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Conversion of glycerol into lactic acid using Pd or Pt supported on carbon as catalyst

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ABSTRACT

The oxidation of glycerol into lactic acid using activated carbon with Pd or Pt as heterogeneous catalysts was study. Several reaction parameters were evaluated: catalyst loading, catalyst weight, NaOH/glycerol molar ratio, temperature and reaction time. The textural and structural properties of the carbon supported catalysts (fresh and spent) were evaluated by N_2 adsorption-desorption isotherms at −196 °C, XRD, SEM, EDX, TEM and XPS. It was possible to achieve a glycerol conversion of about 99% with selectivity to lactic acid of 68% and 74% using 10% Pd/C and 5% Pt/C as catalysts, respectively, at 230 °C of reaction temperature. Moreover, Pd/C and Pt/C catalysts were used in five reaction cycles without significant loss of activity, highlighting the great stability of the prepared catalysts.

1. Introduction

Nowadays, biodiesel production is on a large scale, mainly, due to the government incentives and the development of renewables sources for fuels production. In the transesterification reaction, about, 10% in weight of raw material is converted into glycerin. That is why biodiesel industries are facing a surplus of this main by-product, glycerol, representing 10% (v/v) of the final ester. Due to the government incentives to increase carbon and oil energy independence and meet the growing energy demand, the biodiesel market is expected to reach 37 billion liters in 2016. This production will result in 4 billion liters of crude glycerol, generating a surplus volume that the glycerol market cannot absorb [1,2]. In this way, some studies have been conducted to make the glycerol industry more profitable. Various catalytic conversion processes have been proposed for the transformation of glycerol into chemicals with high added value, such as 1,3 propanediol, 1,2 propanediol, succinic acid, polyesters of lactic acid and polyglycerols [3].

The potential of lactic acid (LA) and its importance as a product in the chemical platform is clearly visible in the chemical market. The LA world production increased from 40,000 t/year in the 1990s to 260,000 t/year in 2008, and these rates are expected to increase substantially. The Plastics Today magazine (2011) predicted an LA market of 329,000 t in 2015 and recent projections announced an estimated production of 830,000 t of poly (lactic acid) (PLA) in 2020 [4].

Lactic acid is conventionally used as an acidulant and/or a conservative in the food industry and it has also been used as a raw material for the production of pharmaceuticals, cosmetics, textiles, leather, and biodegradable polymer (Poly (lactic acid)). The poly (lactic acid) has wide applications in a variety of fields due to their biodegradability and biocompatibility. This organic acid can be produced by chemical synthesis or by bioprocesses. However, the last one is the predominant method for lactic acid production and presents several disadvantages, such as large amount of water costs, low reaction rate and high cost due to their separation and purification in downstream processes. The development of a chemical synthesis route for the production of PLA has stimulated great interest among researchers because of both, the low cost and environmental impact [5].

Nowadays, some researchers have been progressed in the conversion of glycerol into lactic acid by chemical catalysis [6]. Kishida et al. [7], reported that glycerol can be converted into lactic acid in an alkaline medium and hydrothermal conditions (at 300 °C), with NaOH as homogeneous catalyst. Shen et al. [8], reported the effect of different alkali and alkaline earth hydroxides in glycerol hydrothermal conversion into lactic acid at 300 °C, showing that the alkali metal hydroxides were more effective catalysts than alkaline earth metal hydroxides. Ramirez-Lopez et al. [9] studied the use of high glycerol concentrations and equivalent amounts of NaOH, at 280 °C,

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obtaining a yield of 84.5% to LA. This study showed that a high basic concentration to catalyze the conversion using a high glycerol concentration is required. However, due to the high alkalinity and elevated temperature, it is necessary to use specific reactors, to avoid high corrosiveness and relevant concerns on an industrial scale.

According to Chen et al. [10], the use of solid catalysts includes advantages such as, low corrosivity, reuse of the catalyst, low temperature reaction and easily of separation of catalyst/product, thereby reducing chemical wastes.

The conversion of glycerol using mainly supported metal nanoparticles has been extensively studied to obtain other acids (acetic acid, glycolic acid, glyceric acid, formic acid) and have shown that lactic acid can be generated from glycerol using heterogeneous catalysis [11]. Some researchers have reported the formation of lactic acid by using supported catalysts such as: Ru/C, Pt/C, Au/C, PtRu/C and AuRu/C [12,13]; Au/TiO_2 Pt/TiO_2, Pd/TiO_2 and AuPt/TiO_2 [14]; Cu/SiO_2 e CuO/Al_2O_3 [15]; Pt/$CaCO_3$ [16]; Rh/C e Ir/C [17]; and Au/n-CeO_2, Pt/n-CeO_2 and AuPt/n-CeO_2 [18], and Pd/C [19]. In this case, the use of supported catalysts can improve the catalytic performance, tailoring not only the catalytic activity but also the selectivity for the target molecule. In this context, the aim of this study was to investigate the catalytic performance of Pd/C and Pt/C in glycerol conversion into lactic acid. The process conditions such as catalyst loading, catalyst weight, NaOH/glycerol molar ratio, temperature and reaction time were systematically studied. The catalysts were characterized by a variety of experimental techniques in order to better understand the factors governing the catalytic activity of the studied samples.

2. Experimental

2.1. Materials

The chemicals used, palladium(II) chloride ($PdCl_2$-Sigma-Aldrich), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$-Sigma-Aldrich), sodium hydroxide (NaOH-Vetec-Brazil), sulfuric acid (H_2SO_4-Synth), hydrochloric acid (HCl-Synth), nitric acid (HNO_3-Synth), sodium carbonate (Na_2CO_3- Dynamic Contemporary Chemistry), formaldehyde (Vetec-Brazil), glycerol (Vetec-Brazil), lactic acid (Sigma-Aldrich) and activated carbon (Vetec-Brazil) were of analytical grade. Ultrapure water (Milli-Q System, Millipore) was used in all experiments.

