



# The electrooxidation of acetaldehyde on platinum–ruthenium–rhodium surfaces: A delicate balance between oxidation and carbon–carbon bond breaking



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## ARTICLE INFO

### Article history:

Received 6 May 2015

Received in revised form 23 June 2015

Accepted 8 July 2015

Available online 7 August 2015

### Keywords:

Acetaldehyde electrooxidation pathways

Platinum–ruthenium–rhodium

Acidic media

*In situ* FTIR

C–C bond breaking

## ABSTRACT

In this work we investigate the electrooxidation of acetaldehyde in acidic media on platinum–ruthenium–rhodium electrodeposits of several compositions. Combined results of electrochemistry and *in situ* FTIR spectroscopy show that the Ru/Rh ratio plays a pivotal role on the electrooxidation of acetaldehyde on PtRuRh surfaces. The combination of these metals apparently establishes a delicate balance between the ability of a surface to oxidize adsorbed species and to promote the C–C bond breaking. Overall, by estimating the charges involved in each oxidation pathway we were able to mimic the electrochemical behavior as a function of the composition. The global output suggests that the proper combination of platinum–ruthenium–rhodium can lead to the development of active catalysts towards the oxidation of small organic molecules.

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## 1. Introduction

Since the seminal work of Sokolova and coauthors [1], the electrooxidation of acetaldehyde has been the object of several investigations, including the ones on pristine [2] and modified [3] platinum single crystals, Pt bulk electrodes [4] and thin films [5–8], Pt-based electrodeposits [9] and Pt-based supported catalysts [10–13]. Such interest is justified from both technical and basic points of view, because acetaldehyde is one important intermediate of the electrooxidation of ethanol [2,14], and one of the smallest oxygenated molecules that contains a carbon chain [6]. Therefore, its electrooxidation can be considered a model to understand how carbon–carbon bonds can be broken in small molecules containing a methyl group [6].

Concerning multifunctional catalysts, in a core paper Adzic et al. investigated ternary PtRhSnO<sub>2</sub>/C catalysts towards ethanol oxidation [15]. The authors demonstrated that these materials are efficient to cleave C–C bonds of ethanol and promote the production of CO<sub>2</sub> even at room temperature and low overpotentials (compared to pure platinum) [15]. According to the authors, the catalytic property of the ternary electrocatalyst is due to synergistic effects between the constituents [15]. Apparently, SnO<sub>2</sub> strongly interacts with water and

hinders its reaction with Pt and Rh. Consequently, Pt and Rh sites are available to adsorb ethanol [15]. In this paper the authors demonstrate that the efficient oxidation of organic molecules would be achieved when we understand what is the role played by each metal (or oxide) on the surface and how these characteristics affect the pathways of such complex reactions.

Regarding the molecules of interest, by comparing the electrooxidation of ethanol and acetaldehyde with SEIRAS, Koper and coauthors showed that the amount of adsorbed species during their corresponding oxidations is higher for acetaldehyde than for ethanol [6]. Based on these results, the authors suggest that the C–C bond breaking is easier in acetaldehyde [6]. Once acetaldehyde is also formed from ethanol, these findings have important implications on the mechanistic aspects of both electrooxidation reactions and claim for the development of catalysts able to oxidize both species.

In order to address some of these questions, in a previous work we investigate the ability of platinum–ruthenium–rhodium (PtRuRh) ternary electrodeposits to electrooxidize acetaldehyde in acidic media, by using *in situ* FTIR spectroscopy [9]. The results showed that the catalytic activity of PtRuRh is strongly influenced by the composition of the deposits, but in that occasion the spectroscopic results were interpreted in a semi-quantitative way. Here we take a step forward: by using *in situ* FTIR spectroscopy, we estimate the amounts of acetic acid and CO<sub>2</sub> produced during the electrooxidation of acetaldehyde and their respective oxidation charges on six different surfaces. Our analysis allows the

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understanding of the electrode composition-dependence in terms of the oxidation pathways; it further points towards the possibility of using infrared spectroscopy as a probe to design surfaces possessing a finely-tuned composition, envisaging an optimal electrocatalytic performance towards a given reaction.

