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Unexpected Activity for Glycerol Electro-oxidation of Nanostructured Pd-Pt and Pd-Pt-Ru Catalysts


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Abstract: Ruthenium modified palladium/platinum bimetallic materials were synthesized at nanoscale from formic acid method. This soft and surfactant-less chemical approach led to trimetallic catalyst (Pd_{25}Pt_{50}Ru_{25}/C) that displayed excellent ability toward glycerol oxidation and also a favourable capacity for CO oxidation, as probing molecule. In the case of glycerol, the main oxidation peak shifted remarkably from 500 mV towards lower electrode potentials. From cyclic voltammetry combined with in situ infrared spectroscopy experiments, our findings provided evidences of weakly adsorbed carbonaceous species on the trimetallic electrode probably due to the ligand effect.

Glycerol is a cheaper by-product from biomass and can feed a Direct Alcohol Fuel Cells (DAFCs). Platinum is a powerful and widely used catalyst for oxidation of various alcohols with different numbers of carbon atom chains and with one or more hydroxyl groups like glycerol. However its electro-oxidation on Pt electrodes leads to the formation of various intermediates and by-products causing the decrease in the efficiency of the reaction process. It is very well established that binary and ternary Pt based materials improve the catalytic activity and decrease adsorbed oxidation intermediates during oxidation of alcoholic compounds. Several studies reported the use of ruthenium as oxophilic co-catalyst capable of forming oxygenated species (metal-OH) at lower potentials compared to pure Pt, according to a bifunctional mechanism. The metal-OH species act as oxygen source, required in the oxidation of adsorbed reaction intermediates or fragments releasing the Pt sites. Poisoning tolerant Pt-based catalyst can also be achieved through the ligand effect issued from the modification of its band center or to the shift of the Pt 5d electronic states caused by the presence of the second metal, resulting in a weakening of the Pt-adsorbed molecule like Pt-CO interaction. However, the low natural abundance of Pt and Ru is a major drawback of these catalysts for practical applications and in this sense, alternative approaches have been searched. Some of them use carbon-supported Pd-rich platinum electrocatalysts with promising performance, since Pd has interesting catalytic properties. Therefore, the aim of the present paper is the development of alloyed PdPt and PdPtRu catalysts dispersed onto high carbon surface area for studying their activity and selectivity toward glycerol electro-oxidation reaction (GlyOR) in alkaline medium.

Results obtained from EDS analyses are showed in Table 1, values displayed indicate that the bulk compositions evaluated present little discrepancies when compared with the nominal compositions expected from the relative amounts of precursors used in the preparation of the catalysts. These analyses also confirmed that the metal loading on the carbon support was nearly 20 wt.% for all catalysts. The obtained results confirm the effectiveness of the synthesis method employed. The as-prepared nanomaterials containing Pt, Pd and Ru were first characterized by X-ray diffraction and the obtained patterns are displayed in Fig. 1. Their diffractograms present typical reflection planes of face-centered cubic structure of palladium and platinum metals with broad peaks that denote small crystallite sizes. Another peak, which is more pronounced in the Pd_{25}Pt_{50}/C material, and localized at ca. 2θ = 34.0°, is ascribed by Kibis et al. to the crystallographic plane (011) of PdO.

Figure 1. X-ray diffraction patterns of carbon supported Pt and Pd based nanomaterials as-synthesized from the formic acid method.

