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Liquid-Phase Oxidation of Glycerol over a Pt/C Catalyst: Optimization of the Reaction Conditions

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Abstract

Liquid-phase glycerol (Gly) oxidation was investigated systematically over a Pt/C catalyst. The catalyst was prepared by impregnation with a $(NH_4)_2[PtCl_4]$ solution, in order to obtain a 1 wt% Pt. The catalyst was characterized by AAS, TEM and TPR techniques. The reaction conditions were optimized by conducting experiments in the range of temperature from 40 to 60°C, Gly/Pt molar ratio between 4000 and 10000, pH between 5 and 13 and H_2O_2 concentration in order to get between 2.5 and 10 volumes of active oxygen in the reactor. The optimum reaction conditions were identified as 60°C, Gly/Pt = 4000, pH= 5, H_2O_2 concentration enough to obtain 10vol of O_2, 100 mg catalyst and constant stirring. Under these conditions, a maximum glyceric acid (GlyA) selectivity of 57.1% was obtained at 37% Gly conversion.

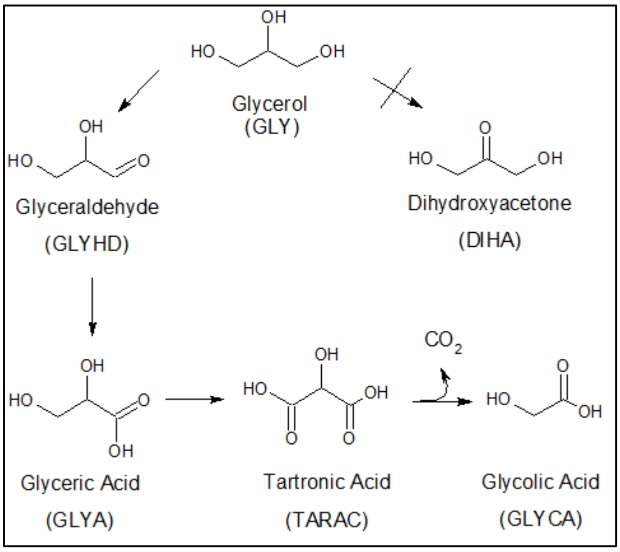
Resumen

La oxidación en fase líquida de glicerol (Gly) se investigó sistemáticamente empleando un catalizador Pt/C. El catalizador se preparó por impregnación con una solución de $(NH_4)_2[PtCl_4]$, con el fin de obtener un 1% en peso de Pt. Se lo caracterizó por AAS, TEM y TPR. Las condiciones de reacción se optimizaron realizando experimentos en el intervalo de temperatura entre 40 y 60ºC, relación molar Gly/Pt entre 4000 y 10000, pH entre 5 y 13 y concentración de H_2O_2como para obtener entre 2.5 y 10 volúmenes de oxígeno activo en el reactor. Las condiciones óptimas de reacción se identificaron como 60°C, Gly/Pt = 4000, pH = 5, concentración de H_2O_2 suficiente para obtener 10vol de O_2, 100 mg de catalizador y agitación constante. Bajo estas condiciones, se obtuvo una selectividad máxima de ácido glicérico (GlyA) del 57.1% con una conversión de Gly de 37%.

Palabras Clave: Glicerol, oxidación, Platino, Carbón, Peróxido de hidrógeno
*Keywords:*Glycerol, oxidation, Platinum, Carbon, Hydrogen Peroxide

1. INTRODUCTION

During the last decade, demand for biodiesel has grown steadily and is expected to continue this way in the coming years driven by the fulfillment of current biofuel policies in the US, Argentina, Brazil, Indonesia and the EU. Glycerol (GLY) is obtained as the main by product in the production of biodiesel (~ 10% by weight) [1]. The current demand for glycerol cannot compensate for its production and therefore, new efficient processes must be found for its transformation into valuable derivatives [2]. For instance, based on glycerol and through oxidation processes, various promising chemicals can be obtained, such as dihydroxyacetone (DHA) and glyceric acid (GlyA) (Scheme 1).



Scheme 1. Reaction network for glycerol oxidation.

