Influence of silver on the glycerol electro-oxidation over AuAg/C catalysts in alkaline medium: a cyclic voltammetry and in situ FTIR spectroscopy study


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1. Introduction

There has been a worldwide urge for clean-energy generation, a theme well encompassed by fuel cells [1]. To date the only fuel cells that perform well enough to be considered for commercial purposes are hydrogen fuel cells [1,2]. However, the use of hydrogen introduces a number of formidable challenges including hydrogen production, storage, and distribution. In order to avoid the difficulties associated with hydrogen fuel, it is then of great interest to develop appropriate anode catalysts for direct alcohol fuel cells [3] amongst which the direct glycerol fuel cell is one of the most interesting because it makes use of a non-toxic and bio-based fuel, at present abundantly co-produced in the biodiesel fabrication [4].

From the thermodynamic viewpoint, direct glycerol fuel cells compete well with methanol and ethanol ones and it is not so far from the hydrogen fuel cells. The theoretical energy density of glycerol is 5.0 kWh kg⁻¹ [5], while those of methanol, ethanol, and hydrogen are 6.1, 8.1, and 32.8 kWh Kg⁻¹ [3], respectively. The challenge in realizing the thermodynamic promise of direct glycerol fuel cells lies in improving their kinetic characteristics. Specifically, new anode catalysts must completely oxidize glycerol to CO₂ at low overpotentials. The optimal glycerol oxidation catalyst would be highly active for cleaving the C-C-C bond of glycerol and simultaneously highly resistant to poisoning by reaction intermediates such as CO [6].

Many studies of the electro-oxidation of glycerol have focused on platinum-based catalysts because platinum is known to oxidize organic molecules in acidic and alkaline solution [7–10]. Nevertheless, there has been a growing interest in gold because in alkaline medium it presents higher activity than platinum for glycerol oxidation [7,11]. This interesting behavior is attributed to the high resistance of gold toward the formation of poisoning surface oxides [12]. For polycrystalline platinum [8,13,14], Pt single crystals [6], Pt/C [5], polycrystalline gold [7,8], and Au/C [5], glycerol oxidation results in CO₂ and partial oxidation products. On these catalysts partial oxidation products prevail, indicating incomplete C-C-C bond cleavage. Furthermore, the oxidation commences at relatively high overpotentials, likely due to catalyst poisoning by CO and other strongly adsorbed residues [6,7]. In a real direct glycerol fuel cell, the evolution of incomplete oxidation products and the high overpotential would result in co-production of other chemicals and low power density.

Alloying Pt with non-noble metals is a known strategy to improve electro-oxidation of alcohols. In particular, the electrocatalytic oxidation of glycerol was studied over carbon-supported...
PtRuSn-based catalysts [15]. The ternary PtRuSn/C catalyst presented noticeable modifications of the geometric and electronic structures in comparison with the Pt/C and PtRu/C catalysts. The structurally modified PtRuSn/C catalyst displayed better electrocatalytic performance for glycerol oxidation than Pt/C and PtRu/C catalysts, as seen by larger peak currents and lower onset potential. Moreover, based on results of CO striping experiments, it was suggested that the PtRuSn/C catalyst was more efficient than Pt/C and PtRu/C catalysts for oxidative removals of CO or CO-like carbonaceous intermediate species produced during the glycerol oxidation reaction. In another study [5], it was verified that bimetallic AuPd catalysts present better catalytic performance than those of monometallic Au and Pd materials, being close to that of platinum at low potentials [5,16]. Such synergetic effect between Au and Pd is still not completely understood, and further studies with different AuPd catalyst structures may help to bring new insights on that. The same group has shown that Bi-modified Pt/C and Pd/C present higher catalytic activity and lower overpotentials to the glycerol oxidation than non-modified materials [17]. Especially the order of activity of catalysts was Pd/C < Pt/C < PdAg50Bi50/C < PtAg50Bi50/C = Pd45Pt45Bi10/C. Therefore the replacement of half of the platinum atoms by palladium atoms resulted in the same catalytic activity. The improvement of the catalytic performance of the Bi-modified materials with respect to non-modified materials was explained in terms of a bifucational mechanism, since no evidence for either bismuth-platinum or bismuth-palladium alloy formation was found in that work. In the proposed bifucational mechanism, the adsorption of glycerol occurs on platinum and/or palladium and the formation of oxygenated species occurs on bismuth [17].

