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Selective oxidation of glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals

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Abstract

The liquid phase oxidation of glycerol with oxygen has been studied using a series of monometallic and bimetallic catalysts based on Au, Pd and Pt metals supported on carbon, in order to study the effect of the metal on the distribution of the products. It was found that by using bimetallic catalysts (Au–Pd, Au–Pt) the distribution of the products could be controlled. Moreover, bimetallic catalysts were by far more active than monometallic catalysts. Selectivity could be tuned by using different preparation method.

Keywords: Glyceric acid; Glycolic acid; Tartronic acid; Liquid-phase oxidation of glycerol; Gold; Palladium; Platinum

1. Introduction

A range of possible products can be formed by oxidising glycerol, such as dihydroxyacetone (DIHA) glyceraldehyde (GLYHYDE), glyceric acid (GLYA), glycolic acid (GLYCA), hydroxypyruvic acid (HPYA), mesoxalic (MOXALA), oxalic acid (OXALA) and tartronic acid (TARAC). Today the market for these chemicals has not developed because of their high cost due to their expensive current syntheses. However, using an oxidation process applied to aqueous solutions using air on recyclable catalysts will lower the cost and also will be beneficial from environmental point of view. In recent years, many studies have been focused on the oxidation of alcohols [1–8] and polyols [9–14] to chemical intermediates. The big challenge associated with these catalytic oxidation reactions is to control and direct the reaction pathway to the desired products.

Thus, glycerol oxidation has been studied in detail by applying different reaction conditions and different metals (Au, Pd, Pt, Pt/Bi) [15–21] supported mainly on carbon in order to control the product selectivity to the desired product. It has been shown that by tuning the reaction conditions, particularly the pH, the selectivity to the desired product could be tuned. Moreover, the right choice of the metal affects significantly the direction of the reaction pathway. Thus, by using acidic conditions, secondary alcoholic groups and dihydroxyacetone [16] and hydroxypyruvic acid [17] were formed, whereas at basic conditions, the primary alcoholic groups were preferentially oxidised and glyceric acid was obtained [18]. Depending on the metal employed, Au [19,20] and Pd [18] metals at basic conditions were more selective towards glyceric acid than Pt [18,21] metal. Doping Pt/C catalyst with Bi gave the highest selectivity to dihydroxyacetone, indicating the change on the direction of the reaction pathway towards to the secondary alcoholic group [18,22].

Recently we have demonstrated [23] that supported gold catalysts can give high selectivity to glyceric acid (>90%) at 100% conversion under alkaline conditions, depending on the preparation method used. In this paper, we have compared the behaviour of monometallic (Au, Pd and Pt) and bimetallic catalysts (Au–Pd, Au–Pt) supported on carbon, in order to study the effect of Pd and Pt on Au.

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2. Experimental

2.1. Materials

Na_2PdCl_4, K_2PtCl_4, $NaAuCl_4 \cdot 2H_2O$ (purity >99.0%) and PVA (Mw = 13,000–23,000, 98% hydrolysed) were from Aldrich.

Stock aqueous solutions of Na_2PdCl_4 ([Pd] = 0.449 M), K_2PtCl_4 ([Pt] = 0.038 M), $NaAuCl_4 \cdot 2H_2O$ ([Au] = 0.036 M), PVA (1%, w/w) and $NaBH_4$ (0.1 M) were prepared. The solutions of PVA and $NaBH_4$ were freshly prepared. Activated carbon was from Camel (X40S; SA = 900–1100 $m^2\,g^{-1}$; PV = 1.5 ml g^{-1}; pH 9–10). Gaseous oxygen from SIAD was 99.99% pure. Glycerol (88 wt.% solution), glyceric acid and all the intermediates were from Fluka. Deionised water (Milli-Q purified) was used in all the experiments.

Before use the carbon was suspended in HCl 6 M and left under stirring for 12 h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6–6.5. At the end the carbon was filtered off and dried for 5–6 h at 150 °C in air. The final water content was evaluated to be <3%.

2.2. Catalyst preparation

2.2.1. Monometallic sol

Au sol: Solid $NaAuCl_4 \cdot 2H_2O$ (0.043 mmol) and PVA solution (1.64 ml) were added to 130 ml of H_2O.

After 3 min, $NaBH_4$ solution (1.3 ml) was added to the yellow solution under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed.

Pd sol: Na_2PdCl_4 stock aqueous solution (0.043 mmol) and PVA solution (880 μl) were added to 130 ml of H_2O, obtaining a yellow-brown solution. After 3 min, $NaBH_4$ solution (860 μl) was added under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed.

Pt sol: Solid K_2PtCl_4 (0.051 mmol) and PVA solution (1.9 ml) were added to 150 ml of H_2O. After 3 min, $NaBH_4$ solution (1 ml) was added to the colourless solution under vigorous magnetic stirring. The light-grey Pt(0) sol was formed after 30 min.

2.2.2. Au–M bimetallic sols (M = Pd, Pt, 1:1 molar ratio)

Preparation method A: Solid $NaAuCl_4 \cdot 2H_2O$ (0.095 mmol) was dissolved in 290 ml of H_2O and PVA solution added (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA). After 3 min, $NaBH_4$ solution (2.9 ml) was added under vigorous magnetic stirring. The red Au(0) sol was immediately formed. After further 3 min, stock aqueous solution of $[MCl_4^{2-}]$ (0.099 mmol) and $NaBH_4$ solution (2.0 ml) were added, obtaining a dark brown sol.

Preparation method B: $[MCl_4^{2-}]$ stock aqueous solution (0.099 mmol) and PVA solution (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA) were added to 290 ml of H_2O. After 3 min, $NaBH_4$ solution (2.0 ml) was added under vigorous magnetic stirring. The dark brown Pd(0) sol was immediately formed. After 3 min, an aqueous solution of $NaAuCl_4 \cdot 2H_2O$ (0.095 mmol) and $NaBH_4$ solution (2.9 ml) were added, obtaining a dark-brown sol.

