

Probing *n*-Propanol Electrochemical Oxidation on Bimetallic PtRh Codeposited Electrodes

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The adsorption and reaction of *n*-propanol was investigated using *in situ* Fourier transform IR spectroscopy and on-line differential electrochemical mass spectrometry on electrodeposited Pt, Rh, and PtRh with different compositions. It has been observed that the bimetallic electrodes were more active than pure platinum below 0.9 V. The pure rhodium electrode was practically inactive. Differences in product yield show that platinum is more active than the bimetallic electrodes for propionic acid formation, but the bimetallic electrodes show higher activity for CO_2 and propanal production. The electrochemical reduction of the strongly adsorbed intermediates on pure platinum and on the two bimetallic electrodes gave products with 1, 2, and 3 carbons, while the pure rhodium electrode produced only methane. The degree of coverage by the irreversibly adsorbed species is about ten times higher on platinum than on the bimetallic electrodes or rhodium, showing that on the bimetallic electrodes the intermediates are not as strongly adsorbed as on pure platinum.

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Manuscript submitted March 21, 2002; revised manuscript received August 13, 2002. Available electronically January 2, 2003.

The electrochemical oxidation of *n*-propanol on platinum electrodes has been the subject of a detailed study¹ using auxiliary techniques like in situ Fourier transform infrared spectroscopy (FTIRS) and on-line mass spectrometry to detect products and intermediates. It was found that the oxidation leads to CO₂, propanal, and propionic acid for the oxidation products. Stable intermediates with C-H stretching bands were observed and the adsorbed species may contain CH₂ and CH₂ stretching vibrations. However, a very characteristic band from adsorbed alkoxy species, the C-O-H deformation band at ca. 1430 cm⁻¹, was not reported and a definitive identification of the adsorbed species was not given. However, it is clear that the reduction of the adsorbed intermediates gives ethane and propane. Ethane is ca. 3.5 more abundant than propane. Detection of ethane and propane show that C2 and C3 adsorbates are very likely, because reduction products from adsorbed CO on platinum electrodes, generally yield only C₁ hydrocarbon compounds.²

The key step for total oxidation of a multicarbon atom alcohol is the C-C bond dissociation and the C-O coupling reactions, while partial oxidation requires only C-H dissociation for propanal and C-H bond dissociation followed by C-O bond formation for the acid. Thus a good catalyst for total oxidation must provide sites for C-H and C-C bond dissociation and sites for active oxygen at low potentials to promote the C-O bond formation, in order to carry out the oxidation to CO_2 . Therefore, a more complete oxidation to CO_2 or acid entails the supply of oxygen species, which may come from the water in solution or from surface oxides formed on the electrode surface at different potentials. Indeed, oxides on platinum electrode surfaces, depending on the oxidation state [Pt-OH, Pt-(OH)₂ and PtO], can be classified as active species. Oxides of platinum at higher oxidation states [Pt(OH)₃ and PtO₂] poison the reaction.³ Ruthenium has been added to platinum electrodes to supply active oxygen at overpotentials lower than platinum. This mechanism has been observed for methanol oxidation in many studies.⁴ It has been a consensus in the literature that ruthenium is one of the most promising second elements in methanol electro-oxidation.⁵⁻⁷ In a recent study, we showed that ruthenium presents also effects on ethanol and *n*-propanol oxidation.^{8,9} Other elements have not been explored extensively. Particularly, the interest in the use of rhodiumcontaining electrodes has been scarce. It has been reported that a pure rhodium electrode has smaller catalytic activity for methanol electro-oxidation than pure platinum electrodes.¹⁰ The catalytic activity of the rhodium and iridium electrodes for ethanol oxidation was compared by Tacconi et al.¹¹ They concluded that the oxidation

As pointed out above, the same has been observed for C_3 alcohols, where propanal and propionic acid are observed parallel to the production of CO_2 .¹ The C-C bond stability increases with the chain length and the oxidation of C_3 alcohols to CO_2 is more difficult than ethanol.³ In a previous communication,⁹ we showed that the surface roughness of platinum electrodes improves the C-C bond dissociation for C_3 alcohols. On the other hand, it would be interesting to find also a combination of metals that could afford a suitable catalyst able to decrease the C-C bond energy and promote a higher yield to the total oxidation of C_3 alcohols.