From a previous work [18] we know that the electro-oxidation of glycerol on AuAg/C occurs at lower overpotential than that of the same reaction on Au/C. This may be explained by the reduction of the gold 5d band occupancy caused by the Ag addition. The question now is whether this electronic effect might alter the reaction mechanism. In the present work we studied the impact of adding silver to gold on the mechanism of glycerol electro-oxidation. The Au:Ag ratio in the catalysts was systematically varied and the glycerol oxidation products were investigated by means of in situ FTIR. An extremely simple synthetic route that makes use of glycerol itself was used for the production of the catalysts. The electrochemical oxidation of glycerol over carbon-supported Au and Ag catalysts was also investigated for comparison.

2. Experimental

2.1. Experimental conditions, reactants and instrumentation

All experiments were performed at room temperature (25 °C ± 1 °C). The chemicals used to prepare the working solutions, namely 0.1 mol L⁻¹ NaOH and 0.1 mol L⁻¹ glycerol in 0.1 mol L⁻¹ NaOH, were high-purity NaOH, glycerol and ultrapure water from Millipore system. The electrochemical experiments were conducted in a conventional three-electrode cell. The counter electrode was a Pt foil. The reference electrode was a reversible hydrogen electrode (RHE) and all potentials in this work are referred to it. The working electrodes consisted of carbon-supported Ag, Au₅₂Ag₂₅, Au₅₀Ag₅₀, Au₇₅Ag₂₅ and Au on a glassy carbon disc. Throughout this paper, these catalysts will be referred to as Ag/C, Au₅₂Ag₂₅/C, Au₅₀Ag₅₀/C, Au₇₅Ag₂₅/C and Au/C. Chemical and physical characterizations of the samples were conducted using a TEM FEI Tecnai with an accelerating potential of 200 kV. Chemical characterization of the samples was also performed by an EDX LINK ANALYTICAL, with a SiLi Pentafet detector and atmosphere thin window, resolution from 133 eV to 5.9 keV and area of 10 mm², coupled with a scanning electronic microscope ZEISS LEI 440. Electrochemical experiments were carried out with either a 1285 Solartron potentiostat/galvanostat controlled by the CorrWare software or an AUTOLAB 30 potentiostat/galvanostat controlled by the GPES software. The FTIR instrument was a Nicolet Nexus 670 spectrometer equipped with liquid nitrogen cooled MCT detector. In situ FTIR spectroscopy experiments were performed in a three electrode spectro-electrochemical cell with an IR transparent and planar CaF₂ window attached to the bottom of the cell. Details concerning the cell are described elsewhere [19]. Briefly, a movable piston supported the working electrode. Through the piston a platinum wire was connected to the working electrode and kept the electric contact. During the in situ FTIR spectroscopy measurements, the electrode was maintained pressed against the CaF₂ window. In such way, a thin liquid film was formed between them, minimizing the absorption of the infrared beam by the solution. The angle of incidence of the IR beam was kept constant at 65°.

2.2. Synthesis of the carbon-supported catalysts

The catalysts were produced directly onto Vulcan carbon without stabilization by surfactants, thus avoiding any influence of them on the reactions under study. The synthesis of the catalysts was conducted as follows: in a flask A 40 mg of XC-72 Vulcan carbon were sonicated for 30 minutes with 50 mL of ultrapure water followed by addition of a fixed amount of AuCl₃ and/or AgNO₃ under stirring. A glycerol-NaOH mixture contained in separate flask B was added to the mixture in flask A to yield the final concentrations presented in Table 1. The black suspensions formed just after the addition of the glycerol containing solution to the metallic precursor solution were kept during 24 h under stirring at room temperature and then washed, filtered and dried at 80 °C for 12 h.

2.3. Experimental procedure

For the transmission electron microscopy (TEM) experiments, cooper coated grids were immersed into the carbon–supported catalysts suspensions containing 1.0 mg of catalytic powder and 5 mL of isopropanol alcohol, and were allowed to dry overnight in a desiccator. The grids were then analyzed by TEM.

For X-ray energy-dispersive spectroscopy (EDS) analysis, the samples were prepared according to the following procedure. About 40 mg of the powdered sample were placed over a glass table. One drop of a Teflon solution was placed over the powder, which was then thoroughly mixed with the help of a stainless steel scoop. The material was subsequently transferred to a pressurizing tube to produce small compact disks of the sample with a smooth surface. The material was fixed over a previously cleansed sample holder. For each one of the samples three distinct areas were analyzed. Based on these data the average chemical composition of the samples and the respective standard deviation were then calculated.