## 2. Experimental

The solutions used in this work were prepared with deionized water (Milli-Q, 18.2 M $\Omega$  cm), HClO<sub>4</sub> (Suprapur, Merck) and CH<sub>3</sub>CHO (P.A., Merck). Before each experimental protocol the electrochemical cell (including its solution) was purged with N<sub>2</sub>. All the experiments were performed at room temperature ( $T \approx 25$  °C). The counter electrode was a platinum sheet of large surface area and all the potentials were measured against a reversible hydrogen electrode (RHE) in a 0.1 M HClO<sub>4</sub> solution.

The details of the procedure for the electrodeposition of binary (platinum–ruthenium) or ternary (platinum–ruthenium–rhodium) surfaces can be consulted elsewhere [9]. Briefly, the electrodeposits were obtained by simultaneous electroreduction of Rh<sup>3+</sup>, Ru<sup>3+</sup> and Pt<sup>4+</sup> ions on a mirror-finished gold disk in 0.1 M HClO<sub>4</sub>, at a potential of  $E = 0.05$  V during 5 min. Overall, six electrodeposits were prepared, three of them containing only Pt and Ru, which served to discriminate the role of Ru during the acetaldehyde electrooxidation. After the best binary composition was found, a second series including Rh was also investigated, in which the relative composition of Ru and Rh (at.%) was changed, following the sequence 26:0 (binary catalyst), 23:4, 14:10 and 8:16. For the ternary catalysts Pt was used as the major component, its composition being kept nearly constant (in the range 73–76 at.%). The compositions of all electrodeposits were determined by electron-probe microanalysis (EPMA), performed on a CAMECA SX50 microprobe. Based on ten different points investigated in each sample, one can assume that the electrodeposits are homogeneous and present a random structure. More details about the characterization can be consulted in [9].

For the estimation of the real surface areas and the analysis of the catalytic activities, the electrodes were saturated with carbon monoxide by bubbling the gas for 10 min at  $E = 0.05$  V in a 0.1 M HClO<sub>4</sub> aqueous solution. The non-adsorbed CO was eliminated from the solution by purging it for additional 10 min with pure N<sub>2</sub>. Afterwards, a cyclic voltammogram was recorded at  $v = 20$  mV s<sup>-1</sup> in the potential range  $0.05 \leq E \leq 0.80$  V. The charge involved in the oxidation of a monolayer of adsorbed CO was used to estimate the surface areas, assuming a charge density of 420  $\mu$ C cm<sup>-2</sup>.

For the electrooxidation of acetaldehyde the potential was kept at  $E = 0.05$  V and acetaldehyde was admitted into the cell to reach a concentration of 0.2 M. Next, chronoamperometric experiments were performed in triplicate by monitoring the (current vs. time) response after the application of a potential step from  $E = 0.05$  to 0.60 V for 20 min.

*In situ* FTIR experiments were performed in the presence of 0.1 M HClO<sub>4</sub> + 0.2 M CH<sub>3</sub>CHO by using a FTIR spectrometer equipped with a MCT detector. The counter electrode was a platinum sheet. Reflectance spectra were collected as the ratio ( $R/R_0$ ) where  $R$  represents a spectrum at a given potential and  $R_0$  is the “reference” spectrum collected at  $E = 0.05$  V. Positive and negative bands represent the consumption and production of substances, respectively [16]. Spectra were collected in the potential range of  $0.05 \leq E \leq 0.80$  V (by successive steps of  $\Delta E = 0.05$  V) and computed from the average of 32 interferograms. The spectral resolution was set to 4 cm<sup>-1</sup>. Further details of the spectroelectrochemical cell and setup can be consulted in [16]. The electrochemical IR cell was fitted with a CaF<sub>2</sub> planar window for the collection of bands. The spectroscopic analysis of the behavior of the catalysts was made by following the formation of CO<sub>2</sub> and acetic acid.

