Behaviour of Bimetallic Pt–Pd Carbon-Supported Catalysts in Methanol Electrooxidation

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Carbon powder supported bimetallic 8w%Pt+8w%Pd/C, 8w%Pt+6w%Pd/C, 8w%Pt+4w%Pd/C, 8w%Pt+2w%Pd/C, 8w%Pt/C and 8w%Pd/C samples were prepared, characterised and tested for the electrooxidation of methanol. The particle sizes were found to depend greatly on the composition and the metal content. With pure palladium and samples rich in palladium, the diameter of the bimetallic particles was around 150 nm, but with pure Pt and samples poor in Pd it was much smaller, below 5 nm. The electrocatalytic activity of these catalysts was determined by cyclic voltammetry and polarization curves. Compounds with 33 and 43 at%Pd were the most active catalysts for the methanol oxidation reaction. A good correlation was obtained between electrochemistry and *in situ* infrared reflectance spectroscopy results.

Key words: Carbon Supported Platinum-Palladium Catalysts, Methanol Electrooxidation, *in-situ* Infrared Reflectance Spectroscopy, SNIFTIRS and SPAIRS

1. Introduction

In acid medium, the electrocatalytic oxidation of methanol needs platinum as a basic component. During the last decades, there has been great interest in this reaction, mainly in relation with the possible use of methanol as a fuel for the direct methanol fuel cell, DMFC [1–3]. Platinum is necessary as an electrode material for the first step of the reaction mechanism which consists of a dissociative adsorption of methanol with the breaking of C–H bonds. Several adsorbed species are then formed [4–5]. Some of these are strongly adsorbed and act as poisons, and others are more weakly adsorbed and act as reactive intermediates, which can be easily removed from the electrode surface to give the final product, carbon dioxide. It is possible to break down the mechanism into two different paths:

a. Methanol → Reactive intermediates → CO_2 at moderate potential
b. Methanol → Poisoning intermediates → CO_2 at high potential

The key role of the poison species is now widely accepted after their identification [1]. Adsorbed CO is the main poison and its presence at the surface inhibits further oxidation of methanol. Therefore, removing of adsorbed CO or prevention of its formation are key parameters to increase the rate of the methanol oxidation reaction.

The reaction step for the removal of adsorbed carbon monoxide at the platinum electrode as carbon dioxide is given below:

$$Pt-CO_{ads} + Pt-OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^-$$
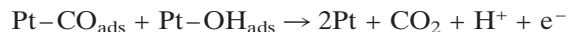
The formation of $Pt-OH_{ads}$ is reputedly difficult, above *ca.* +0.7 V *vs.* RHE, therefore metals, such as Ru [6–8] and Sn [9], which dissociate water at low potentials can be used as catalysts.

In petrochemistry, bimetallic Pt+Pd catalysts are used for the oxidation of carbon monoxide to carbon dioxide [10]. They are also used for the electrocatalytic oxidation of other organic molecules such as methanol [11], formic acid [12] and D-glucose [13]. It was found that addition of palladium to platinum modifies the electrocatalytic behaviour of the electrode drastically because of a decrease in the poisoning species on the catalyst surface. However, only a very limited number of studies on bimetallic Pt+Pd catalysts for methanol oxidation reaction was carried out. Therefore, in this study, the electrooxidation of methanol on carbon supported bimetallic Pt+Pd catalysts, with different percentages of Pt and Pd, has been followed by cyclic voltammetry and in-situ FTIR

studies. Electron microscopy was used to characterise the catalysts.

2. Experimental Section

2.1. Preparation and characterisation of the catalysts

8w%Pt+2w%Pd/C: 0.7 g of carbon powder, Vulcan XC-72, was sonicated 30 min in 300 ml of water. This suspension was then heated to 80 °C and 0.1651 g of $H_2PtCl_6 \cdot 6H_2O$ and 0.0366 g of H_2PdCl_4, dissolved in water, were added separately followed by sufficient $NaHCO_3$ dissolved in water to neutralise the protons liberated from the acidic solutions. After heating for 2.5 h, reduction was carried out by adding an excess of concentrated HCHO solution, and the temperature was maintained for 2 h. After filtration, the sample was thoroughly washed with 1.5 l of boiling water and finally dried at 100 °C overnight.

The other catalysts were prepared according to the same procedure, with the appropriate amounts of $H_2PtCl_6 \cdot 6H_2O$ and H_2PdCl_4 stock solutions and $NaHCO_3$. Pure platinum and palladium on carbon powder (Pt/C and Pd/C) were prepared with the same method for the sake of comparison.

The samples were characterised by transmission electron microscope. A Philips CM 120 instrument with a LaB_6 electron source operating at 200 kW was used to visualise the samples. An electron dispersive X-ray detecting system, EDAX, which is attached to the TEM, was used to analyse the samples. The spatial resolution of the EDAX probe is 0.3 nm.