In this study we are interested in the examination of the role of bimetallic electrodes containing rhodium on the C-C bond dissociation. This can be accomplished by following the production of CO_2 (a measure of C-C bond dissociation). Furthermore, rhodium electrodes produce oxygen adsorption and alcohol oxidation at lower potentials than platinum and this can also improve the C-O bond formation for the total oxidation. In order to investigate these effects we use FTIRS and differential electrochemical mass spectrometry (DEMS) as analytical techniques.

Experimental

Electrodes.-Potentiostatic deposition of Pt or codeposition of Pt and Rh onto a smooth Au substrate (a disk of 0.32 cm^2 geometric area, previously polished to a mirror finish). For DEMS the electrochemical deposition were made on a gold layer (1.13 cm² area, 50 nm thickness) prepared by gold sputtering onto a Scimat membrane (thickness 60 µm, mean pore size 0.17 µm, 50% porosity). All electrodepositions were performed in a 0.1 M HClO₄ solution containing the appropriate amount of Pt and Rh salts for 5 min at 0.2 V vs. reversible hydrogen electrode (RHE). The electrode active area was determined by adsorbing CO and recording the amount of CO₂ by measuring the charge required to oxidize the CO monolayer. This charge was used to calculate the active surface area assuming one CO adsorbed per active site. The active surface area was used to normalize the current in the cyclic voltammograms. The normalization of the FTIRs and DEMS were made by recording the amount of CO₂ released in the solution upon oxidation of the CO monolayer in a potentiostatic step (FTIR) and during a voltammetric cycle (DEMS). The normalization using the FTIR and DEMS results are

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efficiency depends on the electrode material with Ir being a better electrocatalyst than Rh for selectivity and rhodium for the total oxidation of ethanol to CO_2 . The ethanol total oxidation requires C-C bond cleavage, which is energetically more difficult than only the C-H bond dissociation and a parallel route leading to the C_2 partial oxidation products takes place with the production of ethanal and acetic acid. Thus, rhodium seems to provide more active sites for C-C bond dissociation than iridium electrodes.

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Table I. Bulk composition of the different electrodes used for *in situ* FTIR and DEMS experiments obtained by energy dispersive X-ray analysis and the corresponding solution composition used for the electrodeposition of the electrodes.

Electrode	Electrode	Solution composition		
(FTIRS)	(DEMS)	$H_2PtCl_6 \cdot 6H_2O$	$RhCl_3\!\cdot\! 3H_2O$	HClO ₄
Pt	Pt	20 mM		1 M
Rh	Rh		20 mM	1 M
Pt _{0.75} Rh _{0.25}	Pt _{0.75} Rh _{0.25}	20 mM	8.5 mM	1 M
Pt _{0.63} Rh _{0.37}	Pt _{0.55} Rh _{0.45}	20 mM	20 mM	1 M

necessary, since the amount of products detected by these techniques depends on factors other than the active surface area, as discussed in previous publications. $^{\rm 12,13}$

An RHE in the electrolyte solution (0.1 M HClO_4) was used as reference and a platinized Pt foil as counter electrode.

Chemicals.—Solutions were prepared with Millipore Milli Q water and analytical grade chemicals: $HClO_4$ acid (70%), propanol (99.9%), $H_2PtCl_5 \cdot 6H_2O$ (Aldrich), and $RhCl_3 \cdot 3H_2O$ (Aldrich). Nitrogen (99.96%) was used to degas the solutions and CO (99.9%) to carry out the normalization of the electrodes. The electrode compositions were determined by energy dispersive X-ray fluorescence (EDX). The composition of the solutions used for the electrodeposition and the final electrode composition are listed in Table I. The solutions used were 0.1 M HClO₄ as a background electrolyte and a 0.1 M *n*-propanol in 0.1 M HClO₄ for the reaction studies.

Instrumentation and procedures.—The FTIRS was a BOMEM DA8 provided with a liquid nitrogen cooled mercury-cadmium telluride (MCT) detector. A cell made of poly(tetrafluoroethylene) (PTFE) equipped with a CaF₂ window was used for the *in situ* FTIR experiments. Each single-beam spectrum was computed after averaging 256 interferometer scans, taken with 8 cm⁻¹ resolution, at different potentials in the range 0.3-1.2 V. The spectra are presented in the form of the reflectance ratio R/R_0 of a single-beam spectrum, R_0 , obtained at a given potential and a reference spectrum, R_0 , obtained at 0.25 V.

Home-made DEMS equipment was used. The quadrupole mass spectrometer used was a MKS Instrument. Details of this equipment are given in Ref. 13. The electrochemical cell was constructed as described in Ref. 14. The experiment consists in recording simultaneously the current-potential (I-E) and mass intensity-potential voltammograms (potential positive scans and mass signal) for selected values of m/z (mass/charge) ion signals. The potential was cycled in the range 0.05-1.0 V and the scan rate was 0.01 V s⁻¹.