2.2. Catalyst preparation

Palladium catalyst supported on activated carbon was prepared using $PdCl_2$ as metal precursor, according to the method developed by Kubota et al. [20]. Thus, in a typical synthesis, the activated carbon sample was pretreated with a HNO_3 solution (10% v/w – 5 mL g^{-1}) at 80 °C under stirring for 3 h in order to obtain a functionalized surface. The palladium catalysts containing 2.5, 5 and 10 wt% of total metallic charge were prepared with solutions containing $PdCl_2$, where 12 mL of 1 M HCl were added under stirring. 1.0 g of the pretreated carbon was added to the prior solution and stirred for 20 h at 30 °C. The solids were recovered by filtration, mixed with a Na_2CO_3 solution, maintained under stirring for 3 h at 30 °C and reduced with formaldehyde (37%) under stirring for 2 h at 60 °C. The obtained catalyst was recovered by vacuum filtration, followed by washing with Ultrapure water and drying at room temperature for 16 h. The catalysts were denoted as xPd/C-Fresh or Used, for fresh and spent catalysts, respectively, where *x* is the weight percent of metal (2.5, 5 and 10).

Platinum catalysts supported on carbon were prepared using $H_2PtCl_6 \cdot 6H_2O$, following the methodology adapted by Liang et al. [21]. To this end, 1 g of pretreated carbon was added to a solution containing the platinum precursor desired concentration under stirring at 50 °C and reduced with formaldehyde (37%) for 1 h at the same temperature. The obtained catalyst was recovered by vacuum filtration, followed by washing with Ultrapure water and drying at room temperature. The catalysts were denoted as xPt/C-Fresh or Used, for fresh and spent catalysts, respectively, where *x* is the weight percent of platinum (1, 2.5 and 5).

2.3. Characterization

The X-ray powder diffraction (XRD) powder patterns of the Pd/C and Pt/C catalysts were recorded on a diffractometer (PANalytical modelo EMPYREAN) using Cu Kα radiation ($\lambda = 1.54056$ Å), scanning from 10 to 80° (2θ). The phases were identified according to Joint Committee on Powder Diffraction Standards (JCPDS) database.

Scanning electron microscopy (SEM) was performed on a scanning electron microscope (INSPECT 50) operated at an acceleration voltage of 20 kV to characterize the morphology of Pd/C and Pt/C particles. Previously, the samples were deposited on an aluminum sample holder and sputtered with gold and then SEM measurements were conducted.

Transmission Electron Microscope (TEM) images were obtained using a Philips CM 200 Supertwin-174 DX4 microscope operated at an acceleration voltage of 200 kV to characterize the morphologies and the crystal structures of the Pd and Pt nanoparticles supported on carbon. Samples were dispersed in ethanol and a drop of the dispersion was put on a Cu grid (300 mesh).

The textural properties were experimentally determined by N_2 physisorption at −196 °C using an Micromeritics ASAP 2020 analyzer. The samples were previously degassed at 200 °C at a vacuum of 10^{-5} bar. The pore diameter was calculated according to the formula: 4 V/A.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a spectrometer Physical Electronics 5700 using a Mg-Kα source (1253.6 eV) (model 04–548 Dual Anode X-ray Source). The X-ray source was run at a power of 300 W (10 keV and 30 mA). All spectra were obtained using a 720 m diameter analysis area. The specimens were analyzed at an angle of 45° to the surface plane. The X-ray source was located at 54° relative to the analyzer axis at 5.10^{-10} Torr of vacuum.

The palladium and platinum contents in the catalysts were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fischer Scientific, iCAP 6000 model). The standard calibration was carried out using Pd and Pt aqueous solution, prepared in HNO_3 solution 2% (v/v), in concentrations of 0.1, 0.5, 1, 5 e 10 mg L^{-1}. The reaction samples, after one reaction cycle, were dissolved in deionized water. The wavelength used to determine Pd and Pt was 340.4 and 214.4 nm, respectively. The samples were measured five times and the results showed are the average.

2.4. Catalytic tests

The reactions were carried out in a 300 mL capacity stainless steel Parr reactor equipped with a mechanical stirrer (700 rpm). In a typical experiment, several catalyst weights (0.2, 0.4, 0.6 and 0.8 g) were employed. 100 mL aqueous solution of glycerol and an aqueous solution of NaOH (NaOH: glycerol molar ratio = 0.75, 1.1 and 1.25) were charged into the reactor. The reaction was carried out at 200 or 230 °C and the reaction time was 4 h. After that time, the catalyst was separated by vacuum filtration. The reaction parameters were investigated: metal loading (%), catalyst mass (g), NaOH:glycerol molar ratio, temperature and reaction time.

The reaction products were analyzed by comparison with standard samples, using a HPLC Shimadzu equipment using a RI

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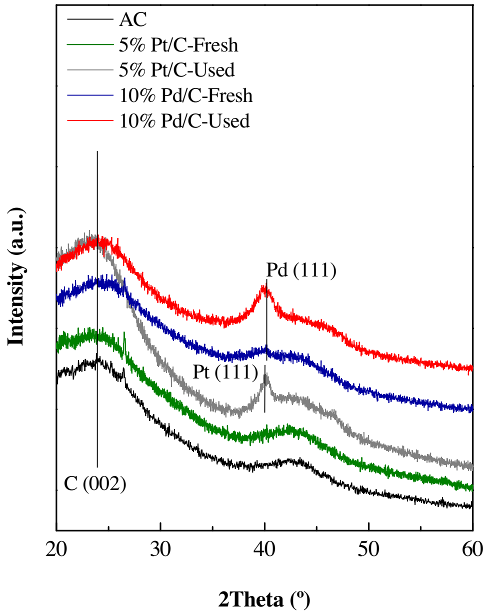

Fig. 1. X-ray diffraction patterns of support (AC), fresh catalysts (Pd/C-Fresh, Pt/C-Fresh) and used catalysts (Pd/C-Used, Pt/C-Used).

detector. The system was equipped with a Biorad Aminex HPX-87H column operating at 60 °C and 5 mmol L^{-1} of H_2SO_4 solution were used as eluent. Samples were eluted at a flow rate of 0.6 mL min^{-1} and the injection volume was 20 µL. Concentrations were determined using calibration curves obtained by injecting standard solutions of known concentrations (0–18 g L^{-1} of glycerol and lactic acid).

