oxidation at potentials below 0.21 V [18,20]. However, the Pt(111)/Os system is more active for methanol oxidation than Pt(111)/ Ru at 0.27 V (and at higher potentials) [54]. Further spectroscopic studies are however needed to evaluate the contribution of anion adsorption effects to the unsatisfactory performance of Pt(111)/Os towards CO oxidation and methanol oxidation below 0.27 V [55].

Recalling data from above and from the Section 3.4.1, the comparison of the data between the CO stripping from Au(111)/Ru (Fig. 15) and from Pt(111)/Ru (Fig. 16A) demonstrates an interesting feature. Namely, the CO stripping peak at 0.23 V from Pt(111)/Ru, which we previously attributed to oxidation of CO at Ru sites and adjacent Pt sites [31], is shifted negatively with respect to the peaks for Ru(0001) and bulk Ru, ca. 0.28 and 0.30 V respectively [51,52], in contrast to the positive shift observed for Au(111)/Ru (Fig. 15). A similar observation was reported by Gasteiger et al. for CO oxidation on well-characterized Pt-Ru alloys versus bulk polycrystalline Ru [49]. As noted above, the Au(111) substrate causes a decrease in the CO oxidation rate due to the strengthening of the Ru–CO bond by the expansion of the Ru lattice relative to bulk Ru [56]. Because Au (0.29 nm) and Pt (0.28 nm) are both larger than Ru (0.27 nm), the peak shift based on lattice expansion alone should be positive for both [53]. In contrast, the modification of Ru by the Pt(111) substrate increases the rate of CO oxidation at lower potentials. This enhancement could occur for a number of well-studied reasons, likely in concert: (1) a weakening of the Ru-CO bond by electronic interactions with Pt, (2) a decrease in the strength of the OH_{ads} bond, [49], or (3) a more loosely packed CO adlattice that allows for more nucleation of OH_{ads} [57], as well as other possible reasons not considered here. The weakening of the Ru-CO bond by electronic effects was observed by our NMR studies of Pt/Ru nanoparticles [58], but it was reported to be rather small. As for a decrease in the OH_{ads} bond strength, Gasteiger et al. [49] attributed the slower CO stripping rate on bulk Ru (after the onset of the reaction) compared to bulk Pt to a stronger OH_{ads} bond on Ru, deduced from UHV studies of OH desorption and adsorption on the surfaces (\sim 330 kJ/mol on Ru(0001) [59] versus \sim 230 kJ/mol on Pt(111) [60,61]). The sharper CO stripping peak appearing at lower potential for the $Pt_{54}Ru_{46}$ alloy was explained by the reduction of the OH_{ads} bond strength due to fewer Ru-Ru neighbors. Supporting Gasteiger et al., but not definitively, DFT studies by Koper et al. [62] show that the OH adsorption energy on Ru(0001) at the atop site (-3.09 eV) is slightly greater than that for a full Ru monolayer on Pt(111) (-3.06 eV) and for Pt_2 Ru alloy (-3.04 eV), and the adsorption energy of OH at the hollow hcp site (the most stable site in this calculation) was also slightly greater for Ru(0001) (-3.49 eV) compared to the Ru monolayer on Pt(111) (-3.47 eV). However, DFT calculations by Liu et al. [63] show that the adsorption energies of OH on Ru(0001) and OH on $Pt_{50}Ru_{50}$ (111) alloy are the same at 0.17 eV. Thus a lower OH_{ads} bond strength for PtRu surfaces versus bulk Ru may play a part in the observed CO stripping behavior, although the results are not yet conclusive and the difference appears to be small. Turning to the structure of the CO adlayer, the sharpness of CO stripping peak corresponding to the Ru islands in our results could perhaps be explained by the existence of a looser CO adlayer structure that allows for more interaction between OH and CO. This would be analogous to the more loosely packed CO structure observed by Lin et al. on PtRu alloy surfaces compared to the tightly packed islands they observed on bulk Ru and Ru(0001) surfaces [52,57]. Future spectroscopic analyses by in situ FTIR and SFG and more theoretical studies specific to our particular system will help determine the relative contributions of such effects.