Preparation method C: $[MCl_4^{2-}]$ stock aqueous solution (0.099 mmol), and PVA solution (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA) were added to a solution of $NaAuCl_4 \cdot 2H_2O$ (0.095 mmol) in 290 ml of H_2O. The yellow-brown solution was stirred for 3 min and $NaBH_4$ solution (4.9 ml) was added under vigorous magnetic stirring, obtaining a dark-brown sol.

Within a few minutes of sol generation, the colloid (acidified at pH 1, by sulphuric acid) was immobilised by adding activated carbon under vigorous stirring. The amount of support was calculated as having a total final metal loading of 1 wt.%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C for 4 h. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

2.3. Alcohol oxidation

Glycerol oxidation was performed at 30 and 50 °C, respectively, using a glass reactor (30 ml capacity), equipped with heater, mechanical stirrer, gas supply system and thermometer. The glycerol solution (0.3 M and NaOH/glycerol ratio = 4, mol/mol) was added into the reactor and the desired amount of catalyst (glycerol/metal ratio = 500, mol/mol) was suspended in the solution. The pressure of the oxygen was 3 atm. Once the required temperature (30 or 50 °C) was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. Samples were removed periodically and analysed by high-performance chromatography (HPLC) using a column (Alltech OA-10308, 300 mm × 7.8 mm) with UV and refractive index (RI) detection in order to analyse the mixture of the samples. H_3PO_4 0.1% solution was used as the eluent. The identification of the possible products was done by comparison with the original samples. The activity of catalysts were reported based on TOF (calculated based on the total metal loading). The kinetic regime has been proved by subsequent experiments, changing the amount of catalyst.

2.4. Characterisation techniques

2.4.1. Sol characterisation

UV–Vis spectra of sols were performed on HP8452 and HP8453 Hewlett-Packard spectrophotometers in H_2O between 190 and 1200 nm, in a quartz cuvette.

2.4.2. Catalyst characterisation

(a) The gold content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24.

(b) X-ray diffraction experiments: Philips X'Pert vertical goniometer connected to a highly stabilised generator, Cu Kα Ni-filtered radiation, a graphite monochromator and a proportional counter with a pulse-height discriminator were used.

The XRPD measurements were done using a sample holder allowing gas flowing [24] to avoid any contamination from the air humidity, the water content changing the XRPD pattern shape. For this reason, the samples were dried with a N_2 flux for 72 h. Drying process was monitored by XRPD measurements comparing run by run the XRPD patterns. This same procedure was applied also to the support.

Then the sample, contained in the XRPD sample holder, underwent a second in situ treatment with H_2 (20 cc min^{-1} 4 h) to reduce PdO that could be present inside the sample to β-PdH. Successively, the β-PdH was washed with N_2 flux and monitored by XRPD until β-PdH disappears and metallic Pd appears.

Eventually, patterns of the sample and of the support were recorded at 295 K on a 10–140° range with a step size of 0.05° (10 s $step^{-1}$). For each sample six runs were done in order to have a final statistic of 60 s for each point. This high number of seconds was used in order to drop the noise of data as much as possible.

(c) XPS measurements were performed in an M-probe instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of 200 × 750 μm and a pass energy of 25 eV, providing a resolution for 0.74 eV. The Au 4f region at 84.0 eV was fully investigated. In order to obtain information about the Pd species, the Pd $3p_{1/2}$ region at 556 eV was studied. The choice to study this very unusual region is due to the following reasons: the classical Pd 3d peaks fall in the same position of Au 4d peaks; Pd $3p_{3/2}$ peak is overlapped with the O 1s.

The accuracy of the reported binding energies (BE) can be estimated to be ±0.2 eV. The quantitative data were also accurately checked and reproduced several times (at least 10 times for each sample).

3. Results and discussion

3.1. Sol characterisation

Monometallic catalysts, based on gold, palladium and platinum, were prepared by immobilising on carbon the corresponding sol. These materials were used as a reference for setting the behaviour of monometallic catalysts. Monometallic colloids, based on the precursors $AuCl_4^-$ $PdCl_4^{2-}$ and $PtCl_4^{2-}$ anions were prepared by reducing the corresponding salt with $NaBH_4$ in the presence of polyvinylalcohol (PVA) as a protective agent. The UV–Vis spectra, recorded in H_2O in the 190–800 nm region, showed the transformation of $AuCl_4^-$ anion (λ_{max} = 222 nm) through the appearance of the plasmon resonance peak of Au(0) sol (490–520 nm); in the case of palladium ([$PdCl_4^{2-}$]: λ_{max} = 210 and 238 nm) or platinum ([$PtCl_4^{2-}$]: λ_{max} = 218 nm), only the disappearance of precursor peaks were observed after reduction as Pd(0) or Pt(0) sols do not present plasmon bands, in agreement with the literature reports [25]. These sols were rapidly adsorbed by carbon producing monometallic catalysts. The bimetallic sols were prepared by three methods, named method A, method B and method C. The former two methods consist in the formation of a metallic sol by reduction of $AuCl_4^-$ or MCl_4^{2-}, (M = Pd, Pt) followed by reduction of the second metal salt, nucleating from the solution onto the preformed metal particles. On the contrary preparation method C consists in the simultaneous reduction of a solution of both salts. The concentrations of the precursor species were always maintained at 3.3×10^{-4} M, with Au/M molar ratio equal to one. The reductions were followed by UV–Vis spectroscopic analyses and the electronic spectra concerning with (Au–Pd) and (Au–Pt) sol generation (using method A) are reported in Figs. 1 and 2, respectively. In both cases, the first step involves the reduction of the $AuCl_4^-$ solution to Au(0) sol [Au plasmon peak λ_{max} = 510 nm]. After the addition of MCl_4^{2-} in the second step, only a further addition of sodium borohydride can reduce the MCl_4^{2-} specie producing the bimetallic sol.

