Deposition of Ru Adatoms on Pt Using Organometallic Chemistry: Catalysts for Electrooxidation of MeOH and Adsorbed Carbon Monoxide

**Christopher E. Lee and Steven H. Bergens***

Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Ru adatoms were deposited on black Pt gauze by hydrogenating $Ru(COD)(\eta^3\text{-}C_3H_5)_2$ (**1**, COD is 1,5-cyclooctadiene) over the gauze at low temperatures in hexanes solution under 1 atm of dihydrogen gas. A series of Pt−Ru$_{ad}$ surfaces were prepared by interrupting the hydrogenation after deposition of 0.05, 0.10, 0.30, 0.32, 0.44, 0.70, and 3.5 equiv of Ru adatoms. The ratio of currents in the "double layer" to those in the "hydride" region in the potentiodynamic responses of these surfaces (0.5 M H_2SO_4, 25 °C, sweep range 0.025−0.70 V, 5 mV/s) increased as the equivalents of Ru adatoms increased. Stripping voltammetry of adsorbed monolayers of carbon monoxide from these surfaces (0.5 M H_2SO_4, 25 °C, sweep range 0.025−0.70 V, 5 mV/s) showed a drop by 120 mV in the CO stripping peak potential upon deposition of 0.05 equiv of Ru adatoms on Pt. Deposition of more Ru adatoms did not cause significant further drops in the CO stripping peak potential. The surfaces were evaluated as catalysts for the electrooxidation of MeOH. The measured currents were normalized to the specific surface areas of the gauzes measured before deposition of Ru adatoms by hydrogenation of **1**. The order of activity of MeOH-poisoned Pt−Ru$_{ad}$ surfaces toward the potentiodynamic oxidation of MeOH (0.5 M H_2SO_4, 25 °C, sweep range 0.025−0.60 V, 5 mV/s) was 0.05 > 0.10 > 0.30 ∼ 0.44 > 0.7 > 0 (Pt) equiv of Ru adatoms. The activity of Pt increased relative to the other surfaces as the potential increased, becoming more active than 0.30, 0.70, and 0.44 equiv Pt−Ru$_{ad}$ at the upper limit of the sweeps. Surfaces with low equivalents of Ru adatoms (from 0.05 to 0.10 equiv) were the most active toward the potentiostatic oxidation of MeOH ($E = 0.4$ V, 0.5 M H_2SO_4, 0.5 M MeOH, 25 °C) with between 50 and 28 times higher turnover numbers than black Pt. The activation energies for oxidation of MeOH over 0.05 and 0.10 equiv of Pt−Ru$_{ad}$ were 37 and 45 kJ/mol, respectively, at 0.4 V, 0.5 M H_2SO_4, and 0.5 M MeOH.

Introduction

We have synthesized black Pt surfaces with adsorbed submonolayer equivalents of Ru adatoms and evaluated these surfaces as catalysts for the electrooxidation of MeOH and adsorbed CO in sulfuric acid electrolytes. The Ru adatoms were deposited on black Pt surfaces using an organometallic reaction between surface platinum−hydrides and a ruthenium−hydrocarbonyl compound dissolved in an alkane solvent. With a previous publication, we reported that black Pt effects the hydrogenation of $(COD)Ru(\eta^3\text{-}C_3H_5)_2$ (**1**, COD is 1,5-cyclooctadiene) in hexanes at $p(H_2) \sim 1$ atm and $T = -25$ to 25 °C. The hydrogenation generates cyclooctane (COA, major C_8 product), octahydropentalene (OHP, <1% of COA), propane, and Ru adatoms that are adsorbed by the surface of Pt (eq 1).[1]
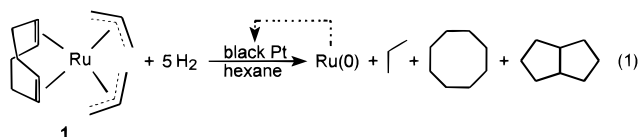
The hydrogenation allows for real-time control over the equivalents of Ru adatoms deposited on Pt, and it provides a convenient method to generate Pt surfaces with known amounts of adsorbed Ru adatoms.

