



J. Serb. Chem. Soc. 76 (11) 1523–1536 (2011)
JSCS–4226

Impact of the modification of carbon-supported, Pt-based catalysts by irreversibly adsorbed Sn, Ru and Rh on ethanol oxidation

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(Received 17 February, revised 7 April 2011)

Abstract: The oxidation of ethanol was studied at Sn_{ad}-, Ru_{ad}- and Rh_{ad}-modified and unmodified PtC, Pt₃Sn/C and Pt₃Ru₂/C catalysts. Potentiodynamic, quasi-steady-state and chronoamperometric measurements were used to investigate the activity and stability of the catalysts. Irreversible adsorption of a small amount of each of the adatoms (≈10 % surface coverage) enhanced the activity of the Pt/C and Pt₃Sn/C catalysts. The onset potential was shifted by ≈50 mV towards lower values and the current densities over the whole studied potential region were up to two times higher with respect to the unmodified catalysts. On the other hand, the addition of Sn_{ad} or Rh_{ad} slightly increased the activity of Pt₃Ru₂/C, while the presence of Ru_{ad} decreased its activity for ethanol oxidation. The catalytic action of Sn_{ad} and Ru_{ad} was associated mostly with their ability to adsorb oxygen-containing species at lower potentials than Pt, permitting a bifunctional mechanism to proceed. Rh_{ad} also acted on the C–C bond breaking activation as well as source of oxygen containing species, increasing in this way the activity of the modified surfaces for ethanol oxidation.

Keywords: ethanol oxidation; Pt nanocatalyst; Pt–Sn nanocatalyst; Pt–Ru nanocatalyst; Pt–Rh nanocatalyst; adatom modification.

INTRODUCTION

Ethanol is a promising candidate to replace methanol in fuel cells due to its higher energy density that corresponds to 12 electrons per molecule in the total oxidation, low toxicity, mass production from renewable sources and easy storage and transportation. The complete oxidation of ethanol entails dehydrogenation, C–C bond cleavage and the stripping of the resulting adsorbed CO. The fragmentation of ethanol on catalyst surfaces generating stable adsorbates has

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doi: 10.2298/JSC110217136L

been the subject of many previous studies using both *in situ* infrared spectroscopy (FT-IR) and differential electrochemical mass spectrometry (DEMS).^{1–5} Although the mechanistic details of ethanol oxidation in acidic solution on a pure Pt electrode still remain unclear, the general view is that acetaldehyde (CH₃CHO) and acetic acid (CH₃COOH) are the main products, with carbon dioxide (CO₂) appearing at very high positive potentials. Thus, the major challenge for the electrocatalysis of ethanol is to achieve its total oxidation to CO₂ at low overpotentials.

Despite of fact that platinum is generally known as one of the best electrocatalyst for alcohol oxidation at low temperatures, it has limited ability for C–C bond scission and is easily poisoned by CO and other carbonaceous intermediates. Different C₁ and C₂ adsorbates formed in the oxidative adsorption of ethanol have been identified.^{1,2,6–8} CO₂ is formed from strongly adsorbed intermediates on the electrode, while the products of partial oxidation, acetaldehyde and acetic acid, are formed from weakly adsorbed intermediates.^{1,9} The efficiency of C–C bond activation in ethanol oxidation is the key to enable this reaction to be useful in fuel cell applications. Hitherto, this efficiency was quite low and partial oxidation products, acetaldehyde and acetic acid, were observed.^{10,11}

The addition of a second metal to Pt by underpotential deposition or by alloying creates bimetallic catalysts and changes the electronic and structural properties of the base material, causing a change of its catalytic activity. It also alters the number of large Pt ensembles on platinum surfaces, which are important for site-demanding processes, such as C–C bond cleavage.

The activity of binary electrocatalysts was attributed to a bifunctional effect (Pt adsorbs alcohol and oxidizes H, while the second metal supplies oxygen-containing species to oxidize the blocking intermediate CO) or to the electronic interaction between Pt and alloyed metals.^{12–14} These effects may influence ethanol oxidation on bimetallic catalyst in a way either to accelerate the oxidation of the CO adsorbate, as in the case of PtSn and PtRu bimetallic electrodes,^{2,3,15,16} or to improve C–C bond activation, as in the case of PtRh.¹⁷ It was shown that PtSn/C bimetallic carbon-supported materials are more active than PtRu/C electrocatalysts for ethanol oxidation.^{15,18} The different promotion effects of PtSn/C and PtRu/C to ethanol oxidation can be explained by the structural effect (difference in alloy phase structure and particle morphology) and by modified bifunctional mechanisms in different potential regions.¹⁸ However, the electro-oxidation of ethanol on PtSn/C or PtRu/C yields almost only partially oxidized products acetaldehyde and acetic acid, *i.e.*, the presence of Sn or Ru did not improve the conversion of ethanol to CO₂. On the other hand, PtRh bimetallic catalysts show significant activity for the production of CO₂ from ethanol, although the reaction currents are almost similar to that of a platinum electrode.^{10,19} It was proposed, from the results of DEMS measurements, that the

strong CO–Rh bond or slow dehydrogenation on Rh diminish the overall ethanol oxidation reaction (EOR) rate.¹⁷