Propanol adsorption experiments were performed in the flow cell under constant potential conditions. Thus, after the activation of the working electrode in the 0.1 M HClO₄, with the electrode polarized at E_{ad} 0.35 V, propanol was added to the cell in order to have a 0.1 M propanol solution. The electrode was held for 5 min in order to generate the stable adsorbed intermediates. After the adsorption time the propanol-containing solution in the cell was replaced by the 0.1 M HClO₄ solution under potential control. Finally, DEMS measurements were performed in the range 0.35 to -0.05 V.

Results

In situ infrared spectroscopic study.—All the *in situ* spectra obtained during the *n*-propanol oxidation presented the same feature as observed before for platinum and PtRu bimetallic electrodes.^{1,9} So here we use only the integrated band intensity for CO₂ (2344 cm⁻¹) and propionic acid (1226 cm⁻¹) as a function of the oxidation potential (Fig. 1a, b, respectively) to evaluate the electrocatalytic activity and selectivity of the electrodes. Clearly the Pt_{0.75}Rh_{0.25} electrode produces the highest band intensity for CO₂ (Fig. 1a).



Figure 1. (a) Normalized integrated band intensity of CO₂ obtained from *n*-propanal oxidation in a 0.1 M propanol in 0.1 M HClO₄ solution on different electrode compositions. (b) Normalized integrated band intensity of propionic acid obtained during oxidation of 0.1 M propanol in 0.1 M HClO₄ solution on different electrode compositions. The symbols are (\blacksquare) Pt, (\blacktriangle) Pt₇₅Rh₂₅, (\blacktriangledown) Pt₆₃Rh₃₇, and (\blacklozenge) Rh.

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Figure 2. Positive scan voltammetry and mass signal-potential curves obtained for the cyclic oxidation of 0.1 M propanol in 0.1 M $HCIO_4$ on electrodeposited Pt electrode.

Comparing the different electrodes for the CO₂ yield in the range between 0.6 and 1.1 V, the electrocatalytic activity for the total oxidation can be arranged in the following sequence: $Pt_{0.75}Rh_{0.25}$ > $Pt_{0.63}Rh_{0.37}$ > Pt > Rh. For the partial oxidation to propionic acid (Fig. 1b), the Pt electrode presents the highest activity over the whole range of potentials studied. The sequence of activities in this case is Pt > $Pt_{0.75}Rh_{0.25}$ > $Pt_{0.63}Rh_{0.37}$ > Rh.

The rhodium electrode presents the lowest activity for the electro-oxidation of propanol. On this electrode the CO_2 band is approximately ten times less intense than observed for the $Pt_{0.75}Rh_{0.25}$ electrode. The rhodium electrode is almost inactive for propionic acid production.

The results of Fig. 1 show a very interesting feature. The CO_2 production reaches a maximum at 0.8 V, while the propionic acid production does not present a maximum. This result shows that the platinum oxide, which is formed above 0.8 V, may act as a poison for the C-C bond dissociation (inhibition of CO_2), but not to C-O coupling, since oxidation to propionic acid is not inhibited.

Differential electrochemical mass spectrometry (DEMS) studies.—The volatile reaction products of the *n*-propanol oxidation were followed by DEMS. In Fig. 2 the mass signal obtained during the electro-oxidation of *n*-propanol on electrodeposited Pt are shown.

The oxidation of *n*-propanol leads to the production of propanal and CO₂, as already reported.¹ The reaction leading to propanal starts at 0.5 V, and it is followed using the mass signals at m/z = 58 and m/z = 29. The former corresponds to the propanal radical cation and the latter is related to the (COH)⁺ fragment, which is the main peak of the mass spectrum of propanal.¹² CO₂, which starts at 0.6 V is followed through the mass signal m/z = 44. However, since m/z = 29 is also found for acetaldehyde, the possibility of acetaldehyde production must be tested. The fragmentation of propanal, under the conditions of the experiments, indicates that acetaldehyde must present also a mass signal at m/z = 43, which is not observed in the mass signal shown in Fig. 2. Likewise, the correction of the m/z = 29 for propanal fragmentation shows that the mass signal m/z = 29 corresponds only to the fragmentation of propanal. In that case, the production of lower aldehydes has been ruled out. Based on this result, it is important to stress that the mass signal m/z = 44 is due only to CO₂, since propanal does not present a mass signal at m/z = 44. The direct consequence of this observation is that once one C-C bond has dissociated, the remaining C2 fragment also reacts to give CO₂.