So far, these compounds are produced using inorganic oxidizing agents or enzymatically. Thus, dihydroxyacetone, which is an active ingredient in self-tanning products, is produced through biocatalytic processes using *acetobacterium gluconobacter suboxidans,* but with only reduced yields [3]. That is why the heterogeneous catalytic oxidation of glycerol is presented as an environmentally friendly alternative to obtain some of these products selectively [4]. These reactions are performed at moderate temperatures and do not use extreme pH conditions [5-7]. Oxidation of glycerol is usually carried out in the liquid phase, using heterogeneous catalysts and air, oxygen or hydrogen peroxide as oxidizing agents, under mild conditions of pressure, temperature and with pH control.

A number of monometallic catalyst systems are known which are able to oxidize the primary hydroxyl group of glycerol, rendering glyceric acid as main product [8,9]. In particular, palladium, platinum and gold particles supported on various materials have been investigated

[6,10-12]. Additionally, bimetallic catalysts such as Pt-Bi and Au-Pt have been mentioned as selective catalysts to produce dihydroxyacetone [2,8,10,13-15].

In the present paper, a detailed study of the heterogeneous catalytic oxidation of glycerol over a Pt/C monometallic catalyst is presented. Experimental data were obtained by varying the operative conditions (temperature, glycerol concentration, H_2O_2 concentration to obtain different volumes of active O_2 in the reactor and pH).

2. MATERIALS AND METHODS

2.1. Preparation of 1 wt.% Pt/C catalyst

The monometallic catalyst was prepared by impregnating the carbon support with a 5 w/v % $(NH_4)_2[PtCl_4]$ aqueous solution. A volume of 2.80 mLof this solution was used to impregnate 10.0091 g of the support, using 50 mL of distilled water as solvent. In this way, the solution had an appropriate concentration such as to obtain 1 wt.% Pt in the final catalyst. After 48 h of contact between the solution and the carbon support, the excess solvent was removed according to the procedure proposed by Coloma *et al.* [16]. Platinum reduction was performed under a H_2 flow at 400°C for 2 h.

2.2. Catalyst characterization

The platinum content was determined by atomic absorption spectroscopy on a Varian AA 240 spectrophotometer after burning away the carbon in air at 700°C and dissolving the residue in *aqua regia*.

Temperature-Programmed Reduction (TPR) tests were carried out in a reactor built in our laboratory, using 50 mg of catalyst, a feed of 5 vol.% H_2 in Ar at a flow rate of 7.3 $cm^3 min^{-1}$ and a heating rate of 10°C min^{-1}, from room temperature to 800°C. H_2 consumption during the reduction was analyzed *on-line* in a Shimadzu GC-8A Gas Chromatograph equipped with a thermal conductivity detector (TCD).

The size distribution of metal particles was obtained by transmission electron microscopy (TEM) using a JEOL 100 CX instrument. The samples were ground and ultrasonically dispersed in distilled water. For the determination of the particle size distribution histogram, more than 200 Pt particles were measured from micrographs taken directly from the screen using the clear field image. The metal dispersion (D) was calculated from the Pt particle size distribution obtained from TEM measurements by the following equation [17], assuming spherical particles:

$$D = \frac{6\,M_{Pt}}{\sigma \rho_{Pt}}\left(\frac{\sum_i n_i d_i^2}{\sum_i n_i d_i^3}\right) \qquad (1)$$

where: M_{Pt} is the molar mass of Pt and ρ_{Pt} its density (21.45 g cm^3), n_i is the number of particles with a diameter d_i and σ is the area occupied by 1 mol of Pt at the surface (3.75×10^4 m^2mol^{-1}).

2.3. Oxidation experiments

Glycerol oxidation reactions were carried out at atmospheric pressure in a 250 mL glass reactor with constant stirring, immersed in a thermal bath. The reactor is charged with the aqueous solution of glycerol, NaOH if necessary, H_2O_2 as oxidizing agent and the temperature is increased to the desired value. Once the set temperature value is reached, 100 mg of catalyst is added and the reaction starts. Experiments were carried out under different conditions, with the objective of evaluating the influence of the reaction variables on glycerol conversion. The oxidation reactions were carried out at temperatures from 40 to 60°C and by varying the glycerol/platinum molar ratio (between 4000 and 10000), pH (between 5 and 13) and H_2O_2 concentration in order to get between 2.5 and 10 volumes of active oxygen. The reaction course was followed by taking samples at suitable time intervals and analyzing them by high performance liquid chromatography (HPLC).