In the bimetallic systems the spectra of Pd(0) or Pt(0) sols are usually superimposed to the one of gold at the end of reduction.

3.2. Catalysts characterisation

3.2.1. XRPD–XPS

In order to calculate the mean size dimensions and the nature of the active phase a proper characterisation has to be done. The main difficulty that can arise in the characterisation of nanometer sized clusters comes from the possible presence of multimodal particle size distribution. If particles having dimensions smaller than 3 nm are present, XRPD patterns could not reveal them, and the mean size dimension calculated is not representing the real situation of the active phase. In order to give a good estimate of the mean size dimensions a modified Rietveld analysis was used [26]. This method is able to evaluate the contribution to the XRPD pattern coming from very small nanoclusters (sizes less than 3 nm) and to quantify the total amount of metal, thus considering both the contribution of bigger clusters and of the smallest ones. The results of the XRPD Rietveld quantitative analysis were compared with the metal amount obtained by atomic absorption to check if all the metal was revealed by XRPD technique, then the profile parameters obtained by the Rietveld refinement were used in the calculation of the mean size dimensions.

Table 1 reports the results obtained after Rietveld analysis of XRPD measurements of (Au–Pd)/C catalysts and the

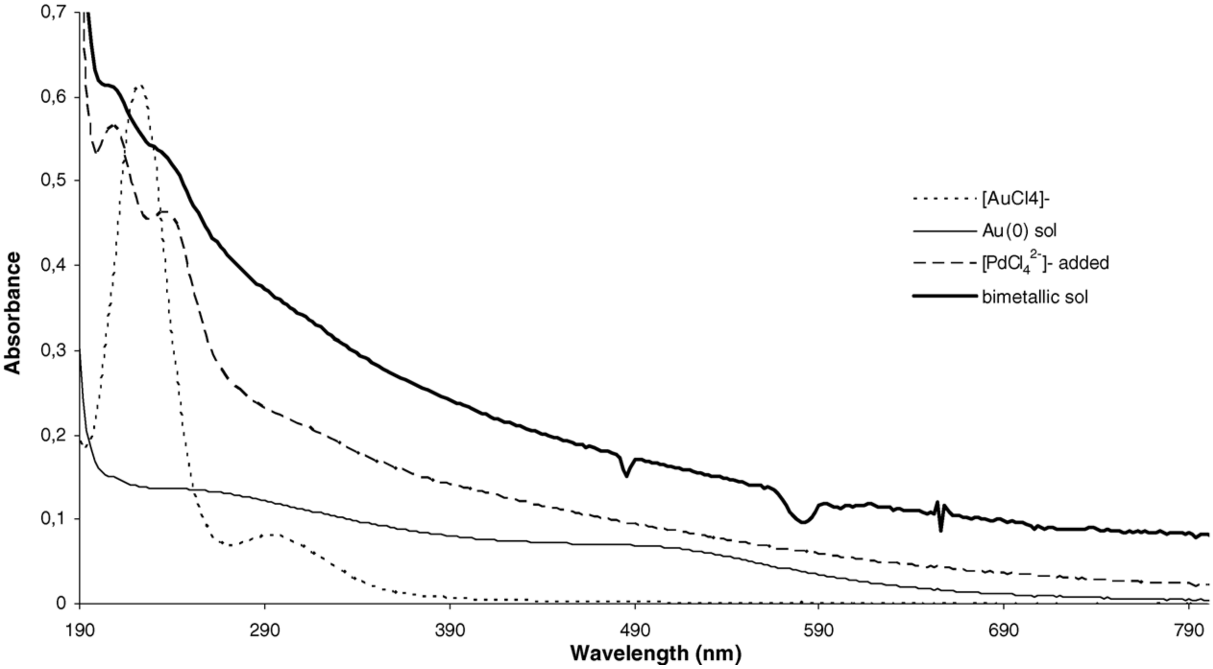


Fig. 1. UV–Vis spectra recorded in (Au–Pd-method A) sol preparation.

quantitative results of XPS analyses in terms of the surface atomic ratio Au($4f_7$)/Pd($3p_1$).

In terms of XRPD, catalyst prepared by method B presents the highest amount of pure palladium corresponding to almost the total Pd. Conversely gold is present only as alloy Au_8Pd_2 and pure gold is not present. Catalyst prepared by method A and C presented almost the same amount of the same alloyed phase Au_6Pd_4; pure palladium in these two catalysts is however reflecting the different loading of the catalyst. Moreover, (Au–Pd)/C prepared by method A presented a very finely dispersed Pd (<2 nm).