As heterogeneous catalysts, Pt−Ru surfaces have been used to effect reactions including the hydrogenation of arenes,[2] the hydrogenolysis of propane,[2] the hydrogenation of CO,[3] and the electrochemical oxidation of MeOH in fuel cells.[4] Unsupported bulk alloys, supported bimetallic particles, and Pt surfaces with adsorbed Ru adatoms (Pt−Ru$_{ad}$) have all been used as precursors to catalysts for the electrooxidation of MeOH. The recent work with bulk alloys includes that of Gasteiger et al., who demonstrated for shiny Pt−Ru alloys with well-defined surface compositions (measured with low-energy ion scattering) and of known surface areas (surface roughness factors ∼1) that the percentage of Ru at the surface (θ_{Ru}) at the maximum activity toward the potentiostatic electrooxidation of MeOH is ∼10% at $E = 0.4$ V ($T = 25$ °C, 0.5 M MeOH, 0.5 M H_2SO_4).[5] They also showed that θ_{Ru} at maximum activity shifts to ∼30% at higher potentials and temperatures. Van Reen et al. reported that $\theta_{Ru} \sim 15\%$ at maximum activity toward the potentiostatic electrooxidation of MeOH over co-electrodeposited Pt−Ru electrodes at $E = 0.48$ V (0.1 M MeOH, 0.5 M H_2SO_4).[6] These authors estimated θ_{Ru} using measurements from electrochemical quartz crystal microbalances and cyclic voltammetry. In their use of cyclic voltammetry, θ_{Ru} was estimated from the potential of the cathodic oxide peak, as first reported by McNicol and co-workers,[7] and from the estimated Coulombic charge corresponding to formation of what was assumed to be surface Ru-$(OH)_2$. Recently, Gilman et al. reported that $\theta_{Ru} \sim 50\%$ at maximum activity normalized to geometric surface areas of

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* To whom correspondence should be addressed.

unsupported Pt−Ru alloys at $E = 0.48$ V ($T = 25$ and 60 °C, 1.0 M MeOH, 0.5 M H_2SO_4).[8]

It is difficult to accurately measure θ_{Ru} of supported Pt−Ru particles. The methods used to obtain information about θ_{Ru} of supported Pt−Ru particles include cyclic voltammetry,[7] CO adsorption/oxidation,[9] and gas titrations.[10] To the best of our knowledge, only cyclic voltammetry has been used with supported Pt−Ru catalysts for the electrooxidation of methanol. The value of θ_{Ru} at maximum activity for electrooxidation of methanol by such systems is often extrapolated from the internal compositions of the particles, the catalyst loading and dispersion, and the geometric surface area of the electrode. The reported values for θ_{Ru} at maximum activity range from ∼12% to 50%.[6a,11] It is believed, however, that the correlation between θ_{Ru} and activity that was observed by Gasteiger et al. using bulk, shiny alloys also applies to supported Ru−Pt alloy particles.[5] This supposition remains to be directly proven by experiment.[12]

The Pt−Ru$_{ad}$ systems studied in the literature consist of Pt electrodes with electrodeposited Ru adatoms.[13] Watanabe et al. reported that $\theta_{Ru} \sim 50\%$ at maximum activity toward the potentiodynamic oxidation of methanol.[13a,c] These authors estimated θ_{Ru} using cyclic voltammetry to assess the Coulombic charge corresponding to formation of what was assumed to be surface Ru−OH.

We have used the hydrogenation of **1** to generate a series of black Pt−Ru$_{ad}$ electrodes with increasing equivalents of Ru adatoms. As described previously,[1] we determined the equivalents of Ru adatoms deposited on Pt by comparing the specific surface area of the black Pt before the hydrogenation[14] to the amount of **1** consumed or to the total COA and OHP formed in solution during the hydrogenation. We now report the electrooxidation of MeOH and adsorbed monolayers of CO over a series of these surfaces in aqueous sulfuric acid.

Experimental Section

General. Argon (Linde, prepurified) was passed through molecular sieves (Anachemia, activated type 4 Å) prior to use. Dihydrogen (Linde, prepurified) and CO (Matheson, ultrahigh purity) were used as received. Water was deionized, distilled from alkaline permanganate under nitrogen, and purged with argon for 30 min prior to use. Hexanes (BDH, HPLC grade) were passed through aluminum oxide (grade 1), hydrogenated ($p(H_2) = 1$ atm) over Pt black for 24 h, and distilled off potassium metal under argon gas through a Vigreux column. The decane internal standard was purified similarly. Methanol (BDH, HPLC grade) was distilled from $Mg(OCH_3)_2$ under argon. Diethyl ether (Calendon) was distilled from potassium/ benzophenone under argon. H_2SO_4 (either BDH ACS grade or Alfa Aesar 99.9999%) was used as received. Rubber septa were extracted for 24 h with HPLC grade hexane in a Sohxlet extractor and dried under vacuum. All glassware was rinsed with a 1:5 mixture of 30% aqueous hydrogen peroxide: concentrated H_2SO_4, water, a 5% mixture of ammonium hydroxide in absolute ethanol, ethanol and then dried in an oven. (η^4-1,5-cyclooctadiene)Ru(η^3-C_3H_5)$_2$ (**1**) was prepared by a literature method[15] and twice sublimed under vacuum immediately before use.

The reactor used for the hydrogenations was a 2.3 × 10.3 cm Pyrex tube containing a 4 × 14 mm Teflon-coated magnetic stir bar and fitted with a rubber septum pierced with a disposable pipet (used as a dihydrogen gas inlet) and a glass tube supporting the blacked Pt gauze.