In order to improve both the activity and selectivity (the overall reaction rate), ternary catalysts, such as PtSnRh/C, PtRuRh/C or PtRuSn/C, were made using different methods of preparation.^{7,19–22} The joint action of the three constituents could explain the large activity of ternary catalysts for ethanol oxidation. In the catalysts containing Rh, the role of Rh was to adsorb and stabilize the key intermediate, which leads to cleavage of C–C bonds, Sn or Ru provides OH species necessary for the oxidation of CO adsorbed on Rh sites, while Pt facilitates ethanol dehydrogenation. It was shown that ternary Pt–Sn–Rh alloy catalysts possess the highest activity for ethanol electro-oxidation at potentials higher than 0.45 V (RHE), as a consequence of geometric and electronic modification due to the formation of a ternary alloy phase.²³ A Pt–Ru–Rh/C catalyst exhibited a compromise between the overall reaction rate and CO₂ yield, *i.e.*, both characteristics were between those of Pt–Ru/C and Pt–Rh/C.¹⁹ In a recent work of Kowal *et al.*,²⁴ it was stated that a ternary Pt–Rh–SnO₂ electrocatalyst was effective in splitting the C–C bond in ethanol at room temperature and caused its predominant oxidation to CO₂ at very low overpotentials. The catalytic property of this ternary electrocatalyst was attributed to the synergistic effect between all three constituents.

On the other hand, the ternary PtRuSn/C catalyst, benefited from the simultaneous presence of Ru and Sn and the positive effect was ascribed mainly to interactions between Sn and Ru oxides.^{17,21,22} The addition of 10 wt. % of Sn to PtRu/C resulted in an excellent performance and a two-fold enhancement compared with PtSn/C.²⁵

The irreversible adsorption of Sn, Rh or Ru at Pt/C does not perturb significantly Pt structurally or electronically, as was shown in spectroscopic studies,^{26–28} although the presence of the second metal alters the number of large Pt ensembles, which may be important for the site demanding process of C–C bond cleavage. The catalytic action of Sn or Ru atoms was associated mostly with their ability to adsorb oxygenated species at lower potentials than Pt, permitting the bifunctional mechanism to proceed.¹⁵ Both of these two metals are inactive for ethanol adsorption. Moreover, Rh alone is inactive for ethanol oxidation, but it is capable of adsorbing and stabilizing the intermediate formed by ethanol dehydrogenation, which leads to cleavage of C–C bonds at a reasonable rate, as well as to act as a source of oxygenated species.¹⁹

Recently, the activity of Pt–Sn/C and Pt–Ru/C in ethanol oxidation was correlated with the degree of alloying. Although the results reported so far are generally not in agreement, most of them indicate that highly alloyed catalysts promote ethanol oxidation.^{3,23,29,30}

In a previous work,³¹ ethanol oxidation was studied at two alloys, Pt₃Sn/C and Pt₃Ru₂/C, as well as on a Pt/C catalyst modified with the corresponding amounts of Sn_{ad} (25 % surface coverage) and Ru_{ad} (40 % surface coverage) in order to simulate the alloy composition of the catalysts. The comparative investigation based on the effects influencing the catalytic properties of these electrodes contributed to a better understanding of the different activities between alloys, as well as between alloys and Pt/C modified by the corresponding amounts of irreversibly adsorbed Sn and Ru.

In the present study, ethanol oxidation was investigated on carbon-supported Pt-based catalysts modified with a small amount (≈ 10 %) of irreversibly adsorbed Sn, Rh and Ru. The idea of such surface modifications arose from the fact that modification of Pt₃Sn/C with a small amount of Sn_{ad} created a powerful catalyst for overall ethanol oxidation,^{31,32} as well as from a previous theoretical study²⁴ in which it was shown that a low Rh content relative to Pt is likely to facilitate C–C bond breaking in the system.

The main goal of the present work was to examine the influence of electrode composition on the electrocatalytic activity toward the electrochemical oxidation of ethanol in order to explain the difference between modified and unmodified Pt-based catalysts and finally, to determine the optimal concentration of the constituents that gives the most active catalyst for the EOR.

