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Pt catalysts modified with Bi: enhancement of the catalytic activity for alcohols oxidation in alkaline media

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Abstract

Recent developments on anion exchange membranes for fuel cell application renewed the interest in the study of alcohol oxidation at high pHs for applications in Anion Exchange Membrane Direct Alcohol Fuel Cells (AEM-DAFC). Although platinum is still the most studied catalyst for oxidation of alcohols in alkaline media, the introduction of one or more metals in order to increase the oxophilicity of the catalyst is a common approach in the development of improved materials for these reactions. In this manuscript, we report the enhancement of the catalytic activity of Pt/C toward ethanol, methanol and propanol oxidation in alkaline media by simple adsorption of Bi surface. The activity was checked by cyclic voltammetry, the reaction products and intermediates were analyzed by “in-situ” infrared spectroscopy. The presence of Bi showed to increase of the activity of Pt toward the oxidation of the referred alcohols by acting as a third body (impeding surface poisoning) and also by an electronic effect (on water adsorption at the surface).

Keywords: platinum catalysts, alcohols oxidation, Bi adsorption, alkaline media, adatoms

1. Introduction

Electro-oxidation of alcohols is one of the most important subjects in electrocatalysis [1, 2]. This importance is due the use of these compounds as fuels in direct alcohol fuel cells (DAFC) that emerged in the last decades as promising alternatives for power sources in portable applications. The use of alcohols as fuels presents several advantages when compared with the “traditional” hydrogen powered fuel cells because, in addition to their high energy densities (comparable to gasoline, from 6.1 kWh/kg for methanol to 8.0 kWh/kg for ethanol) they can be easily handled, stored and transported [3]. However, further development of direct alcohol fuel cell technologies is limited by the sluggish kinetics of the

alcohols oxidation reaction, the formation of catalyst poisoning intermediates (like CO) and undesired final products (acetic acid, propionic acid). From this point of view, investigation and development of low-cost or highly effective electrocatalysts for the oxidation of alcohols at the anode that increase current densities and shows low overvoltage is still a requirement.

Most of the studies concerning alcohols oxidation were performed in acidic media [4-7], though, it is known that the oxidation of organic fuels is faster and has smaller overpotential in alkaline media [6, 8]. Moreover, the use of alkaline conditions is more favorable for the cathode side (oxygen reduction) where a variety of non-noble metal catalysts can be used. Despite all these advantages, the development of alkaline fuel cells has been hindered by the undesirable progressive carbonation of the alkaline electrolyte due to the carbon dioxide from the air or from the oxidation of the fuel. However, recent developments of alkaline solids has allowed the use of anion-exchange membranes (AEM) [9-11] in direct alcohol fuel cells (AEM-DAFC) instead of caustic liquid fuels, renewing the interest in the study of alcohol oxidation at high pHs.

Similarly to acidic environments, in alkaline electrolytes the majority of the studied catalysts are based in noble metals with special attention for platinum and palladium, mono or multimetallic [12-14]. Pt catalysts are considered the most active materials for alcohols electrooxidation in alkaline media due to the capability of Pt to catalyze C-H bond rupture at comparatively low overpotentials. Though, oxidation of the intermediate product CO on a pure Pt surface occurs only at high overpotentials and is therefore rate determining. Alloying these noble metals with more oxophilic elements can lower the electrocatalysts electronic binding energy by facilitating the adsorption of OH at lower potentials and promoting the oxidation of the organic species. The improved performance of binary and ternary electrocatalysts including Pt–Ru [15-17], Pt–Sn [15, 16, 18, 19], PtSnRu [15], PtSnNi [19], PtRuNi [20], PtRuMo [21] and PtCuCo [22] have been extensively studied in both acidic and alkaline media.

Recently, elements as Bi have been found to promote formic acid [23], methanol [24] (at Pt single crystals) and ethanol oxidation [4, 25] (Pt/C nanoparticles) in acidic media. Bi can be spontaneously adsorbed onto Pt surfaces resulting in a stable bimetallic surface in which the surface coverage of the adatom can be easily modified [26]. It has been reported that the presence of the adatom can affect the oxidation path in the mechanism of the reaction inhibiting the poison formation and enhancing the direct oxidation [24, 27]. The enhancement of the reaction in catalysts containing Bi has also been reported in alkaline media for methanol [28], ethanol [25, 29] and ethylene glycol [30] as bi or tri-metals. However, most of these studies concern multimetallic nanoparticles and full understanding on the effect of Bi is still missing.

In this work we report the enhancement of the catalytic activity of Pt/C catalysts with irreversibly adsorbed Bi towards ethanol, methanol and propanol oxidation in alkaline media. In this way the effect of Bi in the catalyst surface can be accessed. The presence of Bi at the catalyst surface increases the catalytic activity of Pt toward the alcohol oxidation (ethanol, methanol and propanol) in alkaline media. Bi showed to have a mixed behavior in the catalyst acting as a third body (impeding Pt surface poisoning) and providing OH for the reaction at lower potentials (bifunctional mechanism). The effect of the Bi coverage was studied, and experiments were performed in conditions close to “in situ” fuel cell measurements aiming to obtain information about performance and durability of the catalyst. The reaction intermediates and products were investigated using in situ infra-red spectroscopy. The enhanced catalysis showed to be dependent on the alcohol and, for Bi coverages around 70% of the Pt surface, the direct oxidation path to CO₂ is preferred in smaller alcohols (methanol and ethanol) and the incomplete oxidation toward other products is favored when increasing the carbon chain in the alcohol (propanol). In any case, Pt/C catalysts modified with Bi irreversibly adsorbed at the surface showed to be a very good candidate for application in AEM-DAFC.

2. Experimental

The working electrode was prepared by deposition of 4 μl of an ink onto a glassy carbon electrode (0.1963 cm^2 of geometric area) previously cleaned by polishing with an alumina suspension and rinsing in an ultrasonic bath. The ink was prepared using 5 mg of carbon supported Pt catalyst (60% wt., Alfa Aesar), 20 μl of Nafion[®] solution (5 wt. % Aldrich) and 200 μl of ethanol (p.a., Altia) that were carefully mixed with a magnetic stirrer and sonicated. The electrodes prepared with this procedure have a Pt loading of ~ 0.02 mg.

The electrochemical experiments were performed in a classical three electrode cell at controlled temperature (20°C) and under nitrogen purge (AGA, 99.999%) (figure 1). A platinum coil was used as a counter electrode and a reversible hydrogen electrode as a reference. The experiments were performed with a potentiostat/galvanostat PGSTAT100 Autolab system and a rotating device from Pine Instruments.

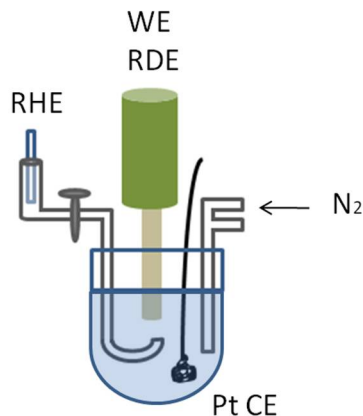


Figure 1 – Scheme of the electrochemical cell used.

Cyclic voltammetry in 0.5 M H_2SO_4 (Merck) was done for the electrochemical characterization of the catalysts and for the electrochemical active area determination. Following the procedure previously described [13], prior to the use of the nanoparticles for alcohol oxidation, they were cleaned by CO (AGA, 99.999%) adsorption and stripping [14]. The active surface area of the Pt nanoparticles was determined

by the charge involved in the so-called hydrogen UPD region assuming 0.23 mC cm^{-2} for the total charge after the subtraction of the conventional current attributed to double layer charging contribution [14].