Electrochemical experiments were performed using a Pine Bipotentiostat Model AFCBP1 controlled with Pinechem 2.00 software or using a homemade potentiostat equipped with a Hewlett-Packard 7004 chart recorder. Inductively coupled plasma spectroscopy (ICP) was performed using a Perkin-Elmer Optima equipped with an atomic emission detector. Gas chromatography−mass spectrometry was performed using a VG-7070E with a Varian 6000 GC fitted with a 30 m J&B DB5 column using a MSS data system. Electrolytes were purged with argon for at least 10 min prior to use, and electrochemical experiments were performed under argon unless stated otherwise. The reference electrode was an anodized silver wire behind a D-porosity glass frit, but potentials are referred to the standard hydrogen electrode. The counter electrode was a blacked Pt wire behind a D-porosity glass frit. The specific surface area of a control blacked Pt electrode decreased by 7% after being held at $E = 0.050$ V for 30 min in our 0.5 M H_2SO_4 electrolyte. Gas chromatography (GC) was performed on a Hewlett-Packard series 530 10 m methylsilicone column # 19057-121 fitted to a Hewlett-Packard 5980A gas chromatograph with a Hewlett-Packard 3392A integrator. ^{1}H NMR spectra were measured on a Bruker AM-400 NMR spectrometer operating at 400.13 MHz.

Procedures. Detailed procedures for the preparation, electrochemical characterization, and manipulation of the blacked Pt gauzes; for carrying out and interrupting hydrogenations of **1**; for potentiodynamic and potentiostatic oxidations of methanol; and for the adsorption and electrooxidation of CO are given in the previous publication.[1] These procedures are also briefly described as appropriate in this report.

Results and Discussion

We used blacked Pt gauzes for this investigation. The specific surface areas of the gauzes were determined from the Coulombic charge in the cathodic hydride region of cyclic voltammograms recorded in 1.0 M H_2SO_4 under argon.[1,16] The lower limits to the surface roughness factors of these gauzes ranged from 250 to 500. These lower limits were determined by comparing the specific surface area of the shiny Pt gauze before blacking to its specific surface area after blacking.[17] It was necessary to use high specific surface area Pt (black) in order to generate sufficient concentrations of COA and OHP in solution during the hydrogenation of **1** to allow reliable quantification by GC when depositing submonolayer equivalents of Ru adatoms on Pt. After electrochemical determination of its specific surface area, the black Pt gauze was protected by surface oxides (by holding the potential at 1.4 V for 2 min in 1.0 M H_2SO_4), washed with purified water under argon, and quickly transferred through air while protected by several drops of purified water to the hydrogenation vessel.

The equivalents of Ru adatoms deposited on Pt was monitored during hydrogenations of **1** by use of gas chromatography (GC) to determine the amount of COA and OHP in solution. Hydrogenations of **1** were interrupted when the desired equivalents of Ru adatoms was deposited on Pt as follows in brief. The Pt−Ru$_{ad}$ surface was lifted above the hexane solution in which the hydrogenation was carried out, it was washed quickly with dihydrogen-saturated hexanes under dihydrogen gas, dried under a stream of dihydrogen gas, and transferred to the electrochemical cell protected by surface hydrides in a drybox under argon. The potential was set to 0.075 V concomitant with immersion of the gauze into the electrolyte. Control experiments using black Pt electrodes and repeating the entire hydrogenation procedure in the absence of **1** showed that little change in surface area occurs during these manipulations (<6% after sweeping to 1.4 V during voltammetry in 0.5 M H_2SO_4).[1] Further controls showed that typically between 10% and 30%

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of the sites on control Pt gauzes became covered by disadvantageous impurities during these procedures, as indicated by the decrease in current of the "hydride region" of voltammograms recorded in 0.5 M H$_2$SO$_4$ (sweeping from 0.025 to 0.70 V at 5 mV/s). The surface impurities behaved as blocking agents, reducing the current in the "hydride region" but not effecting its shape. We could not determine whether the impurities derived from hexanes or from an unknown source. We note that, within experimental certainty, the amount of **1** consumed was equal to the amount of COA and OHP produced in solution during the hydrogenation, indicating that the surface impurities did not derive from **1**.[1] After a hydrogenation, we would first carry out a "dummy" oxidation of adsorbed CO (described below) followed by continuous potential sweeps in 0.5 M H$_2$-SO$_4$ (between 0.025 and 0.70 V at 5 mV/s) to remove as many surface contaminants as possible from the Pt−Ru$_{ad}$ surfaces before carrying out any electrochemical experiments. The lifetimes and further poisoning of these surfaces are discussed in more detail below.