The glycerol conversion (%X), selectivity to lactic acid ($\%S_{LA}$) and lactic acid yield (%Y) were calculated according to the following equations:

$$\%X = \frac{(molGly_{in} - moGly_{out}) \times 100}{molGly_{in}} \tag{1}$$

$$\%S_{LA} = \frac{mol\ of\ desired\ product \times 100}{molGly_{in}} \tag{2}$$

$$\%Y = \frac{\%X \times \%S_{LA}}{100} \tag{3}$$

3. Results and discussion

3.1. The X-ray powder diffraction (XRD) analysis

Fig. 1 shows the X-ray diffraction patterns of the carbon support (C), as-synthesized, and the fresh and used catalysts (Pd/C-Fresh, Pd/C-Used, Pt/C-Fresh, Pt/C-Used). An important parameter in the structural characterization of coals is the interlayer spacing of the stacks (d_{002}), which reflects the distance between the graphene layers in the stacks of the coal. According to Takagi et al. [22], the value of d_{002} is related to the perfection in the stacking structure periodicity, a decrease in this value (d_{002} for the graphite structure is 0.335 nm), is indicative of a more ordered structure.

The broad band located between 2θ = 20–30° is characteristic of amorphous materials. In both diffractograms (activated carbon samples and Pd/C, Pt/C fresh and used catalysts) can be visualized a peak at 2θ = ∼24.1° related to the diffraction plane (0 0 2) of the hexagonal graphitic carbon according the JCPDS card no. 75–1621. This result suggests that the material has a low degree of crystallinity with hexagonal graphite belonging to $P6_3/mmc$ space group with broad peaks at 2θ = 20–30° (0 0 2). These reflections are likely associated with sp^2-bonding carbon lacking in periodicity in the C-axis, which is consistent with graphite [23].

From Fig. 1 it is noted that the X-ray diffractograms of fresh catalysts (Pd/C and Pt/C) are similar to the X-ray diffraction of activated carbon. It could be seen that neither the acid modification nor the introduction of palladium or platinum metals changed the structure of the activated carbon. The diffractogram corresponding to 10% Pd/C-Fresh did not show diffraction peaks related to the tetragonal phase PdO [24] and Pd° cubic [25]. This suggests that the particles of palladium should be well dispersed on the support surface, with a low particle size or in low concentration to be detected by X-ray diffraction [26]. For the 10% Pd/C-Used catalyst a significant peak was observed, at 2θ = 40.1° (1 1 1) (JCPDS

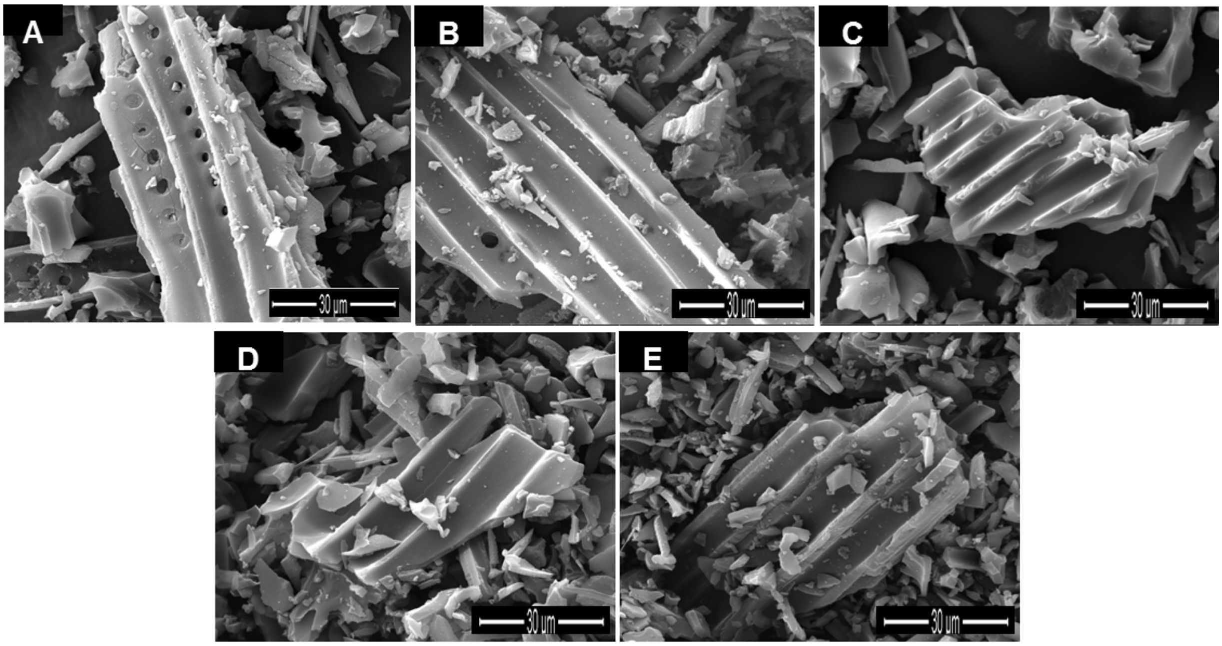

Fig. 2. SEM images: Activated Carbon (A), Pd/C-Fresh (B), Pd/C-Used (C), Pt/C-Fresh (D), Pt/C-Used (E) at magnification of 3000×.