EXPERIMENTAL

Electrode preparation

Commercially available Pt-based catalysts supported on high surface area carbon were used: platinum (Pt/C) with 47.5 wt. % Pt and platinum–ruthenium (Pt₃Ru₂/C) with 33.5 wt. % alloy provided by Tanaka Precious Metals Group (Kikinzoku International K.K) and platinum–tin (Pt₃Sn/C) with 20 wt. % alloy provided by E-Tek, USA. The catalysts were characterized by X-ray diffraction analysis.³¹

The catalysts were applied to a glassy carbon substrate in the form of a thin-film.¹⁵ A suspension of 5 mg of the respective catalyst in a mixture of 1 ml water, 1 ml ethanol and 50 μ l of a 5 % aqueous Nafion solution was prepared in an ultrasonic bath and 10 μ l of the suspension was placed onto the substrate (5 mm diameter) and dried at room temperature to form a homogenous catalyst layer. The resulting metal loading was 25 μ g cm⁻².

To avoid the contribution of any other anions, surface modification by the adatoms was achieved by holding a freshly prepared electrode at -0.2 V in 0.1 M HClO₄ solution containing Sn, Ru or Rh ions, produced by dissolving the required metal from the alloy matrix of Pt₃Sn/C, Pt₃Ru₂/C and PtRh/C, respectively, during cycling (20 cycles) at different anodic limits. The adatom-modified electrode was then rinsed with water and transferred to the electrochemical cell.

Electrochemical measurements

Electrochemical measurements were performed at room temperature in N₂-purged 0.1 M HClO₄ solution in a standard three compartment electrochemical cell with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The reagents used were of p.a. purity (Merck) and solutions were prepared with high purity water

(“Millipore”, 18 M Ω cm resistivity). Ethanol (0.5 M) was added to the solution while holding the electrode potential at -0.2 V. The catalytic activity was measured using the potentiodynamic (sweep rate 20 mV s $^{-1}$), quasi-steady-state (sweep rate 1 mV s $^{-1}$) and chronoamperometric methods. The potentials are given *versus* SCE and the currents were normalized per total mass of metal and are expressed as mA mg $^{-1}$.

The current–time transient curves were recorded during 30 min upon immersion of the electrode in the solution at -0.2 V for 2 s prior to stepping to 0.2 V.

A VoltaLab PGZ402 (Radiometer Analytical, France) was used in the electrochemical experiments.

RESULTS AND DISCUSSION

Polarization curves for ethanol oxidation on unmodified and Sn_{ad}, Ru_{ad} and Rh_{ad} modified Pt/C, Pt₃Ru₂/C and Pt₃Sn/C catalysts in acid solution are shown in Fig. 1. The positive potential limit was set at 0.3 V to prevent any dissolution of Sn, Rh or Ru.

A comparative investigation of ethanol oxidation on the Pt-based catalysts showed that both alloys are more active than Pt/C, as was found previously.³¹ The initial potentials on the Pt₃Sn/C and Pt₃Ru₂/C catalysts were approximately -0.1 V and -0.05 V, respectively, and the reaction rates at the alloyed catalysts were higher than that at Pt/C, particularly at Pt₃Sn/C. On the Pt/C catalyst, the reaction commences at ≈ 0.1 V, when dissociative adsorption of water occurred providing the OH_{ad} species³³ required for the oxidation of the C₁ and C₂ intermediates generated by dissociative adsorption of ethanol.

The activity of the Pt/C catalyst was improved in the presence of irreversibly adsorbed adatoms and reaction commenced at ≈ 0.05 V less positive potentials relative to the unmodified Pt/C (Fig. 1). The negative shift of the starting potential was more pronounced at the modified Pt₃Sn/C electrode (≈ 100 mV), while it was the least expressed on the modified Pt₃Ru₂/C catalyst compared to the unmodified Pt-based alloy catalysts.

The catalytic action of Sn_{ad} or Ru_{ad} on the investigated electrodes was correlated generally to their ability to dissociate water at lower potentials than Pt, enabling the bifunctional mechanism between the adsorbed species on Pt and the OH species adsorbed on the added metals to proceed (Fig. 1a and b).¹² Spectroscopic analysis of Sn_{ad} on Pt/C showed that Sn_{ad} interacted with oxygen species in a similar manner as in the Pt₃Sn/C alloy.²⁸ The high activity of this alloy originates mainly from the electronic effect resulting in weak bonded adsorbate generated by ethanol adsorption on the Pt sites,^{34,35} and an appropriate amount of oxygen-containing species, weakly bound to the Sn sites.^{36,37} On the other hand, the underpotential deposition of Sn on Pt/C did not provoke any significant electronic changes in Pt,²⁷ which means that Sn_{ad} did not interfere remarkably with the ability of Pt to adsorb strongly ethanol or the adsorbate generated by ethanol dissociation. A small amount of Sn (≈ 10 %) irreversibly adsorbed on Pt₃Sn/C (Fig. 1a) improved the activity of the alloy, creating a powerful catalyst for etha-

nol oxidation.^{31,32} The high activity of this catalyst can be explained by a combination of the electronic effect and the easier mobility of Sn_{ad} ,³⁸ with an enhanced amount of oxygen-containing species on the Sn.