We use the equivalents of Ru adatoms rather than θ_{Ru} to designate the Pt−Ru$_{ad}$ surfaces studied in this report. As discussed previously,[1] it appears that complete coverage of the active sites on Pt by Ru adatoms is achieved after hydrogenation of between 1.5 and 2.0 equiv of **1**. That between 1.5 and 2.0 equiv of Ru adatoms was required to cover all sites of a rough, black Pt gauze indicates that the coverage of Pt by Ru is fairly uniform. We therefore believe that the equivalents of Ru adatoms is representative of θ_{Ru} at low coverages (i.e., during the early stages of the hydrogenation), when the likelihood of Ru adatoms being deposited only on Pt is statistically high. At later stages of the hydrogenation, when deposition of Ru adatoms likely occurrs on Ru$_{ad}$ as well as on Pt, the equivalents of Ru adatoms is taken as the upper limit to θ_{Ru}. We have no information about the distribution of the Ru adatoms on the Pt surface or about how this distribution changes upon exposure to different conditions and reactants.

Voltammetry in 0.5 M H$_2$SO$_4$. Figure 1 shows the base voltammograms of black Pt and of 0.05, 0.30, 0.70, and 3.5 equiv of Pt−Ru$_{ad}$ in 0.5 M H$_2$SO$_4$. The current peaks in the "hydride region" become less resolved and increasingly overlap with the enlarging "double-layer" region as the equivalents of Ru adatoms increases. Quite similar behavior was observed of bulk, shiny alloys of known surface compositions by Ticanelli et al.[18] and by Gasteiger et al.[5] As was discussed by these and other researchers,[19] the onset of formation of adsorbed oxides on Ru in the positive going sweeps overlaps with the electrooxidation of surface hydrides, resulting in loss of a clear distinction between these processes. It was proposed for bulk Ru−Pt alloys that the increase in the ratio of currents in the "double layer" to the "hydride" regions with increasing θ_{Ru} results from a progressive lowering of the potential for adsorption of surface oxygen species.[5,18] It appears that increasing the equivalents of Ru adatoms adsorbed by Pt during hydrogenation of **1** also causes formation of surface oxides to occur at progressively lower potentials.

Electrooxidation of Adsorbed CO. The electrooxidation of adsorbed CO over Pt−Ru surfaces has been studied by numerous investigators.[9,20] It was shown for bulk Ru−Pt alloys that the potential of the stripping peak of an adsorbed monolayer of CO during stripping voltammetry is indicative of θ_{Ru}.[20e,j] It was found that θ_{Ru} was ∼50% for such surfaces with the highest activity (lowest stripping peak potential) toward oxidation of adsorbed CO. Frelink et al.[20m] found that a shift in the CO stripping peak to lower potentials by 150−200 mV was caused
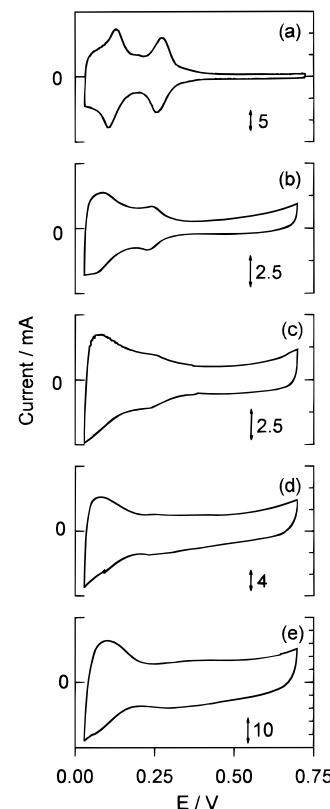

Figure 1. Base voltammograms of black Pt−Ru$_{ad}$ with (a) 0, (b) 0.05, (c) 0.30, (d) 0.70, and (e) 3.5 equiv of Ru adatoms. The voltammograms are the third sweeps recorded after oxidation of a monolayer of adsorbed carbon monoxide measured in 0.5 M H$_2$SO$_4$ (between 0.025 and 0.7 V at 5 mV/s). Absolute currents are shown scaled to illustrate the differences in shape between the voltammograms.
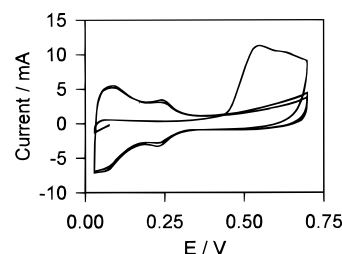

Figure 2. CO stripping voltammetry over 0.05 equiv Pt−Ru$_{ad}$. Shown are the first, second, and third sweeps.