The conversion was determined by monitoring the glycerol concentrationwith time:

$$x_{Gly} = \frac{C^0_{Gly} - C^t_{Gly}}{C^0_{Gly}} \qquad (2)$$

where x_{Gly} is the glycerol conversion, C^0_{Gly} is the initial glycerol molar concentration and C^t_{Gly} is the molar concentration of glycerol at time t (min). The selectivity towards product *i* (S_i) was calculated using the following equation [18]:

$$S_i = \frac{C^t_i}{\left(C^0_{Gly} - C^t_{Gly}\right)} \cdot \frac{n_i}{3} \qquad (3)$$

where C_i^t is the molar concentration of compound *i* at time t (min) and n_i is the number of carbon atoms in compound *i*.

2.4. HPLC analysis

The quantitative analysis of the reaction samples was performed by high performance liquid chromatography using an UHPLC DIONEX UltiMate 3000 chromatograph equipped with both UV (210 nm) and refractive index (RI) detectors. An ion exchange column PhenoSphere 5µSax 80 A (250x4.6mm) at 50°C was employed to separate the eluted compounds. Diluted H_2SO_4 (5.00 mM) was employed as eluent, with a flow rate of 0.6 mL min^{-1}. The products were identified by comparison with pure standards (Sigma Aldrich).

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

Determination of the metal content of the catalyst by atomic absorption spectroscopy yielded 1.05% by weight of Pt, very close to the calculated value.

Figure 1 shows the TPR profile of the Pt/C catalyst. It can be seen that only one broad peak appears at 120ºC, which corresponds to the reduction of the metal precursor from Pt^{2+} to Pt^{0} [19]. At temperatures over 200ºC the hydrogen consumption observed is associated to the partial gasification of the support around the metallic particles, according to what is proposed in the literature [20]. From TEM images information about the dimension and dispersion of the platinum particles can be directly obtained. TEM micrograph for Pt/C catalyst is shown in Figure 2.

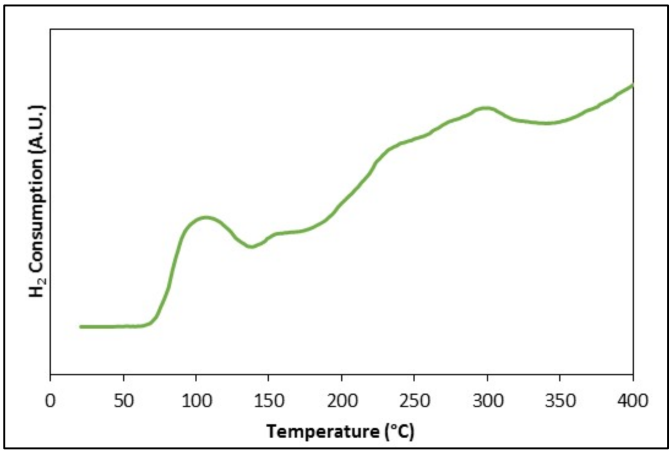


Figure 1: Temperature-programmed reduction profile of Pt/C catalyst.

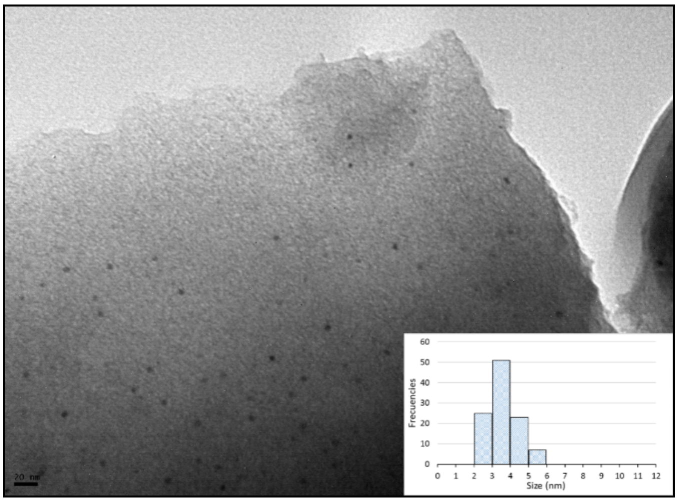


Figure 2: TEM image of the Pt/C catalystand its particle size distribution histogram in the inset.

Dark spots uniformly dispersed on the carbon support can be observed, which correspond to the Pt particles. The mean particle size was calculated using the data obtained from the histogram of the particle size distribution (inserted in the lower right corner of the TEM image in Figure 2) and resulted to be 4 nm. This value was used to estimate the platinum dispersion, according to the expression given in the Materials and Methods section (Eq. 1). A dispersion of 36.5% was determined.