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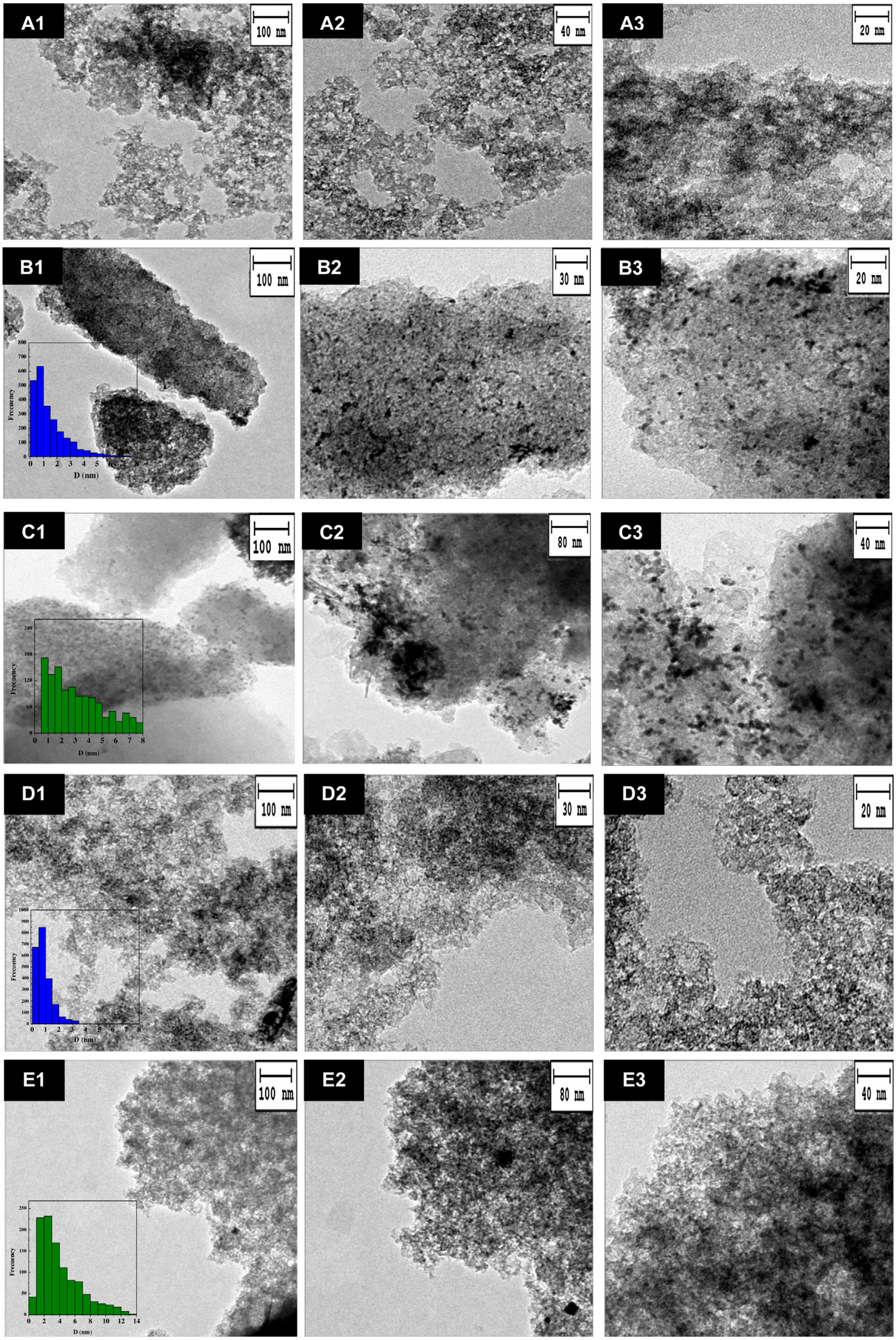

Fig. 3. TEM images: Activated Carbon (A1–3), Pd/C-Fresh (B1–3), Pd/C-Used (C1–3), Pt/C-Fresh (D1–3), Pt/C-Used (E1–3) at different magnifications.

card no. 62-2867), characteristic of metallic palladium. The Pt peak ($2\theta = \sim 39^\circ$) was also absent in the XRD of 5% Pt/C-Fresh, suggesting that the Pt species were uniformly dispersed as minuscule grains or with a low degree of crystallinity. A different XRD pattern was observed for the used catalyst, showing a peak at $2\theta \sim 39^\circ$, assigned to the (1 1 1) reflection of platinum (JCPDS Card no. 04-0802). It is

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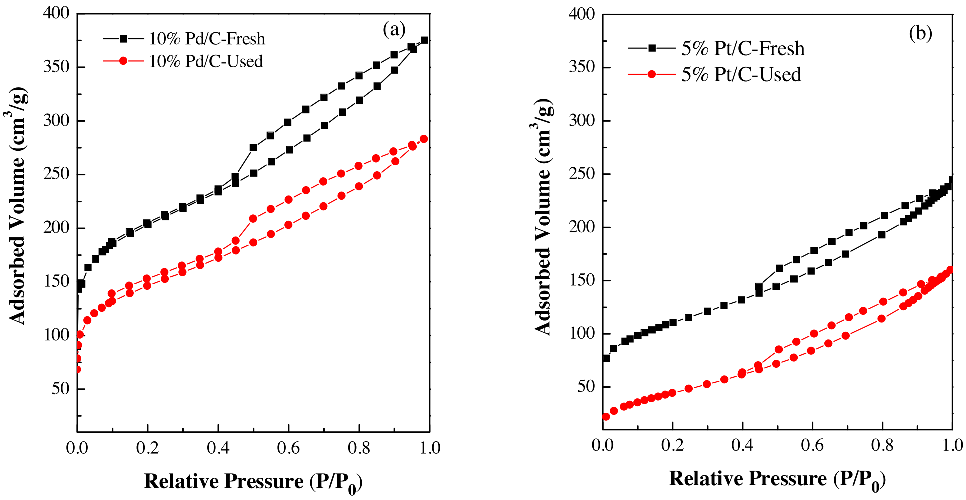

Fig. 4. N_2 adsorption-desorption isotherms corresponding to 10% Pd/C (a) and 5% Pt/C (b) before and after the catalytic reaction.