A slight shift of the diffraction peaks to lower diffraction angles was observed in the XRD patterns for Pd_{25}Pt_{50}/C and Pd_{25}Pt_{50}Ru_{25}/C catalysts as compared to Pd/C, indicating an increase of the lattice parameter as a consequence of the incorporation of platinum and ruthenium atoms into the structure of palladium. Table 1 also includes the calculated values of the XRD lattice parameters. In particular for Pd_{25}Pt_{50}/C catalyst, the obtained lattice parameter is higher than the value calculated for pure Pd and lower than that for pure Pt, which clearly evidences the alloy formation between PdPt. For Pd_{25}Pt_{50}Ru_{25}/C catalyst, the lattice parameter is lower than for pure Pd (0.388355 nm, JCPDS card 5-681). This is likely due to the interactions with the support and/or insertion of Ru, which presents smaller atomic ratio than Pd (134 pm against 137 pm), at the PdPt/C structure. The crystallite sizes were calculated from the Scherrer’s equation. Considering the (220) reflection plane, the obtained values are summarized in Table 1. For Pd/C and Pt/C catalysts the obtained crystallite sizes were 12.2 and 3.1 nm, respectively, while for Pd_{25}Pt_{50}/C and Pd_{25}Pt_{50}Ru_{25}/C materials a 3.2 nm size was obtained for both materials, indicating that greater the degree of substitution of palladium, smaller the average crystallite sizes. This also suggests that the presence of the second metal favors the dispersion of the catalyst on the carbon support avoiding a high kernels growth. It has also been suggested that Ru promoted the dispersion of the electrocatalyst, because unalloyed amorphous metallic or oxide materials that may reside on or near the surface of the alloy particles help to prevent the particle growth during the deposition. No typical reflection of the ruthenium hexagonal structure (hcp) or tetragonal structure feature of RuO_{2} was observed from the XRD patterns. The decrease of the lattice parameter noticed in the tri-metallic material (Table 1) is certainly due to the substitution of Pt and Pd atoms by those of Ru in the fcc structure.
Table 1. Relative atomic composition, crystallite sizes obtained from XRD and TEM and lattice parameters for the Pd-based catalysts.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic composition (%)</th>
<th>d_{XRD} (nm)</th>
<th>d_{TEM} (nm)</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>100</td>
<td>-</td>
<td>4.0*</td>
<td>0.3884</td>
</tr>
<tr>
<td>Pt/C</td>
<td>-</td>
<td>100</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Pd_{50}Pt_{50}/C</td>
<td>49.2</td>
<td>50.8</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Pd_{25}Pt_{25}Ru_{50}/C</td>
<td>28.5</td>
<td>27.2</td>
<td>44.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

* TEM image for the Pd/C material in Figure 2 displays heterogeneous particles and agglomerates due to the crystallographic network formed during the synthesis. The corresponding histogram, given as trend in the shape, was drawn thanks to the counting of small particles.

TEM images of the prepared catalysts are shown in Figure 2. For the Pt/C and Pd_{50}Pt_{50}/C materials, the TEM images display spherical shape nanoparticles, while in Pd_{25}Pt_{25}Ru_{50}/C small size particles were observed but their shape is not well defined. Apart from the Pd/C sample in which only the small particles were taken into account, the average particle sizes obtained from TEM were found to be fair in-line with the crystallite sizes resulting from XRD analysis.

From the physical chemical characterizations and according to the EDS analyses (spectra not showed), the atomic compositions of catalysts were found to be Pd_{49.2}Pt_{50.8}/C, Pd_{99.7}Pt_{0.3}Ru_{0.3}/C, 99.7 and 98.7% for pure Pt/C and Pd/C, respectively. Very little discrepancy was observed relatively to the nominal values.

Figure 3A shows the typical CV profiles for the electrocatalysts in supporting alkaline electrolyte. For the present concern, as the different catalysts showed similar particle size in the order of 3.5 nm, the currents were normalized by metal loading in the catalyst composition. The hydrogen adsorption/desorption region between 0.05 and 0.4 V is not well defined for Pd/C because palladium has ability of also absorbing hydrogen, thus preventing the desorption of H_{ads} species as efficiently as on Pt.\[^{25}\] Pt/C and Pd/C electrode materials exhibit cathodic peak corresponding to the reduction of the oxide formed at their surface during the forward potential scan at around 0.60 V and 0.65 V, respectively. For the Pd_{50}Pt_{50}/C electrocatalyst the CV shows typical surface processes that occur on Pd and Pt. Concerning the Pd_{25}Pt_{25}Ru_{50}/C electrocatalyst it can be observed a broader double layer region compared to the mono- and bi-metallic catalysts because of the Ru oxidation (RuO_{2}) \[^{26, 27}\] with the accentuated formation of oxygenated species detrimental to promote a bifunctional mechanism.\[^{24, 28-30}\]