The adatom layer was adsorbed on the electrode surfaces by contact with a $0.5 \text{ M H}_2\text{SO}_4$ solution containing 10^{-5} M of Bi_2O_3 at open circuit. The electrode was then rinsed with ultra-pure water and transferred to the cell containing the supporting electrolyte ($0.5 \text{ M H}_2\text{SO}_4$) where the voltammogram was recorded. The Bi surface coverage was measured according with previously reported methods [26]. Then the electrode was transferred to the electrochemical cell containing 1 M of the alcohol (ethanol – p.a. Altia, methanol – Merck and propanol – Merck) in 0.1 M NaOH (Merck) where the catalysis was accessed.

Fourier-transform infrared spectroscopy (FTIRS) experiments were performed with a Nicolet Magna 850 spectrometer, equipped with an MCT detector. The spectroelectrochemical cell was provided with a prismatic CaF_2 window beveled at 60° . Spectra shown are composed of 100 interferograms collected with a resolution of 8 cm^{-1} and p-polarized light. They are presented as absorbance, according to $A = \log(R/R_0)$, where R and R_0 are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively [31]. All the spectroelectrochemical experiments were conducted at room temperature, with a reversible hydrogen electrode (RHE) and a platinum wire used as the reference and counter electrodes, respectively. For these experiments a gold collector electrode was used and the inks were prepared without the ionomer (Nafion) in order to avoid the undesirable bands coming from the polymer [32].

The contact of the electrodes with the ethanol solution was performed at controlled potential (0.1 V) where, apparently, no adsorption or reaction process take place. This potential was maintained until the electrode was pressed against the CaF_2 window. After collecting the reference spectrum at this potential, the potential was stepped progressively to higher potentials up to 0.8 V .

3. Results and discussion

3.1. Ethanol oxidation

Figure 2 shows the effect of irreversibly adsorbed Bi on Pt/C catalyst for ethanol oxidation in alkaline electrolyte (0.1 M NaOH) at 0 (A) and 1800 rpm (B). As an inset of the figure, the blank cyclic voltammograms (CV's) obtained for the surfaces in 0.1 M H₂SO₄ after cleaning (with the respective CO stripping) are presented as reference. As it can be observed, the presence of Bi on the surface leads to the decrease of the charge of H adsorption at potentials lower than 0.40 V due to the presence of less free Pt sites, in agreement with previous literature [26]. On the other hand, the redox peaks characteristic from Bi are observed at higher potentials (0.60-0.70 V).

The experiments were performed in unstirred solutions as well as under electrode rotation in order to mimic the real conditions in a fuel cell anode, where the solution is always flowing through the catalyst layer avoiding mass transport limitations for the electrode reactions. The CV's for both of the surfaces in 0.1 M NaOH and 1 M EtOH are presented for 0 and 1800 rpm's in Figure 2. Similarly to what occurs in acidic solutions [33], the presence of irreversible adsorbed Bi also enhances the catalytic activity of Pt in alkaline media. These results are in accordance with those reported previously for ethanol oxidation on PtBi nanoparticles in alkaline media [25, 29].

When the Pt catalyst is modified with Bi, the oxidation currents increase and the onset potential is shifted to less positive potentials when compared with the pristine Pt. Even though the absolute current intensities do not increase significantly, at static conditions (0 rpm), the onset potential shifts from 0.42 V on pure Pt to 0.20 V on PtBi. For PtBi, the oxidation curve presents a maximum at 0.7 V and after that

the current begins to decrease reaching values close to the pure Pt at 0.8 V. Although a significant hysteresis is observed between the positive and negative sweeps, even when the electrode potential is decreased, the oxidation currents are higher with Bi than without it. It is worth to notice that the hysteresis observed for the PtBi surface, is not due to poisoning of the surface as observed in other cases [34, 35]. The hysteresis normally describe for ethanol oxidation is related to the formation of CO at low potentials that decrease the oxidation currents on the positive scan till high enough potentials are reached for oxidizing CO. Then, the electrode surface becomes free causing an increase in the oxidation currents on the negative going scan. In the present case the electrode is more active in the positive scan suggesting a lower degree of poisoning of the surface. When mass transport is improved by rotating the electrode at 1800 rpm, the current intensities are significantly higher at 0.8 V if we compare the clean Pt surface and Pt modified with Bi. The decrease in the onset potential is less pronounced with rotation (from 0.4 to 0.28 mV at 1800 rpm) and there is no maximum in the current intensities. Moreover, the hysteresis is not visible with rotation and both sweeps are totally reversible and have exactly the same currents (note that also in Figure 2-B both forward and backward scans are represented).

1 M EtOH + 0.1M NaOH
10mV/s

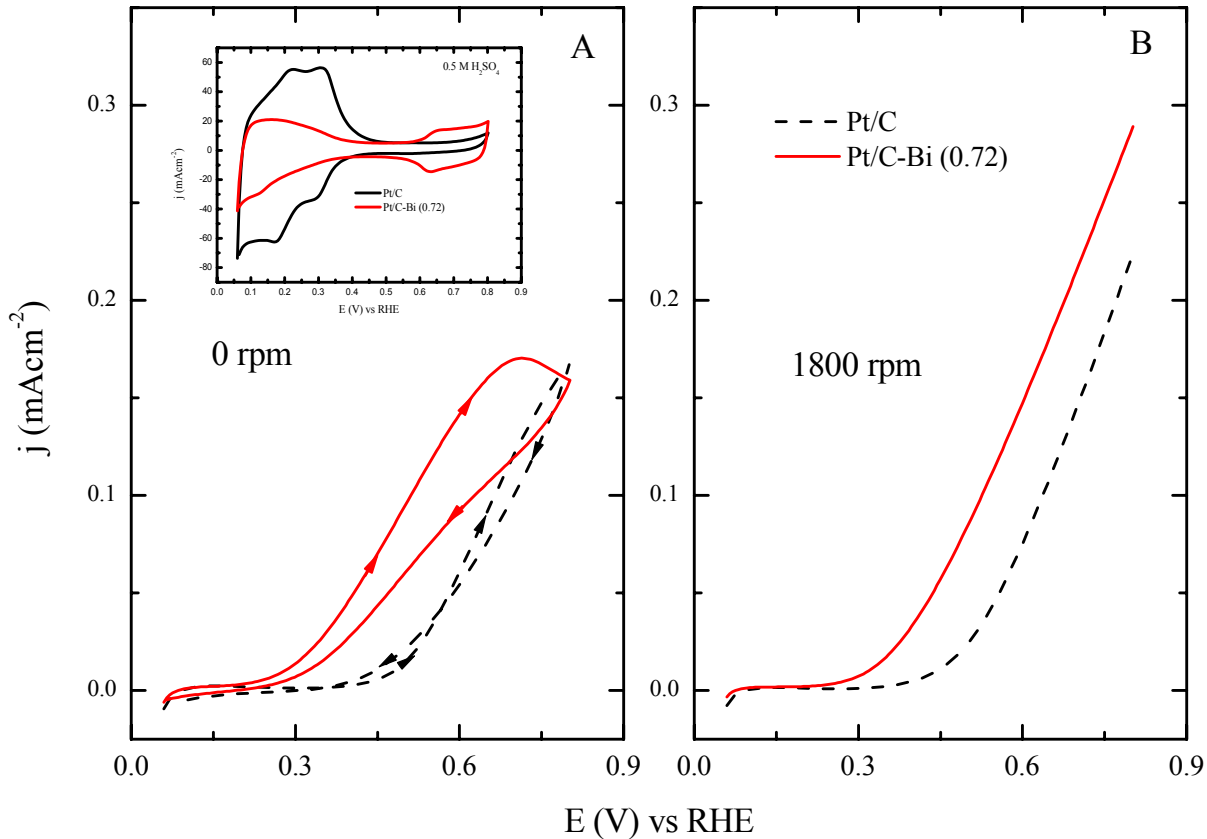


Figure 2 – Cyclic voltammograms obtained for the Pt/C catalyst (dashed line) and Pt/C modified with Bi (straight line) in 0.1M NaOH and 1M EtOH, 10mV/s. (A) at 0 rpm and (B) at 1800 rpm.