3.4.3. CO as a probe of Ru stability on Pt(111)/Ru

Finally, CO is also a good probe to test the stability [55,56] of the Ru deposits before going through the electrochemical stabilization/reduction cycle. Such a behavior is of interest in order to enhance understanding of the spontaneous deposition reaction per se. Shown in Fig. 17, the Pt(111)/Ru was first obtained after a single Ru spontaneous deposition and a successive voltammetric stabilization (reduction) of the Ru deposit (Section 3.2.3), and the solid line shows the CO



Fig. 17. CO stripping from the Pt(111)/Ru surface in 0.1 M H_2SO_4 with (solid line) and without (dashed line) stabilizing of the Ru deposit before CO dosing. The Pt(111) surface was covered by Ru nano-islands via single spontaneous deposition in 1 mM RuCl₃ + 0.1 M HClO₄ solution for 2 min. The stabilized surface: three voltammetric cycles between -0.2 and 0.6 V in 0.1 M H₂SO₄. Without the stabilization: the potential cycles were omitted. Other conditions as in Fig. 16A.

stripping reaction from this surface. Next, the experiment was re-started, and the new Pt(111)surface was exposed to the Ru containing solution, rinsed and transferred to the electrochemical cell. Such a freshly prepared ruthenized electrode was exposed to CO without the electrochemical deposit stabilization. The dashed line in Fig. 17 shows the CO oxidation features obtained from this procedure. The data clearly indicate that most of the freshly prepared Ru precursor was displaced from the electrode by CO chemisorption, similarly to the CO displacement of some underpotentially deposited, apparently unstable metals, as reported by Markovic et al. [64,65]. This gives additional credit to the idea that the electrochemical stabilization is an essential step in the utilization of spontaneous deposition for stable bimetallic electrode (Pt/Ru) preparation. Also, assuming that CO is displacing, but not reacting the Ru precursors, the data show that the amount of metallic ruthenium in the deposit is very low, as only loosely bound surface complexes of ruthenium [66] can be displaced by CO. It conclusively documents that the main mechanism for the deposit precursor formation is the one involving chemisorption (see Section 1) rather than disproportionation proposed in Ref. [66].

4. Summary and conclusions

Ru islands were deposited spontaneously on two single crystal surfaces, Au(111) and Pt(111), and characterized by in situ STM. Os was spontaneously deposited on Pt(111) for comparison. Many new structural details of such nanosized islands were revealed. From such STM data together with methanol oxidation chronoamperometry and CO stripping voltammetry results, the main comparative conclusions of this study are the following:

- The change in morphology of the already reduced and stable Ru deposits on Pt(111) obtained via two spontaneous depositions can be induced by an electrochemical treatment. The treatment involves oxidizing and reducing the islands that leads to the islands becoming smaller both in width and height. The change in the island morphology affects the observed methanol oxidation rates.
- (2) Spontaneous deposition of Ru on Au(111) and Pt(111) occurs via the formation of nanosized Ru islands. On Au(111), deposition of islands on steps dominates, whereas on Pt(111), ruthenium deposits homogeneously. The extent of deposition on the terraces is similar for the respective saturation coverages, but details concerning island topography are quite different.
- (3) For Pt(111), multiple spontaneous depositions were implemented. The existing islands from the first deposition are the preferred sites for Ru deposition during the second (and subsequent) exposure as evidenced by the growth of the islands mainly in height.
- (4) Os on Pt(111), as Ru on Pt(111), is deposited homogeneously. Compared to Pt(111)/Ru, however, Os is deposited on Pt(111) at a much higher rate and it forms a larger proportion of multilayer islands within only a single deposition.
- (5) CO stripping voltammetry from Pt(111)/Ru and Pt(111)/Os was also investigated and the data were compared. The differences were related to the difference in the oxophilicity of the two metals.

- (6) The shift in CV peaks associated with CO stripping from Au(111)/Ru compared to that from the bulk Ru indicates a stronger bond between CO and Ru surface atoms from Au(111)/Ru than between CO and surface Ru atoms from bulk Ru.
- (7) CO stripping activity from the Ru islands also depends on the substrate used, Pt(111) or Au(111). Apparently, the effect of strain in the pseudomorphic Ru lattice on Au(111) increases the strength of the Ru-CO bond, resulting in a positive shift in the CO stripping peak. In contrast, the modification of Ru by the Pt(111) substrate causes the peak to shift negatively, which cannot be due to the lattice expansion. Alternate explanations may involve a weakening of the Ru-OH_{ads} bond strength due to the reduction in Ru-Ru neighbors versus bulk Ru, or a more loosely packed CO adlattice that allows for more OH_{ads} nucleation next to CO-occupied sites.

The work is in progress to investigate the three bimetallic single crystal surfaces discussed in this report by electrochemical XPS [32], to add the electronic characterization to the reactivity and structural studies.

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