by electrochemical deposition of small amounts of Ru adatoms (θ_{Ru} ∼ 15%) on Pt. Deposition of more Ru adatoms did not cause significant further shifts in the CO stripping peak potential. Watanabe et al. found θ_{Ru} to be ∼50% at the maximum activity for the potentiostatic oxidation of CO over Pt−Ru$_{ad}$.[20d] In the present work, CO was adsorbed on Pt−Ru$_{ad}$ surfaces by bubbling CO at 1 atm through the stirred electrolyte (H$_2$SO$_4$, 0.5 M) for 15 min while holding the potential at 0.075 V. The excess CO was then flushed from the electrolyte with argon gas, the stirring was stopped, and the potential was cycled between 0.025 and 0.70 V at 5 mV/s. The first sweep was in the downward direction. Control experiments show that a full monolayer of CO is adsorbed by black Pt after CO gas is bubbled through the electrolyte for 5 min. The potentiodynamic response of the black Pt electrode obtained after flushing the electrolyte with argon gas contained no evidence of free CO in solution. Figure 2 shows the potentiodynamic response of the 0.05 equiv Pt−Ru$_{ad}$ surface. The CO stripping peak potential was 0.543 V, with evidence of a second peak at 0.630 V. The
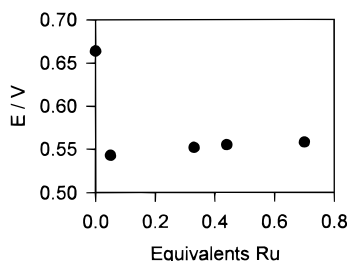
Figure 3. Plot of CO stripping peak potential versus equiv of Ru adatoms over Pt−Ru$_{ad}$.

CO stripping peak potential was 0.664 V over black Pt, ~120 mV higher than the 0.05 equiv Pt−Ru$_{ad}$ surface. Figure 3 shows plots of the CO stripping peak potential versus equivalents of Ru. In accord with the results of Frelink et al.[20m] deposition of more Ru adatoms on Pt by hydrogenation of **1** did not cause significant further shifts in the CO stripping peak potential. Our results and those of Frelink et al. indicate that the maximum shift in the CO stripping peak potential between Pt and Pt−Ru$_{ad}$ occurs at low θ_{Ru} (~5−15%). These results differ with those from the bulk alloys for which θ_{Ru} at the maximum shift is ~50%. We believe these observations represent an intrinsic difference in reactivity between Pt−Ru$_{ad}$ and Pt−Ru alloys toward oxidation of adsorbed CO. Gasteiger et al. provided evidence that the CO stripping peak potential for Pt−Ru alloys depended not only on θ_{Ru} but also on how the Ru atoms were distributed at the surface.[20e] We propose that a difference between the distributions of Ru atoms at the surfaces of Pt−Ru$_{ad}$ and of Pt−Ru alloys is one cause of their divergence in activities toward adsorbed CO. This interpretation is supported by the recent results of Friedrich et al.[20p] which indicate that submonolayers of Ru adatoms electrochemically deposited on Pt(111) exist as islands under adsorbed monolayers of CO. We propose that the Ru adatoms deposited by hydrogenation of **1** over black, polycrystalline Pt also form islands under adsorbed monolayers of CO. If this proposal is correct, and taking into consideration that deposition of small amounts of Ru adatoms produces quite active Pt−Ru$_{ad}$ surfaces toward the electrooxidation of adsorbed CO, our results imply that the surface mobility of at least one of the intermediates was high on the time scale of the electrooxidation under these conditions.

We attempted to determine the Coulombic charge under the CO stripping peak for the Pt−Ru$_{ad}$ surfaces. We could only obtain an approximate value for this charge because the upper potential limit of the sweeps (0.70 V) was too low to oxidize all the adsorbed CO in the first positive going sweep. We attempted to sum the Coulombic CO stripping charges in the successive positive going sweeps until the steady potentiodynamic response was obtained. The specific surface areas of the Pt−Ru$_{ad}$ electrodes determined in this manner were between 50% and 98% that of the specific surface areas of the corresponding black Pt gauze before the hydrogenation of **1**. Use of the Coulombic CO stripping charge is not an accurate method to determine specific Pt−Ru surface areas.[20e,21] Further, our summation of the charges over successive positive going sweeps likely added more error to its measured value. We therefore only propose that major changes in surface area do not occur during hydrogenation of **1** over Pt. We cannot rule out that small to moderate changes in surface area occurred during the hydrogenation and subsequent experiments.

The activities of the Pt−Ru$_{ad}$ surfaces toward the electrooxidation of MeOH described in this work are normalized to the specific surface area of the black Pt before the hydrogenation of **1**. Since we cannot rule out small to moderate changes in
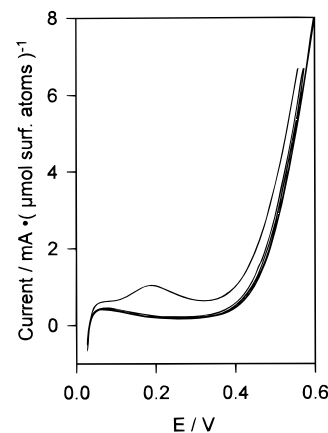