2.2. Electrochemical measurements

Electrodes were prepared from 37.5 mg powder sample (Pt+Pd/C) sonicated in 0.5 ml of Nafion® solution, 5% from Aldrich, dilute in 2.5 ml of water. 0.15 ml of N,N-dimethyl formamide was added in order to obtain a smoother and more homogeneous electrode surface, which is particularly useful for IR measurements. 20 microliter of the resulting ink was dropped on a glassy carbon or gold disk electrode, 0.7 cm diameter, and heated to 40 °C for 20 min and finally to 100 °C for 1 h to eliminate the solvents.

The electrocatalytic activity of the catalysts for the electrooxidation of methanol was measured at room temperature using a Wenking PGS 95 potentiostat/galvanostat in 0.15 M $HClO_4$ (Merck Suprapur grade) aqueous solution, containing 0.5 M CH_3OH (Merck pro analysi). The solution was previously deoxygenated with nitrogen gas of high purity (Air Liquide). The counter and reference electrodes were a glassy carbon sheet and a reversible hydrogen electrode, RHE, respectively. Polarization measurements were carried out using the same equipment, and measurements were taken for each 50 mV during 10 min.

2.3. Infrared measurements

A Bruker IFS 66v instrument with a HgCdTe detector (Infrared Associates) was used to record *in situ* infrared reflectance spectra with a resolution of $4\,cm^{-1}$ [6, 14]. Two different techniques were used to obtain the spectra. These are the Subtractively Normalized Interfacial Fourier Transform Infrared Reflectance Spectroscopy, SNIFTIRS, and the Single Potential Alteration Infrared Spectroscopy, SPAIRS. Information obtained from these two techniques is somewhat different and complementary: SNIFTIRS is suitable mainly to detect adsorbed species, and SPAIRS gives information on the products formed and present in the reaction layer. SPAIRS records a voltammogram at a low sweep rate, typically $1\,mV\,s^{-1}$, and spectra calculated after the averaging of 128 interferograms. The spectrum at a given potential is calculated as $(R-R_{ref})/R_{ref}$, where R_{ref} is the reference spectrum which is taken for example at the lower potential limit of the scan. With the second technique, SNIFTIRS, 128 interferograms are recorded successively at two different potentials, 40 times, and averaged. Resulting spectra were calculated as $[R(E_2)-R(E_1)]/R(E_1)$, where E_1 and E_2 were chosen in the potential region of interest.

3. Results and Discussion

3.1. Characterisation of metal particles

The particle size and distribution of metals, Pt and Pd, on carbon support have been determined by transmission electron microscopy for all samples. For the 8w%Pt/C powder sample the vast majority of the particles are between ~1 and ~5 nm diameter (Fig. 1a). There is also evidence for a very small amount of larger particles including some up to ~10–20 nm. However, electron micrographs of 8w%Pt+2w%Pd/C show the presence of both small, ~2–10 nm, and agglomerated large particles, ~35–65 nm without any one dominating (Fig. 1b). EDAX analysis results on these metal particles are very close to theoretical values such as platinum percentage changes between ~78 to 82% (Fig. 1c). The particle size of
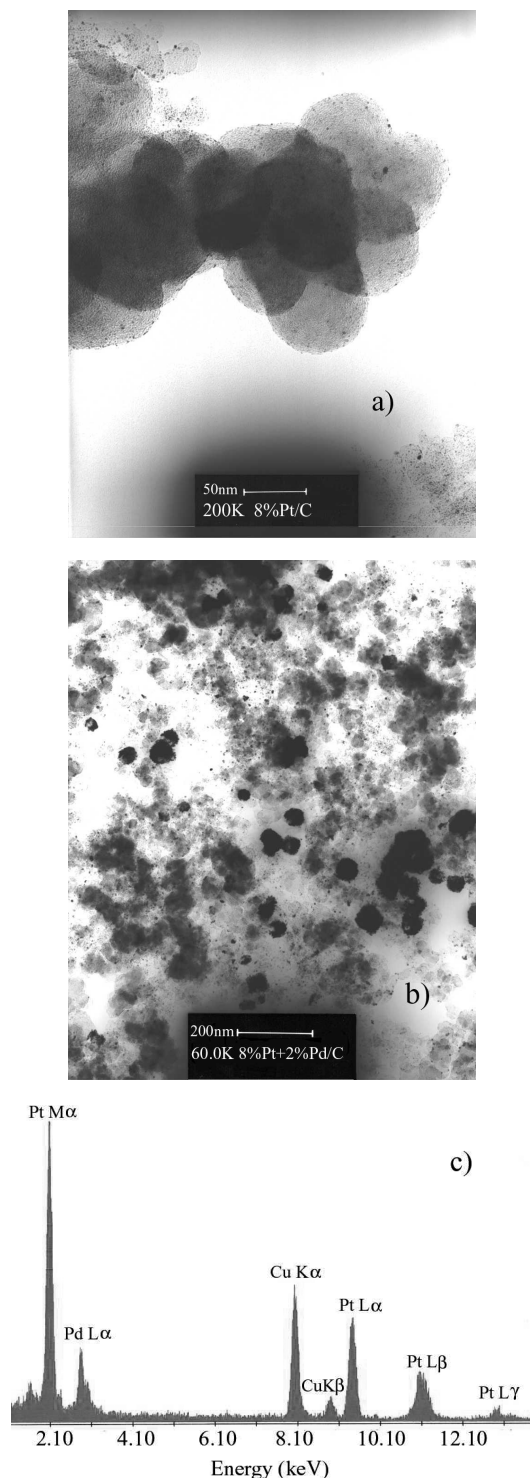
Fig. 1. Electron micrographs of a) 8w%Pt/C; b) 8w%Pt+2w%Pd/C; c) EDAX analysis results for metal particles in 8w%Pt+2w%Pd/C.