Is important to remark that the stability of the modified electrode was achieved by comparing the blank CV after ethanol oxidation with the one obtained before (results not shown) and no significant differences were found.

These results suggest that Bi is promoting the ethanol oxidation reaction at the Pt surface, probably due to a third body effect although and electronic effect or bifunctional catalysis (above onset of oxidation processes on Bi at 0.6 V) cannot be discarded.

In our previous work [36], using similar surfaces for ethanol oxidation in acid media, we suggested that the enhancement of the reaction rate by the presence of Bi on the Pt catalyst surface was due to a third body effect. In this case Bi was acting as an external body blocking specific sites of poison formation (CO) leading to the increase of the incomplete oxidation reaction by enhancing the rate of the reaction per free platinum site. In acidic conditions, the presence of Bi in the catalyst caused a negative shift (higher potentials) on the potential onset for the reaction. This effects was explained by the change on the electronic properties of the surface with consequent stabilization of the adsorbed CO molecule [26, 37] through the increase the electronic back donation phenomena (Bi donates electrons to Pt, causing an increase in the extent of $d\pi_{Pt} \rightarrow 2\pi^*_{CO}$ [38]). However, in the present case, in addition to the current increase there is a positive effect on the onset potential and the oxidation reaction starts more than 0.1 V earlier suggesting some other effect in addition to the third body (that is responsible for the increase of the oxidation currents and hysteresis).

A bifunctional mechanism through Bi mediated OH cannot be excluded, but cannot justify the observed decrease on the onset potential in alkaline media by itself. The catalysis by Bi mediated OH will proceed during the adatom redox process, and this only occurs at potentials higher than 0.6 V. This effect can contribute to the higher current densities for ethanol oxidation on the modified surfaces but only at potentials higher than 0.6 V.

Once none of the previous effects can explain the shift on the onset potential for ethanol oxidation on PtBi, the reason must rely on an electronic effect. As mentioned previously, this electronic effect cannot be related to the adsorbed CO because when Bi is irreversibly adsorbed on Pt single crystals surfaces no enhancement on the CO oxidation is observed. However, the existence of electronic effects related with other intermediate/surface specie can enhance the ethanol oxidation and shift its onset potential to lower values. It was suggested, by Climent et al [39] that Bi adatoms can have a disrupting effect on the

formation of water networks on the platinum surface. Moreover, these authors showed that Bi decreases the Pt work function leading to a displacement of the potential of zero charge to more negative values what also will generate changes on the water absorption on the surface. Based on this assumption we can tentatively suggest that the enhancement on the onset potential on the modified surfaces for ethanol oxidation is related with electronic effects of the adatom on the water adsorption on the surface.

However, further inputs in these observations can be done after analyzing the catalytic effect for ethanol oxidation dependence on Bi coverages at the Pt surface.

3.2. Effect of Bi coverage

The effect of the Bi coverage on the Pt surface for the ethanol electrocatalytic oxidations was accessed in order to help on the understanding of the catalytic properties of these bimetallic electrodes. The results obtained using cyclic voltammetry are shown in Figure 3.

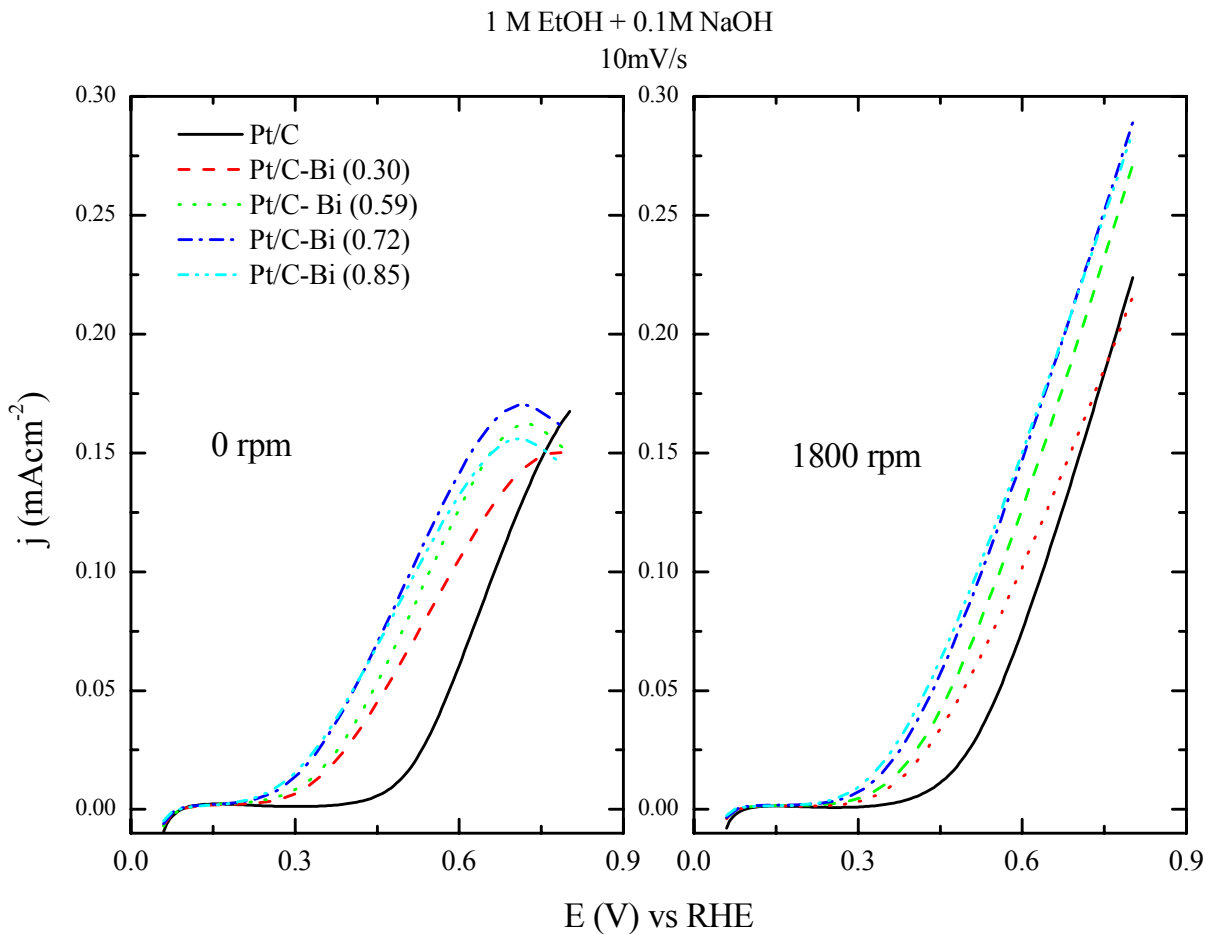


Figure 3 – Cyclic voltammograms obtained in 0.1 M NaOH and 1M EtOH with Pt/C and PtBi/C surfaces with different Bi coverage (coverage indicated in the figure) at 10mV s^{-1} . A) 0 rpm; B) 1800 rpm.

