

# Investigation on the behaviour of Pt(0)/carbon and Pt(0),Au(0)/carbon catalysts employed in the oxidation of glycerol with molecular oxygen in water

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## Abstract

Monometallic and bimetallic catalysts based on Au and Pt metal supported on carbon, were synthesized by varying the nature of Pt precursor and the reducing agent. It was found that the nature of Pt precursor in combination with reducing agent, significantly affected the process of reduction and particle growth. The catalytic performance of the synthesized Pt/C catalysts in the liquid phase oxidation of glycerol was considerably affected in terms of activity and distribution of products. Reduction by H<sub>2</sub> and NaBH<sub>4</sub> depending on the nature of the Pt precursor resulted in the most active and selective catalysts. Improvement of activity was found by addition of Au.

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**Keywords:** Glyceric acid; Glycolic acid; Tartronic acid; Liquid phase oxidation of glycerol; Gold; Platinum; Reducing agent effect

## 1. Introduction

The use of Pt as heterogeneous catalyst in the liquid phase oxidation is very common in academia and industry. Despite the most common synthesis of supported Pt catalysts is based on the impregnation [1–4], immobilization of Pt colloids [5,6] has been used for preparing very active Pt catalysts. Advantages of using this methodology are the reproducible variation of particle size and the control of particle size distribution. However, the most delicate aspects in the synthesis of the Pt colloids is the reduction method of platinum salts and the stabilization of formed Pt colloids normally performed by the use of synthetic polymers. The reduction of aqueous Pt precursors could be performed with H<sub>2</sub> [7–9], or through, photochemical [7,10], pulse-radiolytic [11,12] and thermal means [13,14].

Despite of the large number of applications in liquid phase in which Pt supported on carbon have been used as the catalyst, it has been demonstrated that when dioxygen is used as the oxidant, Pt suffers from irreversible deactivation problems, which can be due either to over-oxidation or poisoning of the metal

surface [15]. Nevertheless, a solution to override this problem is the addition of another metal component, such as Pb or Bi [15,16] that has shown to minimise the poisoning, thus enhancing the lifetime of the catalyst. However, problems of leaching and reconstruction of the catalyst as well as a different product distribution can be seen [15].

Recently, our group has demonstrated that the addition of Au to Pd or Pt metals was not only beneficial in terms of activity/selectivity to various catalytic reactions, but it also enhanced the resistance to poisoning (oxygen or by-product poisoning) with respect to monometallic catalysts [17,18]. The aim of the present study is to investigate the effect of Pt precursor and of the reducing agent in the preparation of monometallic Pt/C catalyst and the role of Au as the secondary metal component on the corresponding bimetallic catalyst systems. The model reaction for this study was chosen to be the liquid phase oxidation of glycerol.

## 2. Experimental

### 2.1. Materials

Aqueous stock solutions of PVA (1%, w/w), NaBH<sub>4</sub> (0.1 M) and N<sub>2</sub>H<sub>4</sub> (0.1 M) were prepared. Fresh solution of K<sub>2</sub>PtCl<sub>4</sub>

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and  $\text{NaAuCl}_4$  were always used. Aged solutions of  $\text{K}_2\text{PtCl}_4$  were prepared upon dissolving  $\text{K}_2\text{PtCl}_4$  in mQ water for 60 h ( $[\text{PtCl}_4^{2-}] = 5 \times 10^{-4}$  M). Activated carbon was from Camel (X40S; SA = 900–1100  $\text{m}^2 \text{g}^{-1}$ ; PV = 1.5  $\text{ml g}^{-1}$ ; 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

**2.2.1.1. Pt-A.** An aqueous solution was prepared upon mixing under vigorous magnetic stirring PVA solution (488  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution), solid  $\text{K}_2\text{PtCl}_4$  (10.3 mg, 0.025 mmol) and 52.0 ml of  $\text{H}_2\text{O}$ . After 3 min,  $\text{NaBH}_4$  solution (5 ml, 0.05 M) was added. A light grey colloid was formed and reacted for 30 min, (Pt =  $4.3 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 10:1$ , PVA/Pt = 1).

**2.2.1.2. Pt-B.** An aqueous solution was prepared upon mixing under vigorous magnetic stirring PVA solution (4.88  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution), solid  $\text{K}_2\text{PtCl}_4$  (10.3 mg, 0.025 mmol) and 52.0 ml of  $\text{H}_2\text{O}$ . After 3 min,  $\text{N}_2\text{H}_4$  solution (250  $\mu\text{l}$ , 0.1 M) was added. A grey colloid was reacted for 15 min, (Pt =  $4.7 \times 10^{-4}$  M,  $\text{N}_2\text{H}_4/\text{Pt} = 1:1$ , PVA/Pt = 1).

**2.2.1.3. Pt-C.** An aqueous solution was prepared upon mixing under vigorous magnetic stirring PVA solution (488  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution), solid  $\text{K}_2\text{PtCl}_4$  (10.3 mg, 0.025 mmol) and 52.0 ml of  $\text{H}_2\text{O}$ . After 3 min,  $\text{H}_2$  (50 ml/min) was bubbled through the solution for 2 h. A dark grey colloid was left to stand for 18 h, (Pt =  $4.7 \times 10^{-4}$  M,  $\text{H}_2/\text{Pt} = \text{excess}$ , PVA/Pt = 1).