Table 1
Textural properties of the support, fresh and spent catalysts: BET Surface Area (S_{BET}), pore volume (Vp) and average pore diameter (Dp).

Sample	S_{BET} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)	D_P (nm)[a]
Activated Carbon	779	0.60	3.0
10% Pd/C-Fresh	758	0.58	3.0
10% Pd/C-Used	534	0.43	3.2
5% Pt/C-Fresh	388	0.36	5.1
5% Pt/C-Used	166	0.24	5.5

[a] Dp: 4 V/A.

interesting to note that these results agree with TEM observations, which suggest that nanoscopic particles embedded in an amorphous matrix can clearly be observed for the used catalyst (See below).

3.2. *Microscopic analyses*

Fig. 2 shows the SEM micrographs corresponding to 10% Pd/C catalyst (Fig. 2B and C) and 5% Pt/C catalyst (Fig. 2D and E) with magnifications of 3000 times, before and after reaction. The activated carbon particles have regular tubular porosity, probably from the vascular structure due to carbon source (Fig. 2A). There was not change in the carbon structure after Pd or Pt deposition (Fig. 2B and D) probably due to the mild deposition conditions used.

It is noteworthy that the spent catalysts (Fig. 2C and E), despite the high reaction temperature (200 and 230 °C), the carbon structure remained stable after the reaction, probably due the chemical and physical activated carbon resistance.

TEM images can directly give us information about the dimension and dispersion of the metallic nanoparticles. TEM micrographs for activated carbon, Pd/C and Pt/C catalysts are shown in Fig. 3. Dark particles uniformly dispersed on the carbon support can be observed, which can be considered embedded metal particles. The results indicate that Pd nanoparticles are well dispersed, with a narrow size distribution in the range of 0.5–2.5 nm as observed in the corresponding histogram, concluding that the methodology used for the catalyst synthesis of Pd/C led to the presence of homogeneously distributed Pd nanoparticles. This dispersion is in good agreement with the conclusion drawn from the XRD results for 10% Pd/C-Fresh, where the diffraction peaks of metallic Pd were not observed. In the case of the used sample, 10% Pd/C-Used (Fig. 3C1–3), it is also observed the existence of some Pd particles agglomerated, indicating some sintering. These results are again in agreement with the XRD analysis, which showed the presence of a diffraction peak (2 theta = 40.1°), related to the reflection plane of Pd°. However, this sintering phenomenum was not considered significant since there was no influence on the catalytic activity for the studied material. The EDX analyses confirmed the presence of Pd with approximately 4.96% ± 0.857% in weight on the surface of the support. This value is approximately about 50% of the experimental loading (10% Pd/C). The particle size distribution shown, without considering the agglomerates observed in Fig. 3 C2 and 3, that the particle size slightly increased.

If Pt catalyst is considered, very small particles were observed in the catalysts 5% Pt/C-Fresh and Used. Barrabés et al. [27] observed that Pt particles were not visible for 0.5% Pt/CeO_2 prepared by the impregnation method, suggesting that the metal particles could be smaller than 1 nm. The particle size distribution revealed a great proportion of particles in the range 0.5–1.5 nm. After the catalytic process (Fig. 3E1–3), the presence of larger particles was observed, and the particle size distribution was broader and moved to higher values. However, the sintering process was less evident than in the case of Pd sample. These data could explain the stability presented by this sample (see below), used in five successive reaction cycles. On the other hand, the amount of Pt calculated by EDX analysis, was about 3.8% (±0.635%) in weight on the support surface. This amount is approximately about 60% of the experimental load (5% Pt/C). According to Marques et al. [19] this difference about metal loading can be explained due to the low reactivity of activated carbon surface, despite the acid wash procedure carried out briefly.

3.3. *Textural properties*

The textural properties of the prepared samples were evaluated from N_2 adsorption-desorption isotherms at −196 °C. The isotherms are represented in Fig. 4. The isotherms obtained are intermediate between type II and IV (according to the IUPAC classification) with the absence of the plateau at high pressures. The hysteresis loop is of type H3 characteristic of mesoporous activated carbon. Moreover, both samples show a great adsorption at low relative pressures, indicating that micropores are also present. This fact is much more important for Pd/C sample, and indicating that carbon support is less affected by Pd incorporation than by Pt. After testing, both samples suffer a decrease of the volume at low pressures and therefore indicating that micropores are those affected by noble metal incorporation. The hysteresis loop hardly changed, indicating that micropores are those affected by the metal

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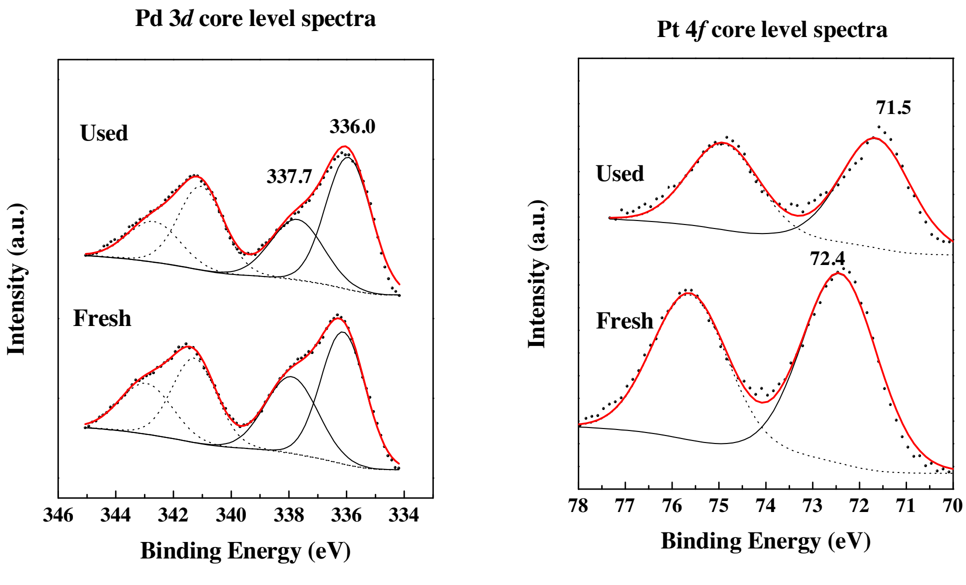

(a) (b)

Fig. 5. (a) Pd 3*d* core level spectra for samples Pd/C-Fresh and Used. (b) Pt 4f core level spectra for sample Pt/C-Fresh and Used.