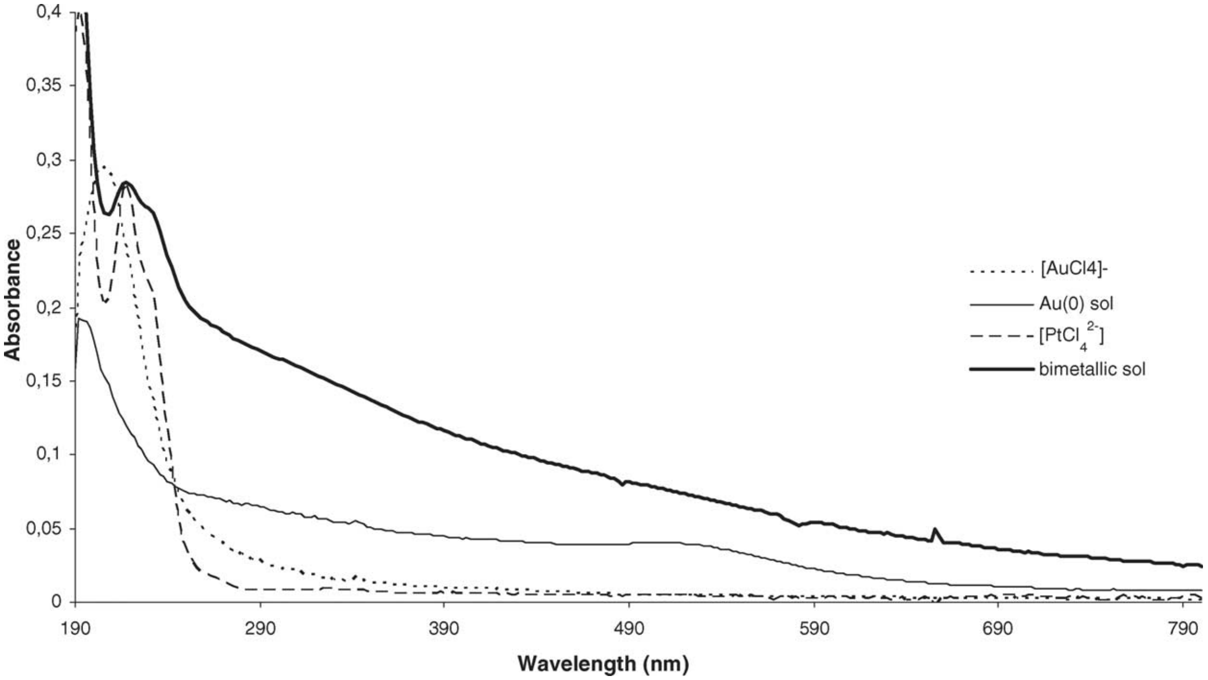


Fig. 2. UV–Vis spectra recorded in (Au–Pt-method A) sol preparation.

Table 1
Catalysts characterisation by XRPD–XPS

XRPD-Rietveld analysis							XPS
	Au[a]	Pd[a]	Au alloyed[b]	Pd alloyed[b]	Ds[c]	Quantitative analyses[d]	Surface atomic ratio $Au(4f_7)/Pd(3p_1)$
Pr.A	–	0.15%	0.60% (Au_6Pd_4)	0.20%	2.6 nm alloy, <2 nm Pd	Au = 0.60%, Pd = 0.35%	0.50
Pr.B	–	0.31%	0.75% (Au_8Pd_2)	0.01%	3 nm alloy, 2 nm Pd	Au = 0.75%, Pd = 0.32%	19.4
Pr.C	–	0.22%	0.61% (Au_6Pd_4)	0.23%	2.5 nm alloy, 3 nm Pd	Au = 0.61%, Pd = 0.45%	0.90

[a] Pure metal as determined by Rietveld analysis.
[b] Alloyed metal as determined by Rietveld analysis.
[c] Surface weighted average dimension for each of the metal phases.
[d] Theoretical metal content: Au 0.65; Pd 0.35%.

Considering these results, we could conclude that contemporary reduction of Au and Pd (method C) is the only method among the three tested that allowed to obtain alloyed phase and pure palladium with similar particle diameter, being palladium almost similarly distributed (0.22% versus 0.23%). The prior reduction of Pd (method B), on the contrary, prevents the formation of a Pd rich alloyed phase. Pd is almost totally presented as pure metal.

In terms of XPS, (Au–Pd)/C prepared by method A showed the lowest ratio $Au(4f_7)/Pd(3p_1)$ whereas (Au–Pd)/C (Method B) the highest. Only from a qualitative point of view, we could say that (Au–Pd)/C (method B) showed a higher surface gold exposure than (Au–Pd)/C (method C) which was higher than (Au–Pd)/C (method A). These results indicate to us that the bimetallic system with the prior reduction of Pd (method B) leads to the highest gold exposure on the surface, whereas the opposite result was observed when gold was firstly reduced.

3.3. Monometallic catalysts

We recently reported [23] that in the glycerol oxidation gold catalysts can be divided in two groups: the first, characterised by well dispersed nanoparticles with a mean diameter centred at 6 nm, that does not maintain the initial selectivity of the oxidation to full conversion; the second, characterised by larger particles (>20 nm), that, on the contrary, maintains constant selectivity from the beginning to the reaction end. Nevertheless, it became apparent that it is not only particle dimension that fulfils an important role in determining the reaction selectivity but also the preparation method, sol immobilisation appearing better than the impregnation or incipient wetness methods. Moreover, the overall selectivity of the reaction does not depend only on the catalyst, but also the experimental conditions play an important role. We stated that reaction conditions optimised for obtaining the highest selectivity were: $pO_2 = 3$ atm, 30 °C, NaOH/S = 4 at S/Au = 500. Using catalyst characterised by larger metal particle, a higher selectivity to glyceric acid up to 92% was achieved.

Thus, in order to correctly compare catalysts based on different metals we had to set up preparation methods able to produce metal particles of similar dimension independently on the metal nature. It is well known that gold, due to its low melting point, has the tendency to form large particles; with palladium, on the contrary, it is quite easy to obtain small particles. We expected that also for palladium the catalytic behaviour could differ by using large or small particles as well as for gold and also that the effect of a second metal could differ as a function of the diameter of the particles themselves. However, on the basis of our experience and expertise, it was simpler for us to obtain gold particles as small as palladium than the opposite; thus we used throughout this work catalysts characterised by “small” particle size (2–3 nm) although this dimension does not optimise the selectivity of the reaction toward glyceric acid.

