Pt catalysts supported on ion exchange resins for selective glycerol oxidation. Effect of Au incorporation

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ABSTRACT

In this paper, bimetallic Pt-Au catalysts were studied for the selective liquid phase oxidation of glycerol. The support used was a macroporous weak anion exchange resin. Two different preparation methods were employed: simultaneous exchange of both metals, and a sequential exchange using the controlled surface reaction technique. PtAu catalysts with a total metal content of 0.4 wt% were prepared, with different Pt:Au molar ratios: 1:1; 2:1 and 1:2. The monometallic Au catalyst resulted inactive for the reaction. Nevertheless, it was found that the addition of Au improved the monometallic Pt catalyst activity. XPS results suggest the formation of a Pt-Au alloy, which could be related with conversion improvement. Not only the presence of Pt-Au alloyed particles, but also the Pt/Au ratio on the catalyst surface influences the activity. When the Au particles reduced on top of Pt (controlled surface reaction method), the Pt amount exposed at the catalyst surface was considerably reduced. For this reason, this Pt-Au sample did not show a significant improvement of conversion with respect to the monometallic platinum.

1. Introduction

In order to ensure the sustainability and profitability of the biodiesel industry, it is compulsory to develop applications of glycerol, the main process by-product. Because of the glycerol oversupply, its price as raw product has been continuously decreasing, and this tendency will probably continue in the near future. This situation has encouraged the development of many investigations aimed at finding routes for the valorization of glycerol. The glycerol molecule is highly functionalized and therefore, an attractive reagent for obtaining several compounds. The glycerol oxidation reaction is important in the synthesis of fine chemicals. One important example is glyceric acid, which is widely used in medicine as glucose metabolite, and it is also used as precursor during some amino acids synthesis, such as serine.

The most widely investigated materials for the heterogeneous glycerol oxidation are carbon supported metal catalysts, which are generally used with pure oxygen as oxidant agent, at moderate temperatures and under basic conditions [1–6].The first catalysts employed for glycerol oxidation were Pt and Pd nanoparticles supported on activated carbon, although more recently gold proved to be very active and selective for this reaction. One of the most important advantages in using Au, if compared to the other noble metals (Pd, Pt), is that it does not lead to over-oxidation under the typical reaction conditions used in this system, when gaseous oxygen as oxidant is used [1,4,5,7]. For this

reason, gold has received special interest for the alcohol liquid phase oxidation, although according to Hashmi et al. [8], it has low selectivity towards the oxidation of the primary alcohol, for complex substrates.

It has been widely reported in the literature that bimetallic catalysts show an improved activity in the glycerol oxidation compared to the corresponding monometallic catalysts [6]. The activity of carbon supported monometallic gold catalysts, for instance, has been improved by promoting the catalysts with platinum [9], allowing the formation of Au/Pt alloys. Also the selectivity resulted affected by introducing a second metal in the Au/C catalysts. Bimetallic $Pt_xAu_y - starch/HT$ (hydrotalcite) showed higher selectivity for the oxidation at the primary hydroxyl groups of glycerol and propylene glycol toward glyceric and lactic acid, respectively, than those of each monometallic samples [10]. Ryabenkova et al. [11] showed that combining Pd or Pt with Au on an activated carbon support, resulted in a significant increase in conversion for the production of lactic acid by propylene glycol oxidation. The same authors reported that bimetallic Pd–Pt catalysts showed enhanced conversion with respect to the monometallic Pd and Pt catalysts. Villa et al. also found a significant enhancement in catalytic activity and selectivity to C3 products without the use of basic conditions, for AuPt alloy nanoparticles supported on H-mordenite [12] or activated carbon [13], in comparison to the monometallic clusters. When alloyed with Au, Pt led to both enhanced glycerol conversion and selectivity towards C3 products relative to Pd. Au–Pt and Au–Pd

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nanoparticles supported on Mg(OH)$_2$ were also reported to be highly active for the selective oxidation of glycerol under base-free conditions at ambient temperature [14]. The performance of monometallic Pt catalysts supported on carbon under base free conditions at room temperature was recently reported [15]. It was found that the modification of carbon surface with some oxygen functional groups can improve Pt dispersion, enhancing the catalytic activity. According to [16], in AuPd/TiO$_2$, Au and Pd may form alloys, which are stable under the experimental conditions, and generate a synergistic effect for glycerol oxidation, resulting in high selectivity These authors also found that Pd/TiO$_2$ was effective for glycerol oxidation, while Au/TiO$_2$ showed little activity. PtCu/C and PtSb/MWCNTs (multiwall carbon nanotubes) showed improved activity and selectivity than the monometallic platinum samples for the selective oxidation of glycerol [17,18]. Hirasawa et al. [19] found that PdAg/C showed higher activity and selectivity to dihydroxyacetone than Pd/C for glycerol oxidation with molecular oxygen.

As regards the support, most authors agree that carbon-supported catalysts are more active than most oxide-supported catalysts [9,20] for selective glycerol oxidation in liquid phase. Among the carbonaceous supports, activated carbon is the most common and studied one [4,5,11,21,22], although graphite [23], carbon nanofibers [6] and carbon nanotubes [24,25] have also been explored, as well as some metal oxides such as TiO$_2$ [16,26], CeO$_2$ [27], and other materials: Mg(OH)$_2$ [28], hydrotalcites [10,29], zeolites [12] and ion exchange resins [30,31]. According to the literature, the size and morphology of the metal nanoparticles can be tuned depending on the support structure and properties. In a previous work [32], we studied platinum catalysts supported on anion-exchange resins for the selective oxidation of glycerol to glyceric acid. These catalysts showed very good activity, and what is also very important, very good stability, maintaining the conversion and selectivity for many reaction cycles. In the present paper, we prepared Pt-Au catalysts, in order to study the influence of the Au addition to the monometallic platinum catalysts.