3.2. Catalytic activity

3.2.1. Effect of the reaction temperature

The influence of temperature on catalytic activity was investigated between 40 and 60ºC, with a Gly/Pt ratio of 6000, H_2O_2 concentration enough to obtain 10vol of O_2 in the reactor and 100 mg of catalyst. Figure 3(a) shows the increase of catalytic activity with temperature. The apparent activation energy (E_a) was determined by numerical regression using an Arrhenius-type function. A value of E_a = 12.8 Kcal/mol has been obtained, which is in good agreementwith the value reported in the literature [21,22].

3.2.2. Effect of the initial Gly concentration

The effect of the Gly initial concentration on catalytic activitywas studied at 60ºC and a H_2O_2 concentration enough to obtain 10vol of O_2. The initial concentration of Gly was varied between 0.2 M and 0.5M. This range was selected considering that the glycerol concentration that most frequently appears in the literature is 0.3 M [4,23-25]. The glycerol molar concentrations used were 0.2 M, 0.3 M and 0.5 M which, expressed as Gly/Pt molar ratio correspond to 4000, 6000 and 10000, respectively. The results are given in Figure 3(b) and show that the catalyst activity decreases by increasing the initial Gly concentration.

Table 1 shows the initial reaction rate calculated at 20% conversion and the maximum conversions obtained for each Gly/Pt ratio.

Table1: Initial Gly reaction rate (v^0_{Gly}) and maximum conversion attained over Pt/C catalyst for the different initial concentration of glycerol employed [Temperature 60°C,H_2O_2 concentration enough to obtain 10vol of O_2, 100 mg catalyst].

Gly/Pt molar ratio	X_{Gly}**%**	v^0_{Gly} **(molGly/sec/g$_{Pt}$)**
4000	37.0	0.040
6000	31.5	0.040
10000	21.8	0.015