Table 2 shows the results of the effect of monometallic catalysts (Au, Pd, Pt) for the selective oxidation of glycerol at 30 and 50 °C. At 50 °C, Au/C exhibited the highest selectivity towards glyceric acid, compared to the other metals. However, its activity was slightly lower than Pd/C. Using Pt/C catalyst full conversion could not be reached, and concentration of glyceric acid was the lowest with respect to the other two metals.

Another interesting point to mark is the distribution of the products (Table 2). At moderate conversion (50%), the major product for Au/C and Pd/C catalysts was the glyceric acid followed by glycolic and tartronic acids, whereas for Pt/C catalyst the formation of glyceric acid and glycolic acid were about at the same levels. At high conversion (90%) a different trend was observed. For Au/C a decrease up to 12% of the selectivity to glyceric acid was observed, whereas for Pd/C catalyst the decrease was up to 44%, followed by a double increase in the selectivity to tartronic acid. This result indicates that glyceric acid was more stable with the Au/C catalyst, while with Pd catalyst further oxidation to tartronic acid was favoured.

The effect of reaction temperature (Table 2) was also studied but only for monometallic Au/C and Pd/C catalysts, since for Pt/C catalyst even at 50 °C deactivation was observed; in fact for Pt/C the reaction did not proceed after 57% conversion even no leaching was observed. The selectivity to glyceric acid for Au/C catalyst was similar either at 30 or 50 °C, which suggests that the reaction temperature did not affect the overall selectivity to glyceric acid. However, a different distribution of the products was

Table 2
Oxidation of glycerol using monometallic catalysts at 30 and at 50 °C[a]

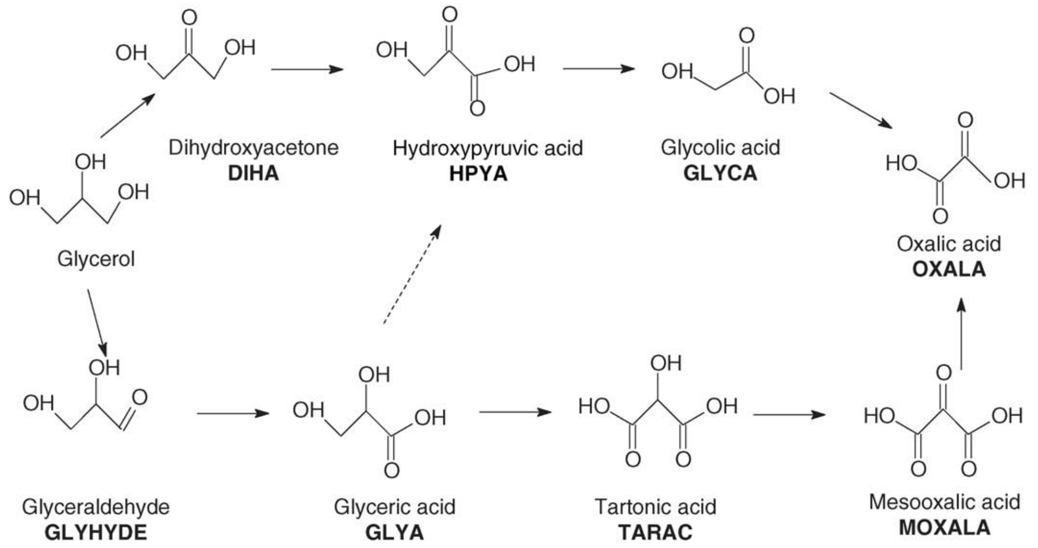
1% M/C	Selectivity (%)							
	S	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	TOF (h^{-1})[b]
1% Au/C-30 °C	S_{50}	61.7	9.8	4.7	2.9	20.8	82.5	779
	S_{90}	48.6	21.7	4.6	1.7	23.4	72.0	
1% Pd/C-30 °C	S_{50}	88.3	0.4	0.0	0.1	11.2	99.5	514
	S_{90}	64.0	7.6	2.7	0.9	24.8	71.6	
1% Au/C-50 °C	S_{50}	64.5	12.2	9.5	4.5	9.2	82.5	1090
	S_{90}	51.8	12.9	23.2	2.5	9.6	72.0	
	S_{100+1h}[c]	45.1	24.2	19.3	1.7	9.7	54.8	
	S_{100+2h}[c]	45.2	20.6	21.5	2.0	10.8	56.0	
1%Pd/C-50 °C	S_{50}	80.6	2.7	0.0	2.3	14.4	99.5	1151
	S_{90}	37.9	23.9	7.5	1.2	29.6	88.8	
	S_{100+1h}[c]	21.4	26.9	11.9	1.2	38.7	60.1	
	S_{100+2h}[c]	21.5	26.2	10.3	1.2	40.9	62.4	
1% Pt/C-50 °C	S_{50}	42.4	31.1	8.2	12.4	5.9	48.3	532
	S_{90}	–	–	–	–	–		

[a] Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 50$ °C, $pO_2 = 3$ atm.

[b] Calculation of TOF (h^{-1}) after 0.25 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

[c] Time indicated after reaching full conversion (100%) S_{50}, S_{90} indicate the selectivity observed at 50 and 90% conversion, respectively.

observed for each temperature. At 30 °C, high and similar values of selectivities to glycolic and tartronic acids were obtained, while at 50 °C, selectivities of these products decreased by a factor of 2–3 and selectivity to oxalic acid increased by a factor of 5, suggesting that at higher temperature on Au/C catalyst, further oxidation of tartronic and glycolic acids to oxalic acid was favoured. Following the reaction Scheme 1, we can hypothesise that at lower reaction temperature (longer reaction time) the formation of tartronic and glycolic acids were favoured; at higher reaction temperature (shorter reaction time) tartronic and glycolic acids were further oxidised to oxalic acid. For Pd/C catalyst, temperature affected in a different way the reaction. At 30 °C, the major product was glyceric acid with tartronic acid to follow, while formation of small amounts of glycolic and oxalic acids were observed. Note that the highest selectivity to glyceric acid with respect to Au and Pt metals was obtained. On the contrary, at 50 °C, selectivity to glyceric acid decreased by a factor of 2 and selectivity to tartronic acid was slightly increased compared to the value at 30 °C, (25% at 30 °C and 29% at 50 °C). The increase in the selectivity to glycolic acid indicates that a higher temperature promoted the formation of glycolic acid with Pd/C catalyst. Following the reaction Scheme 1, we can suppose that in the presence of Pd/C instead of Au/C, at lower reaction temperature the over-oxidation of glyceric



Scheme 1. General reaction pathways.

acid was limited. On the contrary, at higher reaction temperature glyceric acid was rapidly transformed to tartronic acid.