The products observed by FTIR do not allow the discrimination between propanal and propionic acid, but the mass signal m/z = 58 shows unequivocally the production of propanal, as shown before for platinum electrodes. The lack of detection of propionic acid by mass spectrometry can be attributed to the low volatility of propionic acid.¹¹ Recently in a study of ethanol oxidation on Pt and PtRu porous electrodes¹⁵ acetic acid has been detected by DEMS measurements; however, the mass intensity was about 10 times smaller in comparison to acetaldehyde and CO₂.

The results of the propanal and CO₂ yield for four different electrodes are show in Fig. 3. In the range 0.4-0.8 V, all the bimetallic electrodes present higher activity than pure Pt for CO₂ production. Related to the higher current density for the alloys is the onset of the reaction for propanal and CO₂. The partial oxidation to propanal starts at 0.35 V for the most active Pt_{0.75}Rh_{0.25} alloy electrode, while CO₂ production starts at *ca*. 0.5 V. The reaction pathway leading to propanal on pure platinum electrodes starts at *ca*. 0.6 V, at the same potential as for the CO₂ onset. The order of activities, based on the propanal and CO₂ yield, is Pt_{0.75}Rh_{0.25} > Pt_{0.55}Rh_{0.45} > Pt > Rh. These results are in good agreement with those obtained from the FTIR experiments.

The activity of the pure platinum electrode increases for more positive potentials. Specifically the propanal production starts to be more intense for the pure platinum electrode at potentials above 0.9 V. The pure rhodium electrode displays only a very low activity for both CO_2 and propanal.

Although the adsorbed species generated from the dissociative adsorption of the n-propanol were not detected in the *in situ* FTIR spectra, the products obtained from the reduction reaction of the strongly adsorbed species can be a clue to identify the stable reaction intermediates.

The cyclic voltammetric curves (Fig. 4) for the irreversibly adsorbed intermediates show a current density ten times higher for the platinum electrode, compared to the bimetallic ones. The current density is directly proportional to the degree of coverage, it is clear that the surface coverage by the strongly adsorbed intermediates is strongly inhibited on the bimetallic electrodes.

The reduction reaction products obtained for the propanol adsorbed fragments were followed with the mass signals m/z = 43, m/z = 30, and m/z = 15 (Fig. 5). These mass signal account for propane, ethane, and methane (note that the mass signal m/z = 15has been corrected for propane and ethane fragmentation and therefore it is only due to methane). Although the mass signals are corrected for fragmentation, each product has different mass peaks and quantitative determination needs the determination of all fragments. Therefore it is not possible to obtain quantitative data, since the relative amount of products is not known exactly. However, the large difference in current density and mass signals between pure platinum and the bimetallic electrode indicates that a large difference in degree of coverage exists between these two kinds of electrodes.

Except on rhodium electrodes, for which only m/z = 15 is observed, the other electrodes present detectable values for the three



Figure 3. Positive scan current and mass signals as a function of the applied potential obtained during the voltammetric oxidation of 0.1 M propanol in 0.1 M HClO₄ on (——) Pt, (----) Pt_{0.75}Rh_{0.25}, (-----) Pt_{0.55}Rh_{0.45}, and (-----) Rh electrodes. The data are normalized to the integrated CO_2 mass signal generated by a monolayer of adsorbed CO.

mass signals. As in the case of the cyclic voltammetric measurements of the reduction of the stable adsorbed intermediates, platinum presents the largest mass signals for the three adsorbates. It is very difficult to quantify the total amount of adsorbed material from the mass signal, including the relation between the different species.

It is interesting that on rhodium, no C_2 and C_3 adsorbates were observed. On the other hand, the adsorbates on rhodium present by far the lowest degree of coverage. In general, it can be concluded that rhodium practically does not present any meaningful electrocatalytic activity.