2. Experimental

2.1. Materials

The resin used was Mitsubishi WA-30, a macroporous weak anion exchange resin, with tertiary amine functional groups in a styrene divinylbenzene polymer matrix. The resin exchange capacity is 1.6 equiv. L^{-1} and the BET surface area lower than 50 m^2 g^{-1}, as reported by the manufacturer. It is stable at pH values between 0 and 9. Gold (III) chloride solution (30 wt% in dilute HCl), chloroplatinic acid hydrate (purity > 99.9%) and hydrazine hydrate were purchased from Sigma-Aldrich. Glycerol (99.5% purity) and NaOH were obtained from Ciccarelli. Gaseous oxygen from Indura (99.99% purity) was used.

2.2. Catalyst preparation

Pt and Au monometallic catalysts, and Pt-Au bimetallic catalysts were prepared. Table 1 shows a list of the catalysts studied in this work. Before the metal exchange, the support was pretreated with hydrochloric acid (1.4 M) with the objective of incorporating chloride anions in the resin exchange sites. The concentration and type of competitor ion were selected in previous works [32,33]. Chloride was subsequently exchanged by the anions containing the corresponding active metal: (PtCl$_6$)$^{2-}$ for platinum and (AuCl$_4$)$^-$ for gold. After the exchange step, the metals were reduced using hydrazine solution, at pH 14. Reactions involved in the resin pretreatment, the metal exchange and reduction have been previously described [32]. Following this procedure, Pt (0.4 wt%) and Au (0.4 wt%) monometallic catalysts were prepared. The exchange was complete in both cases, since no Pt or Au were detected in the final solution by X-ray fluorescence.

Two different preparation methods were employed for the

Table 1
Catalysts prepared for this work.

Catalyst	Pt content (wt%)	Au content (wt%)	Exchange	Pt:Au molar ratio
Pt 0.2	0.20	–	–	1:0
Pt 0.4	0.40	–	–	1:0
Au	–	0.40	–	0:1
PtAu 1:1	0.20	0.20	Simultaneous	1:1
PtAu 2:1	0.27	0.13		2:1
PtAu 1:2	0.13	0.27		1:2
Pt- Au	0.20	0.20	Sequential	1:1
Au- Pt	0.20	0.20		1:1

bimetallic catalysts: simultaneous exchange of both metals, and a sequential exchange using the controlled surface reaction technique. The former catalysts were obtained similarly to the monometallic ones, by adding the exact amount of the solutions containing Pt and Au in the same exchange step. Using this procedure, PtAu catalysts with a total metal content of 0.4 wt% were prepared, with different Pt:Au molar ratios: 1:1; 2:1 and 1:2. It should be noted that since platinum and gold molar weights are very similar, the molar ratio is almost in coincidence with the weight ratio. For the catalysts prepared by sequential exchange, after the first metal exchange and reduction, the second metal was incorporated by the controlled surface reaction method [34]. The monometallic catalyst obtained in the first step was stripped with N$_2$ for 30 min and then H$_2$ for two hours. Afterwards, the solution containing the second metal was added, while treating in H$_2$ flow for another two hours. The fixation involved the reduction of the second metal (Pt or Au) on the active metal sites previously deposited, by reaction with chemisorbed hydrogen. According to previous reports [34,35], this method allows the second metal to deposit on the surface of the first one. After that the bimetallic catalysts were reduced with hydrazine in strong basic medium. Finally, the samples were filtered and washed with NaCl solution until neutral pH in the eluted solution. By this method, Pt-Au (0.4 wt%) and Au-Pt (0.4 wt%) catalysts were prepared, both with Pt:Au 1:1 molar ratios. It should be highlighted that all of the bimetallic samples contained 0.4 wt% of active metal/s, referred to the mass of wet support.

2.3. Catalysts characterization

2.3.1. Metal loading

The samples were analyzed by Energy-dispersive X-ray fluorescence (XRF). Using a Shimadzu equipment, model EDX-720, by energy dispersion. Samples were dried in an oven at 80 °C and the measures were performed under vacuum.

2.4. Microscopic analysis

the catalysts were analyzed using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM analyses were carried out with a JEOL microscope model 100CXII operated at 100KV. The SEM equipment was a JEOL JSM 35C model. The observation was made using an accelerating voltage of 20 kV. Elemental chemical analyses were also carried out by X-ray, using an electron probe micro-analysis (EPMA) technique with energy-dispersive system (EDAX), attached to the SEM.

2.5. X-ray diffraction

crystalline phases of fresh catalysts were identified by powder X-ray diffraction (XRD) analysis using a Shimadzu XD-D1 diffractometer, equipped with a CuKα radiation source and using a scanning rate of 1 min^{-1}.

2.6. X-ray photoelectron spectroscopy

The surface species were analyzed by X-ray Photoelectron Spectroscopy (XPS) using a multitechnique system (SPECS), equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV and an Al anode operated at 100 W. The pressure was maintained below 2.10^{-8} mbar during the analysis. The samples were supported on Cu double sided tape and evacuated in the prechamber for 12 h before analysis. The spectra were processed using the software Casa XPS (Casa Software Ltd., UK). The binding energy was calibrated with respect to the C1s peak (284.6 eV) of contaminated carbon.

2.7. Activity tests

Glycerol (GOH) oxidation reactions were carried out in liquid phase, using a 150 mL capacity stainless steel reactor. The reactor was discontinuous in the liquid phase and continuous in the gas phase. Pure oxygen was used as oxidant, which was fed from the reactor bottom with a pressure of 150 kPa. The glycerol/metal molar ratio (GOH/M^0) was 700, and the sodium hydroxide/glycerol molar ratio (NaOH/GOH) was varied between 2 and 3. Reactions were carried out at 303 K and 323 K. The concentration of the reactant and products were followed by high pressure liquid chromatography (HPLC), using a BioRad HPX-87H column with UV and refractive index (RI) detector. The mobile phase used was 5 mM H_2SO_4 with a flow rate of 0.6 ml·min^{-1}. Products were identified and quantified by comparison with the original samples, after obtaining the calibration curves.