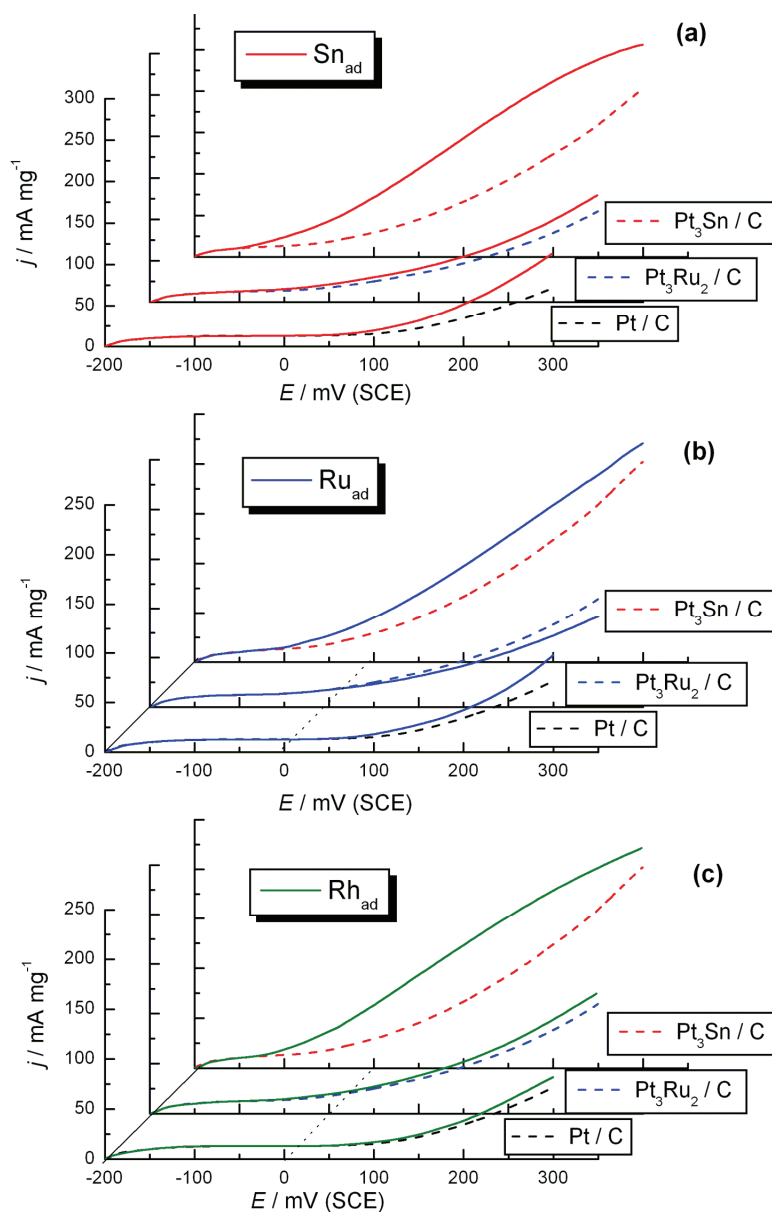


Fig. 1. Potentiodynamic curves for the oxidation of 0.5 M $\text{C}_2\text{H}_5\text{OH}$ in 0.1 M HClO_4 at Pt/C, $\text{Pt}_3\text{Ru}_2/\text{C}$ and $\text{Pt}_3\text{Sn}/\text{C}$: a) unmodified and modified with 10 % Sn_{ad} ; b) unmodified and modified with 10 % Ru_{ad} ; c) unmodified and modified with 10 % Rh_{ad} . $v = 20 \text{ mV s}^{-1}$.

Irreversible adsorption of Ru on Pt/C or Pt₃Sn/C did not provoke significant electronic changes in Pt^{26,27} and therefore ethanol oxidation on respective catalysts obeyed the conditions relevant for the bifunctional mechanism (Fig. 1b). The addition of 10 % Ru improved slightly the activity of these catalysts due to the increased amount of oxygen-containing species on the Ru sites. On the contrary, the decreased activity of Pt₃Ru₂/C modified by 10 % Ru was the consequence of the disturbance of the conditions relevant for the bifunctional mechanism, *i.e.*, the appropriate ratio between Pt sites, which adsorb ethanol, and Ru sites, which nucleate oxygen containing species necessary to oxidize the adsorbates. The ratio between Pt and Ru that provides the best catalytic performance is 60:40, is fulfilled in the Pt₃Ru₂/C catalyst.³⁹