Discussion

The use of a normalization procedure allows a confident comparison of the electrode activity for the electro-oxidation of n-propanol on Pt, Rh, and PtRh coelectrodeposited electrodes with



Figure 4. Cyclic voltammograms obtained for the products obtained upon reducing electrochemically the irreversibly adsorbed intermediates in the absence of *n*-propanol in solution: (----) Pt, (----) Pt_{0.75}Rh_{0.25}, (------) Pt_{0.55}Rh_{0.45}, and (------) Rh electrodes. The irreversibly adsorbed intermediates were formed by contacting the electrode polarized at 0.35 V in 0.1 M propanol in 0.1 M HClO₄ for 5 min and then replacing the solution by 0.1 M HClO₄. The data are normalized by the area occupied by adsorbed CO on each electrode (active surface area).

different bulk composition. The bimetallic electrodes presented the best electrocatalytic activity for *n*-propanol oxidation at potentials lower than 0.9 V. The best composition tested in the present paper is $Pt_{0.75}Rh_{0.25}$. The overall electrocatalytic activity correlates well with the CO_2 and propanal yield for the electrodes studied, meaning that those products control the overall reaction rate for potentials below 0.9 V.

The composition of the bimetallic electrode is the bulk composition and not the surface composition. For bimetallic PtRu electrodes it has been reported that the surface composition differs from the bulk. There is platinum enrichment of the surface, depending on the surface pretreatment.¹⁶ Surface enrichment for PtRh can also be expected, but no data on the differences in surface and bulk composition exists for these electrodes. Independent of the final surface composition, note that in an early study, using bimetallic PtRh as CO-tolerant electrode for H₂ oxidation, it was suggested that the increased electrocatalytic effect for H₂ oxidation is related to an electronic effect instead of a bifunctional mechanism. Therefore, addition of rhodium is not only to supply active oxygen. In that case the composition at the surface may not be so important as it is in the case of a bifunctional mechanism. In our case strong evidence that the bifunctional mechanism is not so important, like in the case of PtRu bimetallic electrodes, is that the addition of rhodium to the electrode composition strongly shifts the onset potential for propanal, but not for CO₂. Production of propanal entails only C-H bond dissociation and not C-O bond formation, for which the presence of oxygen at lower potentials does not affect the reaction rate. On the other hand, on PtRu bimetallic electrodes the effect of ruthenium on the onset potential for CO_2 ⁹ is in good harmony with the bifunc-



Figure 5. Mass signals obtained during the negative scan for reducing the strongly adsorbed intermediates in 0.1 M HClO₄: The symbols are (\longrightarrow) Pt, ($\cdot \cdot \cdot \cdot$) Pt_{0.75}Rh_{0.25}, (- - -) Pt_{0.55}Rh_{0.45}, and ($- \cdot - \cdot -$) Rh. The irreversibly adsorbed intermediates were formed by contacting the electrode polarized at 0.35 V in 0.1 M propanol in 0.1 M HClO₄ for 5 min and then replacing the solution by 0.1 M HClO₄. The data are normalized to the integrated CO₂ mass signal generated by a monolayer of adsorbed CO.

tional mechanism already proposed for methanol oxidation for this alloy. Unfortunately the propanal and CO_2 production cannot be compared with PtRu bimetallic electrode, since no DEMS results are reported for this system. Only *in situ* FTIR results have been reported,⁹ but in this case the differences in CO_2 and propanal yield can be due to the differences in surface area.^b

A remarkable result is the difference in the current and mass signal of the stable adsorbates on the different electrodes. Pure platinum electrodes present the highest degree of coverage for strongly adsorbed intermediates on all the electrodes. In addition, the highest electrocatalytic activity of the bimetallic electrodes indicates that the important intermediates are only weakly adsorbed and these adsor-



Figure 6. Possible general reaction scheme for the oxidation of n-propanol on platinum and PtRh bimetallic electrodes in acid solutions. The (s) means strongly bonded and (w) weakly bonded intermediates. C1, C2, and C3 are for fragments of the adsorbed intermediates containing one, two and three carbon atoms, respectively.

bates control the overall reaction rate, even for CO_2 production, as already anticipated before for pure platinum electrodes.¹ Evidence connected to this observation is the result that the oxidation of the isolated stable adsorbates produces only CO_2 , as published before.¹ If CO_2 would be produced only from the strongly adsorbed intermediates, a higher CO_2 yield should be expected for platinum. Therefore, a lower degree of coverage by the strongly adsorbed intermediates on the bimetallic electrodes facilitates both the total and partial oxidation via the weakly adsorbed intermediates.

Summarizing, propanal and CO_2 can be produced via weakly adsorbed intermediates, but CO_2 can originate from the strongly bonded intermediates as well. Additionally, simultaneous observation of propanal, CO_2 , and propionic acid suggests that the reaction follows parallel pathways on all the electrodes. A tentative general reaction scheme is proposed in Fig. 6.