As shown in Figure 3, the current density for ethanol oxidation increases till very high Bi surface coverages. However, when amounts of Bi close to the total coverage of the Pt surface are reached, the oxidation currents show a decrease, revealing that the catalytic reaction needs both Pt and Bi pair to precede and that Bi by itself is not active toward ethanol oxidation. A summary of the most important values obtained from the data in Figure 3 is presented in Table 1.

The results show clearly an increase on the oxidation currents for Bi coverages till 0.72. When higher coverages are reached, the currents show a small decrease, being in any case much higher than in the

pure Pt surface. It is also interesting to notice that the maxima in the currents, observed for the static measurements, decrease with the increase of Bi coverage at the electrode surface. It means that higher currents are obtained at lower potentials with increasing Bi amounts. At the same time, the onset potentials also decrease with increasing Bi coverage, showing to be dependent on its amount on the Pt surface.

Table 1 – Summary of the potential onsets and maximum current intensities for EtOH oxidation in Pt surfaces with different Bi coverage.

Bi coverage	E onset (5μA) / V	I max / mA cm⁻²	E at I max / V	E onset @1800 rpm / V
0	0.443	0.166	0.800	0.403
0.30	0.280	0.150	0.773	0.322
0.59	0.260	0.162	0.722	0.304
0.72	0.240	0.170	0.714	0.278
0.85	0.233	0.155	0.700	0.261

In a bifunctional catalytic mechanism, the onset potential for the reactions should not be dependent on the adatom coverage at the surface. In the present case, the onset potential of the reaction shifts almost 50 mV from coverages of 0.3 to 0.85, what supports the initial idea that no bifunctional mechanism exists due to Bi once that its redox process is higher than the onset for ethanol oxidation.

The oxidation currents for ethanol oxidation at 0.5 V were plotted as a function of the Bi coverage on the Pt electrode (Figure 4). In agreement with the results shown previously, the catalytic activity from the Bi adatoms is observed even for low coverages (0.3). Then the oxidation currents appear to increase almost linearly with the amount of Bi at the surface and the maximum is obtained for significantly high

coverages. For coverages higher than 0.72 the currents start to decrease. Leiva *et al* [27] published a simple model for describing the adatom effect on the electrocatalytic enhancement for formic acid oxidation on Pt modified single crystals that was satisfactory when compared with the experimental results. If we try to explain our results under this framework we can assume that in this particular case, Bi combines two effects for enhancing the EtOH oxidation on Pt/C – third body and electronic effect.

Assuming that ethanol adsorption requires several neighboring Pt sites and dissociates to form the poison (CO) [40], it could be expected that adatoms could act as a third body disturbing this poison formation by blocking some fraction of the surface sites. In a third body effect, adatoms are electrocatalytically inert and prevent the poisoning of the surface only by steric effects. As explained, poison formation is precluded at isolated sites or even small atomic domains free of adatoms. These are the only sites delivering a contribution to the increase on the oxidation current. The remaining wide areas of empty sites become completely poisoned. In this situation, negligible oxidation currents are expected at low coverage, since the probability of formation of catalytic units consisting of a substrate site surrounded by adatoms is very low. Appreciable activity appears when the coverage of adatoms increases over a threshold $\theta_{ad} > 0.5$, and a maximum is observed at $\theta_{ad} \approx 0.7$ in the case of ethanol.

On the other hand, for a true catalytic effect the adatom influence is expected to be observed for low coverages and increase linearly till at least half of the surface becomes covered by the adatom. Then, a maximum activity should be observed followed by a decrease of the catalytic currents due to the diminution of the uncovered, albeit very active, free platinum surface sites close to the adatoms.

In the present situation, the ethanol oxidation is enhanced already at low Bi coverages and the current increase is almost linear with the amount of adatom at the platinum surface. Based on these results we can suggest, due to the mixed behavior of the current intensity dependence on the Bi coverage that, Bi

irreversibly adsorbed on Pt/C in alkaline media enhances ethanol oxidation through a third body and an electronic effect (probably related with water adsorption as mentioned above).

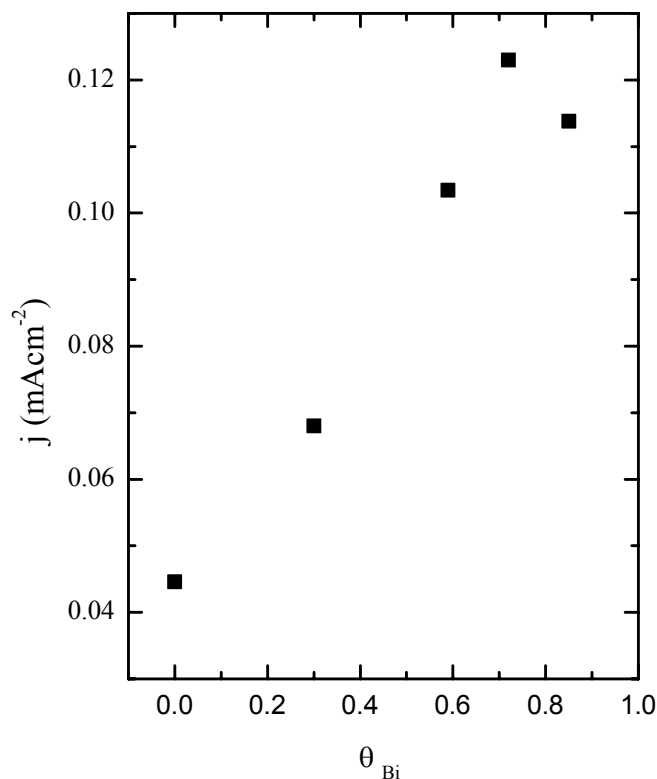


Figure 4 – Current intensity for ethanol oxidation at 0.5 V (vs. RHE) vs. Bi coverage at the Pt/C surface.

In order to gain further insights on the ethanol oxidation mechanism in alkaline media on PtBi surfaces FTIR experiments were performed. In the spectra presented in this paper, positive bands correspond to the products formed during ethanol oxidation, while negative bands account for the consumption of species present at the reference potential. The results obtained under controlled potential conditions for Pt and PtBi (with different coverages indicated in the corresponding figure labels) are presented in Figure

5, for two sample potentials, namely 0.4 and 0.7 V. Several bands can be observed in the spectra, a broad one between 2500 and 3000 cm^{-1} corresponding to the C-H region (2700–3000 cm^{-1}) which overlaps with other wide band denoting OH from carboxyl group between 2500 and 3000 cm^{-1} , a sharp band at 2341 cm^{-1} due to the asymmetric stretching of CO_2 and the bands at 1554 and 1417 cm^{-1} from O-C-O symmetric and asymmetry stretching (respectively) from acetate. The band corresponding to carbonate (possible reaction product) arises from the C-O stretching at 1390 cm^{-1} . However, it is likely overlapped with the acetate bands and can only be assigned after proper analysis, as it will be explained below.