The stability of product distribution was also studied after reaching full conversion and prolonging reaction time (1–2 h) (Table 2). It can be indicated that with both of Au and Pd catalysts, glyceric acid was not practically over-oxidised. The only difference between the two metals is that with Au further oxidation of glycolic acid to oxalic acid proceeded, whereas with Pd, only a slight increase of the tartronic acid was observed, as the sum of glycolic and tartronic acid is constant. These results are only in partial agreement with what we observed during the reaction (drop in selectivity to glyceric acid as the reaction proceeded), which indicates the possibility of another reaction pathway. Further investigations are needed on this topic.

3.4. Bimetallic catalysts

Having in mind the catalytic data of the monometallic catalysts, we continued with the study of the bimetallic catalysts based on (Au–Pd)/C and (Au–Pt)/C at the same reaction conditions.

3.4.1. (Au–Pd)/C

The main product for the (Au–Pd)/C catalysts either at 30 or 50 °C was glyceric acid followed by the formation of tartronic, glycolic, hydroxypyruvic and oxalic acids. The reaction profile of (Au–Pd)/C at 30 °C (method C) is shown as an example (Fig. 3). It can be seen that as the conversion increased the selectivity to GLYA decreased and the main by-products were TARAC and GLYCA. However, depending on the preparation method and the temperature chosen, a different distribution of products was observed for each catalyst (Table 3).

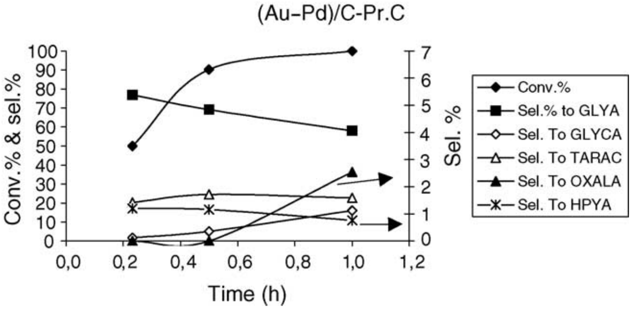


Fig. 3. Selective oxidation of glycerol in the presence of 1% (Au–Pd)/C-Pr.C. Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 30$ °C, $pO_2 = 3$ atm.

Depending on the reaction temperature, the catalytic data showed that at lower temperature (30 °C), the major product was glyceric acid (70–58% selectivity at 90% conversion) followed by tartronic and glycolic acids, indicating that the main loss of selectivity to glyceric acid was due to the formation of tartronic acid. At higher temperature (50 °C), glyceric acid was still the major product (55–57% selectivity at 90% conversion) but with lower selectivities to glyceric and tartronic acids. The formation of glycolic acid was increased by a factor of 1.2–3.7, indicating that the enhancement of the oxidation of glycerol to glycolic acid

Table 3
Oxidation of glycerol using (Au–Pd)/C catalysts at 30 and 50 °C[a]

1% (Au–M)/C	Selectivity (%)							
	S	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	TOF (h^{-1})[b]
(Au–Pd)/C-Pr.A-30 °C	S_{50}	67.9	4.7	0.0	1.9	25.5	93.4	1234.3
	S_{90}	58.5	9.6	0.0	1.5	30.4	88.9	
(Au–Pd)/C-Pr.B-30 °C	S_{50}	69.7	3.9	0.0	1.0	25.4	95.1	1444.6
	S_{90}	56.8	8.2	0.0	1.0	34.0	90.8	
(Au–Pd)/C-Pr.C-30 °C	S_{50}	76.8	1.7	0.0	1.2	20.3	97.1	1077.4
	S_{90}	69.3	5.1	0.0	1.2	24.5	93.8	
(Au–Pd)/C-Pr.A-50 °C	S_{50}	77.2	4.5	0.0	0.7	17.6	94.8	1774.5
	S_{90}	57.7	11.9	0.0	1.1	29.2	86.9	
	S_{100+0h}[c]	49.0	24.6	2.1	0.8	23.6	72.6	
	$S_{100+0.5h}$[c]	47.9	24.1	2.0	0.8	25.1	73.0	
(Au–Pd)/C-Pr.B-50 °C	S_{50}	76.5	5.9	0.0	0.7	16.8	93.3	1765.2
	S_{90}	56.7	14.2	0.0	1.2	27.9	84.6	
	S_{100+0h}[c]	48.3	22.3	2.2	0.8	26.4	74.7	
	$S_{100+0.5h}$[c]	44.6	21.3	3.6	0.8	29.8	74.4	
(Au–Pd)/C-Pr.C-50 °C	S_{50}	76.7	5.0	0.0	1.4	16.9	93.6	1510.0
	S_{90}	55.7	18.8	0.7	1.7	23.1	78.8	
	S_{100+0h}[c]	47.1	27.0	1.9	1.5	22.6	69.7	
	$S_{100+0.5h}$[c]	46.1	23.4	2.5	1.0	27.0	73.1	

[a] Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 30$, 50 °C, $pO_2 = 3$ atm.