8w%Pt+4w%Pd/C can be divided into three groups. The first group comprises a small amount of large square particles, ~200 nm, with a ~50w%Pd and ~50w%Pt composition. Other groups include two types of agglomerated particles with different constitution such as ~5–10 nm particles with a ~5–15w%Pd and 95–85w%Pt, and ~25–35 nm particles with a 25–40w%Pd, 75–60w%Pt composition. Transmission electron micrographs of powder samples of 8w%Pd+6w%Pd/C show two types of particle distributions. One which has platinum rich particles, ~96–93w%Pt, with a smaller size ~4–20 nm compared to the other which has ~40–110 nm particle size with a ~40–50w%Pd and ~60–50w%Pt compositions. The particles observed in TEM studies of the 8w%Pt+8w%Pd/C powder sample show a different trend to that found in the other powder samples. Almost all particles are in the range of ~60–100 nm diameter, and are uniformly distributed on carbon support. The particle compositions changes between ~55–45w%Pt and ~45–55w%Pd which is in agreement with the theoretical values. The final type of distribution is found for the 8w%Pd/C powder sample. The electron micrographs show that most of the particles are between ~50–250 nm diameter, with a small number of extremely small particles, up to 0.5 nm diameter. The different particle sizes and the estimated surface area are summarized in Table 1 for the different catalysts.

From the TEM observations, it is clear that the size of the particles changes mainly with the composition, but the calculated area of the electrode also varies from 0.6 cm^2 for pure Pd to 17.7 cm^2 for pure platinum. Moreover, as the amount of both metals is known from the initial amount used for the synthesis and by taking into account the composition of each kind of particles as determined by EDAX, it becomes possible to estimate the real surface area of the electrodes. For these estimations, the particles are taken as small ideal spheres (Table 1).

3.2. Electrocatalytic activities

The electrocatalytic activities of the catalysts were evaluated by cyclic voltammetry. The results for 8w%Pt/C, 8w%Pt+4w%Pd/C and 8w%Pt+2w%Pd/C, in supporting electrolyte, 0.15 M

Samples	Particle size in nm	Composition in w%Pd	Estimated electrode active area in cm^2 if only one kind of particles were present
8w%Pt/C	1 to 5	0	17.7
8w%Pt+2w%Pd/C	2 to 10	18 to 22	12.2
	35 to 65	18 to 22	1.5
8w%Pt+4w%Pd/C	200	50	0.5
	5 to 10	5 to 15	11.1
	25 to 35	25 to 40	3.1
8w%Pt+6w%Pd/C	4 to 20	4 to 7	8.0
	40 to 110	40 to 50	1.7
8w%Pt+8w%Pd/C	60 to 100	45 to 55	1.7
8w%Pd/C	50 to 250	100	0.6

Table 1. Size and composition of the different particles observed by TEM for the supported catalysts. Estimated electrode active area by assuming particles as spheres.

$HClO_4$, at 5 mV s^{-1}, are given in Fig. 2. Hydrogen adsorption and evolution are observed with a broad and sharp peak in the cathodic region for 8w%Pt/C. Conversely, the formation of adsorbed hydrogen is not detected for catalysts containing a significant amount of palladium. It is well known that Pd does not adsorb hydrogen, but formation of palladium hydride is generally observed with bulk Pd [15]. No such phenomena was observed for the catalysts in this work, possibly due to the dispersion of the metal particles onto carbon. The broad peak for hydrogen desorption observed for 8w%Pt/C disappears as the amount of Pd increases. Finally, a shift in potential is observed for the cathodic peak corresponding to the reduction of metal oxide formed during the anodic sweep.