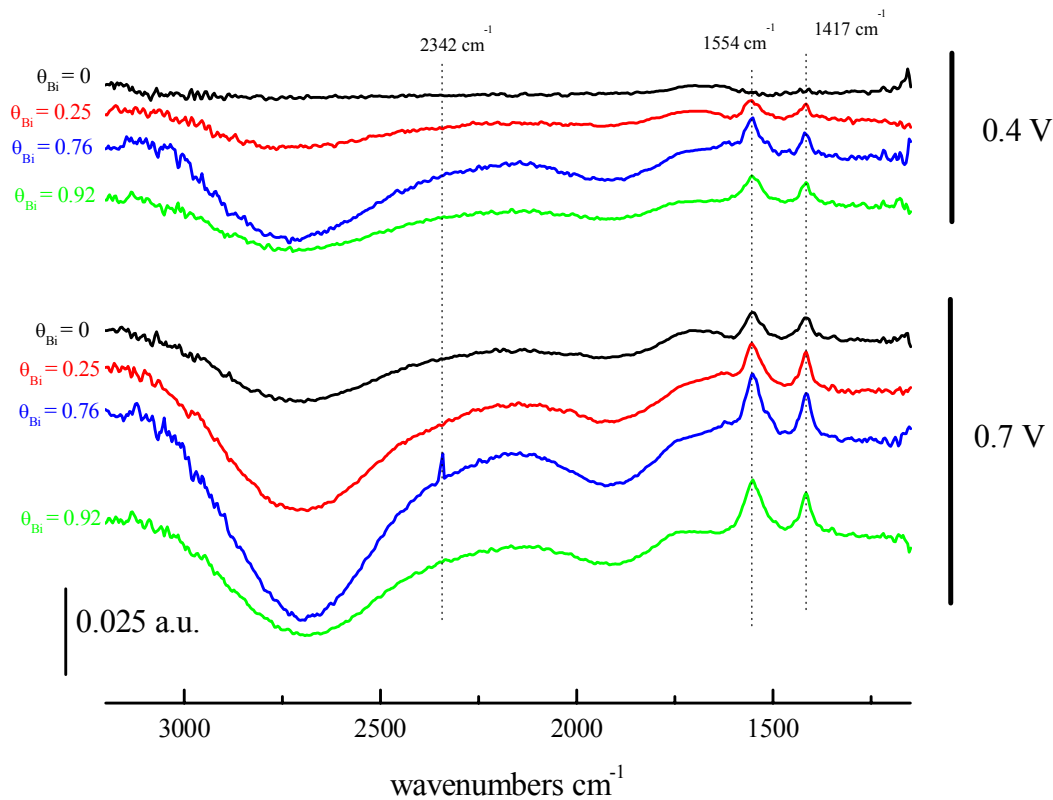


Figure 5 - Spectra obtained for ethanol oxidation on Pt and PtBi catalyst (coverage indicated in the figure), in 1M ethanol and 0.1 M NaOH with 100 scans and 8 cm^{-1} of resolution. The sample potential of each spectrum is indicated in the Figure. The reference spectrum was obtained at 0.1 V.

A first look into the spectra in Figure 5 shows that no drastic changes in the spectra are observed when comparing the surfaces with and without Bi. This results support our previous assumptions that the reaction mechanism is mainly the same in the presence of the adatom. In the pristine Pt electrode, at 0.4 V no bands due either to products formation or reactant consumption are observed, while bands at 1554 and 1417 cm^{-1} start emerging at this potential for Bi coverages as low as 0.25. When the Bi coverage increase these bands increase also, but at high Bi coverages (0.92) their intensity decreases again. The same behavior is observed in the broad band at 2500-3000 cm^{-1} , corresponding to ethanol consumption. These results support the previous findings from the cyclic voltammetry, showing that the presence of Bi in the electrode surface leads to a shift of the onset potential of the reaction to less positive potentials, in agreement with the appearance of product bands at lower potentials.

At 0.7 V, the behavior follows the same trend, higher band intensities are observed when increasing the Bi contents on the surface, followed by a subsequent decrease for coverages close to the surface saturation. Is worthwhile notice, that an unexpected band from CO_2 is observed for Bi coverage of 0.76 at 0.7 V. In alkaline media it is expected that all the formed CO_2 is hydrolyzed to carbonate band of which is difficult to distinguish from the acetate band appearing, as referred before, in the same wavenumbers. According with other reports [41] during EtOH oxidation a change on the local pH will exist due to the neutralization of the NaOH from the H^+ produced during the reaction. This effect is more pronounced in thin layer configuration, especially when high amount of CO_2 is produced. For these reasons, we assume that if the amount of the oxidized EtOH is high, more CO_2 is produced and higher pH changes will be observed, justifying the appearance of a band due to CO_2 in the IR spectra.

With the aim of shedding some light in the possible formation of carbonate (CO_3^-) by the catalysts a subtraction analysis of the spectra was done (Figure 6), following the procedure described by Zhou *et al* [41]. For this analysis, the transmission spectra of the acetate (A in Figure 6) was subtracted from the

reference spectra (B and D in Figure 6) resulting in spectra (C and E in Figure 6) where the acetate contribution was ruled out. A factor of 0.98 was introduced in this calculation in order to normalize the transmission spectra with the FTIR spectra. To find the appropriate value (that depends on the system configuration and the properties of the instrument) the transmission spectrum was subtracted from the sample spectra multiplied by different values till the value that suppressed the band at 1554 cm^{-1} was obtained. As it is possible to observe in Figure 6, when carbonate is produced (spectra E for PtBi) a band can be observed in the spectra resulting from the subtraction of the transmission spectrum from the sample spectrum.

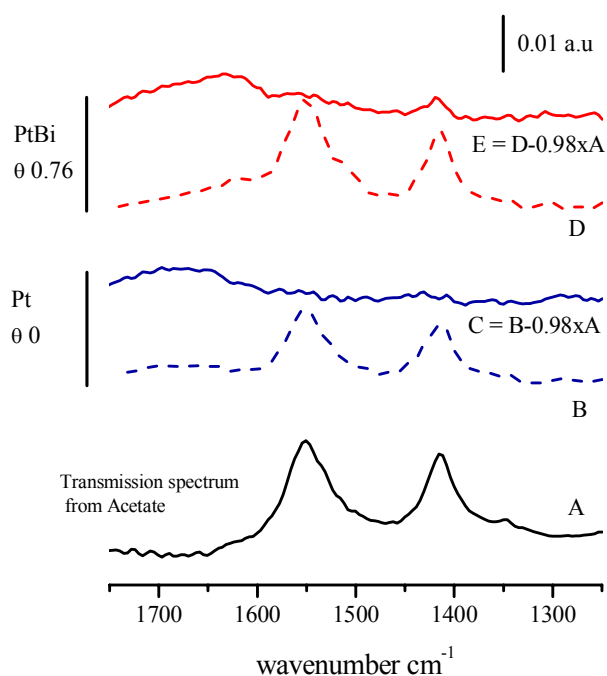


Figure 6 – Subtraction analysis for the identification of the carbonate band during ethanol oxidation for pure Pt and PtBi (0.76). A) transmission spectra for acetate; B) sample spectra at 0.7 V for Pt; C) spectra

resulting from the subtraction of A from B; D) sample spectra at 0.7 V for PtBi (coverage 0.76); E) spectra resulting from subtraction of A from D.

An overview of the results obtained with this analysis is given in Figure 7, where the area of bands for carbonate (from the subtraction), acetate at 1554 cm^{-1} and acetate + carbonate 1417 cm^{-1} are plotted as a function of the electrode potential for Pt and Pt with different Bi coverages on the surfaces.

The results in Figure 7 clearly show that PtBi with coverage of 0.76 is the electrode that leads to higher bands area for all the products in all the potentials, as expected from the fact that this surface gives higher current values for ethanol oxidation. The amount of carbonate for the unmodified Pt is almost negligible; suggesting the surface favors the incomplete ethanol oxidation into acetate. However, for all the surfaces with Bi, carbonate can be observed and at Bi coverage of 0.76 the largest band area for this compound are found. This results support our previous assumption that when the reaction rate is higher and more CO_2 is produced, the pH change in the surface is significant and in addition to the carbonate, CO_2 can also be observed in the FTIR spectra.