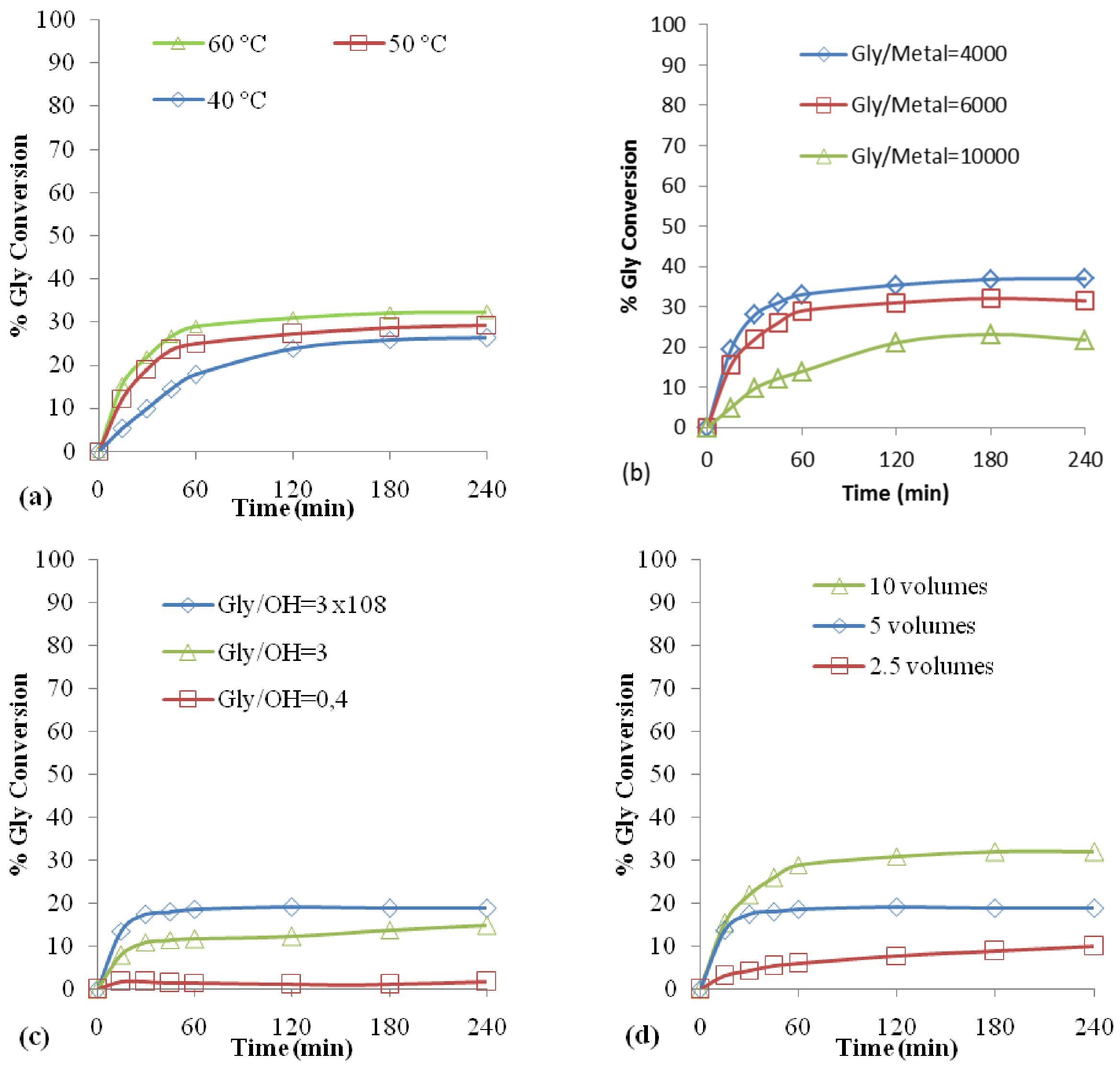


Figure 3: Effect of **(a)** temperature [Gly/Pt ratio of 6000, H_2O_2 concentration enough to obtain 10 vol of O_2]; **(b)** Gly initial concentration [Temperature 60°C,H_2O_2 concentration enough to obtain 10 vol of O_2]; **(c)** pH [Gly/Pt= 6000, Temperature 60°C,H_2O_2 concentration enough to obtain 10 vol of O_2]; **(d)** H_2O_2 concentration [Gly/Pt= 6000, Temperature 60°C,] on Pt/C activity (100 mg catalyst; constant stirring).

The reaction order with respect to Gly was determined with an empirical power-law model using the v_{Gly}^{0} values given in Table 1:

$$v_{Gly}^{0} = k.\left(C_{Gly}^{0}\right)^{n} \tag{4}$$

$$\ln(\,v_{Gly}^{0}) = \ln k + n.\,ln(C_{Gly}^{0}) \tag{5}$$

The value calculated for *n* was obtained by plotting the $\ln(\,v_{Gly}^{0})$ as a function of $ln(C_{Gly}^{0})$ (Figure 4).

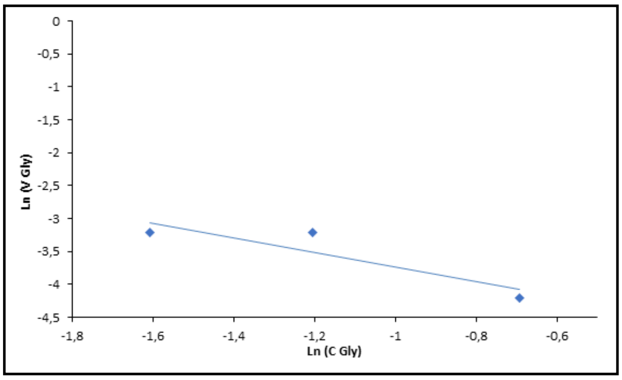


Figure 4. $\ln(v^0_{Gly})$ versus $ln(C^0_{Gly})$ for pseudo-homogeneous model with Pt/C catalyst, Temperature 60°C,H_2O_2 concentration enough to obtain 10vol of O_2

The value obtained for *n* was -1.1. The negative value for the order of reaction indicates that Gly is strongly adsorbed on the catalytic active sites of the catalyst. From the data observed in Figure 4 it can be derived that up to a certain concentration value of Gly, the active sites of the catalyst are covered with strongly adsorbed Gly molecules. Then, the oxidation of Gly occurs as if the reaction order with respect to Gly was apparently zero. It would appear as the initial Gly concentration increases, the initial amount of Gly that would be strongly adsorbed on the surface of metallic Pt particles would also increase and thus the initial availability of free active sites is lower, which would explain the lower observed rate.