In the presence of 0.5 M of methanol in 0.1 M $HClO_4$ solution, current peaks demonstrate significant activity of these materials for the electrooxidation of methanol (Fig. 3). All currents given in Fig. 3 are rough currents recorded with the electrodes as mentioned in the experimental section. No corrections for the metal amount or the real area were made for this figure. Methanol oxidation on the 8w%Pt/C electrode is observed during the anodic sweep around 400 mV after the hydrogen desorption region. Above 930 mV methanol oxidation is inhibited and the anodic current decreases prior to the increase in the region where the metal oxide is formed. During the reverse scan, methanol oxidation starts again around 700 mV, *i.e.* after the reduction of platinum-oxide. The methanol oxidation starting potential and the maximum potential of the oxidation peak are shifted towards more negative potentials for bimetallic catalysts especially for 8w%Pt+4w%Pd/C. Methanol oxidation starts near 300 mV and reaches its maximum around 800 mV for this cata-
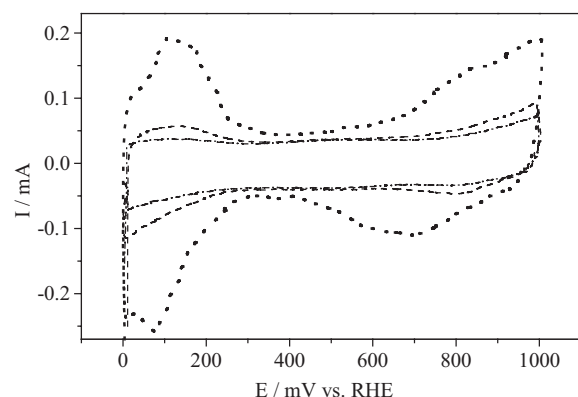

Fig. 2. Voltammograms of 8w%Pt/C (…), 8w%Pt+4w%Pd/C (– . –) and 8w%Pt+2w%Pd/C (– –) electrodes in 0.15 M $HClO_4$ at a sweep rate of 5 mV s^{-1} and at room temperature.
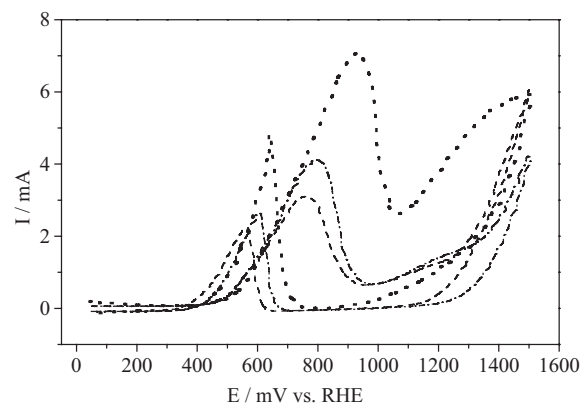

Fig. 3. Voltammograms of 8w%Pt/C (…), 8w%Pt+4w%Pd/C (– . –) and 8w%Pt+2w%Pd/C (– –) electrodes in 0.15 M $HClO_4$ + 0.5 M CH_3OH at a sweep rate of 5 mV s^{-1} and at room temperature.

lyst. Fig. 4 displays a comparison of the voltammograms recorded for all samples prepared in this work, in the potential region 200–500 mV *vs.* RHE. 8w%Pd/C is not considered in this figure as it does not show any electrocatalytic activity towards methanol oxidation in this region, as expected from previous observations in acidic medium. The poor activity observed from the 8w%Pt+8w%Pd/C should be noted, which is an unexpected finding, probably related to the size of the particles, which leads to a rather low active area compared to the other samples.

One other way to evaluate the electrocatalytic activity of the electrode is to acquire the polarization curves at different potentials, *i.e.* to record the variation of the current at constant potential during a given time. Figures 5a, b and c give a comparison of the behaviour of the different catalysts, excluding Pd, for three different times, 20 s, 1 min and 10 min. Such a comparison shows possible modifications of the activities with time in correlation with the metal composition. If we focus on the region where the oxidation of methanol begins, *i.e.* between 250 and 500 mV, it clearly appears that the 8w%Pt+4w%Pd/C catalysts is again the most efficient one. With this composition the oxidation of methanol begins at the lowest potential. As already noticed above, the 8w%Pt+8w%Pd/C catalyst exhibits a poor activity, even in this potential region, in contrast to 8w%Pt+6w%Pd/C which is more active than 8w%Pt/C. Finally, 8w%Pt+2w%Pd/
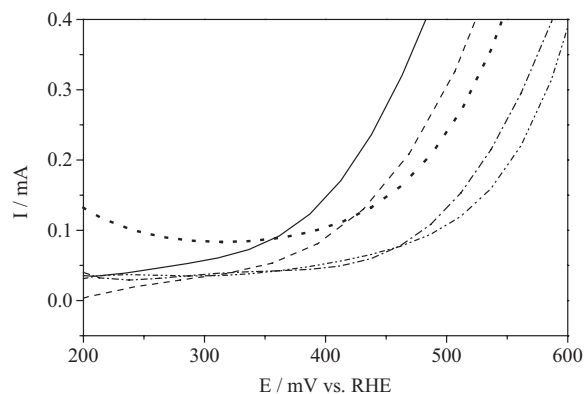