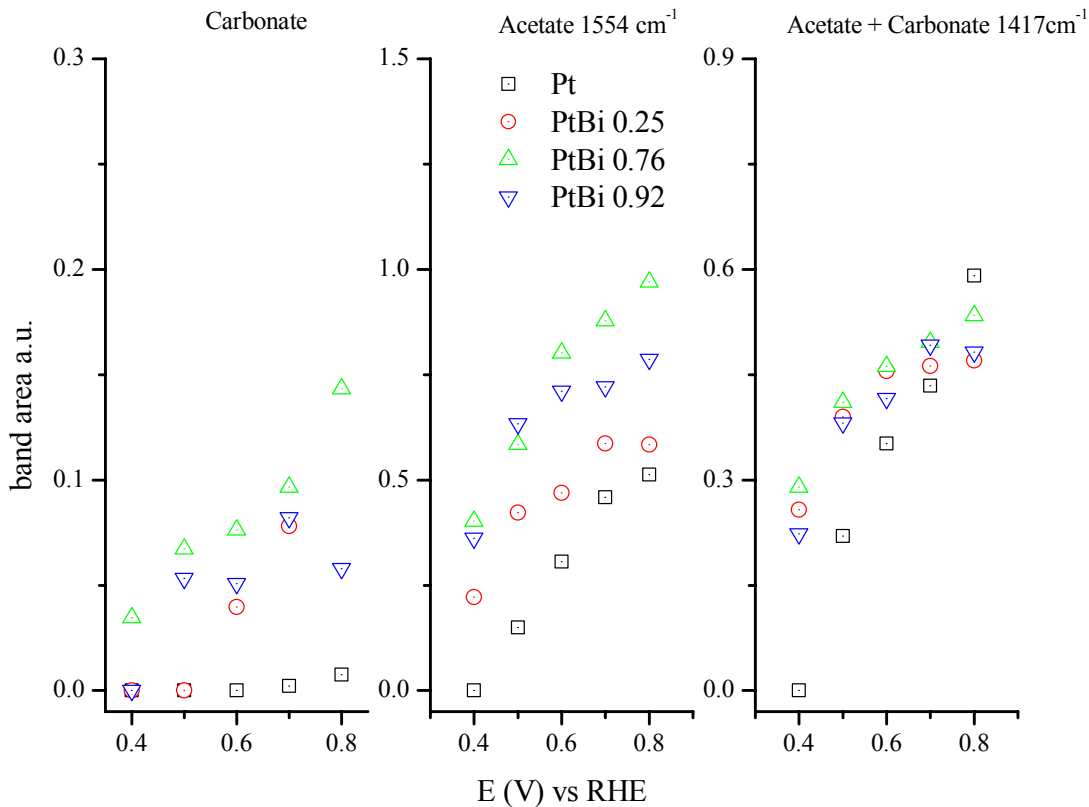


Figure 7 - Area of the bands for carbonate (from subtracted spectra), acetate (1554 cm^{-1}) and acetate + carbonate (1517 cm^{-1}) for Pt and PtBi (0.25, 0.76 and 0.92).

The FTIR results show, in agreement with cyclic voltammetry, that Bi enhances the reaction mechanism for the ethanol oxidation not only by a third body but also by an electronic effect (related with water adsorption). Bi provides necessary a surface ensemble with optimum adsorption energies of intermediates for the reaction to proceed at lower potentials and through the total oxidation of ethanol to CO_2 with optimum coverages being those when more than half of the Pt surface is covered by Bi adatoms. Results on the influence of the size of the carbon chain of the alcohol on the catalytic effect promoted by Bi irreversibly adsorbed on Pt catalysts are presented in the next section.

3.3. Other Alcohols

The results obtained for Pt and PtBi surfaces as catalysts for ethanol, methanol and propanol oxidation are presented in Figure 8. Methanol and propanol were chosen in order to have a smaller and a bigger molecule than ethanol.

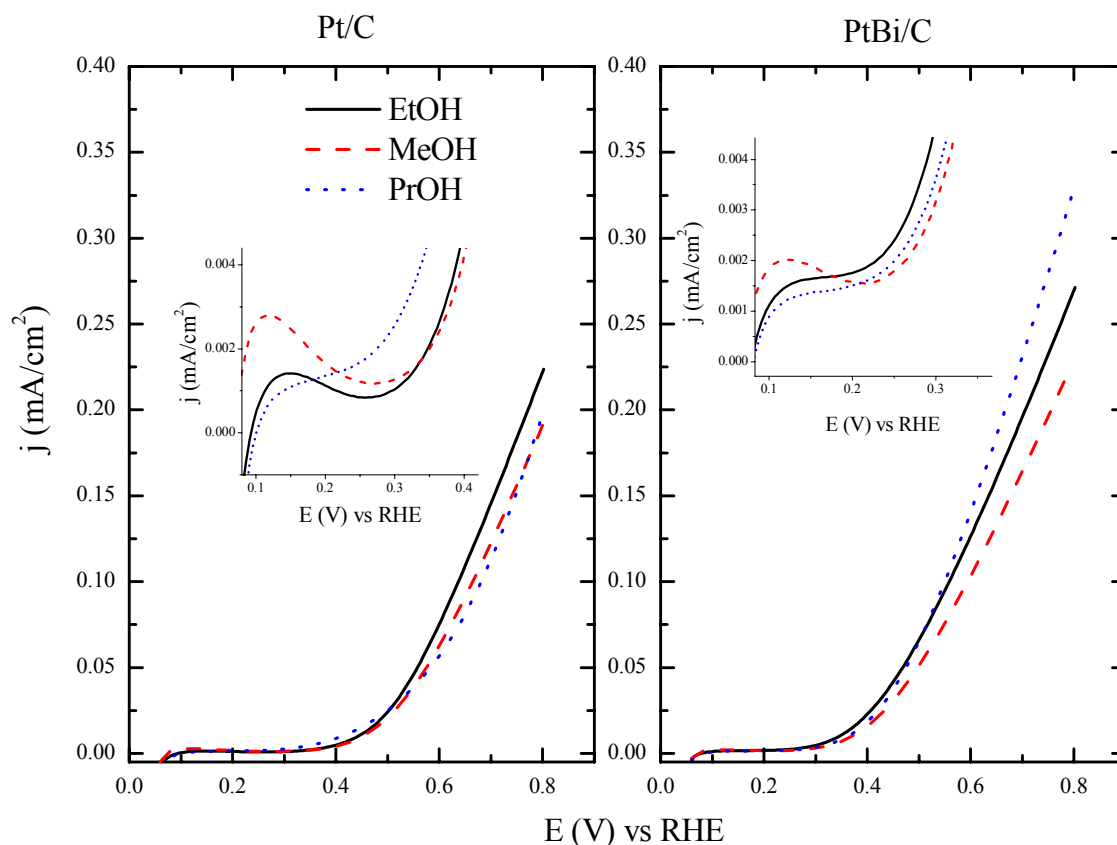


Figure 8 – Cyclic voltammograms for 1M ethanol, methanol and propanol oxidation in 0.1M NaOH at Pt and PtBi surfaces (Bi coverage: 0.72 – ethanol; 0.70 - methanol; 0.76 - propanol). Scan rate 10mV s^{-1} , 1800 rpm. For simplifying the figure only the positive sweeps are shown.