The addition of Rh slightly enhanced the reaction rate on all the investigated catalysts. The effect of Rh_{ad} on Pt/C was less expressed compared to Sn_{ad} or Ru_{ad} (Fig. 1c). The role of Rh is to adsorb C₂ intermediates formed by ethanol dehydrogenation, to stabilize them and permit the cleavage of C–C bonds.⁴⁰ Nevertheless, Rh is less efficient for the dehydrogenation reaction compared to Pt; thus a relatively high-energy barrier for the dehydrogenation can hinder C–C bond scission necessary for the formation of CO.¹⁰ Thereby, the CO coverage during the reaction must be lower on surfaces containing Rh. At the same time, the presence of OH_{ad} species on Rh at lower potentials compared to Pt could enhance the oxidation of reaction intermediates. The present results are consistent with a small enhancement of the catalytic effect in ethanol oxidation observed on carbon-supported PtRh (9:1) catalyst relatively to Pt/C and the role of Rh on bimetallic PtRh electrodes was associated with the changes in the electronic properties caused by the addition of Rh to Pt.^{10,41}

The catalytic activity of all the investigated catalysts at $E = 0.2$ V are summarized in Table I. The most active was Pt₃Sn/C modified with Sn_{ad}, which was 1.7 times more active than Pt₃Sn/C and even 6 times more active than Pt/C. It is also notable that the Ru modified Pt₃Ru₂/C electrode was less active than Pt₃Ru₂/C by almost 15 %.

TABLE I. Mass-specific current densities ($j / \text{mA mg}^{-1}$) of the respective catalysts at $E = 0.2$ V (SCE)

Catalyst	Unmodified	Sn _{ad}	Rh _{ad}	Ru _{ad}
Pt/C	34.7	52.5	38.4	42.2
Pt ₃ Sn/C	124.2	212.4	180.0	160.2
Pt ₃ Ru ₂ /C	63.6	160.2	70.8	56.0

From a practical point of view, not only is the initial activity of catalysts an important factor, but also the improvement of their poisoning tolerance. This is possible to illustrate by measuring the current densities of ethanol electro-oxidation at a constant potential as a function of time. In this sense, chronoampero-

metric experiments were performed (Fig. 2). The highest initial current density at 0.2 V on Pt₃Sn/C compared to the other two unmodified catalysts is in accordance with the potentiodynamic measurements (Fig. 1). The currents decayed rapidly at the Pt/C and Pt₃Ru₂/C catalysts, reaching their steady state values within a few minutes. On the contrary, at the Pt₃Sn/C catalyst, the initial current decreased slightly and stabilized in the experimental period of time at a value which was about two times higher than at the Pt₃Ru₂/C catalyst. The Pt₃Sn/C catalyst is evidently less poisoned than Pt₃Ru₂/C or Pt/C, since weaker bound adsorbate on the electronically modified Pt in Pt₃Sn/C could be more easily oxidized than on Pt₃Ru₂/C or Pt/C.

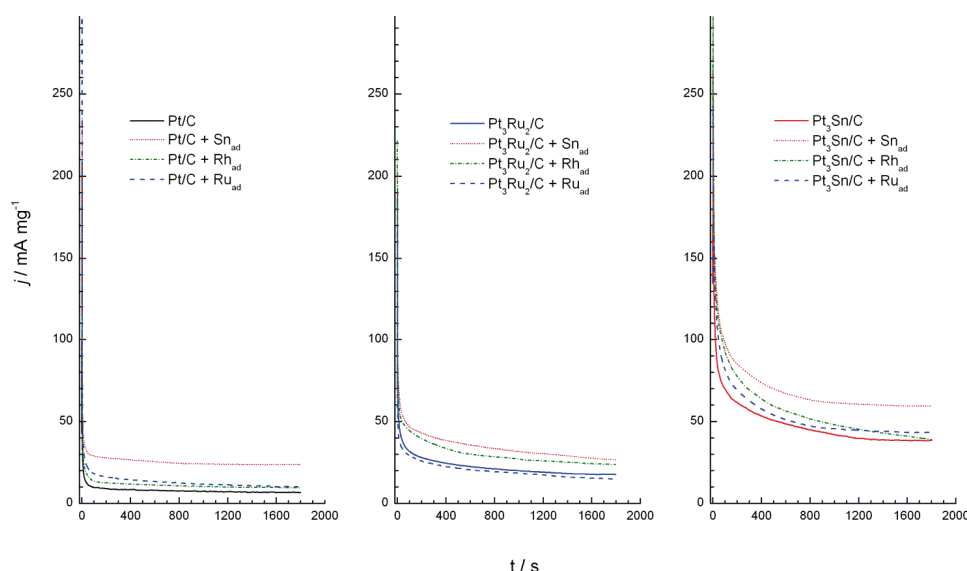


Fig. 2. Chronoamperometric curves for the oxidation of 0.5 M C₂H₅OH in 0.1 M HClO₄ at 0.2 V at: a) Pt/C unmodified and modified with 10 % Sn_{ad}, Ru_{ad} and Rh_{ad}; b) Pt₃Ru₂/C unmodified and modified with 10 % Sn_{ad}, Ru_{ad} and Rh_{ad}; c) Pt₃Sn/C unmodified and modified with 10 % Sn_{ad}, Ru_{ad} and Rh_{ad}.