Figure 4. Positive-going sweeps of the potentiodynamic oxidation of methanol over 0.10 equiv Pt−Ru$_{ad}$. The curves are a composite of two experiments containing the first, second, and third sweeps from one and the fourth and fifth sweeps from the other experiment.
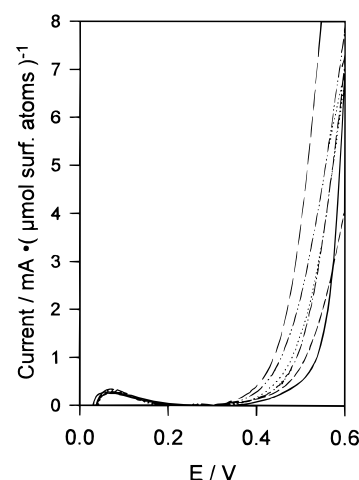

Figure 5. Third current-normalized positive going sweeps for the potentiodynamic oxidation of methanol over 0.0 (−), 0.05 (− −), 0.10 (− ·· −), 0.30 (− · −), 0.44 (···), and 0.70 (− − −) equiv Pt−Ru$_{ad}$.

surface area, the comparisons of normalized activities presented in this work are best taken as approximate rather than precise representations of the relative activities of the Pt−Ru$_{ad}$ surfaces.

Potentiodynamic Oxidation of MeOH. Figure 4 shows the positive going sweeps obtained with the 0.10 equiv of Pt−Ru$_{ad}$ surface ([MeOH] = [H$_2$SO$_4$] = 0.5 M, 25 °C, sweep rate = 5 mV/s, sweep range = 0.025 to 0.60 V). The first sweep contains a significant anodic peak in the hydride region that apparently overlaps with the onset of MeOH oxidation at ~0.2 V. The subsequent sweeps do not contain this peak and are appreciably lower in current than the first sweep at all potentials. The decreases in current after the third sweep were small, indicating the potentiodynamic response had stabilized. Quite similar behavior was observed by Gasteiger et al. using a shiny bulk Ru−Pt alloy with θ_{Ru} ~ 10%.[5] As was discussed by these authors,[5] who referred to results of radiotracer experiments by Horányi et al.[22] and to results of infrared measurement by Kunimatsu,[23] both the decrease in current and the loss of the hydrogen desorption peak after the first positive going sweep were likely caused by an accumulation of surface organic residues from the electrooxidation of MeOH. These residues are not significantly desorbed at lower potentials. Figure 5 shows the third positive going sweeps (normalized for specific surface area and corrected for (pseudo) capacitive current densities) for Pt and for 0.05, 0.10, 0.30, 0.44, and 0.70 equiv Pt−Ru$_{ad}$. Further decreases in current after the third sweep were
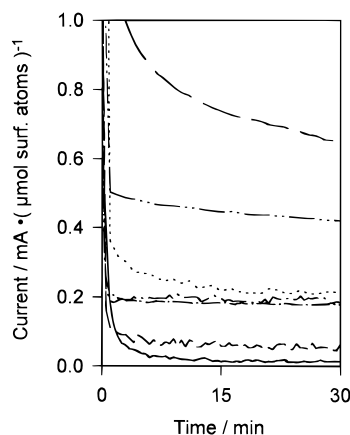
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Figure 6. Normalized current versus time for the potentiostatic oxidation of methanol over 0.0 (—), 0.05 (− −), 0.10 (− ·· −), 0.30 and 0.32 (− · −), 0.44 (···), and 0.70 (− − −) equiv Pt−Ru$_{ad}$.

small for these surfaces, indicating that the potentiodynamic responses shown in Figure 5 approximate the behavior of MeOH poisoned surfaces. The onset of oxidation was lower than Pt for all the Pt−Ru$_{ad}$ surfaces. The order of activity was 0.05 > 0.10 > 0.30 ∼ 0.44 > 0.70 equiv Pt−Ru$_{ad}$ > Pt over most of the potential range. The relative activity of Pt increases with potential, becoming more active than the 0.30, 0.44, and 0.70 equiv surfaces near the upper limit of the sweeps. This behavior is reminiscent of that obtained by Gasteiger et al. using bulk alloys under similar conditions (after 10 sweeps at 20 mV/s).[5] These workers found that θ_{Ru} at maximum activity decreased as the electrode potential increased. The reported order of activity was θ_{Ru} = 33% > 7% > 44% > 0% at ∼0.45 V and 7% > 33% > 44% > 0% at 0.55 V. Assuming that the equivalents of Ru adatoms on Pt−Ru$_{ad}$ is comparable to θ_{Ru} determined by Gasteiger et al., these results indicate that Pt−Ru$_{ad}$ and bulk, shiny Pt−Ru alloys behave similarly toward the potentiodynamic oxidation of methanol under these conditions.