[b] Calculation of TOF (h^{-1}) after 0.25 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

[c] Time indicated after reaching full conversion (100%) S_{50}, S_{90} indicate the selectivity observed at 50 and 90% conversion, respectively.

Table 4
Oxidation of glycerol using (Au–Pt)/C catalysts at 30 and 50 °C[a]

1%(Au–M)/C	Selectivity (%)							
	S	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	TOF (h^{-1})[b]
(Au–Pt)/C-Pr.A-30 °C	S_{50}	58.1	35.3	1.2	2.7	2.7	60.8	1434.7
	S_{90}	45.7	39.8	2.2	3.0	9.3	55.0	
(Au–Pt)/C-Pr.B-30 °C	S_{50}	53.7	36.3	1.9	2.0	6.1	59.8	922.8
	S_{90}	53.1	31.8	2.4	2.4	10.3	63.4	
(Au–Pt)/C-Pr.C-30 °C	S_{50}	47.3	45.1	1.4	2.7	3.4	50.7	1034.8
	S_{90}	50.9	35.9	2.0	2.3	8.9	59.8	
(Au–Pt)/C-Pr.A-50 °C	S_{50}	72.8	22.7	0.6	0.9	2.9	75.7	1953.4
	S_{90}	50.4	40.3	1.3	1.7	6.4	56.8	
	S_{100+0h}[c]	37.5	40.6	2.9	1.9	17.2	54.7	
	$S_{100+0.5h}$[c]	25.9	40.0	4.5	1.8	27.7	53.6	
(Au–Pt)/C-Pr.A-50 °C	S_{50}	72.3	17.6	1.1	0.9	8.1	80.4	1986.8
	S_{90}	49.2	31.5	2.2	1.6	15.5	64.7	
	S_{100+0h}[c]	30.7	34.7	4.6	1.7	28.3	59.0	
	$S_{100+0.5h}$[c]	21.3	33.1	6.2	1.5	37.8	59.1	
(Au–Pt)/C-Pr.B-50 °C	S_{50}	42.6	52.8	0.8	1.5	2.2	44.8	1257.7
	S_{90}	36.9	54.2	0.9	1.7	6.3	43.2	
	S_{100+0h}[c]	37.0	51.9	0.8	1.7	8.6	45.6	
	$S_{100+0.5h}$[c]	27.0	48.8	2.4	1.5	20.4	47.4	

[a] Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 30$, 50 °C, $pO_2 = 3$ atm.
[b] Calculation of TOF (h^{-1}) after 0.25 h of reaction. TOF numbers were calculated on the basis of total loading of metals.
[c] Time indicated after reaching full conversion (100%) S_{50}, S_{90} indicate the selectivity observed at 50 and 90% conversion, respectively.

was happening at higher temperature. In terms of activity, a higher temperature enhanced the rate of reaction by a factor up to 1.4 as the TOF showed. Comparison with the monometallic Au and Pd catalysts shows that (Au–Pd)/C catalysts were generally more active than both monometallics by a mean factor of 1.5, indicating a "synergetic" effect between Au and Pd. Depending on the preparation method, at 30 °C (Au–Pd)/C catalyst prepared with preparation method C, gave the highest selectivity to glyceric acid compared to preparation methods A and B. However, at higher temperature this trend was not observed and all bimetallic (Au–Pd)/C catalysts exhibited similar selectivity to glyceric acid. In terms of activity, catalysts prepared by using method A and B possessed higher activity than catalyst prepared by method C irrespective of reaction temperature. The mean value of decrease in activity for catalyst prepared by method C was up to 1/5 with respect to catalysts prepared by method A and B.

After reaching full conversion we let the reaction to proceed for 1h. The results showed (Table 3) that glyceric acid was quite stable with (Au–Pd)/C and only a small degradation observed at the expense of tartronic acid, in line with the data of Pd/C catalyst in terms of selectivity and of Au/C in terms of stability.

On the basis of XRPD and XPS data we tried to make a rough correlation between nature of the (Au–Pd)/C catalysts and their catalytic performance, knowing that a deeper characterisation should be done for an appropriate evaluation. This correlation is not an easy task since we observed not only the presence of an alloy but also the presence of free Pd metal on the catalyst.

Monometallic Au catalyst at 30 °C showed a higher activity than Pd, probably because Pd/C has been fast poisoned as the reaction rate rapidly declined. By increasing the temperature at 50 °C, Pd/C became more active and the effect of poisoning resulted less evident. On the contrary, all bimetallic catalysts presented higher activity, the most active at 30 °C being (Au–Pd)/C catalyst (method B). As this catalyst contains the highest amount of pure palladium we expected a faster deactivation with respect to the other bimetallic systems. (Au–Pd)/C (method A) and (Au–Pd)/C (method C) catalyst activities also appeared to be correlated to pure palladium amount: (Au–Pd)/C (method A) was more active than (Au–Pd)/C (method C) as it contains a finely

Table 5
Reaction data for the physical mixture 1% Au/C + 1% Pd/C at 30 °C[a]

		GLYA	GLYCA	OXALA	HPYA	TARAC	TOF (h^{-1})[b]
30 °C	S_{50}	71.9	6.6	–	1.9	19.6	755.0
	S_{90}	57.7	11.4	7.6	1.2	22.2	

[a] Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 30$ °C, $pO_2 = 3$ atm.
[b] Calculation of TOF (h^{-1}) after 0.25 h of reaction S_{50}, S_{90} indicate the selectivity observed at 50 and 90% conversion, respectively.