We can observe that the presence of Bi enhances the catalytic properties of Pt surfaces for the oxidation of all the studied alcohols. The onset potential of the reaction decreases and the maximum current densities are always higher in the presence of Bi. These results support the idea that Bi acts mainly as a

third body for the oxidation of these alcohols due to the non-specificity for the alcohol itself. In any case, other specific effects for each alcohol cannot be excluded. A deeper analysis of the Bi effect can be done by comparing these results with those reported in the literature for bimetallic PtBi nanoparticles. For methanol oxidation, PtBi nanoparticles have been studied in both alkaline and acid media [42-44]. In acidic media, no activity was shown by the PtBi intermetallic nanoparticles [43], however in alkaline media the activity was shown to be higher than for PtRu [44]. In relation to the onset potential values, Yang [42] reports only a small decrease when compared with Pt and Matsumoto [44] observed an increase of 100 mV of the onset in comparison with a PtRu catalyst. In our results, the methanol onset potential decreases 80 mV from 346 mV on pure Pt to 265 mV on PtBi (at 1800 rpm). When compared with results reported previously in our group for PtRu catalysts [45], the onset potential on PtBi is still 20 mV lower. We can suggest that the difference in these results is due to the structure of the catalysts. In the nanoparticles Pt and Bi are as an alloy or an intermetallic compound, in which Bi will be randomly distributed in the entire particle. In the Pt catalysts with irreversibly adsorbed Bi, the adatom is mainly on the surface of the catalyst. This fact is probably the reason for the higher activity observed, meaning that Bi is more effective on the Pt surface than when distributed in the whole particle.

The propanol oxidation has also demonstrated to be catalyzed by irreversibly adsorbed Bi on the Pt surface. Although the shift on the onset potential for this alcohol is smaller (only 20 mV) the increase on the current densities is the highest for the three investigated alcohols.

Chronoamperometric measurements at a fixed potential were performed in order to study catalyst poisoning [45] in the oxidation of ethanol, methanol and propanol. The electrode potential was stepped from 0.1 V to 0.5 V and was held at this potential (at which alcohols oxidation currents are observed in the CV) for over 30 min (2000 s) and the current was recorded versus time. The results are shown in Figure 9.

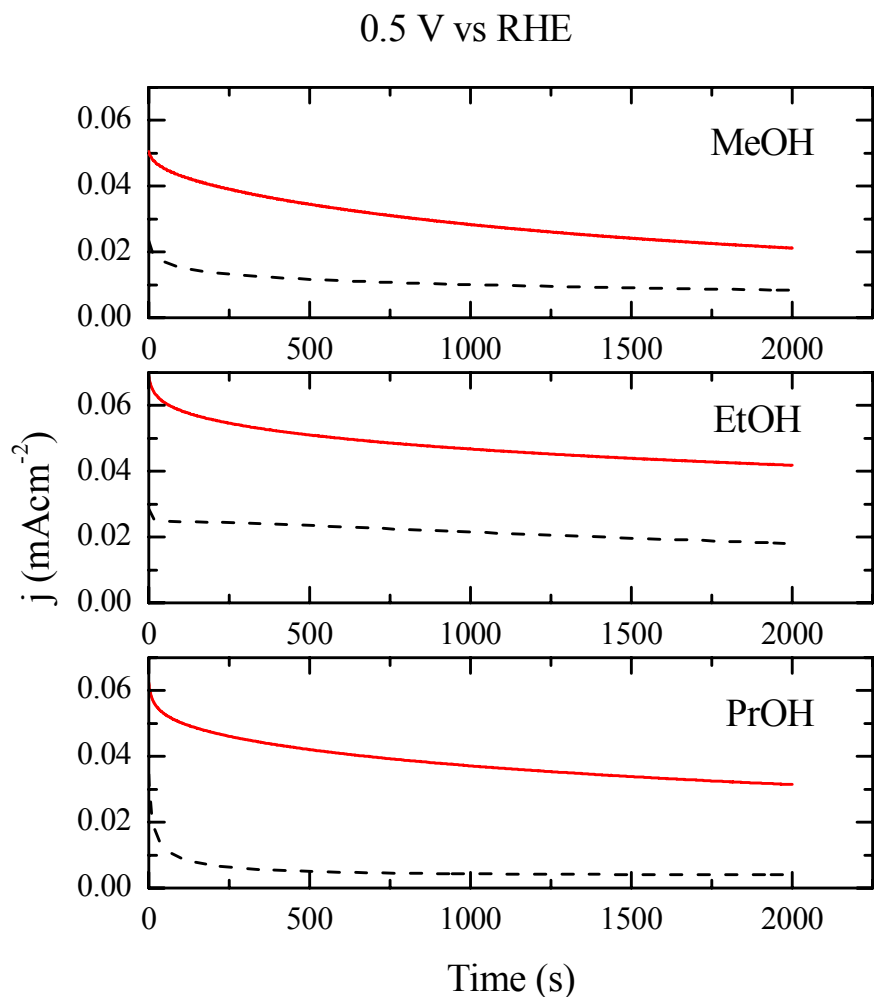


Figure 9 - Chronoamperometric curves for Pt/C (dashed) and PtBi/C (solid) for 2000 s at 0.5 V (vs. RHE) for ethanol, methanol and isopropanol 1M in 0.1 M NaOH, (Bi coverage: 0.72 – ethanol; 0.70 - methanol; 0.76 - propanol).

The enhancement of the catalytic activity for all the three alcohols when Pt is modified with Bi is clearly observed. Nevertheless, is interesting to observe that for MeOH, the deactivation of PtBi is faster than for the other two alcohols. In the first 250 s, the current is more than 3 times higher for PtBi than for pure Pt, however, after 30 min of the measurement this is only 2 times higher. This deactivation of the PtBi

surface also occurs for ethanol and propanol although it is not so pronounced. Table 2 summarizes the major results obtained for these alcohols oxidation at Pt and PtBi surfaces.

Table 2 – Shift on the onset potential and increase in the current intensities in Pt/Bi surfaces for methanol, ethanol and propanol.

Alcohol	Shift on the E onset @1800 rpm / mV	Increase in I at 0.5V after 2000 s
MeOH	- 81	2 x
EtOH	- 117	2.5 x
PrOH	- 20	8 x

FTIR measurements were also performed for Pt and PtBi surfaces for methanol and propanol oxidation (Figure 10) in order to evaluate the reaction products and intermediates of these reactions in the presence and absence of Bi on the Pt catalysts. Spectra for 0.4 and 0.7 V are given to compare the onset of the reaction and the potential where the full oxidation occurs on both catalysts.

For the methanol oxidation several bands can be observed in the spectra. Formate ions and carbonate are expected products from methanol oxidation at Pt surfaces [46]. The IR bands for these compounds are at 1587 and 1385 cm^{-1} for asymmetrical and symmetrical stretching of formate ions, respectively, and 1360 cm^{-1} for the carbonate ions (that can arise either directly from methanol oxidation or from hydrolysis of CO_2 in alkaline media). The latest can overlap with the band at 1385 cm^{-1} corresponding to formate. At 0.4 V, a band at 1587 cm^{-1} can be observed in the spectrum for Pt, suggesting that some formate starts to be produced at this electrode potential. However, for PtBi more bands are observed: a sharp band at 1574 cm^{-1} and two overlapped ones at 1385 and 1360 cm^{-1} . These bands clearly show that, first, more products is formed at this potential on the PtBi catalyst, and second, that in addition to formate also carbonate is

being formed, suggesting that Bi also favors the direct path for methanol oxidation. A few wavenumbers difference exists in the bands that we assigned to the formate asymmetric stretching on both the catalysts. This difference can be understood by the fact that formate is a species that adsorbs on the Pt surface, and as an adsorbed specie its vibration frequency will be sensitive to all the electronic changes on the surface (for example, adsorbed species band frequency decreases with the electrode potential due to the increase of the back donation mechanism between the molecule and the metal). The fact that the frequency of the formate asymmetric band decreases in the presence of Bi reveals the change on the electronic properties of the substrate Pt due to the adatom.