For the electrochemical experiments, a glassy carbon disc with 5 mm of diameter (0.196 cm² geometric area) was used as substrate to support the catalytic layers of the carbon–supported materials. For the preparation of the catalytic layer, 2.0 mg of the catalytic powder (Ag/C, Au₅₂Ag₂₅/C, Au₅₀Ag₅₀/C, Au₇₅Ag₂₅/C and Au/C) were suspended in a mixture containing 1 mL of isopropyl alcohol and 20 μL of a Nafion solution (5 wt % in low aliphatic alcohol, from DuPont). After ultrasonic homogenization, 20 μL of this ink were deposited onto the glassy carbon disc and the solvent was then evaporated at room temperature. Electrochemical measurements were performed in oxygen-free working solutions.

Previous to the experiments with Au and Ag-based catalysts, the cleanliness of the electrolytic solution was tested by the stability.
Table 1
Concentration of the metallic precursors, NaOH and glycerol used in the synthesis of the carbon-supported catalysts.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Au(^{3+}) concentration (mmol L(^{-1}))</th>
<th>Ag(^{+}) concentration (mmol L(^{-1}))</th>
<th>NaOH concentration (mol L(^{-1}))</th>
<th>Glycerol concentration (mol L(^{-1}))</th>
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</thead>
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<tr>
<td>Ag</td>
<td>0.0</td>
<td>0.4</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Au(<em>{25})Ag(</em>{75})</td>
<td>0.1</td>
<td>0.3</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Au(<em>{50})Ag(</em>{50})</td>
<td>0.2</td>
<td>0.2</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Au(<em>{75})Ag(</em>{25})</td>
<td>0.3</td>
<td>0.1</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Au</td>
<td>0.4</td>
<td>0.0</td>
<td>0.01</td>
<td>1.0</td>
</tr>
</tbody>
</table>

of the characteristic voltammetric features of a standard Pt electrode in pure electrolyte. The Pt electrode was then replaced by the working electrode that was introduced into the cell at 0.05 V vs. RHE. In the sequence, cyclic voltammetry or FTIR spectroscopy (first series of increasing potential steps) was performed. Cyclic voltammograms were obtained in the potential range between 0.05 V and 1.6 V at 0.05 V s\(^{-1}\). Given the arbitrary nature of some of the normalization methods commonly adopted by the literature, as for example mass of catalyst or active area of an element of the catalyst, we have chosen not to use any normalization method for the faradaic currents. Nevertheless all measures have been made with the same electrode geometry surface area and catalyst load, assuring the comparison of them. FTIR spectra were taken in the wavenumber region between 4000 cm\(^{-1}\) and 1000 cm\(^{-1}\), first at 0.05 V and then from 0.1 V to 1.6 V in 0.10 V steps. Spectra were computed from the average of 128 interferograms. The spectral resolution was set to 8 cm\(^{-1}\). Reflectance spectra were calculated as the ratio between R and R\(_0\) (R/R\(_0\)), where R represents a spectrum at the sample potential and R\(_0\) is the spectrum collected at 0.05 V.

All experiments were made at least in duplicate and the results were reproducible in the limit of the experimental error.

3. Results and Discussion

3.1. Physical and chemical characterization of the carbon-supported catalysts

Transmission electron microscopy (TEM) images (Fig. 1) show that Au/C and Ag/C catalysts have distinct mean particle sizes. Au/C catalyst has a mean particle size of 7.3 nm and Ag/C catalyst has a mean particle size of 34 nm. The bimetallic catalysts have a mean particle size smaller than that of Au catalyst. Au\(_{25}\)Ag\(_{75}\)/C and Au\(_{50}\)Ag\(_{50}\)/C catalysts have both a mean particle size of 4.7 nm. However, the standard deviation of the particle size distribution of the Au\(_{75}\)Ag\(_{25}\)/C catalyst is 1.8 nm while that of the Au\(_{50}\)Ag\(_{50}\)/C catalyst is 1.4 nm. Notably, 85% of the particles of the Au\(_{75}\)Ag\(_{25}\)/C catalyst and 90% of the particles of the Au\(_{50}\)Ag\(_{50}\)/C catalyst are 6.0 nm or less. Also the TEM images of the Au\(_{25}\)Ag\(_{75}\)/C catalyst provide no evidence for particles greater than 8 nm. Au\(_{50}\)Ag\(_{50}\)/C has a mean particle size of 5.5 nm and the standard deviation of the particle size distribution is 1.8 nm. Approximately 6% of the particles of the Au\(_{25}\)Ag\(_{75}\)/C catalyst are larger than 8 nm. Therefore these results clearly show that by increasing the Ag content from 0 at. % up to 50 at. % the catalyst particle size decreases and the particle size distribution becomes narrower than that of the Au/C catalyst. In opposition by increasing the Ag content from 50 at. % up to 75 at. % the catalyst particle size increases and the particle size distribution becomes broader than that of the Au\(_{50}\)Ag\(_{50}\)/C catalyst.