**2.2.1.4. Pt-A'.** The pink solution, formed upon dissolving solid  $\text{K}_2\text{PtCl}_4$  (10.3 mg, 0.025 mmol) in 52.0 ml of  $\text{H}_2\text{O}$  was let to age for 60 h. Then, PVA solution (488  $\mu\text{l}$  of 1% (w/w) aqueous stock solution) and  $\text{NaBH}_4$  solution (750  $\mu\text{l}$ , 0.1 M) were added under vigorous magnetic stirring. The mixture was led to react for 45 min forming a grey–brown sol, (Pt =  $4.7 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 3$ , PVA/Pt = 1).

**2.2.1.5. Pt-B'.** The pink solution formed upon dissolving solid  $\text{K}_2\text{PtCl}_4$  (10.3 mg, 0.025 mmol) in 52.0 ml of  $\text{H}_2\text{O}$  was let to age for 60 h. Then, PVA solution (488  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution) and  $\text{N}_2\text{H}_4$  solution (1 ml, 0.1 M) were added under vigorous magnetic stirring. The mixture was let to react for 45 min forming a grey sol, (Pt =  $4.7 \times 10^{-4}$  M, Red/Pt = 4, PVA/Pt = 1).

### 2.2.2. Au–Pt bimetallic sols

**2.2.2.1. (Au–Pt)-A1.** PVA solution (3 ml of a 1% (w/w) aqueous stock solution) was added to 226.5 ml of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (30.6 mg, 0.077 mmol) aqueous solution, under vigorous magnetic stirring. After 3 min,  $\text{NaBH}_4$  solution (2.3 ml, 0.1 M) was added. A ruby red sol was immediately formed. After 5 min, 2.0 ml of  $\text{K}_2\text{PtCl}_4$   $3.85 \times 10^{-2}$  M aqueous solution (0.077 mmol) and  $\text{NaBH}_4$  solution (1.5 ml, 0.1 M) were added. A red–brown sol was formed and was let to react for 15 min, (Au/Pt =  $3.3 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 2$ ,  $\text{NaBH}_4/\text{Au} = 3$ , PVA/Pt = 1).

**2.2.2.2. (Au–Pt)-A2.** PVA solution (3 ml of a 1% (w/w) aqueous stock solution) was added to 226.5 ml of  $\text{K}_2\text{PtCl}_4$  (32.0 mg, 0.077 mmol) aqueous solution. After 3 min,  $\text{NaBH}_4$  solution (1.5 ml, 0.1 M) was added. A grey sol was formed. After 15 min, 2.0 ml of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  ( $3.85 \times 10^{-2}$  M) aqueous solution (0.077 mmol) and  $\text{NaBH}_4$  solution (2.3 ml, 0.1 M) were added. A dark brown sol was formed and was let to react for 5 min, (Au/Pt =  $3.3 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 2$ ,  $\text{NaBH}_4/\text{Au} = 3$ , PVA/Pt = 1).

**2.2.2.3. (Au–Pt)-A3.** Solid  $\text{K}_2\text{PtCl}_4$  (32.0 mg, 0.077 mmol) and  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (30.6 mg, 0.077 mmol) were added to 226.5 ml of  $\text{H}_2\text{O}$ . Then, PVA solution (3 ml of a 1% (w/w) aqueous stock solution) and  $\text{NaBH}_4$  solution (3.9 ml, 0.1 M) were added. A dark brown sol was formed and was let to react for 15 min, (Au/Pt =  $3.3 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{M} = 5$ , PVA/Pt = 1).

**2.2.2.4. (Au–Pt)-A'1.** PVA solution (152.0  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution) was added to 231.0 ml of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (30.6 mg, 0.077 mmol) aqueous solution, under vigorous magnetic stirring. After 3 min,  $\text{NaBH}_4$  solution (2.3 ml, 0.1 M) was added. A ruby red sol was immediately formed. After 5 min, 2.0 ml of a 60 h “aged”  $\text{K}_2\text{PtCl}_4$   $3.85 \times 10^{-2}$  M solution (0.077 mmol) and PVA solution (150.0  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution) were added. After 3 min,  $\text{NaBH}_4$  solution (1.5 ml, 0.1 M) was added. The mixture was let to react for 45 min forming a red–brown sol, (Au/Pt =  $3.3 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 2$ ,  $\text{NaBH}_4/\text{Au} = 3$ , PVA/Pt = 1).

**2.2.2.5. (Au–Pt)-A'2.** A pink solution was formed upon dissolving solid  $\text{K}_2\text{PtCl}_4$  (10.4 mg, 0.025 mmol) in 52.0 ml of  $\text{H}_2\text{O}$  and was let to age for 60 h. Then, PVA solution (490  $\mu\text{l}$  of a 1% (w/w) aqueous stock solution) and  $\text{NaBH}_4$  solution (500  $\mu\text{l}$ , 0.1 M) were added under vigorous magnetic stirring. The mixture was let to react for 45 min forming a dark solution. Then, PVA solution (490  $\mu\text{l}$ ), 3.12 ml of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  ( $8 \times 10^{-3}$  M) aqueous solution (0.025 mmol) and  $\text{NaBH}_4$  solution (750  $\mu\text{l}$ , 0.1 M) were added. It was let to react for 30 min forming a dark brown sol, (Au =  $4.6 \times 10^{-4}$  M, Pt =  $4.7 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt} = 2$ ,  $\text{NaBH}_4/\text{Au} = 3$ , PVA/M = 1).