At 0.2 V, the initial current densities at the Sn_{ad}-modified Pt₃Sn/C were significantly increased compared to the unmodified catalyst and they were much higher than at the other catalysts studied with or without Ru_{ad} and Rh_{ad}. The current decayed slower at the Sn_{ad}-modified than on the unmodified Pt₃Sn/C catalyst, indicating less accumulation of CO_{ad} species. Finally, two times higher current densities were achieved at the Sn_{ad}-modified Pt₃Sn/C than on Pt₃Sn/C, which was about 9 times more active than Pt/C. This corresponds with the results obtained in the potentiodynamic measurements (Fig. 1).

The electrocatalytic activity of the catalysts studied for ethanol oxidation after 30 min increased in the sequence: Pt/C < Pt/C+Rh_{ad} < Pt/C+Ru_{ad} < Pt₃Ru₂/C

+ Ru_{ad} < Pt₃Ru₂/C < Pt/C + Sn_{ad} < Pt₃Ru₂/C + Rh_{ad} < Pt₃Ru₂/C + Sn_{ad} < Pt₃Sn/C < Pt₃Sn/C + Ru_{ad} < Pt₃Sn/C + Rh_{ad} < Pt₃Sn/C + Sn_{ad}, suggesting that the activity of the supported Pt-based catalysts can be associated with their CO tolerance, which was the most pronounced at the Sn_{ad}-modified Pt₃Sn/C catalyst.

Moreover, a $(di/dt) = f(t)$ plot at small time values allows an evaluation of the initial poisoning rate, the greater the slope, the greater the initial poisoning of the electrode surface. The initial poisoning rates for the Pt-based catalysts with and without Sn_{ad} are presented in Fig. 3. It appears that Sn_{ad} leads to less poisoning, since the experimental slopes with added Sn were lower by a factor of 1.1, 1.22 and 1.6, compared to those obtained without the addition of Sn_{ad} to Pt/C, Pt₃Ru₂/C and Pt₃Sn/C, respectively.

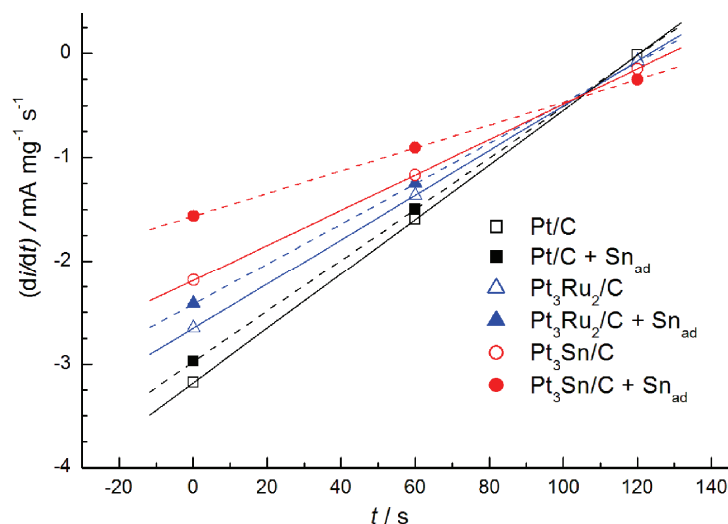


Fig. 3. $di/dt = f(t)$ Curves for Pt/C, Pt₃Ru₂/C and Pt₃Sn/C catalysts with and without 10 % Sn_{ad}.

The quasi-steady-state results of ethanol oxidation on the investigated catalysts are given in Fig. 4. The Tafel slopes of $\approx 120 \text{ mV dec}^{-1}$ obtained at the Sn_{ad}- and Rh_{ad}-modified electrodes and at the unmodified Pt₃Sn/C catalyst indicate that the first electron transfer could be the rate determining step.²⁹ The higher Tafel slopes of $140\text{--}150 \text{ mV dec}^{-1}$ at the Ru_{ad}-modified electrodes and the unmodified Pt₃Ru₂/C and Pt/C catalysts could be caused by large poisoning of the Pt.⁴²

Hitherto, the mechanism of ethanol oxidation on bimetallic catalysts has been discussed mainly in terms of a bifunctional effect^{12,39} and/or electronic effects.^{34,35} Since the investigated irreversibly adsorbed adatoms did not change significantly the performance of the supported catalysts regarding ethanol adsorption, their promotional or inhibiting effect (as in the case of Ru_{ad} on Pt₃Ru₂/C) on ethanol oxidation requires additional explanation.