The conversion was determined by monitoring the glycerol (GOH) concentration with time:

$$x_{GOH} = \frac{M_{GOH}^0 - M_{GOH}^t}{M_{GOH}^0} \tag{1}$$

where: xGOH is the glycerol conversion; M_{GOH}^0 is the glycerol molar initial concentration; and M_{GOH}^t is the glycerol molar concentration at t time.

Selectivity to compound i was determined as follow:

$$S_i = \frac{M_i^t}{(M_{GOH}^0 - M_{GOH}^t)} \cdot \frac{n_i}{3} \tag{2}$$

where M_i^t is the i compound molar concentration at t time and n_i is the carbon atoms number of the corresponding compound.

Finally, process yield was calculated according to equation 3:

$$R_i = S_i \cdot x_{GOH} = \frac{M_i^t}{M_{GOH}^0} \cdot \frac{n_i}{3} \tag{3}$$

2.8. Stability tests

The catalyst stability was determined by running ten consecutive reaction cycles, and comparing the glycerol conversion and selectivity to glyceric acid obtained in each test. Between cycles, the system was just rinsed with deionized water. The reaction condition chosen for these tests were 50 °C and NaOH/GOH ratio of 3. Additionally, the chemical stability of the metal function in the used catalyst was studied by TEM, FRX and XPS, and compared with the fresh sample.

3. Results and discussion

3.1. Catalysts characterization

The resin support, as well as the mono and bimetallic catalysts, were analyzed by X-ray diffraction (results not shown). No signals corresponding to the noble metals were observed, indicating that the crystal
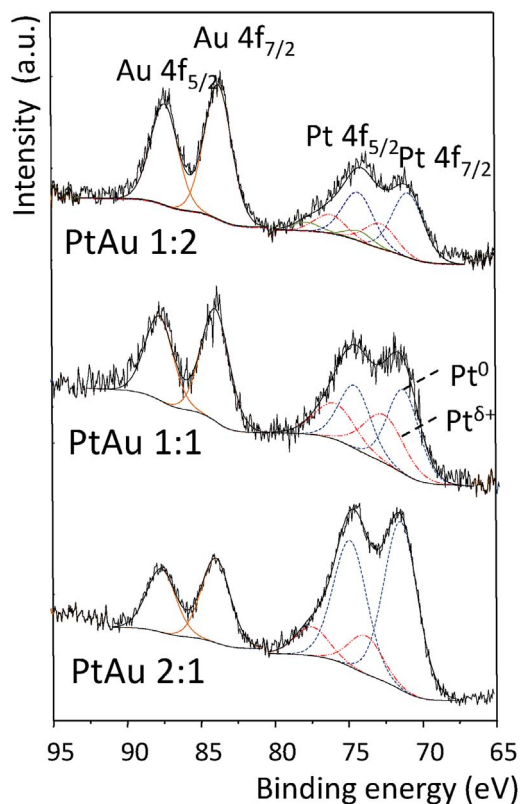

Fig. 1. XPS spectra in the Pt 4f-Au 4f region. Simultaneous metals exchange.

Table 2
XPS results for the different mono and bimetallic catalysts.

Catalyst	B.E. Pt 4f$_{7/2}$ (eV)	B.E. Au 4f$_{7/2}$ (eV)	(Pt/Au)$_s$
Pt	71.6		
Au		84.1	
PtAu 2:1	71.5 (81%)	84.0	3.08
	73.9		
PtAu 1:1	71.3 (57%)	84.0	1.60
	72.6		
PtAu 1:2	70.9 (72%)	83.7	0.85
	72.7		
Pt- Au	71.6 (82%)	83.8	0.20
	73.4		
Au- Pt	71.5 (79%)	84.1	1.52
	73.7		
Au- Pt used	71.1 (64%)	83.7	1.23
	73.6		

sizes of the metal particles were very small, and could not be detected by this technique.

The XPS spectra of the bimetallic catalysts are shown in Fig. 1 (simultaneous exchange) and 2 (sequential exchange). Also, Table 2 presents the results obtained by the deconvolution of Pt and Au peaks in the 4f region. The Pt 4f signal presents two main peaks at 71.6 and 75.0 eV, corresponding to the doublet 4f$_{7/2}$-4f$_{5/2}$ of the Pt° specie. The spin-orbit separation is approximately 3.3 eV. In all the bimetallic samples, simultaneously or sequentially exchanged, the Pt 4f signal presents two contributions that correspond to Pt^0 and Pt$^{\delta+}$, being the major contribution the corresponding to the Pt^0 species. These signals are indicated in Fig. 1.

The binding energies corresponding to the reduced Pt are slightly higher than the expected values of 71.1 eV [36]. However, this shift could be attributed to the fact that the platinum particles are of nanometric size, giving an apparent higher binding energy than the measured for bulk materials, provoked by the final state effect [11].
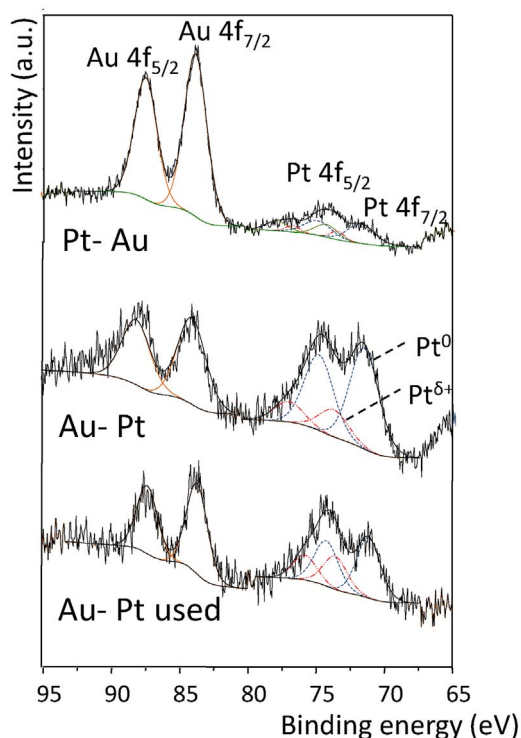
Fig. 2. XPS spectra in the Pt 4f-Au 4f region. Sequential metals exchange.