Fig. 2 shows the XRD patterns of the different catalysts. All the materials display the peaks feature of metallic face-centered cubic (fcc) crystalline structure. For the AuAg based materials all reflections are similar to those of monometallic Au and Ag since both metals have very similar lattice constants (0.4078 for Au and 0.4086 for Ag) [20]. Therefore, no shift of reflections for the AuAg bimetallic materials was observed, as would be expected for alloyed materials. The average crystallite sizes for all materials were estimated through the (220) reflection peak [21] by the application of the Scherrer’s equation [22]:

\[
D = \frac{k\lambda}{B \cos \theta}
\]

where D is the average crystallite size in Å, k is a coefficient taken here as 0.9, λ is the wavelength of the X-rays used (1.5406 Å), B is the width of the diffraction peak at half height in radians, and θ is the angle at the position of the peak maximum. All the crystallite
size values are in the range of 10–20 nm (Table 2). These values are higher than those obtained by TEM. Usually one expects that the average crystallite size should be smaller than the average particle size. A possible explanation for the different trend observed here may be related to the fact that TEM is a local tool whereas XRD gives average information about the catalyst.

X-ray energy-dispersive spectroscopy (EDS) results are shown in Fig. 3. The mean atomic percentage of Au in the Au25Ag75/C, Au50Ag50/C and Au75Ag25/C catalysts is 11, 32 and 53, respectively, thus below the nominal values. These results indicate that during the synthesis of the catalysts Au ion reduction is less effective with respect to the Ag ion reduction. The inset of Fig. 3 shows the weight percentage of metal on carbon for the distinct catalysts. The mean weight percentage of metal on carbon varies from 3.8 for the Ag/C catalyst to 8.4 for the Au50Ag50/C catalyst, being 7.0, 6.6 and 7.2 for Au25Ag75/C, Au75Ag25/C and Au/C catalyst, respectively. These data reveal that the Au-containing catalysts have at least 1.7 times more metal than the Ag one.

3.2. Electrochemical characterization of the carbon-supported catalysts

Stable cyclic voltammograms (CV) of the glycerol oxidation over the Ag/C, Au25Ag75/C, Au50Ag50/C, Au75Ag25/C and Au/C in alkaline medium are shown in Fig. 4. CVs in pure electrolytic solution for each catalyst (insets of Fig. 4) presented typical features corresponding to the surface oxidation and surface oxide reduction and are in accord with the curves previously published [18]. For the Ag/C catalyst similar profiles were observed in the absence and in the presence of glycerol. Markedly, in the presence of glycerol the redox peaks of silver oxides were significantly shifted to higher potentials and no reactivation current of glycerol electro-oxidation was clearly evidenced in the negative-going potential scan. These results indicate that the Ag/C is a very poor catalyst for the glycerol electro-oxidation in alkaline medium. Contrarily the Au/C catalyst is quite active for this reaction as evidenced by its CV in Fig. 4. For the Au/C catalyst, the alcohol electro-oxidation in the positive-going potential scan begins close to 0.70 V. The maximum oxidation current is 4.8 mA.
The voltammetric profiles corresponding to the electrochemical oxidation of glycerol over the AuAg/C catalysts in alkaline medium are remarkably different in comparison with those of the monometallic catalysts. In the positive-going potential scan one verifies two peaks for the glycerol electro-oxidation over the AuAg/C catalysts, which implies that the reaction mechanism on the bimetallic catalysts is different from those on the monometallic materials. For the Au25Ag75/C, Au50Ag50/C and Au75Ag25/C catalysts the onset potential is 0.67 V, 0.60 V and 0.61 V, respectively, representing an advantageous overpotential reduction with respect to the pure Au/C catalyst (onset potential close to 0.70 V). Therefore, the presence of Ag in the bimetallic materials provided a more efficient catalyst in terms of the ability to oxidize glycerol at relatively low potentials. This improvement in the glycerol electro-oxidation onset observed for the AuAg/C catalysts may be attributed to the distinct Au 5d states occupation due the presence of Ag. Recently Garcia et al. [18] reported that the Au50Ag50/C catalyst presents more vacant gold 5d states than the Au/C catalyst. The presence of Ag atoms on the bimetallic catalysts was found to reduce the Au density of states close to the Fermi level. This electronic modification might tune the adsorption strength of adsorbates on the Au surface and eventually lead to lower the onset potential for the bimetallic catalysts.