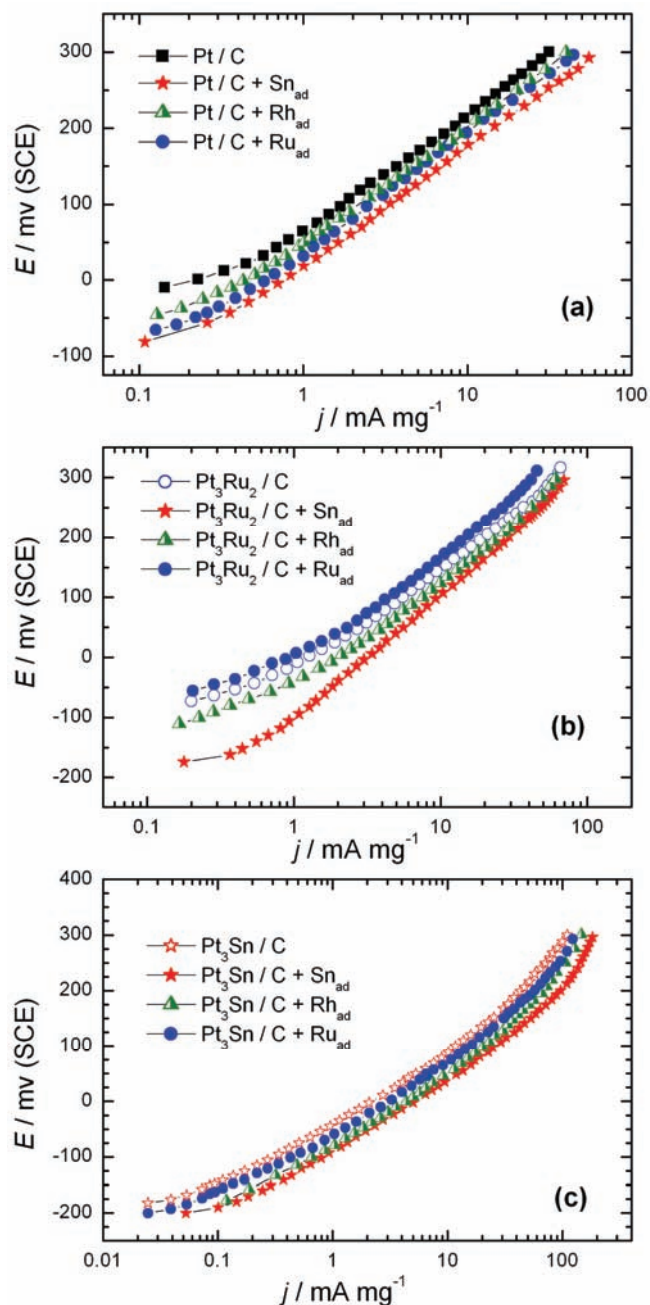


Fig. 4. Tafel plots for oxidation of 0.5 M C₂H₅OH in 0.1 M HClO₄ solution at: a) Pt/C unmodified and modified with 10% Sn_{ad}, Ru_{ad} and Rh_{ad}; b) Pt₃Ru₂/C unmodified and modified with 10% Sn_{ad}, Ru_{ad} and Rh_{ad}; c) Pt₃Sn/C unmodified and modified with 10% Sn_{ad}, Ru_{ad} and Rh_{ad}. $\nu = 1 \text{ mV s}^{-1}$.

With the underpotential deposition of Sn, Ru and Rh, it was intended that different adsorption sites on the Pt particles be occupied. As Sn adatoms are mobile on a Pt surface,³⁸ it is reasonable to assume that they tend to nucleate on the edges of the Pt particles, preventing strong adsorption of poison and simultaneously providing for the adsorption of OH species on Sn_{ad} at lower potentials than on Pt/C, enabling the oxidation of the intermediates (C₁ and C₂ fragments) on the facet sites. This characteristic of Sn_{ad} should be more pronounced on Pt₃Sn/C than on Pt₃Ru₂/C or on Pt/C due to the change in the electronic structure of Pt on the alloyed surface.

Considering the irreversible adsorption of Ru, it was observed that Ru creates two-dimensional (2D) nanosized and catalytically active islands.⁴³ There was no preferential deposition of this metal on surface steps under both electro-deposition⁴⁴ and spontaneous deposition⁴⁵ conditions, indicating that the Ru nucleation does not occur preferentially at crystallographic defects, and that the Ru islands are randomly dispersed over the electrode surface (on facets and step sites), permitting the adsorption of poisoning and reactive species on the Pt active step sites. Although the capability of Ru atoms to dissociate water is larger than that of Sn atoms, Ru-modified surfaces (by irreversible adsorption or alloying) creates catalysts less active than Sn-modified surfaces because of the higher poisoning.²⁶ This refers to the all the investigated Pt-based catalysts.