**2.2.2.6. (Au–Pt)-A'3.** A pink solution was formed upon dissolving solid  $\text{K}_2\text{PtCl}_4$  (10.4 mg, 0.025 mmol) in 52.0 ml of  $\text{H}_2\text{O}$  and was let to age for 60 h. Then, solid  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (9.9 mg, 0.025 mmol), and PVA solution (980  $\mu\text{l}$  of a 1% (w/w) aqueous

stock solution) were added.  $\text{NaBH}_4$  solution (1.25 ml, 0.1 M) was added and was let to react for 45 min under vigorous magnetic stirring forming a dark brown sol, ( $\text{Au}/\text{Pt}=4.6 \times 10^{-4}$  M,  $\text{NaBH}_4/\text{Pt}=2$ ,  $\text{NaBH}_4/\text{Au}=3$ ,  $\text{PVA}/\text{M}=1$ ).

2.2.2.7. (Au–Pt)-B. Solid  $\text{K}_2\text{PtCl}_4$  (31.5 mg, 0.076 mmol) and  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (30.2 mg, 0.076 mmol) were added to 224.0 ml of  $\text{H}_2\text{O}$ . After 3 min, PVA solution (3 ml of a 1% (w/w) aqueous stock solution) and  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  solution (3.1 ml, 0.1 M) were added. A blue sol was formed and was let to react for 15 min, ( $\text{Au}/\text{Pt}=3.3 \times 10^{-4}$  M,  $\text{N}_2\text{H}_4/\text{Pt}=2$ ,  $\text{N}_2\text{H}_4/\text{Au}=2$ ,  $\text{PVA}/\text{Pt}=1$ ).

2.2.2.8. (Au–Pt)-C. PVA solution (1.5 ml of a 1% (w/w) aqueous stock solution) was added to 238.0 ml of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (30.4 mg, 0.076 mmol) aqueous solution, under vigorous magnetic stirring. After 3 min,  $\text{NaBH}_4$  solution (2.3 ml, 0.1 M) was added. A ruby red sol was immediately formed. After 5 min, 3.17 ml of  $\text{K}_2\text{PtCl}_4$  aqueous solution ( $2.4 \times 10^{-2}$  M, 0.076 mmol) and PVA solution (1.5 ml of a 1% (w/w) aqueous stock solution) were added. After 3 min,  $\text{H}_2$  (50 ml/min) was bubbled through the solution for 2 h. A dark grey colloid was left to stand for 18 h, ( $\text{Au}=3.2 \times 10^{-4}$  M,  $\text{Pt}=3.1 \times 10^{-4}$  M,  $\text{H}_2/\text{Pt}=\text{excess}$ ,  $\text{NaBH}_4/\text{Au}=3$ ,  $\text{PVA}/\text{M}=1$ ).

### 2.2.3. Immobilization

Within a few minutes of sol generation, the colloids (acidified at pH 1, by sulphuric acid) were immobilized 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  $120^\circ\text{C}$  for 4 h. ICP analyses were performed on the filtrate using a Jobin Yvon JY24 to verify the metal loading on carbon.

### 2.3. Oxidation tests

Glycerol oxidation was performed at  $50^\circ\text{C}$  using a glass reactor (30 ml capacity), equipped with heater, mechanical stirrer, gas supply system and thermometer. The glycerol solution (0.3 M and  $\text{NaOH}/\text{glycerol}$  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 ( $50^\circ\text{C}$ ) was reached under inert atmosphere, the gas supply was switched to oxygen (3 atm) 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  $\times$  7.8 mm) with UV and refractive index (RI) detection in order to analyse the mixture of the samples.  $\text{H}_3\text{PO}_4$  0.1% solution was used as the eluent. The identification of the possible products was done by comparison with the original samples. The activities of catalysts were reported based on TOF (calculated based on the total metal loading).

## 2.4. Characterization techniques

### 2.4.1. Sol characterization

UV-visible spectra of sols were performed on HP8452 and HP8453 Hewlett-Packard spectrophotometers in  $\text{H}_2\text{O}$  between 190 and 1200 nm, in a quartz cuvette.

### 2.4.2. Catalyst characterization

- The metal content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24. The M/C samples were heated with a 5:1 (v/v) mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  till carbon was burnt off. Then a 3:1 (v/v) mixture of concentrated  $\text{HCl}$  and  $\text{HNO}_3$  was added for the transformation of  $\text{M}(0)$  into  $[\text{M}^{x+}\text{Cl}_4]^{x-4}$ . The corresponding solution was then concentrated and diluted with Milli-Q water.
- X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with  $\text{Cu K}\alpha$  radiation, equipped with a graphite monochromator in the diffracted beam. The crystallite sizes of gold were estimated from peak half-widths by using Scherrer's equation with corrections for instrumental line broadening.

## 3. Results and discussion

### 3.1. Sol characterization

“Fresh”  $\text{K}_2\text{PtCl}_4$  aqueous solutions were reduced by  $\text{NaBH}_4$ ,  $\text{N}_2\text{H}_4$  and  $\text{H}_2$ . Different reaction rates were observed following the reaction by UV spectroscopy. With  $\text{N}_2\text{H}_4$  reduction was completed in 15 min and with  $\text{H}_2$  in 18 h. With  $\text{NaBH}_4$  we observed a variation in the reaction time, being the reduction completed in few minutes or hours. The absence of the plasmon resonance peak of  $\text{Pt}(0)$  sol was observed (Fig. 1), in agreement with literature reports [19].