In addition to differences with respect to the onset potential, disparities between kinetics of glycerol electro-oxidation over the bimetallic catalysts and Au/C catalyst can also be observed in Fig. 4. The maximum current of the most pronounced oxidation peak for the Au25Ag75/C, Au50Ag50/C and Au75Ag25/C catalysts is 0.11 mA, 0.56 mA and 0.5 mA, respectively, at least nearly ten times lower than that observed for Au/C. According to these electrochemical results, the carbon-supported bimetallic catalysts are less promising than Au/C with respect to the reaction rate. The difference between the oxidation currents for the bimetallic catalysts and that of the Au/C catalyst may not be explained by the amount of metal on carbon for the different catalysts, since considering the error bars in the inset of Fig. 3 it varies by at most a factor of 1.6. Therefore, this difference is more likely to be related to effects of the catalysts composition. A possible explanation would be the presence of silver segregated on the nanoparticle surface of the bimetallic catalysts, as evidenced by EXAFS results [18]. Silver oxidizes marginally glycerol, as seen in Fig. 4, and the remaining silver uncovered gold surface of the bimetallic materials might promote the reaction with limited rate. Detailed structure of these bimetallic particles is being investigated by our group and will be the scope of another work. In parallel we are also working to avoid silver segregation on the Ag/C catalyst are significantly lower than those related to the reaction on AuAg/C and Au/C catalysts. This is consistent with the fact that Ag/C was evidenced by cyclic voltammetry to be a poorer catalyst for glycerol oxidation than AuAg/C and Au/C catalysts (Fig. 4). In the FTIR spectra of Ag and Au-based catalysts the absence of a peak close to 2050 cm$^{-1}$, which is typically attributed to the CuO stretching vibration mode of CO species linearly bonded to the catalyst surface, implies that the reaction over these catalysts does not include the CO formation as an intermediate, as previously evidenced for Au catalysts [5,7].

Solutions of expected products from glycerol oxidation were independently explored at alkaline pH conditions by ex situ FTIR spectroscopy in order to produce standard FTIR spectra. The considered products were: glyceraldehyde, dihydroxyacetone, glyceric acid, tartronic acid, mesoxalic acid, pyruvic acid, hydroxypyruvic acid, malonic acid, glyoxylic acid, glycolic acid, oxalic acid and formic acid. Additionally, sodium carbonate solution was also analyzed, since it is a product of CO$_2$ reaction with NaOH. Standard FTIR spectra are displayed in Fig. 7.

In situ FTIR results in conjunction with the standard FTIR spectra indicate that the electro-oxidation of glycerol on the Ag/C, Au25Ag75/C, Au50Ag50/C, Au75Ag25/C and Au/C catalysts proceeds through the formation of several reaction products, since no single product can explain the complex vibrational spectra presented in Figs. 5 and 6, specially those of the Au/C catalyst.

Evident common features in the FTIR spectra of Ag/C, Au25Ag75/C, Au50Ag50/C, Au75Ag25/C and Au/C catalysts at high potentials are peaks at about 1350 cm$^{-1}$, 1380 cm$^{-1}$ and 1580 cm$^{-1}$. They can be attributed to symmetric (1350 cm$^{-1}$ and 1380 cm$^{-1}$) and asymmetric (1580 cm$^{-1}$) O-C-O stretching vibration modes of carboxylates [23] and are mostly likely related to the formation of formic acid. However, the pronounced peak close to 1580 cm$^{-1}$ is also typical of dihydroxyacetone, glyceric acid, hydroxypyruvic acid and glycolic acid in alkaline medium (Fig. 7) and may include contributions of bands between 1570 cm$^{-1}$ and 1605 cm$^{-1}$ that are representative of mesoxalic acid, tartronic acid, oxalic acid, glyoxylic acid, malonic acid and pyruvic acid in alkaline medium (Fig. 7). The presence of these species can not be confirmed only with basis on the peak at ca. 1580 cm$^{-1}$, but the validation of their presence with basis on the other peaks between 1550 cm$^{-1}$ and 1600 cm$^{-1}$ is not straightforward since firstly some peaks are common to different species and secondly many peaks are superimposed in this wavenumber range.