Fig. 4. Voltammograms of 8w%Pt/C (…), 8w%Pt+2w%Pd/C (−..−), 8w%Pt+4w%Pd/C (—), 8w%Pt+6w%Pd/C (− −), 8w%Pt+8w%Pd/C (−.−) electrodes in 0.15 M HClO$_4$ + 0.5 M CH$_3$OH at sweep rate of 5 mV s^{-1} and at room temperature. Only expanded part of the curves are shown here, 200–500 mV *vs.* RHE.
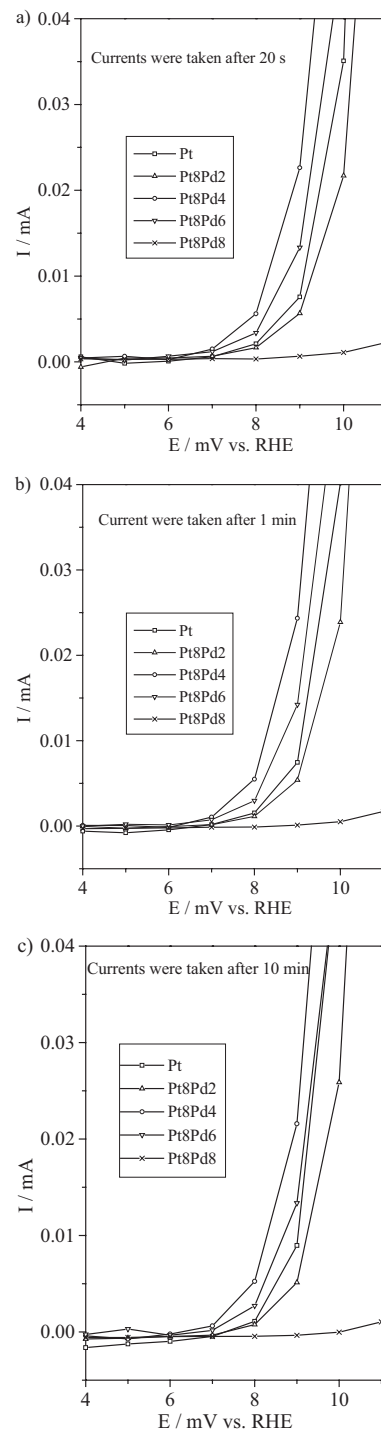

Fig. 5. Polarization curves of different metal/C electrodes in 0.15 M HClO$_4$ + 0.5 M CH$_3$OH, for currents taken after: a) 20 s; b) 1 min; c) 10 min at a given potentials. Potential range: 200–550 mV *vs.* RHE. Rough current values are given.

C appears slightly less active than pure platinum. This confirms that Pd acts similarly to other metals, such as Ru, Sn and Mo [16], which have been proposed to enhance the activity of platinum for the oxidation of methanol. Pd is efficient only in the potential region below 600 mV, *i.e.* in a region where it favours the coverage of the electrode by adsorbed OH species, necessary to oxidize species adsorbed on the platinum sites.

The general trend is confirmed when the current is corrected with the real surface area, as estimated in Table 1, and of the total metal amount present in each electrode preparation. It should be noted that the amount of Pt in the carbon powder was kept constant for all catalysts, 8%, with addition of 2 to 8% of Pd. Figures 5a, b and c were redrawn considering the real surface area and composition of the metal as shown in Figures 6a, b and c. Except for 8w%Pt+8w%Pd/C which is the least active one, the two other bimetallic compounds are more active than Pt, with an advantage for 8w%Pt+4w%Pd/C. However, at a potential above 550 mV the difference in the activity of the catalysts is not so clear if we take into account the estimated active area, (Fig. 7b). The pure platinum electrocatalyst presents the highest current, but with only small differences from the three bimetallics having 2, 4 and 6w%Pd/C. 8w%Pt+8w%Pd/C is clearly the least active. Concerning these polarization experiments, a final remark relates to the active area. It is clear that an accurate estimation of the real active area of the metals is difficult, but with a simple calculation as done above it is possible to compare the true activities of the electrodes. The currents in a wide range of potential, Fig. 7a, may lead to the conclusion that Pt is clearly the most active electrocatalyst, which however is not the case in the low potential range.