Table 3

Nominal and bulk Pt/Au ratios for the bimetallic catalysts prepared.

Catalyst	Pt/Au nominal ratio	Bulk (XRF)		
		Pt	Au	Pt/Au
PtAu 1:1	1	0.26	0.21	1.20
PtAu 2:1	2	0.34	0.16	2.10
PtAu 1:2	0.5	0.20	0.29	0.69
Pt- Au	1	0.23	0.23	1.00
Au- Pt	1	0.24	0.21	1.20

Monometallic Pt catalyst also showed this shift in the signals corresponding to the Pt^0 specie, at 71.6 and 74.9 eV. The XPS results showed that Au is present on the surface in the metallic state for all of the catalysts analyzed, with binding energies in the range 83.7–84.1 eV for the Au $4f_{7/2}$ and 87.4–88.1 eV for Au $4f_{5/2}$, which according to the literature correspond to Au^0 [37].

Standard X-ray sources are not monochromatic. Besides the principal $K_{\alpha1,2}$ line, magnesium and aluminum targets also produce a series of lower intensity lines, referred to as X-ray satellites [38]. According to Krause and Ferreira [39], when using an Al anode, the major satellite line is the $K_{\alpha3}$, which appears at 9.6 eV from the $K_{\alpha1,2}$ line, and have a relative intensity of 7.8%. Because Pt 4f signals are very close to those of Au 4f, for those samples in which the Au peaks are much bigger than the Pt peaks, the contribution corresponding to the Au satellites peaks in the Pt region is not negligible. For this reason, the Pt 4f deconvolution for the PtAu 1:2 sample (Fig. 1) shows three pairs of peaks; two of them correspond to Pt species (Pt^0 and $Pt^{\delta+}$) and the third to the contribution of the $K_{\alpha3}$ Au satellite peak. The same occurs for the Pt −Au sample spectra, presented in Fig. 2.

Fig. 1 and Table 2 shows that the BE of Pt $4f_{7/2}$ shifts to lower BE as Au content increases, being 71.6 eV for the monometallic catalyst, and 71.5, 71.3, and 70.9 eV for the PtAu 2:1, 1:1, and 1:2, respectively. This shift indicates that there is a decrease in the d-band center, decreasing the strength of the interaction between the adsorbates and the catalyst [40]. There is also a down-shift in the BE of Au $4f_{7/2}$ (see Table 2). These results suggest that there is an alloy formation, as previously found in PtAu catalysts supported on carbon [41,42].

The Pt and Au contents of the bimetallic catalysts, prepared by simultaneous exchange and controlled surface reaction, were analyzed by energy-dispersive X-ray fluorescence (XRF), using the fundamental parameters method. The results obtained are shown on Table 3, where the Pt/Au bulk ratio was calculated using the values obtained by XRF. Based on these values, it is possible to conclude that with both preparation procedures the metals were deposited on the support (resin) with a ratio very closed to the nominal one. On the other hand, the Pt/Au surface ratios obtained by XPS (see Table 2) for the samples prepared by simultaneous exchange were higher than the nominal values.

This indicates either that platinum located preferentially on the metal particle surface even when both metals were exchanged in the same step, or that Pt particles have higher dispersion than Au particles. A similar result was obtained for the Au-Pt sample, prepared by surface controlled reaction, having a Pt/Au atomic surface ratio of 1.52, similar to the ratio of 1.60 obtained for the PtAu 1:1. In this case, taking into account the preparation procedure employed for this catalyst, the deposition of platinum on the gold could be expected, since the Pt should be reduced on top of the Au. However, Schwank et al. [43] reported that in the Pt-Au/SiO_2 system at room temperature, gold alone does not show any significant uptake of H_2, since gold atoms have not displayed the capacity to dissociate molecular hydrogen at room temperature. According to these authors, and based on the XPS results, that showed that the spectrum for Au-Pt and for PtAu 1:1 are very similar, it could be concluded that the surface distributions of Pt and Au on the Au-Pt and PtAu samples are very similar. During the preparation of the Au-Pt catalyst, since Au lacks of H_2 chemisorption capacity, platinum is exchanged on the support sites, and not on the Au metallic sites. This means that the exposed amount of platinum and gold is similar when comparing these two catalysts, prepared by the two different procedures. On the other hand, for the other sequential sample (Pt-Au), the Pt/Au surface ratio was only 0.20, indicating that the deposition of the Au particles over the platinum ones was actually effective in this case. It should be remarked that for both samples, the Pt/Au ratio obtained by XRF was close to the nominal value. It can be observed that in the XPS spectrum of Pt-Au, the signal that corresponds to the Pt 4f is clearly less intensive than that for Au 4f.

Fig. 3 shows the metal radial concentration for the catalyst prepared by simultaneous exchange. These distributions were obtained using an energy-dispersive X-ray analysis (EDX) system attached to the SEM instrument. Samples have been conditioned before the analysis as was described in [32]. In Fig. 3 it can be seen that there is a metal reach zone, even visible to the naked eye. In this area the metal loading is clearly higher than nominal value, i.e. it is an egg shell metal distribution. In all cases it can be seen that the metal concentration decreases monotonically. SEM micrographs taken on the metal reach area showed that the resin morphology was not affected. This is in accordance with observation carried out on the monometallic catalyst previously studied in [32].