Figure 3B displays the voltammograms of the same four electrocatalysts in 1 mol L\(^{-1}\) NaOH containing 0.1 mol L\(^{-1}\) glycerol. On Pd/C and Pt/C electrocatalysts, during the forward scan the onset potential of the GlyOR occurs at 0.5 V and 0.4 V with a maximum peak at around 0.9 V and 1.1 V, respectively. The currents involved in this reaction process at the Pt/C surface are higher than those generated on Pd/C. During the backward scan.
the reactivation of the electrode surface starts at 0.73 and 0.9 V vs. RHE for Pd/C and Pt/C, respectively. On Pd\textsubscript{50}Pt\textsubscript{50}/C, the onset potential value is centered at ca. 0.30 V vs. RHE, which represents an improvement of 250 mV and 150 mV compared to the corresponding ones found on the monometallic catalysts. Ruthenium leads to a more drastic catalytic effect towards GlyOR. Indeed, on the surface ternary electrode material Pd\textsubscript{25}Pt\textsubscript{25}Ru\textsubscript{50}/C, the onset potential occurs at around 0.17 V vs. RHE and a peak current of 31.5 A g\textsuperscript{-1} provide sound evidences on its better electrocatalytic activity amongst the studied catalysts. Ruthenium (or Ru oxide) promotes effectively the formation of oxygenated species at lower potentials, as shown in Figure 3A. They act directly on the intermediate adsorbed species such as the CO to release the active sites of the electrode, required for adsorption and oxidation of glycerol according to the Langmuir-Hinshelwood mechanism.\cite{31} As can be seen in Figure 3B, a 520 mV potential shift towards low values and the impressive increase in currents on Pd\textsubscript{25}Pt\textsubscript{25}Ru\textsubscript{50}/C result in the beneficial promotion of the glycerol oxidation due to a combination of ligand/geometry effects in the electrode material and a surface structure involved by the alloying contribution.\cite{32, 33}

The formation of alloy and its interaction with oxygen changes the local density of states around each individual metal site; however, alloying platinum with palladium and / or ruthenium increases the Pt 5d band center of Pt, which leads to modification of the adsorbed intermediate species on the two metals.\cite{31, 38, 39} Therefore, it can be concluded that on the Pd\textsubscript{25}Pt\textsubscript{25}Ru\textsubscript{50}/C electrocatalyst electronic effects may also be involved in the enhancement of the glycerol electro-oxidation albeit much less pronounced than the bifunctional mechanism.\cite{7, 38, 40}

In order to investigate further insights into the glycerol electro-oxidation on these materials, \textit{in situ} spectroelectrochemical measurements have been undertaken in a 1 mol L\textsuperscript{-1} alkaline solution. P-polarized light was used for the reflection-absorption experiments. The set of spectra in Fig. 4 indicates that the GlyOR proceeds through the formation of several reaction products. As can be seen, four main absorption bands, coming from the glycerol oxidative conversion at the surface of Pd containing electrode materials, appear in the spectral domain 2000 – 1000 cm\textsuperscript{-1}. In previous works we have attributed these
bands, after comparison to reference spectra, to the presence of oxalate and formate ions (Table 2). In all these spectra, the band at ca. 1583 cm$^{-1}$, which is characteristic of the presence of asymmetric stretching vibration of O-C-O in carboxylate ions is enlarged by the contribution of the water bending vibration. The production of very small amounts of CO$_2$ at low potential (0.2 V), concomitant to the appearance of a band assigned to formate (1352 cm$^{-1}$) is observed. Although the glycerol oxidation occurs in alkaline medium, CO$_2$ appears as a band in the spectra. This can be explained by the formation of carboxylic acids in a thin electrolytic film between the electrode and the CaF$_2$ window.

Figure 4. In Situ FTIR spectra of glycerol electro-oxidation reaction obtained for (A) Pd/C, (B) Pt/C, (C) Pt$_{50}$Pd$_{50}$/C and (D) Pt$_{25}$Pd$_{25}$Ru$_{50}$/C electrocatalysts as function of the potential.

Otherwise its weak intensity and the absence of another band attributable to adsorbed CO in the range 2100 – 1800 cm$^{-1}$ reveals that not only the glycerol oxidation leads to few degradation of the molecule skeleton, but also that the poisoning species are easily removed from electrode surface of the...
synthesized materials. The band characteristic of carbonate in the 1380-1430 cm\(^{-1}\) region (partially overlapping with the formate ion band) provides further evidences to the CO\(_2\)-to-CO\(_3^{2-}\) neutralization by diffusion in the electrolyte. The behavior observed for the Pt/C was slightly different (Fig 4B) as the main reaction product is carbonate.