3.2.3. Effect of NaOH/Gly molar ratio

The influence of pH on glycerol conversion was investigated. Like any reaction involving acidic or basic products, pH is an important factor to study. That is why the Gly oxidation was performed varying the initial pH in the range of 5 to 13. This was accomplished by adding an appropriate volume of a concentrated NaOH solution before the starting the reaction, keeping constant all the other operating conditions. The plot of Gly conversion as a function of time is shown in Figure 3(c), obtained at different pH values, expressed as NaOH/Gly molar ratio. In this graph it can be seen that an increase in pH decreases the conversion of glycerol, obtaining the best results at pH = 5. Very dissimilar results were found in the available literature. For example, Varma and co-workers who studied this same reaction with a PtBi/C catalyst in a pH range from 2 to 11.5, obtained the best conversion when a basic pH was employed [3]. Previously in 1997, Gallezot had studied the catalytic activity in the glycerol oxidation of a carbon-supported platinum catalyst at pH values between 6 and 11.48. Their results indicated that the catalyst was significantly less active when used under acidic conditions [8]. Oxidation of glycerol using carbon-supported platinum catalysts in acid media was also studied by Kimura [14], Liang [26] and Villa [27]. While Kimura reported little activity for this catalyst, Liang observed a glycerol conversion of 50% and Villa even of 78%. In fact, it is difficult to clearly assess the catalytic results because the reaction conditions are too different. But,what is clear is that the conversion of glycerol using platinum-based catalysts strongly depends on the pH of the reaction medium.

3.2.4. Influence of the concentration of the oxidizing agent

Another variable that was studied was the amount of oxidizing agent, H_2O_2, added to the reactor so that a concentration of 2.5, 5.0 and 10 volumes of active O_2 could be obtained. An increase in glycerol conversion from 10.0% to 32.0% was obtained as the amount of O_2 in the reactor was increased, as seen in Figure 3(d).

The low conversion obtained with the lowest H_2O_2 concentration used may be due to an insufficient amount of O_2 available for the oxidation reaction. Concerning the shape of the curves, it is well known that the platinum group metal catalysts have a marked tendency to be poisoned by oxygen, either by simple blocking of the adsorption sites or by the migration of adsorbed oxygen atoms into the Pt lattice [28]. Hydrogen peroxide releases oxygen during decomposition, which under the experimental conditions in which the catalytic oxidation reaction was carried out adsorbs dissociatively on Pt [29]:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$$O_2 + 2^* \rightarrow 2O^*$$

where * is an adsorption active site.

3.2.5. Performance of Pt/C catalyst in optimum conditions

Based on the above-described results, the optimum conditions for the Gly oxidation reaction over the Pt/C catalyst are: 60°C, Gly/Pt = 4000, pH= 5, H_2O_2 concentration enough to obtain 10vol of O_2, 100 mg catalyst and constant stirring. Using these experimental conditions, a conversion of 37% of Gly was obtained, with glyceric acid (GlyA) and dihydroxyacetone (DIHA) as the main products (Scheme 1). The selectivity to these products were 57.1% and 26.0%, respectively.This result is consistent with the literature in thatcarbon-supported Pt monometallic catalysts preferentially oxidize the primary alcohol group of glycerol, obtaining GlyA as the main product [30,31].

The performance of a different noble metal-based catalyst, namely Pd/Al_2O_3 has also been studied by our research group in the liquid-phase oxidation of glycerol, obtaining a maximum Gly conversion of *ca.* 19% under similar operating conditions [32]. The lower activity of the Pd catalyst compared to that of Pt is attributed to its lower redox potential, which leads to a greater oxygen coverage of the surface, thus reducing the probability of adsorption of the organic substrate. Thus, metals with lower redox potentials, such as ruthenium, are almost inactive in this reaction, due to an almost complete poisoning of their surface with oxygen [33]. Analogous results have been observed by other authors in the oxidation of glyoxal [33] and methanol [28] using carbon-supported palladium and platinum catalysts.

4. CONCLUSIONS

Catalytic oxidation of glycerol overPt/C was investigated. Reaction conditions such as temperature, hydrogen peroxide concentration and initial pH, were optimized. A negative order respect to glycerol was estimated by fitting the initial experimental data with a pseudo-homogenous model. This result indicated that glycerol was strongly adsorbed on the surface of metal Pt particles, in accordance with the catalytic deactivation observed. Under the optimized conditions, a GlyA selectivity of 57.1% was achieved at 37% glycerol conversion.

Acknowledgments

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