By dissolving  $\text{K}_2\text{PtCl}_4$  in Milli-Q water for 60 h a partial substitution of chlorides by  $\text{H}_2\text{O}$  molecules takes place giving rise to  $\text{PtCl}_2(\text{H}_2\text{O})_2$  complex [20] which is reported to be kinetically

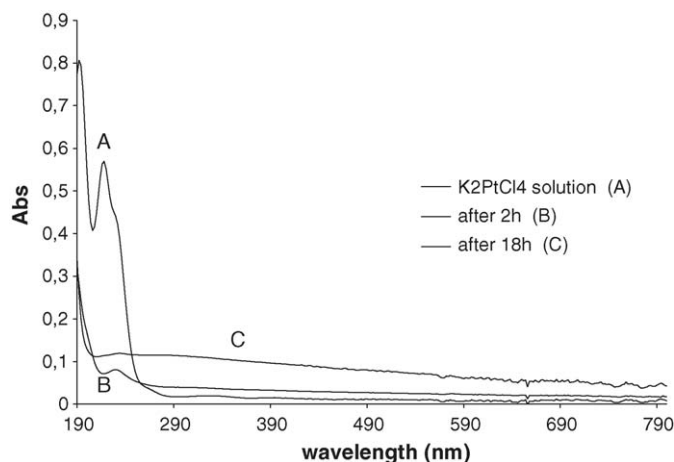


Fig. 1. UV spectrum in  $\text{H}_2\text{O}$  of the initial  $\text{PtCl}_4^{2-}$  solution (A). Pt sol obtained by reduction of (A), in the presence of PVA, by  $\text{H}_2$  after 2 h (B) and 20 h (C).

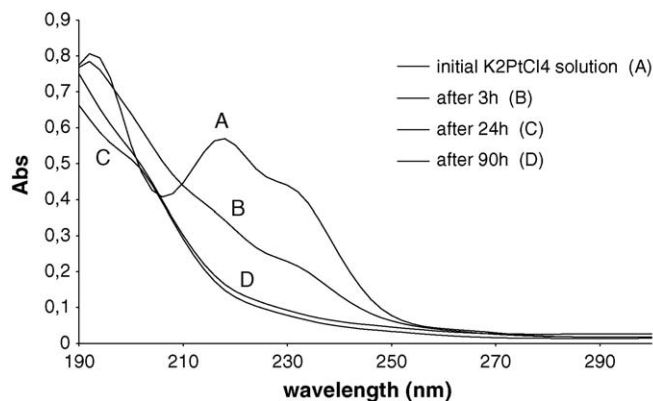


Fig. 2. UV spectrum in H<sub>2</sub>O of the formation of the PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complex: initial PtCl<sub>4</sub><sup>2-</sup> solution (A), after 3 h (B), 24 h (C) and 90 h (D).

more prone to reduction than PtCl<sub>4</sub><sup>2-</sup> [21]. We called this latter solution as “aged” Pt solutions. The formation of PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> was followed by UV spectroscopy that reveals only the disappearing of the UV peak at 218 nm without the appearance of a new characteristic band (Fig. 2). The “aged” Pt solution was reduced by NaBH<sub>4</sub>, N<sub>2</sub>H<sub>4</sub> or H<sub>2</sub>, in the presence of PVA, in order to obtain the metallic sol. The agglomeration and precipitation of black particles were obtained by H<sub>2</sub> reduction probably due to the high rate of reduction process. Different reduction rates were observed by using N<sub>2</sub>H<sub>4</sub> or NaBH<sub>4</sub>, being the first completed in 15 min while the second in 30 min. In both cases similar grey sols have been obtained.

Bimetallic Au–Pt sols were prepared by using “fresh” and “aged” PtCl<sub>4</sub><sup>2-</sup> solutions. Two methodologies already published [18] were employed (using PVA as stabilizer and NaBH<sub>4</sub> as reducing agent): (a) co-reduction of the solution of the two precursors, (b) reduction of a metal precursor in the presence of the preformed sol of the other metal. The “aged” Au–Pt sols were prepared applying the same conditions as the “fresh” ones. However, “fresh” Pt precursor solutions were used for the Au–Pt sols in which Pt precursor was reduced by H<sub>2</sub> or N<sub>2</sub>H<sub>4</sub> since the reduction time was not significantly affected.

### 3.2. Catalyst characterization

#### 3.2.1. XRPD

The crystallite size dimension (XRPD data) of the monometallic and bimetallic catalysts is shown in Table 1. In

Table 1  
Crystallite size dimension of the studied catalysts

Catalysts	Reducing agent	<i>d</i> (nm) XRPD
Monometallic “fresh”		
Pt/C-A	NaBH <sub>4</sub>	n.d.
Pt/C-B	N <sub>2</sub> H <sub>4</sub>	6.7
Pt/C-C	H <sub>2</sub>	2.0–3.0
Monometallic “aged”		
Pt/C-A'	NaBH <sub>4</sub>	2.0–3.0
Pt/C-B'	N <sub>2</sub> H <sub>4</sub>	8.4
Bimetallic “fresh”		
(Au–Pt)/C-A1	NaBH <sub>4</sub>	2.0–3.0
(Au–Pt)/C-A2	NaBH <sub>4</sub>	2.0–3.0
(Au–Pt)/C-A3	NaBH <sub>4</sub>	2.0–3.0
(Au–Pt)/C-B	N <sub>2</sub> H <sub>4</sub>	n.d.
(Au–Pt)/C-C	NaBH <sub>4</sub> /H <sub>2</sub>	n.d.
Bimetallic “aged”		
(Au–Pt)/C-A'1	NaBH <sub>4</sub>	2.0–3.0
(Au–Pt)/C-A'2	NaBH <sub>4</sub>	2.0–3.0
(Au–Pt)/C-A'3	NaBH <sub>4</sub>	2.0–3.0