3.3. Spectroscopic measurements

In situ infrared reflectance spectroscopy is widely known to be a suitable method to observe species adsorbed at the surface of an electrode during the electrochemical process (poisons and intermediates) and to follow modifications in their distributions during potential sweeps. The best results are obtained for smooth surfaces with good reflectivity. It is obvious that the electrodes considered in this work are not ideal for this purpose,
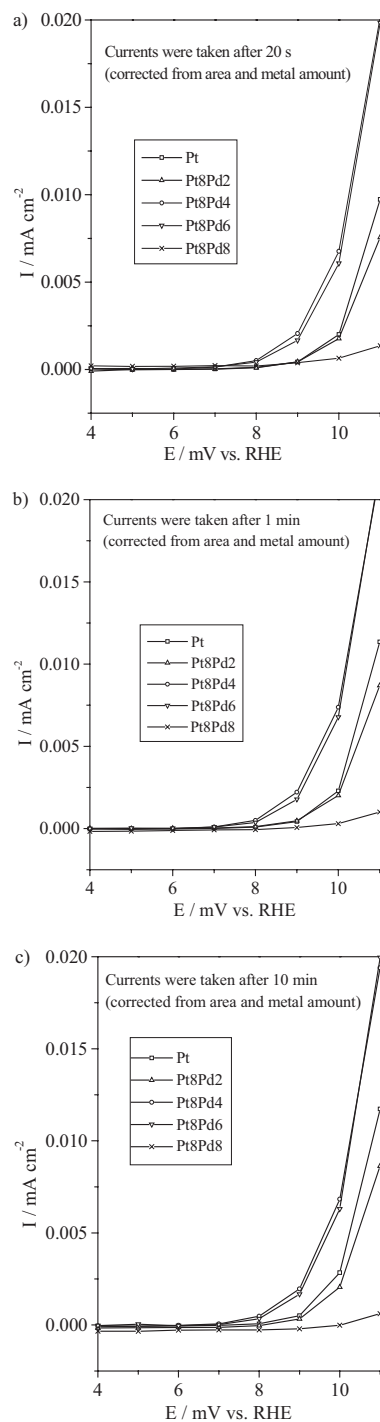

Fig. 6. Polarization curves of different metal/C electrodes in 0.15 M $HClO_4$ + 0.5 M CH_3OH, for currents taken after: a) 20 s; b) 1 min; c) 10 min at a given potential. Potential range: 200–550 mV *vs.* RHE. Current densities after estimation of the real active area.
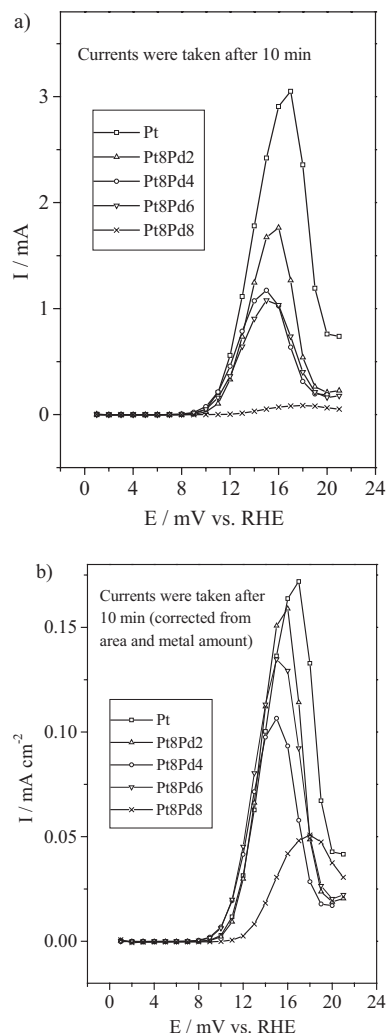
a)

b)

Fig. 7. Polarization curves of different metal/C electrodes in 0.15 M HClO$_4$ + 0.5 M CH$_3$OH, for currents taken after 10 min at a given potential. Potential range: 0–1050 mV *vs.* RHE. a) curve with rough current; b) after correction with the estimated active area.

but it was demonstrated recently [17] that even with rather poor reflectivity properties, FTIR reflectance spectroscopy is a good tool to obtain information about the surface to allow mechanistic considerations.

As mentioned in the experimental section, two different ways to record the spectra were used during this work. By SPAIRS, the information obtained is not only for the surface but also for the products formed and present close to the surface. The SNIFTIRS technique is more efficient to get insights about the adsorbed species present during the electrocatalytic reaction.

Typical SPAIR spectra are given in Fig. 8 for 8w%Pt/C and the four bimetallic compounds 8w%Pt with 2, 4, 6 or 8w%Pd. In addition to bands corresponding to the electrolyte, perchlorate around 1110 cm^{-1}, and interfacial water, 1640 cm^{-1}, the main band at 2350 cm^{-1} observed during this work corresponds to the formation of carbon dioxide. Table 2 summarises the values of the potential at which the formation of carbon dioxide occurs for the different electrodes studied.