In this scheme, the basic difference between platinum and PtRh bimetallic electrode is that on the bimetallic electrodes the coverage by the strongly bonded intermediates is much less than for platinum electrodes and the pathways leading to the weakly bonded intermediates prevail, leading to a higher reactivity.

The higher degree of coverage with strongly adsorbed intermediates on platinum electrodes must relate to the higher reaction onset potential and lower electrocatalytic activity for propanol oxidation on platinum, compared to the bimetallic electrodes. As mentioned above, the strongly adsorbed intermediates poison the electrode surface, requiring higher oxidation potential to cause the reaction to proceed. The production of propanal starts at 0.35 and 0.45 V on the Pt_{0.75}Rh_{0.25} and Pt_{0.55}Rh_{0.45} electrodes respectively, while pure platinum presents the onset for propanal at *ca.* 0.6 V. Thus, poisoning by the strongly bonded intermediates inhibits not only the C-C bond dissociation but also the C-H bond dissociation.

Another important observation in relation to the reaction pathways is the difference in propionic acid and propanal yield as shown by the FTIR and DEMS results. Propionic acid presents the best yield on pure platinum electrodes, while the best yield for propanal is observed for the Pt_{0.75}Rh_{0.25} bimetallic electrode. If propionic acid would originate exclusively from propanal oxidation, then it should be expected that the best propanal yield detected by DEMS would lead also to the best propionic acid yield detected by *in situ* FTIR spectroscopy. That pure platinum favors the pathway to propionic acid, while the Pt_{0.75}Rh_{0.25} favors propanal production, indicates that there are parallel pathways for propanal and propionic acid instead of a purely sequential pathway as suggested before.¹ The sequential pathway may also be another way to produce propionic acid, but the main pathway is the direct oxidation of propanol to the acid. On the other hand, the higher propionic acid yield on platinum electrodes than on the bimetallic electrodes suggests that the production of propionic acid may be related also to the adsorbed C₃ stable adsorbate, since the production of propanal seems not to depend on the C₃

^b The *in situ* FTIR can be strongly affected by the total surface area of the electrode, since the reaction occurs in a very thin layer of solution between the electrode and the infrared window, which is practically disconnected from the bulk solution in terms of diffusion. In that case a larger area will produce larger reactant depletion with a consequent change in the propanal/CO₂ ratio.

stable adsorbate coverage. However, no direct evidence can be supplied from the present experiments.

The rhodium electrode is practically inactive compared to pure platinum or to the codeposited Pt-Rh electrodes. In this connection it is interesting to discuss the C-C bond dissociation efficiency on these electrodes. It is clear that, although pure rhodium electrodes are practically inactive for n-propanol oxidation, the contact of *n*-propanol with the rhodium surface gives rise only to stable C_1 fragment adsorbates. This contrasts with pure platinum or the codeposited PtRh, where C₁, C₂, and C₃ fragments were found. The lack of C3 adsorbates on rhodium electrodes indicates that the rhodium stabilizes only adsorbates with C1 fragments. Indeed, in a previous study,¹⁷ it was found that the presence of rhodium in the electrode composition increases the C-C bond dissociation for ethanol oxidation. This higher ability to dissociate the C-C bond was assigned to a modified electronic structure caused by the presence of rhodium on the electrode. However for the case of *n*-propanol the CO₂/propanal ratio between the bimetallic electrodes and platinum are comparable. This means that the C-C bond dissociation is not as effective as in the case of ethanol.¹⁵ On the other hand, the higher yield both for propanal and CO₂ on the bimetallic electrodes clearly indicates a better catalytic efficiency of these materials. As mentioned above, this superior catalytic activity seems to be related to the lower adsorption energy of the reaction intermediates on the bimetallic electrodes, allowing a higher turnover frequency for the bimetallic electrodes.

Conclusions

Bimetallic platinum-rhodium electrodes present a superior electrocatalytic activity than the pure platinum electrode for applied potentials below 0.9 V. The best electrocatalytic activity is for the $Pt_{0.75}Rh_{0.25}$. The pure rhodium electrode is practically inactive for *n*-propanol oxidation.

The reaction rate below 0.9 V is governed by the weakly bound intermediates. Above 0.9 V the C-C bond dissociation is inhibited

by the platinum oxide, but not the dehydrogenation reaction and the C-O bond formation, since propionic acid shows an increasing yield on the pure platinum electrode.

Acknowledgments

The authors would like to acknowledge the FAPESP, CNPq, and CAPES agencies for financing the project and fellowships.

The University of São Paulo assisted in meeting the publication costs of this article.

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