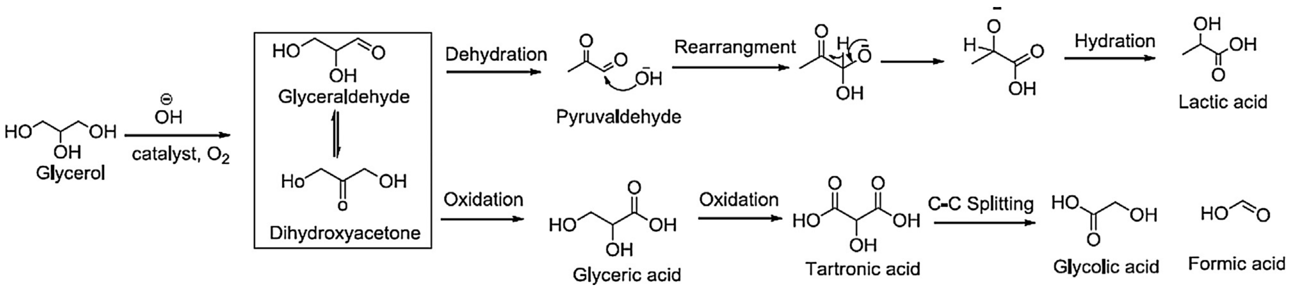

Fig. 6. Proposed reaction mechanism of Glycerol conversion [18].

deposition-sintering in accordance to the low particle size observed for these samples.

Table 1 shows the values of the textural properties before and after use. Comparing the values of area BET, it is noted a reduction of the catalysts compared to the bare support (Pt/C-Fresh approximately 43% and Used approximately 21.3%) and (Pd/C-Fresh approximately 97.3% and Used approximately 68.5%), caused by clogged micropores by metal deposition. Moreover, a decrease is also noticed after testing. This reduction is accompanied with a reduction in the pore volume, indicative of the accumulation of reactants and products after the reaction process inside the pores.

3.4. *X-ray photoelectron spectroscopy*

In order to know the chemical states of the palladium and platinum on 10% Pd/C and 5% Pt/C catalysts, the surfaces were characterized by XPS analysis (Fig. 5a and b). The Pd 3*d* signal is formed by two doublets Pd $3d_{5/2}$ and Pd $3d_{3/2}$ (Fig. 5a). The Pd $3d_{5/2}$ signal is composed of two contributions at 336.0 and 337.7 eV assigned to Pd° and Pd^{2+}, respectively [28–30]. These are the typical valence states for Pd and the peaks values are comparable with the literature. According to the deconvoluted profiles for fresh and used Pd catalysts, shown in Fig. 5, Pd would be present in two different oxidation states. A fraction of the metal would be as $PdCl_2$ (337–338 eV) [31]. This percentage is very similar in the fresh and used catalyst, which indicates that the presence of palladium chloride is related to the precursor used in the catalyst manufacture.

Fig. 5b shows the Pt 4*f* XPS spectra for the 5% Pt/C-Fresh and Used samples. The decomposition of the spectra gives rise to one doublet in both cases: $4f_{7/2}$ component-solid line and $4f_{5/2}$ component-dotted line. The Pt $4f_{7/2}$ component is located at 72.4 eV for the fresh sample and at 71.5 eV for the used one and attributed to Pt^{2+} and Pt°, respectively, suggesting that the Pt species were present as Pt^{2+} in the fresh sample and reduced during the course of the reaction [25,32].

4. Catalytics tests

As stated before, the prepared catalysts were studied in the reaction of conversion of glycerol into lactic acid. Fig. 6 shows the possible reaction mechanism proposed by Purushothamana et al. [18]. The reaction mechanism involves the initial oxidative dehydrogenation of glycerol to glyceraldehyde. In basic conditions, glyceraldehyde is in equilibrium with dihydroxyacetone. It is well known that trioses like glyceraldehyde and dihydroxyacetone undergo rearrangement into lactic acid under alkaline conditions.

An optimal catalyst for the conversion of glycerol into lactic acid therefore should have a strong oxidative dehydrogenation capacity under mild conditions and at the same time being a highly inefficient oxidation catalyst for the conversion of glyceraldehyde into glyceric acid and subsequent oxidation products [18].

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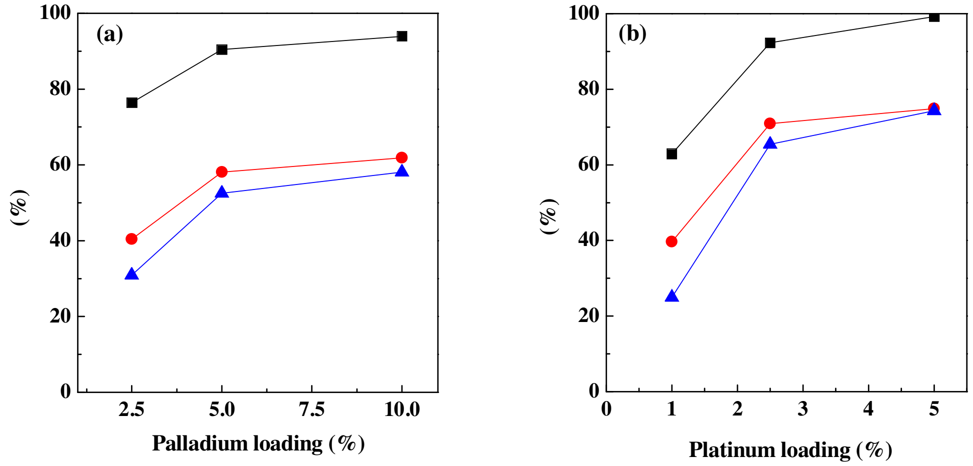