As CO$_2$ is the final product of the electrooxidation of methanol, a first approach to interpret these values is to correlate the appearance potential with the oxidation process. However, if we compare these values with the observations described above for the electrocatalytic activity, some discrepancies are obvious. The 8w%Pt+ 4w%Pd/C and 8w%Pt+6w%Pd/C samples appeared to be the most electroactive at low potentials from pure electrochemical studies (see above), however, the carbon dioxide formation for these samples is observed at rather high potentials, which is unexpected. On the other hand, CO$_2$ is formed at high potentials on 8%wPt+8w%Pd/C which confirms its low electroactivity.

The differences in the results between these two techniques can be related to the mechanism of the electrocatalytic oxidation. Although carbon dioxide is clearly the final oxidation products in all the cases, some other intermediates such as formic acid or more probably formaldehyde can also be formed mainly with the bimetallic compounds, 8w%Pt+4w%Pd/C and 8w%Pt+6w%Pd/C. It is well known from fundamental works that aldehyde intermediates are formed during the oxidation of methanol on platinum [1, 2]. On pure plati-

Electrode	8w%Pt/C	8w%Pt+ 2w%Pd/C	8w%Pt+ 4w%Pd/C	8w%Pt+ 6w%Pd/C	8w%Pt+ 8w%Pd/C
Potential (mV)	450	550	550	500	600

Table 2. Starting potential for CO$_2$ formation as determined by SPAIRS.

num, the oxidation continues rapidly towards carbon dioxide for potentials greater than 0.6 V *vs.* RHE. In the presence of palladium, it seems that the oxidation peak observed at rather low potential during pure electrochemical measurements is not only due to the formation of CO_2, but probably also to the formation of a significant amount of formaldehyde. Unfortunately, the SPAIRS spectra recorded during this work are too noisy (due to the poor reflectivity of the electrodes containing carbon powder) to give a definitive answer concerning the presence of aldehyde groups. Bands in the region around 1720 cm^{-1} are expected which are not detectable in Fig. 8.

SNIFTIR spectra are presented in the Fig. 9 for the same electrodes. As in the previous case, it is possible to list the potential values corresponding to the formation of carbon dioxide (Table 3).

Even if some differences exist with the SPAIRS results, the trend is similar and 8w%Pt+8w%Pd/C is the least active electrocatalyst and 8w%Pt+2w%Pd/C gives poor results. For the three other electrodes, the potentials at which carbon dioxide appears are similar, possibly since SNIFTIRS
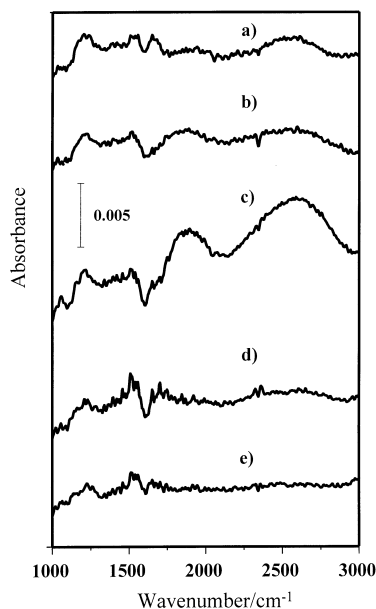

Fig. 9. SNIFTIR spectra taken in 0.15 M $HClO_4$ + 0.5 M CH_3OH as a function of the potential modulation from top to bottom: a) 8w%Pt/C [0.15 V−0.45 V], [0.35 V−0.65 V], [0.55 V−0.85 V]; b) 8w%Pt+2w%Pd/C [0.15 V−0.45 V], [0.35 V−0.65 V], [0.45 V−0.75 V], [0.55 V−0.85 V]; c) 8w%Pt+4w%Pd/C [0.15 V−0.45 V], [0.35 V−0.65 0.65 V], [0.55 V−0.85 V], d) 8w%Pt+6w%Pd/C [0.15 V−0.45 V], [0.35 V−0.65 V], [0.55 V−0.85 V].