TEM analyses of the monometallic Pt and Au samples are presented in Fig. 4A and B, respectively. In addition, Table 4 shows the corresponding average diameter values, calculated from the data obtained by TEM. The calculations are based on the data obtained by measuring 110–120 particles for each sample analyzed. The microscopic analysis evidenced that the preparation technique used allows obtaining very small platinum and gold particles, in most cases below 3 nm diameter, and with a narrow size distribution. Fig. 5 shows the TEM images obtained with the three different bimetallic samples with Pt:Au 1:1 ratio. As it can be observed in the figure, and the values presented in Table 4, the metal particles obtained in the bimetallic samples are bigger, and with a wider size distribution. This could be indicating the formation of a PtAu alloy in the bimetallic samples, as also observed with the XPS analyses. These bimetallic particles are in most cases under the 20 nm diameter. It should be noted that similar results were obtained for all of
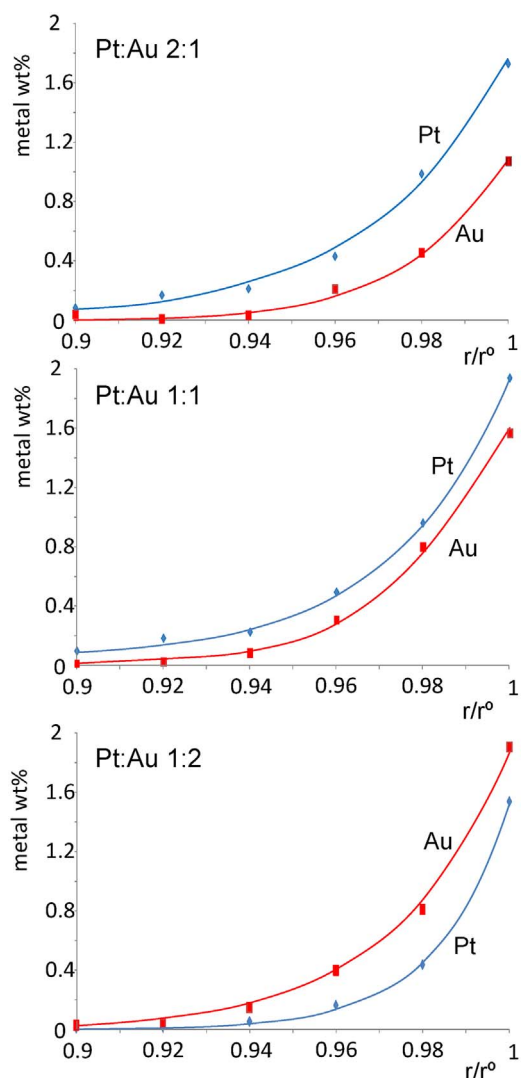
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Fig. 3. Metal radial concentration for the catalysts prepared by simultaneous exchange.
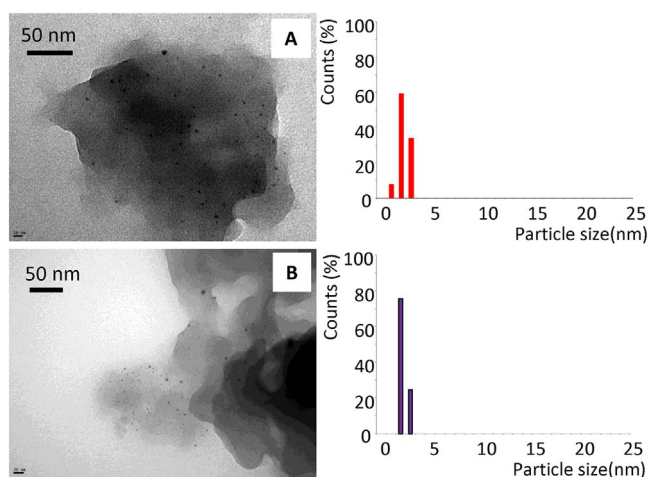

Fig. 4. TEM images and particle size distribution of monometallic resin supported catalysts. A) Pt 0.4; B) Au;.

the bimetallic catalysts, regardless the preparation method employed for metals deposition. The two contributions in the XPS spectra of the bimetallic catalysts, attributed to Pt^0 and $Pt^{\delta+}$, could be indicating the presence of Pt^0 in the surface of metal particles and $Pt^{\delta+}$ in the bulk particle. According to this, since the metal particles are bigger in the

Table 4
Average metal particle sizes calculated from TEM.

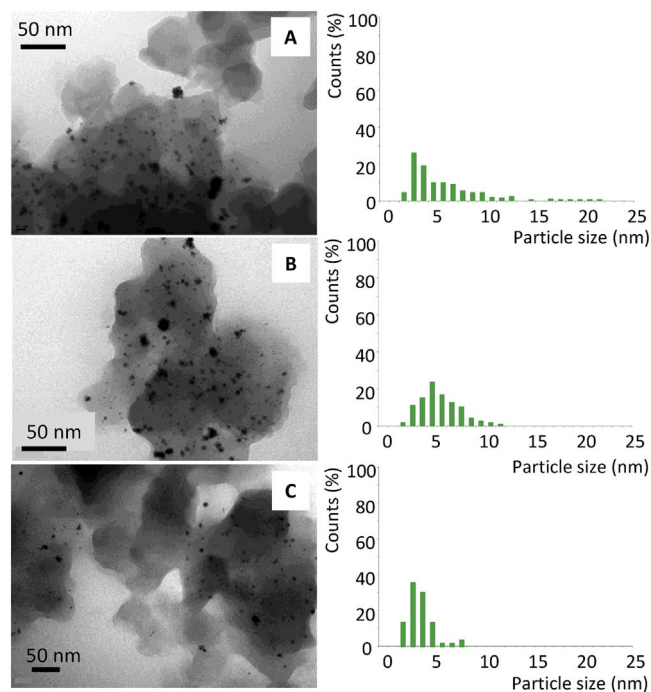| Catalyst	Average diameter (nm)
Pt	1.9
Au	1.9
PtAu 1:1	5.4
Pt- Au	5.3
Au- Pt	3.6

Fig. 5. TEM images and particle size distribution of bimetallic catalysts. A) PtAu 1:1; B) Pt- Au; C) Au- Pt.

bimetallic samples, in the reduction step during catalysts preparation, N_2H_4 only reduces the superficial metal. These results are in concordance with Balakrishnan et al. [43], who reported that the addition of Au to Pt catalysts causes a decrease in the Pt dispersion.