Fig. 7. Effect of metallic loading on glycerol conversion% (■), selectivity% to LA (●) and Yield% of LA (▲). (a) Effect of palladium loading (0.2 g of catalyst) and (b) Effect of platinum loading. (0.5 g of catalyst). Reaction conditions: 100 mL of 0.5 mol L^{-1} glycerol solution, 0.55 mol L^{-1} NaOH, 230 °C, 3 h.

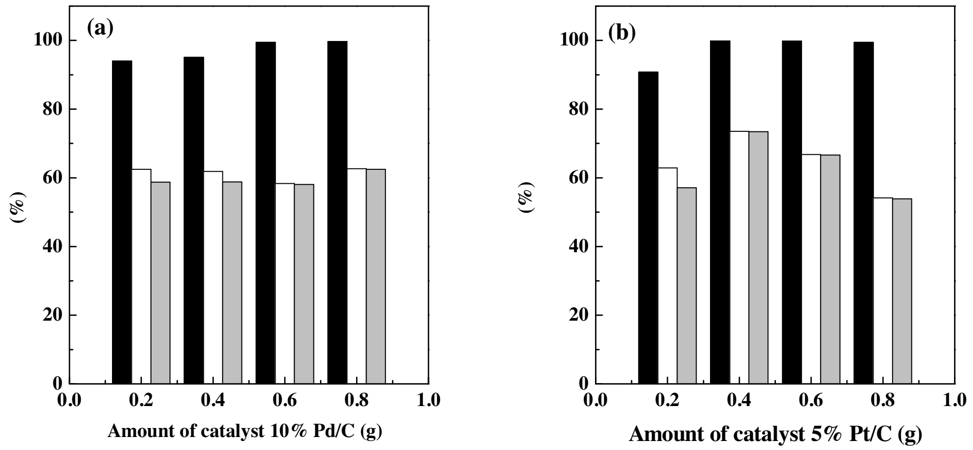

Fig. 8. Effect of catalyst amount (g) on glycerol conversion% (■), selectivity% to LA (□) and Yield% of LA (▨). (a) 10% Pd/C catalyst and (b) 5% Pt/C catalyst. Reaction conditions: 100 mL of 0.5 mol L^{-1} glycerol solution, 0.55 mol L^{-1} NaOH, 230 °C, 3 h.

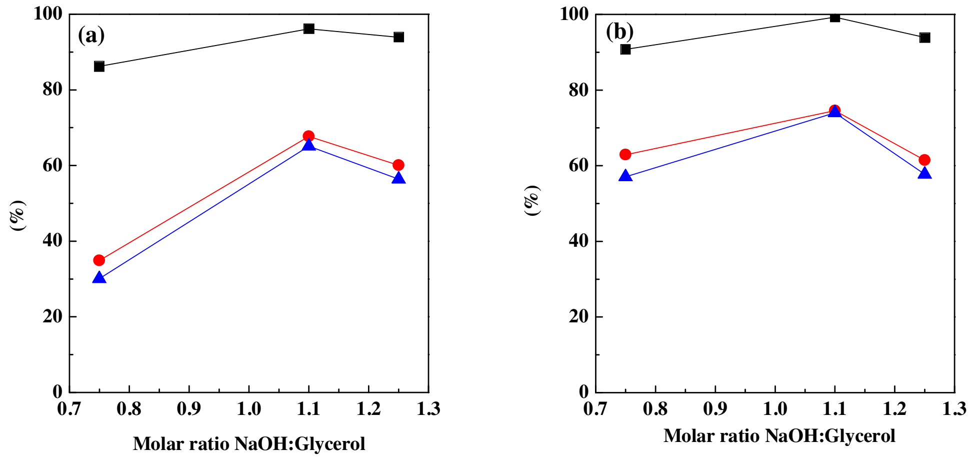

Fig. 9. Effect of NaOH/glycerol molar ratio on glycerol conversion% (■), selectivity% to LA (●) and yield% of LA (▲). (a) 10% Pd/C (0.2 g of catalyst) and (b) 5% Pt/C (0.4 g of catalyst). Reaction conditions: 100 mL of 0.5 mol L^{-1} glycerol solution, 230 °C, 3 h.

4.1. Effect of Pd and Pt loading

The effect of metal loading on the support (activated carbon) is shown in Fig. 7a (palladium) and b (platinum). The conversion of glycerol showed a gradual increase with increasing the metallic loading on the support. The results showed that at the highest loading of Pd and Pt the highest conversions were attained, 93.8% and

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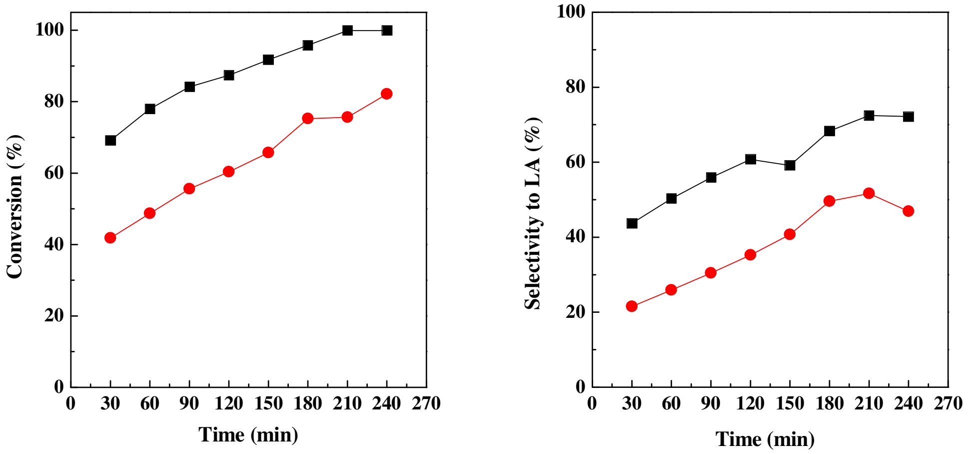