## 3. Results and discussion

### 3.1. (Current vs. time) analysis

Fig. 1 depicts an overview of the behavior presented in current–time curves for all catalysts. These curves were previously published in [9] and will be not showed here. As PtRu surfaces become richer in Ru, the current densities increase and reach a maximum for PtRu (74:26). However, this maximum is exceeded when a minor amount of Ru is replaced by Rh in PtRuRh (73:23:04). The current densities observed for PtRuRh (73:23:04) are four times higher than those of the worst catalysts. If more Rh is added, the catalytic activity rapidly drops and the current densities for those catalysts richer in Rh become comparable to those for non-optimized binary compositions.

Overall, it is noticeable that the mean current densities are strongly sensitive to the composition of the catalyst. More importantly, because the Pt atomic composition was kept virtually constant throughout the ternary series, Fig. 1 suggests that the activity of the catalysts is mainly dependent on the proportion between Ru and Rh on the surface. This observation, in turn, implies that both metals play crucial roles on the mechanism of oxidation of acetaldehyde. Aiming to get further insights about this issue, an *in situ* FTIR analysis was performed, as presented and discussed below.

### 3.2. *In situ* FTIR analysis of the acetaldehyde electrooxidation

Fig. 2 shows *in situ* FTIR spectra collected during the electrooxidation of acetaldehyde ( $0.05 \text{ V} \leq E \leq 0.80$ ) for five representative compositions (indicated in the figure). The main features of the spectra are the bands relative to CO<sub>2</sub> (2343 cm<sup>-1</sup>) and acetic acid (1280 cm<sup>-1</sup>) [8]. These bands are observed for all compositions investigated. Also, a minor band at  $\sim 2050$  cm<sup>-1</sup> relative to on-top CO (the exact frequency depends on the electrode potential considered) can be seen between  $E = 0.3$  and 0.6 V [8]. Other features in the spectra are the bands at 1733 cm<sup>-1</sup> (C=O stretching) [8], and 1386 cm<sup>-1</sup> (coupled C–O stretching and O–H deformation from acetic acid) [8]. No analysis can be made for the carbonyl band (1733 cm<sup>-1</sup>) since it is present on both acetaldehyde and acetic acid, so its magnitude depends on the

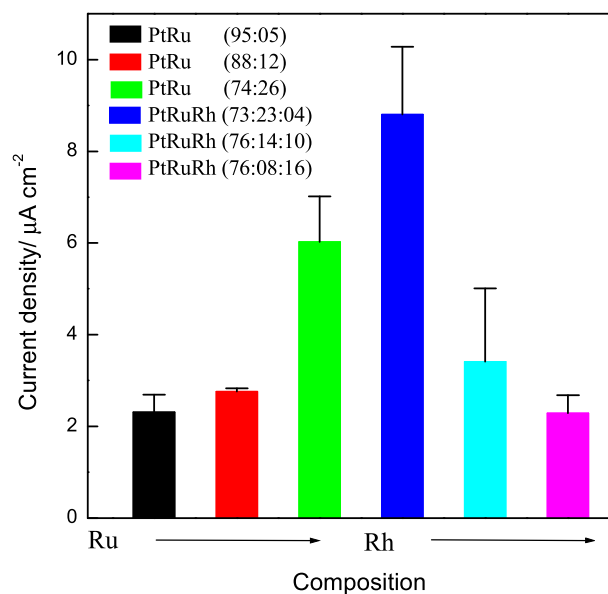


Fig. 1. Average current densities measured after 20 min of polarization at 0.6 V in 0.1 M HClO<sub>4</sub> + 0.2 M acetaldehyde for all the compositions investigated. The compositions of the electrodeposits are indicated in the figure.

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