Careful inspection of the peaks behavior as a function of the applied potential (Figs. 5 and 6) allowed us to qualitatively distingusish different peaks. Table 3 summarizes the main peaks seen in the FTIR spectra. In general the observed features are assigned to bending or stretching vibration modes of alcohols, ketones, aldehydes, carboxylic acids, enols, carboxylates and carbonates [23].

Comparison between standard FTIR spectra presented in Fig. 7 and in situ FTIR spectra shown in Figs. 5 and 6 may lead to some assignments of products. The formation of glyceraldehyde and dihydroxyacetone on the Au and Ag-based catalysts investigated here cannot be excluded, but there is no unambiguous evidence of their presence in the FTIR spectra.

3.3. In situ FTIR spectroscopic characterization of the glycerol electro-oxidation over carbon-supported catalysts in alkaline medium

Sets of FTIR spectra in the wavenumber range from 2500 cm$^{-1}$ to 1000 cm$^{-1}$ corresponding to the glycerol electro-oxidation over the Ag/C, Au/C, Au25Ag75/C, Au50Ag50/C and Au75Ag25/C catalysts are shown in Figs. 5 and 6. The spectra were obtained as a function of increasing potential steps from 0.05 V to 1.60 V. Positive and negative bands seen in the spectra are associated with chemicals formed and consumed during the glycerol oxidation, respectively, and their occurrence depends on the applied potential. By increasing the applied potential the intensity of the bands increases, indicating that species are gradually produced or consumed. For instance, in the sets of spectra presented in Figs. 5 and 6, two negative bands are clearly visible at approximately 1045 cm$^{-1}$ and 1110 cm$^{-1}$. They are assigned to C=O stretching vibration modes of primary and secondary alcohols [23]. These two bands were identified independently by ex-situ FTIR spectroscopy with a glycerol solution in alkaline medium (Fig. 7) and correspond to glycerol consumption during the reaction. Generally intensities of the bands corresponding to the products of the electro-oxidation of glycerol on the Ag/C catalyst are significantly lower than those related to the reaction on AuAg/C and Au/C catalysts (Fig. 4). In the FTIR spectra of Ag and Au-based catalysts the absence of a peak close to 2050 cm$^{-1}$, which is typically attributed to the CuO stretching vibration mode of CO species linearly bonded to the catalyst surface, implies that the reaction over these catalysts does not include the CO formation as an intermediate, as previously evidenced for Au catalysts [5,7].
Fig. 5. In situ FTIR spectra (128 scans, 8 cm$^{-1}$ resolution) of carbon-supported Ag and Au in 0.1 mol L$^{-1}$ NaOH + 0.1 mol L$^{-1}$ glycerol. The reference spectrum was collected at 0.05 V vs. RHE and the sample spectra were measured at 0.05 V and after applying potential steps towards more positive potentials, as indicated in the figure.

Fig. 6. In situ FTIR spectra (128 scans, 8 cm$^{-1}$ resolution) of carbon-supported Au$_{25}$Ag$_{75}$, Au$_{50}$Ag$_{50}$ and Au$_{75}$Ag$_{25}$ in 0.1 mol L$^{-1}$ NaOH + 0.1 mol L$^{-1}$ glycerol. The reference spectrum was collected at 0.05 V vs. RHE and the sample spectra were measured at 0.05 V and after applying potential steps towards more positive potentials, as indicated in the figure.
The resulting spectra for Ag/C might reveal the formation of formic acid, carbonate and/or glyoxylic acid. The latter presents a characteristic band at 1080 cm\(^{-1}\). The absence of expressive bands between 1350 and 1200 cm\(^{-1}\) discards the formation of significant amounts of hydroxyppyrvic acid, glycric acid and glycolic acid.