At 0.7 V, in pure Pt, formate and carbonate (overlapped with formate symmetric band) are observed as products of methanol oxidation as reported previously [46]. But, for the PtBi catalyst a very sharp band for CO₂ is observed at 2342 cm⁻¹ together with a band at 1360 cm⁻¹ due to carbonate formation. Formate is almost absent at this potential for PtBi, suggesting that Bi favors the direct path of methanol oxidation to CO₂ similarly to the observed previously for ethanol oxidation (section 3.2) but likely with higher selectivity, because other products are practically absent.

For propanol, the spectra show much more bands in the region between 1800 and 1200 cm⁻¹ when compared with ethanol or methanol. The first thing to notice, in the spectra for propanol, is the absence of CO₂ related bands for any of the catalysts. Similar bands are obtained for Pt and PtBi that only differ in intensity. At 0.4 V no bands are shown in the spectra for Pt, but they can be already observed for PtBi, showing the higher catalytic activity. At 0.7 V the same bands are present for both catalysts but they are more intense for PtBi, as expected.

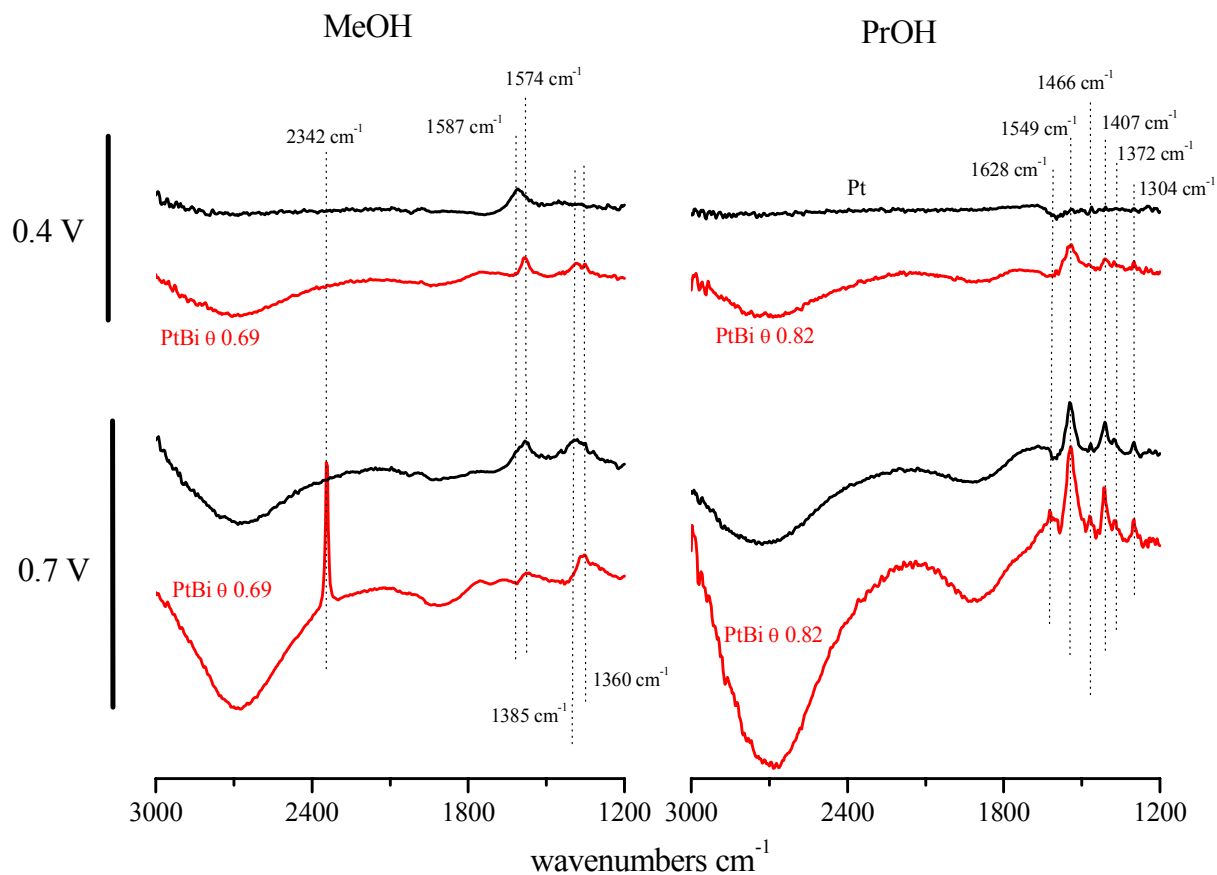


Figure 10 - Spectra obtained for methanol and propanol oxidation on the Pt and PtBi catalyst (coverage indicated in the figure), in 1M alcohol and 0.1 M NaOH with 100 scans and 8 cm^{-1} of resolution. The sample potential of each spectrum is indicated in the Figure. The reference spectrum was obtained at 0.1 V.

According with Schnaidt *et al.* [47], the bands present in the spectra can be attributed to: 1640 cm^{-1} C=O vibration mode from adsorbed propionyl species; 1466 , 1407 , 1372 and 1304 cm^{-1} to OCO stretching and CH_x bending modes from adsorbed propionate. The band at 1549 cm^{-1} was assigned to the C=O modes of some other, strongly bonded adsorbate product, from propanol oxidation. From these, we can

suggest that propionyl and propionate are the main products from propanol oxidation at Pt and PtBi catalysts in alkaline media, and the oxidation follows the same mechanism in both the catalysts although with higher rates at PtBi.

Summarizing, the FTIR experiments show that the reaction mechanism on the Pt/C modified by Bi adatoms follows different paths depending on the alcohol. For methanol (smallest carbon chain) the oxidation reaction on PtBi undergoes preferentially by the complete oxidation path and CO₂ (or carbonate) is the main oxidation product. In the case of propanol, although the activity is enhanced, the mechanism is still the incomplete oxidation to propionyl and propionate and no CO₂ was observed with the PtBi catalyst. For ethanol, PtBi leads to the increase of the oxidation rate with an intermediate behavior: CO₂ (carbonate) can be obtained in the presence of Bi on the platinum surface, though other less oxidized products (acetate) are also formed. In this case, both complete and incomplete oxidation paths coexist.

3.4. Conclusions

This work reports the enhancement of the catalytic activity of Pt/C modified with irreversibly adsorbed Bi in alkaline media. The presence of the adatom increases the catalytic oxidation of ethanol, and also methanol and propanol, both in current intensities and onset potentials. Bi increases the activity of Pt toward the oxidation of the referred alcohols by acting as a third body (impeding Pt surface poisoning) and by an electronic effect disruption of the water network on the platinum surface. Comparing the results obtained for the three studied alcohols, we can say that Pt surfaces modified with Bi are more active for the oxidation reaction for all of them when compared with pure Pt. The increase in the reaction rate increases with the size of alcohol and the catalytic effect follows the order methanol < ethanol < propanol. Nevertheless, the catalytic activity toward the direct oxidation of the alcohol to CO₂ follows the reverse

trend propanol<ethanol<methanol. In any case, Pt/C catalysts modified with irreversibly adsorbed Bi are definitely good candidates as catalyst for practical fuel cell applications.

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