the case of the monometallic catalysts either “fresh” or “aged”, the effect of the same reducing agent is similar. Thus, using NaBH<sub>4</sub> and H<sub>2</sub> as reducing agent, small particles are formed, whereas using N<sub>2</sub>H<sub>4</sub>, substantial increase of particle size was observed (6.7–8.4 nm). In the case of the bimetallic catalysts, the mean crystallite size dimension was similar (about 2–3 nm).

#### 3.3. Monometallic catalysts (“fresh” PtCl<sub>4</sub><sup>2-</sup> solution)

Table 1 shows the catalysts obtained by reduction of “fresh” K<sub>2</sub>PtCl<sub>4</sub> aqueous solution. Table 2 summarizes the catalytic data for the Pt/C catalysts. Depending from the reducing agent used (NaBH<sub>4</sub>, N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, labelled A, B and C, respectively) a different catalytic behaviour was observed in terms of activity and distribution of products. The order of activity was the following: Pt-C > Pt-A ≅ Pt-B. Having in mind the mean crystallite size dimension (XRPD data, Table 1), we can observe that increase of activity was obtained with a parallel decrease of crystallite size. Comparison at similar conversion (e.g. 54–57%) showed that the following order in terms of selectivity to glyceric acid was obtained: Pt/C-B ≅ Pt/C-C > Pt/C-A. In addition, the distribution of the by-products was affected considerably, depending on the catalyst used. Thus, in the case of using Pt/C-C and Pt/C-

Table 2  
Oxidation of glycerol using monometallic Pt/C catalysts at 50 °C<sup>a</sup>

1% M/C	Selectivity (%)							TOF (h <sup>-1</sup> ) <sup>b</sup>
	Conversion (%)	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	
Pt/C-A	57.3	45.6	27.4	7.5	11.7	7.9	53.5	218
Pt/C-B	50.4	65.5	22.0	2.4	2.0	8.1	87.5	212
Pt/C-C	79.7	60.9	21.8	3.0	2.1	12.2	73.2	332
Pt/C-A'	81.6	50.0	34.9	2.8	2.1	10.2	60.9	472
Pt/C-B'	9.3	61.3	33.7	0.0	1.9	3.10	64.4	31

<sup>a</sup> Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50 °C, pO<sub>2</sub> = 3 atm, reaction time 4 h.

<sup>b</sup> Calculation of TOF (h<sup>-1</sup>) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

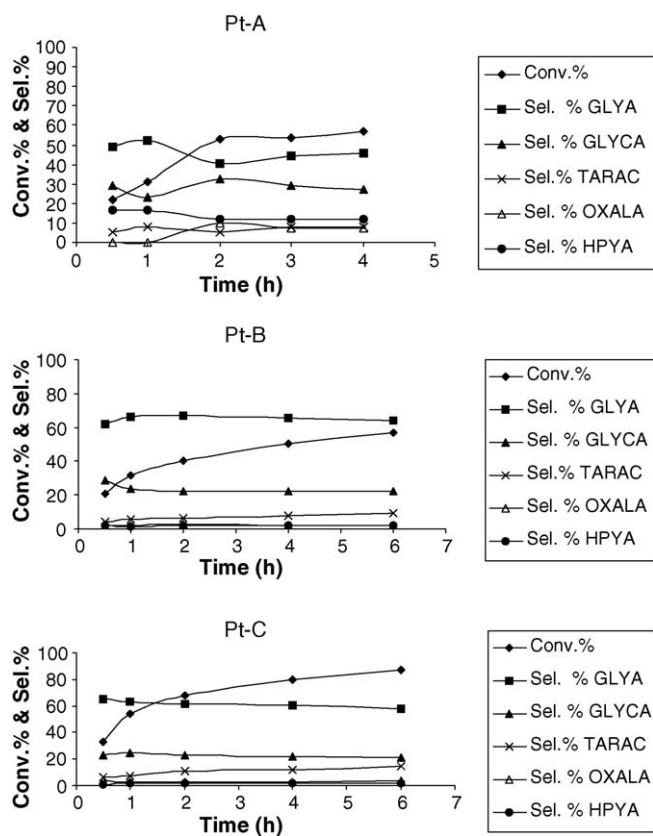


Fig. 3. Selective oxidation of glycerol in the presence of 1% Pt/C: (a) 1% Pt/C-A, (b) 1% Pt/C-B and (c) 1% Pt/C-C. Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4,  $T = 50^\circ\text{C}$ ,  $p\text{O}_2 = 3\text{ atm}$ .