3.2. Catalytic activity

Fig. 6 shows the conversion vs time profiles obtained with different mono and bimetallic catalysts at 30 °C and NaOH/GOH ratio of 2. The three bimetallic catalysts with the same nominal composition (Pt/Au 1:1) but prepared using different preparation procedures are included,
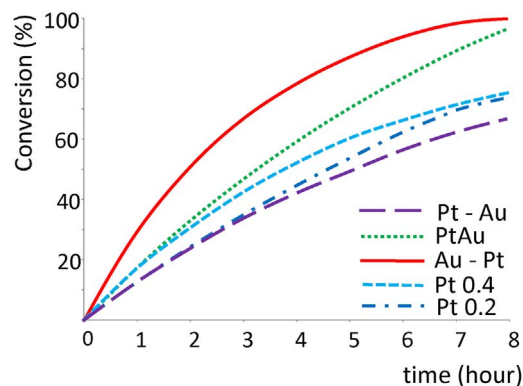

Fig. 6. Glycerol conversion with monometallic and bimetallic catalysts. Reaction conditions: NaOH/GOH: 2, T: 30 °C.

as well as the Pt monometallic catalysts. The Au 0.4% catalyst was almost inactive for the reaction (results not shown), although Au particles size in this sample was closed to that of Pt 0.4% (see Table 4). These results are in accordance with those obtained by Tongsakul et al. [10], who reported no activity for Au catalysts at room temperature and small activity for this catalyst at 333 K, although other authors found that Au catalysts were active for glycerol oxidation. According to Tongsakul et al. [10], when Au nanoparticles are too small, they became inactive for aqueous phase oxidation. Similarly, Xu et al. [16] observed no activity for Au monometallic catalysts. On the other hand, the monometallic Pt 0.4% sample displayed a good catalytic performance, and after 8 h, the glycerol conversion obtained with this catalyst was 75%. At low reaction time, or low conversion level, the activity of these catalysts are as follows: Pt 0.2 ≈ Pt-Au < Pt 0.4 ≈ PtAu < Au-Pt. Initial reaction rates are: $3.84 \cdot 10^{-6}$; $3.92 \cdot 10^{-6}$; $5.18 \cdot 10^{-6}$; $5.3 \cdot 10^{-6}$ and $8.96 \cdot 10^{-6}$ mmol cm^{-3} s^{-1} respectively. Taking into account that Au for itself did not present activity for the reaction, and that the bimetallic PtAu catalyst only have half the platinum content than the monometallic Pt 0.4 catalyst, it can be concluded that there is an important effect of Au on the Pt activity. Comparing the bimetallic PtAu catalyst with the Pt 0.2% sample, i.e., the catalyst with identical Pt content, a 38% increase in the initial reaction rate was found in the bimetallic catalyst compared to the monometallic one. This beneficial effect of Au incorporation became more pronounced as the reaction proceeded. For this reason, the final conversion (8 h reaction) obtained with the bimetallic PtAu catalyst was quite higher than the one corresponding to the Pt 0.2% sample (95% vs 77%). Fig. 7 shows the selectivity to glyceric acid obtained with the different catalysts. It can be seen that for all of them the selectivity value is almost constant, i.e., it does not depend on the conversion value (time). Furthermore, the selectivity to other reaction products presents the same behavior. Fig. 8 shows the product distribution obtained with the Au-Pt catalyst at 30 °C and NaOH/GOH ratio of 2. The bars in Fig. 8 represent the selectivity to different products. As above mentioned, the selectivity is practically constant as a function of time, being these bars representative of the results observed during this experiment. These results, selectivity value independent of time or conversion, were also obtained with Pt monometallic catalyst prepared with different ion competitors [32]. It can be seen that the overoxidation compounds are formed with selectivities below 10%. It should be remarked that with the other catalysts the same products were obtained, with minor differences in the product distribution depending on the catalyst employed.

3.3. Effect of the exchange sequence

The Pt-Au sample, prepared by the controlled surface reaction, did not show a significant improvement of conversion with respect to the monometallic platinum (Pt 0.2), i.e., the reaction rates obtained with both catalysts were similar at low conversion level. At higher times, this
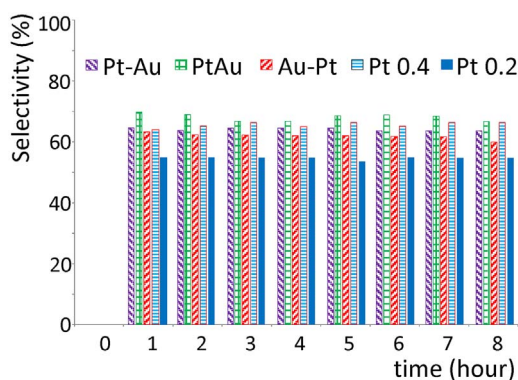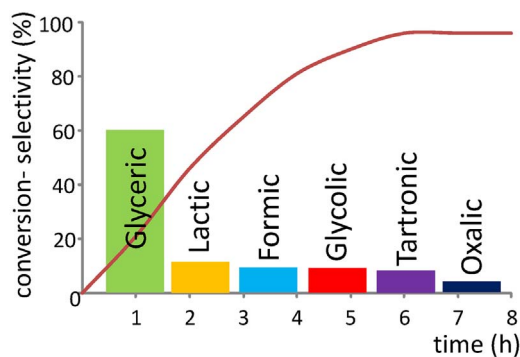
Fig. 8. Glycerol conversion and product distribution (8 h).Au-Pt catalyst. Reaction conditions: NaOH/GOH: 2, T: 30 °C.

catalyst displayed the lowest catalytic activity, while the selectivity remained almost unchanged compared with the other mono and bimetallic samples. Although the Pt:Au nominal and bulk ratio in this sample was similar to the value of the other bimetallic catalysts presented in Fig. 6, according to the XPS results the Pt amount exposed at the catalyst surface is considerably lower (see Table 2). Therefore, the platinum coverage with gold hinders the glycerol conversion and decreases the catalyst performance, although at low reaction times this catalyst has practically the same activity as the monometallic one.