The electro-oxidation of glycerol on the Au/C catalyst may lead to the formation of hydroxyppyrvic acid, mesoxalic acid, glycric acid, tartronic acid, glycic acid, glycic acid, oxalic acid and formic acid. Additionally, the band at 2346 cm\(^{-1}\), which is characteristic of asymmetric stretching vibration of O-C-O [23], indicates the formation of CO\(_2\). In alkaline medium, the production of CO\(_2\) instead of CO\(_3^{2-}\) may be explained by the lowering of the local pH inside the thin layer due to the dehydrogenation of glycerol at high oxidation rates, as recently shown by Camara and co-workers [24].

Finally, the reaction on the AuAg/C catalysts may form glycric acid and glycolic acid, as seen by the occurrence of bands between 1350 cm\(^{-1}\) and 1300 cm\(^{-1}\). The pronounced thin band at 1080 cm\(^{-1}\) is an additional evidence for the formation of glycric acid. Bands at ca. 1380 cm\(^{-1}\) and 1350 cm\(^{-1}\) are shouldered and suggest formation of formic acid, carbonate and/or glyoxylic acid. The thin band at 1310 cm\(^{-1}\) indicates the production of oxalic acid. The absence of bands at around 1724 cm\(^{-1}\), 1600 cm\(^{-1}\) and 1200 cm\(^{-1}\) discards the formation of detectable amount of tartronic acid, mesoxalic acid and hydroxyppyrvic acid, respectively, observed for the Au/C catalyst. Furthermore, the most important feature of the FTIR spectra of the AuAg/C catalysts is that the formation of formic acid is selectively favored in comparison with other products, as seen by the relative intensities of the bands close to 1580 cm\(^{-1}\), 1380 cm\(^{-1}\) and 1350 cm\(^{-1}\). Among the bimetallic catalysts, Au\(_{75}\)Ag\(_{25}\)/C is the fewest selective for the formic acid production and the most selective for the glyoxylic acid and oxalic acid production, as seen by the relative intensity of the bands at ca. 1380 cm\(^{-1}\) and 1310 cm\(^{-1}\), respectively.

Comparing the different sets of products assigned by in situ FTIR spectroscopy and their relative production for the Ag, Au and AuAg catalysts, it is possible to affirm that the presence of Ag in the bimetallic catalysts favors the formation of 1-C atom product.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Assignment of the main bands in the spectra of the Figures 3-5 [23].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (cm(^{-1}))</td>
<td>Au(<em>{75})Ag(</em>{25})</td>
</tr>
<tr>
<td>---------</td>
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</tr>
<tr>
<td>1045</td>
<td>1047</td>
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<tr>
<td>1080</td>
<td>1080</td>
</tr>
<tr>
<td>1110</td>
<td>1114</td>
</tr>
<tr>
<td>1175–1330 (broad band centered at 1262)</td>
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<tr>
<td>1132</td>
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<tr>
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\(^{a}\) Notation used for mode description: \(\nu\), stretching; \(\delta\), deformation.

\(^{b}\) Subscripts indicate the type of mode: s – symmetric, as – asymmetric.

Fig. 7. Standard FTIR spectra of dihydroxyacetone, glyceraldehyde, glycric acid, tartronic acid, mesoxalic acid, pyruvic acid, hydroxyppyrvic acid, malonic acid, glycyclic acid, glycolic acid, formic acid and glycerol in alkaline medium and standard FTIR spectra of sodium carbonate in water.
This result clearly demonstrates that the bimetallic catalysts are more prone to break the C-C-C bond of the glycerol molecule than the monometallic Au/C and Ag/C catalysts, leading to improved electronic yield per glycerol molecule. This might be particularly interesting for fuel cell applications.

Based on the evidences presented in the current work, a tentative mechanism of the electro-oxidation of glycerol on Ag/C, Au25Ag75/C, Au50Ag50/C, Au75Ag25/C and Au/C catalysts in alkaline solutions is proposed in Fig. 8.

4. Conclusions

The main conclusions of the present work are:

- The presence of Ag in the bimetallic materials provides a more efficient catalyst in terms of the ability to electro-oxidize glycerol at relatively low potentials;
- On the other hand, the bimetallic catalysts are less promising than the Au/C catalyst with respect to the reaction rate;
- Silver influences the mechanism of glycerol electro-oxidation, favoring the C-C-C bond breaking, as evidenced by the selective formation of formic acid on the bimetallic catalysts;
- The impact of Ag on the glycerol electro-oxidation over AuAg/C may be driven by electronic modifications and Ag segregation on the catalysts surface.

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