B, where similar selectivities to glyceric acid were obtained, the main by-product was glycolic acid, followed by tartronic acid. It is worth wise to note the reaction profiles for these two mentioned catalysts (Fig. 3). The selectivity to glycolic acid was almost steady in the whole reaction evolution, whereas for glyceric acid a small decline was observed. At the same time selectivity to tartronic acid followed a progressive increase. In the case of Pt/C-A, although the major product was glyceric acid,

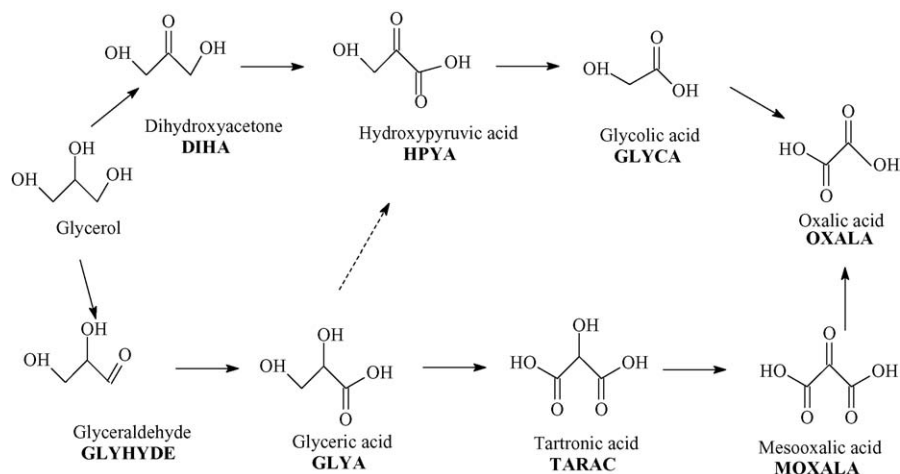
the selectivity was 20% less than the values obtained with the previous mentioned catalysts. Moreover, the major by-products were glycolic and hydroxypyruvic acids followed by oxalic and tartronic acids (Fig. 3). Having in mind the reaction network of glycerol oxidation two major routes exist for glycerol oxidation, (Scheme 1). One, through the oxidation of the primary OH group leading mainly to glyceric acid and the other through the oxidation of the secondary OH group leading to glycolic acid. From the above results, we can suggest that with Pt/C-B and Pt/C-C catalysts the primary OH group is preferred oxidised than the secondary OH group. In the case of Pt/C-A the opposite trend was observed. Although Pt/C-B and Pt/C-C catalysts showed much higher activity than Pt/C-A, in all the cases a decrease in activity was observed as the reaction time was progressing, indicating deactivation of the Pt/C catalysts.

### 3.4. Monometallic catalysts (“aged” $\text{PtCl}_4^{2-}$ )

Table 1 shows the catalysts obtained by reduction of “aged”  $\text{K}_2\text{PtCl}_4$  aqueous solution. In this case the same preparation methods were utilized instead that for the Pt precursor the “aged” solution of  $\text{K}_2\text{PtCl}_4$  was used. As it was mentioned in the sol characterization section (see Section 3.1), reduction by  $\text{H}_2$  resulted in the precipitation of the colloid; in consequence, we were unable to support on carbon. Thus, results are reported only for Pt/C-A' and Pt/C-B' catalysts (Table 2). Fig. 4 illustrates the reaction profiles of these two samples. In terms of activity Pt-A' is much more active than Pt-B', with the latter showing very poor catalytic performance. These results are in agreement with the previous ones, demonstrating that a high catalytic performance could be obtained only with a small crystallite size (below 3 nm).

### 3.5. Comparison of “fresh” and “aged” Pt/C catalysts

Significant changes in the catalytic performance of the “fresh” and “aged” catalysts were found in the oxidation of glycerol (Table 2). Comparison on the basis of the same



Scheme 1. General reaction pathways.

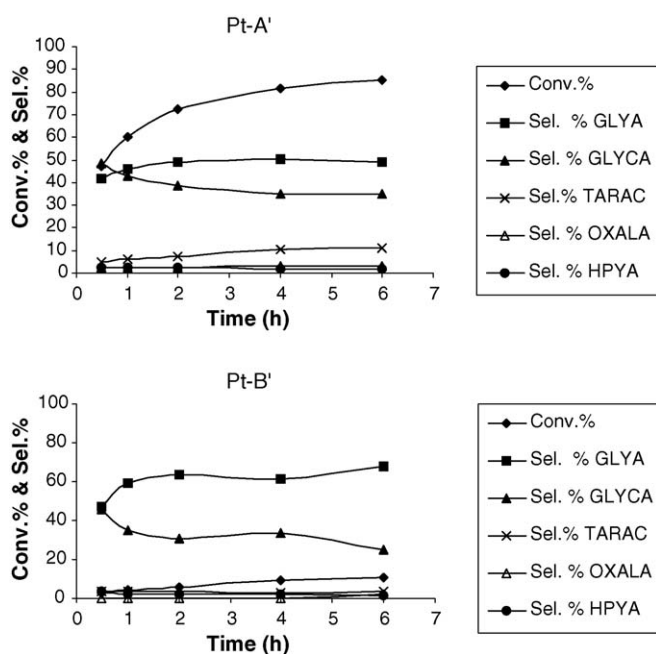


Fig. 4. Selective oxidation of glycerol in the presence of 1% Pt/C: (a) 1% Pt/C-A' and (b) 1% Pt/C-B'. Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4,  $T = 50\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 3\text{ atm}$ .

preparation method (A, B, C) the following points could be highlighted. Preparation method A (PVA/NaBH<sub>4</sub>) gave better catalytic results in terms of activity (almost twice in order of magnitude) using the “aged” precursor instead of the “fresh”. Selectivity to glyceric acid did not change significantly.