On the other hand, the Au-Pt sample (sequential preparation process) was the most active catalyst among the samples studied here. It should be remarked that the Pt amount exposed on this catalyst surface is very similar to the value of the PtAu sample (co-deposition), yet the former was more active. As it was previously discussed, metallic Au does not chemisorb H_2 and therefore, Pt particles are not formed preferentially on the Au metallic particles. For this reason, the Pt/Au surface ratio for this catalyst (Au-Pt) is similar to that of the PtAu one, where both metals were simultaneously exchanged and reduced. Nevertheless, according to the activity results, the incorporation of Au and Pt in sequential steps (first Au, then Pt) provokes a Pt-Au interaction that is more beneficial for the glycerol oxidation reaction. TEM micrographs of both catalysts showed that the bimetallic particles are slightly higher than the individual monometallic Pt or Au particles. In addition, the PtAu catalyst presented a wider particle size distribution, with a small fraction of particles between 10 and 20 nm, while in the Au-Pt catalyst all particles were under 9 nm. These two catalysts have similar Pt/Au ratio on the surface, but different particle size. According to these activity results, the catalyst with the smaller metallic particles has better activity. Besides, comparing the XPS results of PtAu (1:1) (Fig. 1) and Au-Pt (Fig. 2), it is evident that the fraction of Pt^0 is higher in the latter, and this is another factor for activity improvement. Apparently, with the surface reaction method more control can be exerted over the bimetallic particles size, and this could be the cause of the improved performance of this catalyst.

3.4. Effect of temperature and NaOH/GOH ratio

To study how the temperature and NaOH/GOH ratio affect the catalyst selectivity and activity, a set of experiments were made using the Au-Pt catalyst, which had shown the best catalytic performance. The results are shown in Fig. 9. It can be seen that initially there is no apparent influence of the parameters analyzed on the reaction rate. With the progress of the reaction, the higher conversion values are obtained with lower sodium hydroxide content. Similar results were obtained by Ryabenkova et al. [11], in the oxidation of 1,2 propanediol using Pt-Au catalysts supported on C. These authors explained this behavior based on a higher adsorption of the alkaline metal on Pt. Besides, when the concentration of OH$^-$ in water increases, the oxygen solubility decreases, with the consequent negative effect on the reaction rate. In both cases, with NaOH/GOH ratio of 2 or 3, a temperature
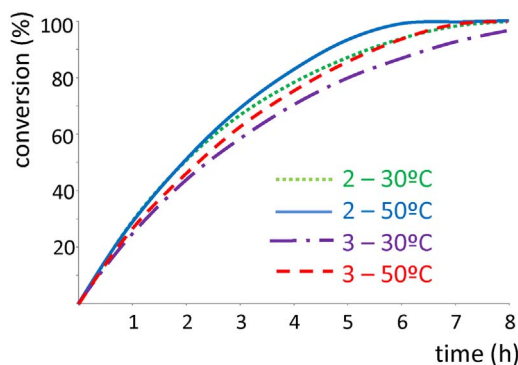
Fig. 7. Glyceric acid selectivity with monometallic and bimetallic catalysts. Reaction conditions: NaOH/GOH: 2, T: 30 °C.

Fig. 9. Glycerol conversion at different reaction conditions. Au-Pt catalyst.

increase causes an improvement in the conversion. A temperature increase has two opposite effects on the reaction rate: on one hand, it decreases the dissolved oxygen concentration, and on the other hand, it favors the reaction kinetic, according to Arrhenius law. Taking into account the results presented in Fig. 9, it can be concluded that for this particular catalytic system, the second effect prevails over the first.

3.5. Effect of Pt/Au ratio

Table 5 displays the results obtained with the bimetallic catalysts prepared by simultaneous exchange, with different Pt/Au ratios, and also the corresponding to the monometallic Pt 0.4 sample, after 8 h of reaction. At these high reaction times PtAu formulations were slightly more active and selective to glyceric acid than the monometallic one. The bimetallic alloyed particles supported on the ion exchange resin are more effective than the platinum particles for the transformation of glycerol into glyceric acid. Among the bimetallic samples, the one with 1:2 Pt:Au ratio showed improved selectivity to glyceric acid at the two temperatures and NaOH/GOH ratios employed. As a consequence, the highest yields were obtained with this catalyst, although all of the samples showed good performances for the reaction. It has to be kept in mind that the Pt content in this series of bimetallic catalysts is not constant. In fact, the 1:2 Pt:Au catalyst has the lowest Pt content (0.13 wt%) and has very high activity and, under several experimental conditions, is the most active. In all cases, it is the most selective. The XPS analyses showed that this catalyst is really different from the other

three, with a BE of Pt $4f_{7/2}$ of 70.9 eV, being 71.6, 71.5 and 71.3 for the Pt (monometallic) and the PtAu 2:1 and 1:1 respectively. This electronic change in the Pt is the cause of this difference in the catalytic performance. Data shown in Table 5 indicates that the there are no significant differences in the selectivity to glyceric acid among the Pt, and the PtAu 2:1 and 1:1, while the activity followed different trends depending upon the reaction conditions. This is because the catalysts contain not only a different Pt/Au ratio, but also a different Pt content, and therefore, a different turnover frequency referred to the exposed Pt atoms, is compensated by a different amount of the active sites.

It was also observed that at the same NaOH/GOH ratio, a temperature increase from 30 to 50 °C, although improves the activity, provokes a slight decrease in the selectivity. Therefore, the glyceric acid yield remains almost invariable.