Potentiostatic Oxidation of MeOH. Figure 6 shows plots of normalized current versus time for the potentiostatic electrooxidation of MeOH over Pt−Ru$_{ad}$ surfaces at E = 0.4 V (0.5 M H$_2$SO$_4$, 0.5 M MeOH, 25 °C). The surfaces all suffered from an initial rapid decrease in current followed by a region of more stable activity, in which the current slowly decreased. This behavior was reported for bulk alloys, and it is interpreted as an initial, rapid dehydrogenation of MeOH followed by a slower oxidation of CO or related species derived from MeOH.[5a,13a,4m,n,r,24] The 0.05 equiv Pt−Ru$_{ad}$ surface was the most active, but it also suffered from the most rapid decrease in activity in the "stabilized" region of the oxidation, after the initial rapid decrease in current. This curve is reproducible: the oxidation was repeated using the same electrode several days later and displayed the same behavior. The activities of two ∼0.30 equiv Pt−Ru$_{ad}$ surfaces (0.30 and 0.32 equiv, prepared independently) were nearly identical, demonstrating that preparation of Pt−Ru$_{ad}$ by hydrogenation of **1** over Pt is somewhat reproducible. Figure 7 represents the activities as turnover numbers versus equivalents of Ru adatoms. The turnover numbers were calculated from the moles of MeOH (assuming 6 electrons/mol) consumed per mole of surface site from time = 17 to 25 min (a period after the initial burst). The turnover numbers are plotted for both potentiostatic oxidations of methanol over the 0.05 equiv Pt−Ru$_{ad}$ surface. The order of activity among the Pt−Ru$_{ad}$ surfaces was the same as that for the MeOH-poisoned surfaces toward the potentiodynamic electrooxidations. Surfaces with low equivalents of Ru adatoms
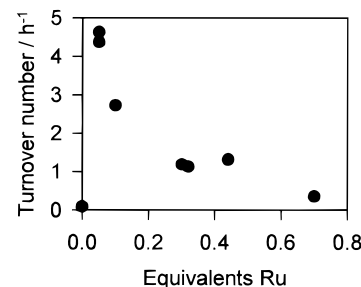

Figure 7. Turnover numbers versus equivalents of Ru adatoms for the potentiostatic oxidation of methanol over Pt−Ru$_{ad}$.
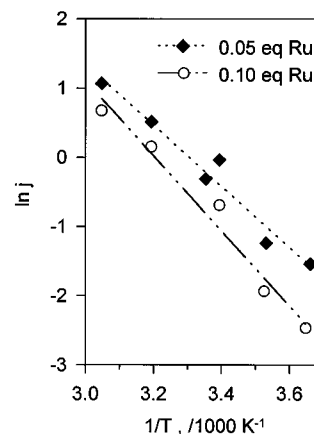

Figure 8. Arrhenius plots of ln(j) versus 1/T for the potentiostatic oxidation of methanol over 0.05 and 0.10 equiv Pt−Ru$_{ad}$.

are the most active: the turnover numbers of the 0.10 and 0.05 equiv Pt−Ru$_{ad}$ surfaces being between 28 and 50 times that of bare Pt. Our results for the potentiostatic oxidation of methanol are reminiscent of those of Gasteiger et al. using bulk alloys (θ_{Ru} ∼ 10% at maximum activity, 25 °C, 0.4 V, 0.5 M MeOH, 0.5 M H$_2$SO$_4$) and to those of van Reen et al.[6] using co-electrodeposited Ru−Pt (θ_{Ru} ∼ 15% at maximum activity, 0.48 V, 0.1 M MeOH, 0.5 M H$_2$SO$_4$). These similarities indicate that bulk Pt−Ru alloys and Pt−Ru$_{ad}$ surfaces generated by hydrogenation of **1** have similar optimum surface compositions toward the electrooxidation of MeOH under these conditions.

Variable Temperature Studies. The potentiostatic electrooxidation of MeOH (E = 0.4 V, 0.5 M MeOH, 0.5 M H$_2$SO$_4$) was effected using the 0.05 and 0.10 equiv Pt−Ru$_{ad}$ surfaces at various temperatures. Figure 8 shows Arrhenius plots of ln(j) versus 1/T using the current measured after 5 min, 30 s.