On the other hand, preparation method B (PVA/N<sub>2</sub>H<sub>4</sub>) with the “fresh” precursor gave much higher activity than the “aged” precursor, whereas selectivities to glyceric acid were similar.

For the preparation method C no comparison was possible since it was not achievable to support on carbon the “aged” precursor.

The most promising catalysts with respect to activity and selectivity to glyceric acid were Pt/C-C and Pt/C-A' catalysts. However, as it was mentioned before in all the cases deactivation was observed at prolonged reaction time (decrease in TOF as reaction was proceeded). The trend of activity should not be correlated only with particle dimension, but some other factors depending on Pt precursor could be involved.

### 3.6. Bimetallic catalysts

We have recently shown [18] that by incorporating Au with Pd or Pt an improvement in terms of activity was found. However, only with Pd improvement in the selectivity to glyceric acid was observed, whereas with Pt dramatically decrease in the selectivity to glyceric acid at the expense of glycolic and tartronic acid was found. In addition, from the catalytic data of the monometallic Pt/C catalysts as discussed in the previous section, we concluded that reduction of the “fresh” Pt precursor by H<sub>2</sub> and of the “aged” precursor by NaBH<sub>4</sub> resulted in the most active Pt/C catalysts.

Thus, based on this concept and using the same preparation methods as mentioned in our previous work [18], we synthesized bimetallic catalysts using in the one case “aged” PtCl<sub>4</sub><sup>2-</sup> precursor solutions (Au–Pt/C-A'1, Au–Pt/C-A'2, Au–Pt/C-A'3) and in the other case using “fresh” Pt precursor and reduced by H<sub>2</sub> and N<sub>2</sub>H<sub>4</sub> (Table 1). For comparison, the Au–Pt/C catalysts obtained by “fresh” PtCl<sub>4</sub><sup>2-</sup> precursor solutions reduced by NaBH<sub>4</sub> are also reported in Tables 1 and 3 (i.e. Au–Pt/C-A1, Au–Pt/C-A2, Au–Pt/C-A3).

### 3.7. Comparison between “fresh” and “aged” (Au–Pt)/C catalysts based on the same preparation method

Table 3 summarizes the catalytic data for the bimetallic catalysts synthesized by using “fresh” (Au–Pt/C-A1, Au–Pt/C-A2, Au–Pt/C-A3) and “aged” Pt precursors (Au–Pt/C-A'1, Au–Pt/C-A'2, Au–Pt/C-A'3). Comparison of these data shows some significant remarks. In both cases (“fresh” versus “aged” Pt precursor) and using the same methodology, high activity and full conversion was reached. Specifically, activity (TOF) was high in both cases and higher in the case of “fresh” (Au–Pt)/C catalysts.

On the distribution of products a similar trend was found except in the case of (Au–Pt)/C-A'2. The reaction profiles of the rest of the bimetallic catalysts were found to be similar to (Au–Pt)/C-A2. The reaction profile of (Au–Pt)/C-A2 and (Au–Pt)/C-A'2 are shown as example, (Fig. 5). In the case of (Au–Pt)/C-A'2 there was substantially formation of glyceric acid (60% at 90% conversion), while with (Au–Pt)/C-A2 the selectivity to glyceric acid varied between 50% and 40%. Nevertheless, only with this preparation method (referred as A2 and A'2) the highest selectivity to glyceric acid was obtained, comparing between the same Pt precursors (“fresh” or “aged”).

Table 3  
Oxidation of glycerol using bimetallic (Au–Pt)/C catalysts at 50 °C<sup>a</sup>

1% M/C	Selectivity (%)							TOF (h <sup>-1</sup> ) <sup>b</sup>
	Conversion (%)	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	
(Au–Pt)/C-A1	75.8	34.7	59.9	0.6	2.1	2.7	37.4	758
(Au–Pt)/C-A2	87.8	43.3	42.1	2.1	0.3	12.2	55.5	878
(Au–Pt)/C-A3	74.4	36.1	57.7	0.7	2.5	3.0	39.1	744
(Au–Pt)/C-A'1	79.1	39.0	53.4	0.8	1.9	4.9	43.9	791
(Au–Pt)/C-A'2	69.3	58.3	32.6	1.8	2.8	4.5	62.8	693
(Au–Pt)/C-A'3	69.6	39.2	55.8	0.8	0.2	4.0	43.2	697

<sup>a</sup> Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4,  $T = 50\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 3\text{ atm}$ , reaction time 0.5 h.

<sup>b</sup> Calculation of TOF (h<sup>-1</sup>) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 4  
Oxidation of glycerol using bimetallic (Au–Pt)/C catalysts at 50 °C<sup>a</sup>

1% M/C	T (h)	Selectivity (%)							
		Conversion (%)	GLYA	GLYCA	OXALA	HPYA	TARAC	Σ GLYA + TARAC	TOF (h <sup>-1</sup> ) <sup>b</sup>
(Au–Pt)/C-C	0.5	98.3	39.8	46.9	1.4	1.6	10.3	37.4	983
(Au–Pt)/C-B	4	19	61.5	26.3	5.4	2.0	4.8	66.3	62

<sup>a</sup> Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50 °C, pO<sub>2</sub> = 3 atm.