Table 2. Assignment of FTIR absorption bands recorded during glycerol electro-oxidation

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Molecular group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1074</td>
<td>C-H bending out of plane (formate ion)</td>
</tr>
<tr>
<td>1108</td>
<td>C-O stretching (aldehyde or alcohols)</td>
</tr>
<tr>
<td>1308</td>
<td>C-O stretching and/or COO rocking (oxalate ion)</td>
</tr>
<tr>
<td>1353</td>
<td>C-O stretching (formate ion)</td>
</tr>
<tr>
<td>1385</td>
<td>Symmetric COO(^{-}) stretching (carboxylate ion)</td>
</tr>
<tr>
<td>1582</td>
<td>Asymmetric COO(^{-}) (carboxylic ions)</td>
</tr>
</tbody>
</table>

We have reported a facile approach in synthesizing nanoparticles by chemical reduction of the metal precursor salts with formic acid. The resulted trimetallic catalysts composed of palladium, platinum and ruthenium exhibited beneficial promotion toward the glycerol oxidation reaction (GlyOR). A marked shift of 520 mV in the peak potential and elevated oxidation currents were observed, as the main ensemble effects of the atomic arrangement in the electrode material. Oxygenated adsorbed species formed on the ternary catalyst has a detrimental effect by acting directly on the reaction intermediate adsorbed species, during the oxidation of glycerol; according to the bifunctional mechanism, although some electronic effect may also be involved. As a result, adsorbed intermediate species such as CO are easily removed from the surface electrode through the oxidative conversion to carbonate at lower potentials, releasing the active sites from poisoning compounds. The weak intensity of the CO\(_2\) band clearly indicates the ability of the as-prepared materials toward glycerol oxidation without high degradation of the initial molecule skeleton.

Experimental Section

Pd/C, Pt/C, Pd\(_{50}\)Pt\(_{50}/\)C and Pd\(_{50}\)Pt\(_{50}\)Ru\(_{50}/\)C materials with 20 wt.% metal loadings were prepared by the formic acid reduction method.[9] Briefly, it consists in dissolving an appropriate amount of metal precursors (H\(_2\)PtCl\(_6\), PdCl\(_2\) and RuCl\(_3\), Alfa Aesar) in water, which was drop-wise added, under stirring, to aqueous suspension Vulcan XC-72 (Cabot) carbon containing 0.5 mol L\(^{-1}\) formic acid at 80 °C. Physical chemical characteristics of all materials were performed by X-ray diffraction (XRD) using a Rigaku diffractometer to analyze the average crystallite size and by a transmission electron microscopy (TEM) FEI Tecnai with an accelerating potential of 200 kV equipped with a X-ray dispersive spectroscopy (EDS) for analyzing the morphology / shape and the composition of all as-prepared materials.

For the electrochemical measurements, a slab of glassy carbon (GC) and Reversible Hydrogen Electrode (RHE) in 1.0 mol L\(^{-1}\) NaOH were employed as counter and reference electrodes, respectively. The working electrode was prepared with 20 µL of catalytic ink ([1:1 powder: isopropyl alcohol] deposited onto a 8 mm diameter GC disk. The experiments were performed in 1.0 mol L\(^{-1}\) NaOH (Sigma-Aldrich 97%) + 0.1 mol L\(^{-1}\) glycerol (Sigma-Aldrich ≤ 99%) solutions prepared with ultrapure water. They were conducted with a computer-controlled potentiostat (AutoLab PGSTAT 302N). Cyclic voltammetry (CV) was carried out in the potential range of 0.05 to 1.4 V vs. RHE at 10 mV s\(^{-1}\) scan rate after deoxygenating the solution with N\(_2\).

In situ Fourier transform infrared spectroscopy (FTIRS) measurements were performed in a Buerk IFS 66v spectrometer with a MCT (HgCdTe) type detector in a beam reflection configuration.[40] The whole system was maintained under vacuum in order to avoid interferences from atmospheric water and CO\(_2\). The spectral resolution was of 4 cm\(^{-1}\) and the FTIR spectra were recorded in 1000-4000 cm\(^{-1}\) MIR region. A three-electrode spectreo-electrochemical cell, fitted with a transparent window (CaF\(_2\)) at the bottom was used in a thin layer configuration. The potentiostat and all electrodes were the same used in electrochemical experiments. Spectra were acquired according to the SPAIRS (Single Potential Alteration IR Spectroscopy) method, performed in the range of 0.05-1.4 V vs. RHE and the reflectivity R\(_0\) was recorded at the different potentials, E, each separated by 0.05 V during the voltammogram recorded at 1 mV s\(^{-1}\) scan rate. CO stripping in a 1.0 mol L\(^{-1}\) NaOH solution was also investigated under the similar operating conditions described above. CO was adsorbed at 0.3 V vs. RHE until the current intensity reached the capacitive current level (herein 5 min). Afterwards the solution was deaerated with N\(_2\) during 25 min to expel all free CO before CV experiments. CO oxidation was assessed at 1 mV s\(^{-1}\).

Acknowledgements

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Keywords: glycerol electro-oxidation • alkaline medium • Pd-Pt-Ru catalyst • in situ FTIR spectroscopic measurements


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