Fig. 8. SPAIR spectra recorded during the oxidation of 0.5 M CH_3OH in 0.15 M $HClO_4$. Reference spectra taken at 0.0 V. a) 8w%Pt/C at 0.45 V *vs.* RHE; b) 8w%Pt+2w%Pd/C at 0.55 V *vs.* RHE; c) 8w%Pt+4w%Pd/C at 0.55 V *vs.* RHE; d) 8w%Pt+6w%Pd/C at 0.50 V *vs.* RHE; e) 8w%Pt+8w%Pd/C at 0.60 V *vs.* RHE.
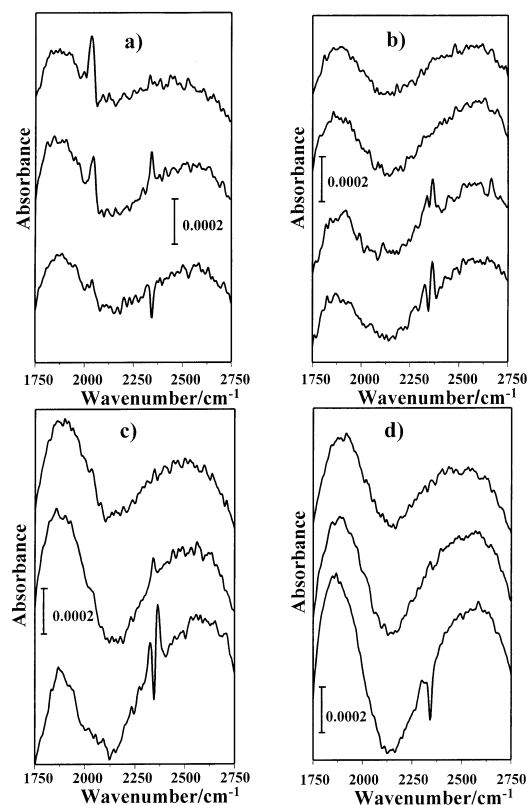
needs a potential modulation with a difference of 300 mV, which can not be decreased further due to the rather weak signal from the rough surface of the electrode. The result is a lack of accuracy in the determination of the potential at which a band appears.

In Fig. 9 an important band is clearly visible for 8%Pt/C, at 2050 cm^{-1} which corresponds to adsorbed CO. This band is the fingerprint of a poisoning phenomenon, adsorption of CO, observed during the electrooxidation of various oxygenated organic compounds. Adsorbed CO is also visible in the SNIFTIR spectra for 8w%Pt+2w%Pd/C and 8w%Pt+4w%Pd/C samples, but the corresponding band is much weaker than for 8w%Pt/C. Conversely, with 8w%Pt+6w%Pd/C no band cor-

Table 3. Starting potentials for CO_2 formation, determined by SNIFTIRS. Average values corresponding to the two potential modulation limits.

Electrode	8w%Pt/C	8w%Pt+ 2w%Pd/C	8w%Pt+ 4w%Pd/C	8w%Pt+ 6w%Pd/C	8w%Pt+ 8w%Pd/C
Potential (mV)	500	600	500	500	700

responding to adsorbed CO can be detected, suggesting an absence of poisoning.

Finally, with the 8w%Pt+8w%Pd/C sample, no CO bands are visible. In this case, it seems that the dissociation of the methanol molecule is difficult on this catalyst. This finding is quite surprising and can be related to the large particle size. Although EDAX analyses suggest the presence of both Pt and Pd in almost equal amounts for all particles, it is possible that palladium is mainly on the surface of the particles. Thus, the number of platinum sites present at the electrode surface is small enough to inhibit the dissociative adsorption of methanol. Moreover, it is well known that palladium is a very poor catalyst for methanol oxidation when used alone [4].

Conclusions

The aim of this study was to find electrocatalysts better than pure platinum for the electrooxidation of methanol. The addition of palladium appears to have a particularly positive effect on the electrode activity.

TEM analyses and EDAX measurements on Pt/Pd particles on carbon have shown that the size of the particles depends greatly on the overall composition of the catalyst. The larger the palladium content is, the larger the particles are. The real surface area of the electrode has been estimated as related to the total metal amount of the electrode. Although the accuracy of these estimations is questionable, it is the only way to obtain a suitable comparison of the real electroactivity of the different samples.

8w%Pt+4w%Pd/C and 8w%Pt+6w%Pd/C were found to be more active than 8w%Pt/C in the low potential regions. For example, the current densities observed at 0.5 V *vs*. RHE are 3.4 and 3.0 times larger for 8w%Pt+4w%Pd/C and 8w%Pt+6w%Pd/C than for 8w%Pt/C. These values are taken from the polarization curves after 20 s. The trend is similar after 10 min at fixed potential, (2.4 and 2.2) even if a slight decrease of these differences is observed.

In situ infrared reflectance spectra suggest that the formation of carbon dioxide, which is the final reaction product, is detected sooner for 8w%Pt/C, but the current density increase due to oxidation of methanol is observed earliest for 8w%Pt+4w%Pd/C by the electrochemical method. This discrepancy between pure electrochemical and spectroscopic data can be interpreted by the formation of intermediate oxidation products such as formaldehyde before the final oxidation into carbon dioxide for 8w%Pt+4w%Pd/C and 8w%Pt+6w%Pd/C.

The poor activity of 8w%Pt+8w%Pd/C observed in electrochemical as well as in IR studies may be related to the size of the particles of this composition, ~60–100 nm diameter, which leads to a rather small active area with a redistribution of palladium towards the surface of the metal particles which is inactive for methanol electrooxidation.

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