Straight lines were obtained with both electrodes, indicating that these surfaces are sufficiently stable to allow for studies of this type. The calculated Arrhenius activation energies were 37 kJ/mol for the 0.05 equiv surface and 45 kJ/mol for the 0.10 equiv surface. The analogous activation energy over the bulk alloy with θ_{Ru} ∼ 7% was 30 kJ/mol as determined by Gasteiger et al., who postulated that surface migration of adsorbed methanol dehydrogenation fragments was rate determining under these conditions.[5b]

Stability of Pt−Ru$_{ad}$. We found that these surfaces could be used for several experiments without appreciable loss of electrochemical activity provided that certain precautions were taken. For example, we used the 0.10 equiv Pt−Ru$_{ad}$ surface for the experiments described in this paper as well as for potentiostatic and potentiodynamic electrooxidations of ethanol, ethylene glycol, and D-glucose.[25] The electrode was stored as described below between experiments. Excluding idling in the
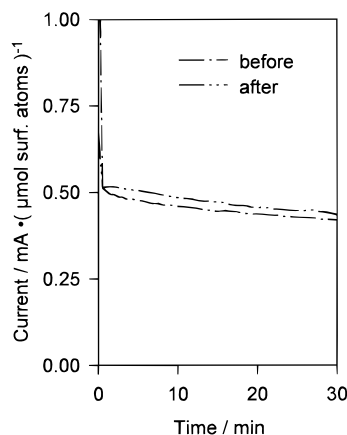
Figure 9. Potentiostatic oxidation of MeOH over 0.10 equiv Pt−Ru$_{ad}$ before and after 16 h of electrochemical activity.

electrolyte at $E = 0.075$ V, this surface was operated electrochemically in the presence of various fuels and at various temperatures for a total of 16 h. As shown in Figure 9, this surface exhibited quite similar activities toward the potentiostatic oxidation of MeOH before and after these experiments.

To maintain the activity of these surfaces, it was important to ensure that the potential never exceeded 0.7 V. Dissolution of Ru above ∼0.9 V quickly destroyed these surfaces. Further, the electrodes were held at 0.075 V whenever in contact with the electrolyte except during the recording of data for experiments. When required, the electrodes could be stored for periods of days by first holding the potential at 0.075 V for at least 2 min, and second, by rinsing the electrode with argon-saturated purified water, drying the electrode under a stream of argon, and storing it at −30 °C in a glovebox freezer. Poisoning by disadvantageous species did not often effect the activities of the surfaces if these and the procedures described previously were followed. A factor in the apparent resistance of these surfaces to trace poisons is their large specific surface areas, which ranged from 2800 to 3700 cm^2. Serious poisoning did occur on occasion during these studies, as evidenced by a precipitous loss in electrochemical activity and by an absence of any features in the hydride region of voltammograms recorded in 0.5 M H$_2$SO$_4$. A procedure that was often successful in restoring these poisoned surfaces was to carry out a potentiostatic oxidation of MeOH (25 °C, 0.4 V), replace the electrolyte with clean 0.5 M H$_2$SO$_4$, and perform continuous potentiodynamic sweeps (5 mV/s, 0.025 to 0.60 V) until the base potentiodynamic response (Figure 1) was obtained.

Conclusions

Hydrogenation of **1** over Pt represents a unique method to prepare Pt−Ru$_{ad}$ surfaces as catalysts for the electrooxidation of MeOH and of adsorbed CO. Our results imply that the hydrogenation produces rough Pt−Ru$_{ad}$ surfaces of known specific surface areas and with reasonable control over the surface stoichiometry. The specific surface area and surface stoichiometry of rough bimetallic surfaces are in general notoriously difficult to measure and to control, and a knowledge of these values is fundamental to the understanding of how such systems operate as catalysts. Further, the electrochemical activities of the Pt−Ru$_{ad}$ surfaces were noticeably stable (up to 16 h) under the conditions used for this study, illustrating that certain metal−metal$_{adatom}$ systems are suitable for long-term studies under the appropriate conditions. Although we do not know the lifetimes of the Pt−Ru$_{ad}$ surfaces under these conditions, they do not immediately decompose by surface segregation or by dissolution of Ru.[26]

Our results indicate that the equivalents of Ru adatoms controls the activity of Pt−Ru$_{ad}$ surfaces toward the electrooxidation of MeOH and of adsorbed CO. Surfaces with between 0.05 and 0.10 equiv of Ru adatoms appear the most active under the conditions used for this study. The apparent control over surface stoichiometry and the knowledge of specific surface area offered by hydrogenation of **1** allows comparisons between these Pt−Ru$_{ad}$ surfaces and the bulk alloys studied by Gasteiger et al. On the main, the optimum surface composition of the Pt−Ru$_{ad}$ surfaces prepared by hydrogenation of **1** is comparable to that reported for the shiny bulk Pt−Ru alloys. One notable difference is in their activities toward the electrooxidation of adsorbed monolayers of CO, which may result from differences between the distributions of Ru atoms at the surfaces of Pt−Ru alloys and Pt−Ru$_{ad}$ under these conditions.

The hydrogenation of **1** appears to generate prototypic Pt−Ru$_{ad}$ surfaces with real time control over the equivalents of Ru adatoms. Since the hydrogenation requires a Pt surface to occur, it will in principle self-direct the deposition of Ru adatoms (or mixtures of Ru and Pt adatoms) on the surfaces of Pt clusters supported by an inert substrate. We are in the process of extending these studies to Pt−Ru$_{ad}$ particles supported on carbon substrates and to other metal systems.

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