dispersed Pd particles. A physical mixture of Au/C and Pd/C presented a comparable activity (Table 5) as gold monometallic catalyst, not showing any effect of poisoning. Thus, we could conclude that the presence of gold is beneficial for palladium activity even not alloyed. This conclusion could also explain the behaviour of (Au–Pd)/C (method B) that resulted very active in spite of the high content of pure palladium. As bimetallic were by far more active than physical mixture of Au/C and Pd/C, we emphasised also the importance of alloyed phases. At 50 °C, except from (Au–Pd)/C (method C), the activities of bimetallic catalysts resulted comparable. From the selectivity point of view we obtained the best result using (Au–Pd)/C prepared by method C. In this case, pure palladium is presented with a mean diameter similar as the alloyed phase. On the contrary with method A we had a very dispersed palladium and an alloyed phase similar in terms of both atomic ratio (6:4) and amount (0.61–0.60) with respect to method C. As the selectivity in these cases differs a lot, we ascribed this difference to the mean diameter of Pd particles. In fact (Au–Pd)/C (method B), which contains the highest amount of Pd (0.31%) with a mean diameter in between the Pd mean diameter of (Au–Pd)/C prepared by methods A and C, showed an intermediate selectivity. On the basis of our previous results [23], we have demonstrated that particle size affected both activity and selectivity, with larger particle size to yield a better initial selectivity (S_{50}), and also to a lower over-oxidation of glyceric acid (S_{90} similar to S_{50}), whereas activity to follow a decrease with the increase of particle size.

3.4.2. *(Au–Pt)/C*

By using Pt instead of Pd for the bimetallic catalysts, a different trend in the distribution of products was observed (Table 4). At 30 °C, the major product was still glyceric acid (45–50% selectivity at 90% conversion), but with lower selectivity than (Au–Pd)/C catalysts (Fig. 4). However, the second major by-product was not tartronic acid as it was with (Au–Pd)/C catalysts but glycolic acid. Slight decrease in selectivities was observed also at 50 °C, with the only difference being the slight higher amount of glycolic acid formed. In terms of activity a higher temperature lead to the enhancement of the activity (TOF) by a mean factor of 1.4, similar to the value obtained for (Au–Pd)/C catalysts. These results indicate that the effect of reaction temperature is mainly on the enhancement of the activity of the catalysts, while the selectivity of glyceric acid slightly decreased with increase of the temperature. By using different preparation methods at the same temperature, the selectivity to glyceric acid and activity were similar for catalysts prepared by method A and B. On the contrary, for catalyst prepared by method C selectivity to glyceric acid was higher (51%) at 30 °C and lower (36%) at 50 °C. Activity was much lower by an average factor of 1/3, as it was happening for (Au–Pd) catalysts comparing with the same preparation method. Especially at 30 °C, on catalyst prepared by method C, selectivity to glyceric acid was constant until full conversion.

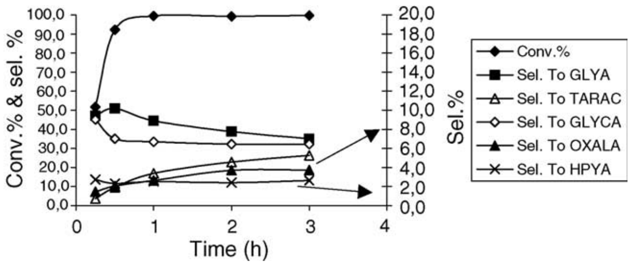


Fig. 4. Selective oxidation of glycerol in the presence of 1% (Au–Pt)/C-Pr.C. Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, $T = 30$ °C, $pO_2 = 3$ atm.

Comparison of the product distribution after reaching full conversion with the (Au–Pt)/C catalysts a different trend was established with (Au–Pd)/C catalysts. The results of the sum of selectivity of glyceric and tartronic acids as reported in Table 4, indicate that glyceric acid underwent consecutive oxidation to tartronic acid, while at the same time, decrease of glycolic acid at the expense to oxalic acid was observed.

4. Conclusions

This study has shown that depending upon the nature of the metal and the reaction conditions, it is possible to direct the distribution of the products for the oxidation of glycerol. In terms of activity either at 30 or 50 °C, bimetallic catalysts are more active than monometallic catalysts, indicating that a synergetic effect exists between Au and M (Pd or Pt). This effect was especially significant in the case of Pt as the monometallic was poisoned before reaching full conversion. In terms of selectivity to glyceric acid, (Au–Pd) catalysts showed in general better selectivity than (Au–Pt) catalysts, with Pd mainly to promote the formation of tartronic acid and Pt to glycolic acid. The overall selectivity to glyceric acid increased using bimetallic (Au–Pd)/C catalysts with respect to monometallics.

From the results obtained studying the behaviour of the catalysts after reaching full conversion (prolonged contact time), we have concluded that glyceric acid was not practically over-oxidised by Au and Pd catalysts (mono or bimetallics), whereas by Au and Pt catalysts (mono or bimetallics), consecutive oxidation to tartronic acid proceeded. Thus, since a drop in the selectivity to glyceric acid happened during the duration of the reaction, we have to suppose another reaction pathway for the formation of glycolic and tartronic acids, except from the over-oxidation of glyceric acid (Scheme 1). Comparison of the different preparation methods indicates that methods A and B with Pd or Pt catalysts gave similar catalytic results, suggesting that the preparation method of the catalyst did not affect significantly the overall selectivity to glyceric acid. On the contrary, by using method C, a different trend in terms of activity and also selectivity was observed. Thus, using (Au–Pd)/C prepared by method C, at 30 °C we obtained the best result in terms of selectivity to glyceric acid (69% at 90% conversion). XRPD characterisation of the (Au–Pd)/C catalysts highlighted the importance of the presence of both (Au–Pd) alloy and of dispersed free Pd in determining the highest selectivity observed. Further characterisation of the (Au–Pt)/C catalysts is underway in order to correlate nature of the catalyst with its activity/selectivity properties as we did for (Au–Pd)/C.

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