Even though the differences in selectivities are not very high, the tendency is very clear, with an improvement in selectivity when decreasing the temperature, being the 1:2 Pt:Au catalyst the most selective to glyceric acid. The NaOH/GOH ratio does not affect the selectivity, but modifies the conversion since the alkaline metal adsorbs on Pt and the OH^- modifies the oxygen solubility, as above discussed.

3.6. Catalytic stability

The catalyst chosen to study the stability was the Au-Pt sample, and it was used in ten consecutive reaction cycles at 50 °C and 3 NaOH/GOH molar ratio. The only operation performed between each cycle was the rinsing of the catalytic bed with distilled water. No significant changes were observed in the values of selectivity and activity between the consecutive reaction cycles as can be seen in Table 6. This is in agreement with the results obtained with Pt monometallic catalysts supported on resin and reported in a previous study [32]. TEM micrographs of Au-Pt catalyst after ten reaction cycles showed a metal particle size of 3.75 nm, very closed to the value obtained for the fresh catalyst (3.64 nm, see Table 4). Moreover, according to the FRX analysis, the Pt/Au ratio of the used catalyst was 1.17, also very similar to the value reported for the fresh catalyst, which was 1.20, as shown in Table 3. These minor changes in the particle size and Pt/Au ratio confirms the remarkable stability of the bimetallic catalysts prepared for this work. The XPS spectra of the Au-Pt used in 10 reaction cycles is shown in Fig. 2. As shown in this figure and from the values reported in Table 2, it is evident that there is a shift to lower BE both in Au 4f and Pt 4f signals, what according to above discussion, indicates that there is formation of alloy during the use of these catalysts.

4. Conclusions

Pt-Au supported on WA30 anion exchange resin as catalysts were studied for the selective liquid phase oxidation of glycerol. The bimetallic catalysts were prepared using different procedures that affect the Pt-Au interaction, and therefore, the catalytic performance. The XPS spectra of the bimetallic samples suggest the formation of a Pt-Au alloy,

Table 5
Catalytic performance of bimetallic and monometallic catalysts at different reaction conditions. Reaction time: 8 h.

Reaction conditions		Catalyst	Glyceric Acid Selectivity (%)	Conversion	Glyceric Acid Yield (%)
T(°C)	r[a]				
30	3	PtAu 1:2	73.5 ± 0.1	0.95 ± 0.02	69.8
		PtAu 1:1	66.3 ± 0.1	0.86 ± 0.01	57.0
		PtAu 2:1	64.0 ± 0.1	0.92 ± 0.02	58.9
		Pt 0.4	64.5 ± 0.2	0.86 ± 0.01	55.5
50	3	PtAu 1:2	69.3 ± 0.3	1.00[b]	69.3
		PtAu 1:1	59.4 ± 0.2	0.95 ± 0.01	56.4
		PtAu 2:1	64.3 ± 0.1	0.98 ± 0.01	63.0
		Pt 0.4	58.2 ± 0.2	0.92 ± 0.02	53.5
30	2	PtAu 1:2	70.7 ± 0.1	0.98 ± 0.01	69.3
		PtAu 1:1	66.0 ± 0.1	0.93 ± 0.02	61.4
		PtAu 2:1	65.5 ± 0.2	1.00[b]	65.5
		Pt 0.4	66.2 ± 0.1	0.80 ± 0.01	53.0
50	2	PtAu 1:2	71.7 ± 0.1	0.93 ± 0.01	66.7
		PtAu 1:1	63.7 ± 0.2	0.94 ± 0.01	59.9
		PtAu 2:1	63.5 ± 0.1	1.00[b]	63.5
		Pt 0.4	59.0 ± 0.1	0.90 ± 0.02	53.1

[a] r = NaOH/GOH molar ratio.
[b] Total conversion was achieved before the 8 h reaction time.

Table 6
Catalytic performance of Au-Pt catalyst in successive reaction cycles. Reaction time: 8 h; 50 °C and NaOH/GOH 3.

Reaction cycle	GOH conversion	Gliceric acid selectivity (%)
#1	0.98	61.5
#2	0.99	62.2
#3	0.98	61.4
#4	0.97	62.8
#5	0.96	61.7
#6	0.98	62.5
#7	0.97	62.0
#8	0.97	62.3
#9	0.98	61.8
#10	0.98	62.3

with both of the preparation methods employed. By the controlled surface reaction, the metals are incorporated in a sequential exchange. The Pt-Au sample prepared by this method showed moderate activity, similar to Pt 0.2 monometallic sample. This was attributed to the surface coverage of platinum with gold, which by itself did not show catalytic activity. On the contrary, this phenomenon was not observed when gold was the first metal incorporated during the catalyst preparation (Au-Pt catalyst). This is because metallic Au does not show H_2 chemisorption capacity and therefore, Pt particles can not be formed preferentially on the Au metallic particles. For this reason, the amount of Pt exposed at this catalyst surface is similar to that of the PtAu one, where both metals were simultaneously exchanged and reduced. Nevertheless, according to the activity results, the Au-Pt catalyst, prepared by the sequential exchange of Au, and then Pt, was more active than the sample with the same contents of Au and Pt but prepared by simultaneous exchange. These two catalysts have similar Pt/Au ratio on the surface, but TEM results showed that metallic particles are slightly smaller in the Au-Pt catalyst. All the bimetallic catalysts prepared by simultaneous exchange are more active and selective than the monometallic Pt catalysts, due to the modification of the electronic structure as revealed by the XPS spectra. The 1:2 Pt:Au catalyst is the most selective, and is the most active under reaction conditions in spite of having the lowest Pt content. The BE of Pt 4f7/2 in this catalyst is significantly lower than in the other bimetallic and monometallic catalysts, and therefore, displays a superior catalytic performance.

It can be concluded that when the surface reaction method is employed, more control can be exerted over the bimetallic particles size, resulting in an improved catalytic performance.

Acknowlegments

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