Rhodium adlayers also grow in islands, but primarily on the facets, leaving large domains of the surface uncovered, including steps and defect sites.^{46,47} As Rh adatoms in the periphery of the islands form steps with the platinum substrate, the islands boundaries (Pt–Rh adsorption sites) could have an enhanced reactivity toward OH and ethanol dissociative adsorption, *i.e.*, the periphery of the islands would contain bifunctional catalytic centers.

In spite of the capability of Ru and Rh atoms to dissociate water at lower potentials with respect to Pt, thereby providing oxygen-containing species to oxidize adsorbed fragments generated from ethanol, the Rh_{ad}-modified Pt/C catalyst was less active than the Ru_{ad}-modified Pt/C catalyst, most likely due to the slightly stronger bond between the adsorbate and Rh.¹⁷

On both alloys, the effect of Rh_{ad} was more expressed compared to Ru_{ad}. The possible explanation is the presence of larger amount of C₁ and C₂ intermediates in the presence of Rh, which could be oxidized with OH species weakly bound on Sn or Ru sites in the corresponding alloys. This assumption must be supported by quantitative measurements; hence additional study is a necessity.

CONCLUSIONS

In this work, ethanol oxidation was investigated on carbon-supported Pt-based catalysts modified with a small amount ($\approx 10\%$) of irreversibly adsorbed Sn, Rh or Ru. The concept of such surface modification was to provide more

sites for the adsorption of oxygen-containing species necessary for the oxidation of reaction intermediates and at the same time to maintain large Pt ensembles important for C–C bond scission.

The irreversible adsorption of all types of adatoms enhanced the activity of the Pt/C and Pt₃Sn/C catalysts. The onset potential was shifted by ≈ 50 mV towards lower values and the current densities over the whole studied potential region were up to two times higher in respect to the unmodified catalysts. On the other hand, the addition of Sn_{ad} or Rh_{ad} slightly increased the activity of Pt₃Ru₂/C, while the presence of a Ru_{ad} adlayer decreased its activity for ethanol oxidation. The catalytic actions of Sn_{ad} and Ru_{ad} were associated mostly with their ability to adsorb oxygen-containing species at lower potentials than Pt, permitting the bifunctional mechanism to proceed. Rh adatoms acted on the activation of C–C bond scission and were a source of oxygen-containing species, increasing in this way the activity of the modified surfaces for ethanol oxidation.

Electrochemical measurements revealed that Sn_{ad} had the most pronounced effect on ethanol oxidation on all the investigated Pt-based catalysts. The most active was Pt₃Sn/C modified with Sn_{ad} which was two times more active than Pt₃Sn/C and even 9 times more active than Pt/C according to chronoamperometric measurements. At the same time this catalysts was less prone to poisoning, suggesting a high CO tolerance.

Tafel slopes of ≈ 120 mV dec⁻¹ obtained at the Sn_{ad}- and Rh_{ad}-modified electrodes and at the unmodified Pt₃Sn/C catalyst indicated that the first electron transfer could be the rate determining step. Higher Tafel slopes of 140–150 mV dec⁻¹ at the Ru_{ad}-modified electrodes and the unmodified Pt₃Ru₂/C and Pt/C catalysts could be caused by a large poisoning of Pt.

Acknowledgements. This work was financially supported by the Ministry of Education and Science of the Republic of Serbia, Contract No. H-172060.

ИЗВОД

УТИЦАЈ МОДИФИКАЦИЈЕ ПЛАТИНСКИХ НАНОКАТАЛИЗАТОРА ИРЕВЕРЗИБИЛНОМ АДОРПЦИЈОМ Sn, Ru И Rh НА ОКСИДАЦИЈУ ЕТАНОЛА

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Оксидација етанола је испитивана на Pt/C, Pt₃Sn/C и Pt₃Ru₂/C катализаторима модификованим иреверзибилно адсорбованим Sn_{ad}, Ru_{ad} и Rh_{ad} адатомима. Њихова активност и стабилност испитивана је потенциодинамичким, хроноамперометријским и квази-стационарним мерењима. Добијени резултати су показали да мала количина иреверзибилно адсорбованих адатома (10 %) повећава активност Pt/C и Pt₃Sn/C катализатора. Почетак реакције је померен ка негативнијим вредностима за ≈ 50 mV и добијене су око два пута веће густине струје у поређењу са немодификованим катализаторима. Додатак Sn_{ad} или Rh_{ad} мало повећава активност Pt₃Ru₂/C катализатора, док додатак Ru_{ad} смањује његову активност за оксидацију етанола. Каталитичка активност адатома Sn и Ru се углавном везује са њиховом спо-

собношћу да адсорбују ОН честице на нижим потенцијалима од Pt и на тај начин побољшавају бифункционални механизам реакције. Повећана активност катализатора модификованих адатомима Rh може се објаснити лакшим кидањем C–C везе у етанолу, као и повећаном количином OH_{ad} честица на Rh местима.

(Примљено 17. фебруара, ревидирано 7. априла 2011)

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