<sup>b</sup> Calculation of TOF (h<sup>-1</sup>) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

In addition, prolonged reaction time (4–6 h) after reaching full conversion resulted in the over oxidation of glyceric acid to tartronic acid (35–40% loss after 5 h of reaction). Only in the case of (Au–Pt)/C-A'2 glyceric acid over oxidation was substantially much slower (7% loss after 5 h of reaction). Note that the preparation method of (Au–Pt)/C-A'2 and (Au–Pt)/C-A2 requires firstly the reduction of “aged”/“fresh” PtCl<sub>4</sub><sup>2-</sup> and then the addition and reduction of AuCl<sub>4</sub><sup>-</sup> precursor. In addition, the “aged” Pt precursor gave better selectivity to glyceric acid, thus we can remark not only the importance of the sequence of addition of the metals but furthermore, the role of the Pt “aged” precursor.

### 3.8. Comparison of bimetallic catalysts using “fresh” Pt precursor

Since we found that monometallic Pt catalysts obtained by H<sub>2</sub> or N<sub>2</sub>H<sub>4</sub> reduction of “fresh” PtCl<sub>4</sub><sup>2-</sup> solution improved activity and selectivity to glyceric acid, we therefore synthesized bimetallic catalysts based on these two reducing agents. In the preparation of the bimetallic Au–Pt/C-C only Pt precursor was reduced by H<sub>2</sub>, whereas Au by NaBH<sub>4</sub>, because the reaction

of H<sub>2</sub> by AuCl<sub>4</sub><sup>-</sup> yielded a black precipitate. In the case of Au–Pt/C-B, both of the metal precursors were reduced using N<sub>2</sub>H<sub>4</sub>.

Catalytic data of the bimetallic catalysts synthesized as mentioned above, are summarized in Table 4. Comparison of results (Tables 3 and 4) for the (Au–Pt)/C prepared using “fresh” Pt precursor showed that the most active bimetallic system was the one in which the Pt reduction was performed using H<sub>2</sub>. In terms of selectivity all the bimetallic catalysts synthesized by the “fresh” Pt precursors showed low selectivity to glyceric acid, which was not maintained at prolonged reaction time after reaching full conversion and it was further transformed to tartronic acid. The only exception to this catalytic behaviour was the bimetallic catalyst Au–Pt/C-B prepared by precursor reduction with N<sub>2</sub>H<sub>4</sub>. High selectivity to glyceric acid was observed (62%), selectivity remaining constant through the progress of the reaction.

## 4. Conclusions

This study has shown that depending on the nature of Pt precursor (“fresh”, “aged”) and reducing agent (NaBH<sub>4</sub>, N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>) for monometallic Pt/C catalysts, the activity and the distribution of the products on the liquid phase oxidation of glycerol could significantly influenced.

In the case of “fresh” Pt/C catalysts, reduction method by H<sub>2</sub> was the most effective in terms of activity and selectivity to glyceric acid, whereas for “aged” Pt/C catalysts, it was by NaBH<sub>4</sub>, suggesting that different nanoparticles can be produced tuning the reductive method. However, in all the cases of monometallic Pt/C catalysts a deactivation progress took place during the reaction. In order to improve the activity and to overpass the deactivation problem, Pt/C catalysts were modified with addition of Au. It was found that activity was significantly enhanced, reaching full conversion in all cases (“fresh” and “aged”). In terms of selectivity, selectivity to glyceric acid was low and it was decreasing as the reaction was proceeding mainly at the expense of glycolic and tartronic acids. However, prior addition and reduction of the “aged” Pt precursor with respect to Au precursor obtained the catalyst that showed the highest selectivity to glyceric acid among the bimetallic catalysts. Finally, the most active bimetallic catalyst was obtained when H<sub>2</sub> was the reducing agent for Pt precursor.

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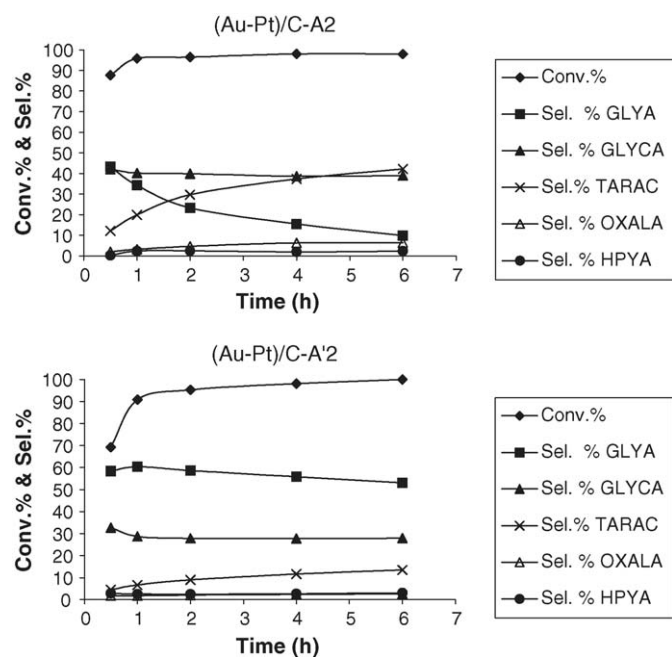


Fig. 5. Selective oxidation of glycerol in the presence of 1% (Au–Pt)/C: (a) 1% (Au–Pt)/C-A2 and (b) (Au–Pt)/C-A'2. Reaction conditions: water 10 ml, 0.3 M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50 °C, pO<sub>2</sub> = 3 atm.

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