Fig. 10. Effect of reaction temperature 200 °C (●), 230 °C (■) and reaction time on: (a) Glycerol conversion and (b) selectivity to LA for 10% Pd/C catalyst. Reaction conditions: 100 mL of 0.5 mol L^{-1} glycerol solution, 0.55 mol L^{-1} of NaOH, 0.2 g of catalyst.

99.2%, respectively. Meanwhile, the selectivity to lactic acid was 61.9% for 10% Pd/C and 74.9% for 5% Pt/C one.

Therefore, to study other experimental parameters, 10% Pd and 5% Pt containing catalysts were employed.

4.2. *Effect of the catalyst amount (g)—10% Pd/C and 5% Pt/C*

The effect of catalyst amount is shown in Fig. 8a (10% Pd/C), and b (5% Pt/C). It is seen that by increasing the amount of 10% Pd/C catalyst from 0.2 to 0.8 g, the conversion (93.9–99.6%) and selectivity to LA (62.6–62.6%) did not change significantly. A similar trend was observed for the yield (58.8–62.4%). In the case of 5% Pt/C catalyst, a similar behavior was observed. By increasing the amount of catalyst from 0.4 to 0.8 g, it did not provoke a significant change in the conversion values (99.8–99.4%). However the selectivity and yield of lactic acid decreased, 62.9–54.2% and 57.1–53.9, respectively. Therefore, 0.2 g was the amount of Pd catalyst and 0.4 g that Pt one, for the following experiments.

4.3. *Effect of molar ratio NaOH/glycerol (Pd/C and Pt/C)*

Dusselier et al. [33] explain that generally the reaction mechanism for the conversion of glycerol into lactic acid formally requires an oxidation and a dehydration/rehydration step (as presented in the reaction mechanism in Fig. 6). The oxidation may be performed by a dehydrogenation under reductive or inert conditions, by oxidation with oxidants or electrochemically. Dehydration usually requires acidic conditions, but many glycerol reactions have been reported in alkaline media.

According Roy et al. [15] the base accelerates lactic acid formation due to two factors (1) favoring the transformation of pyruvaldehyde to lactic acid, and (2) shifting the equilibrium toward lactic acid formation (by reducing the lactic acid concentration as a result of Na-lactate formation and lactate formation reduces the effective base concentration in the reaction mixture).

The effect of NaOH/glycerol molar ratio is shown in Fig. 9a (10% Pd/C) and b (5% Pt/C). Using a molar ratio of 0.75 the values of glycerol conversion were of 86% and 90%, using 10% Pd/C and 5% Pt/C catalysts, respectively. By increasing the ratio until 1.25, the conversions achieved were higher and approximately the same for both samples, 93%. However, the highest glycerol conversion was obtained for a molar ratio of 1.1, 96% and 99% for 10% Pd/C and 5% Pt/C catalysts, respectively. According to Shen et al. [8], that investigated the effects of different bases as, alkali metals and alkaline-earth metals on hydrothermal glycerol to lactic acid conversion, concluding that alkali-metal hydroxides were more effective than alkaline-earth-metal hydroxides. A glycerol conversion of ~90% was obtained at 300 °C with NaOH or KOH as an homogeneous catalyst.

Ramirez-Lopez et al. [9] reported a glycerol conversion of ~98% achieved at 280 °C with a 1.1 NaOH/glycerol molar ratio, but using a higher glycerol concentration of 2.5 M.

In this study, the performance presented by 10% Pd/C and 5% Pt/C catalysts are promising since high conversion values were attained but at lower reaction temperature and lower glycerol concentration (0.5 M) than the values found in literature. In a previous study on the synthesis of lactic acid from glycerol by using 5% Pd/C, it was obtained 95% of glycerol conversion with 1.1 NaOH/glycerol molar ratio [19].

High selectivity values were also observed with the NaOH/glycerol ratio equal to1.1, 68% (10% Pd/C) and 74% (5% Pt/C). Increasing the molar ratio from 1.1 to 1.25, there was a decrease in the selectivity to lactic acid (LA). According to Marques et al. [19] this behavior indicates that by increasing the molar ratio NaOH/glycerol it is favored the reactions involving the formation of other lactic acid products or the degradation of lactic acid preformed.

Moreover, the presented results are promising since it is claimed in literature, the development of active catalysts capable of operating under less corrosive conditions, such as lower —OH concentration as well as lower reaction temperatures to minimize the severe corrosion of stainless steel reactors, making the process suitable for use in industrial production.

4.4. *Effect of the reaction time and temperature and catalyst stability*

The influence of temperature on the conversion and yield of the lactic acid was studied at two temperatures (200 and 230 °C) for 4 h with a NaOH/glycerol = 1.1, with 10% Pd/C and 5% Pt/C catalysts (Figs. 10 and 11).

The temperature is expected to affect the selectivity of the reaction, since the selectivity to lactic acid is improved at high temperatures as showed in Figs. 10 and 11, for both catalysts. Ftouni et al. [34] studied the conversion of glycerol to lactic acid using Pt/ZrO_2 catalyst, however also detected the presence of other reaction products such as formic acid, 1.2-PDO, 1.3-PDO, ethylene glycol, acetic acid and ethanol in small amounts, at 180 °C and under the He pressure of 30 bars. In the present study, the possible presence of the products listed in the previous study was not detected,

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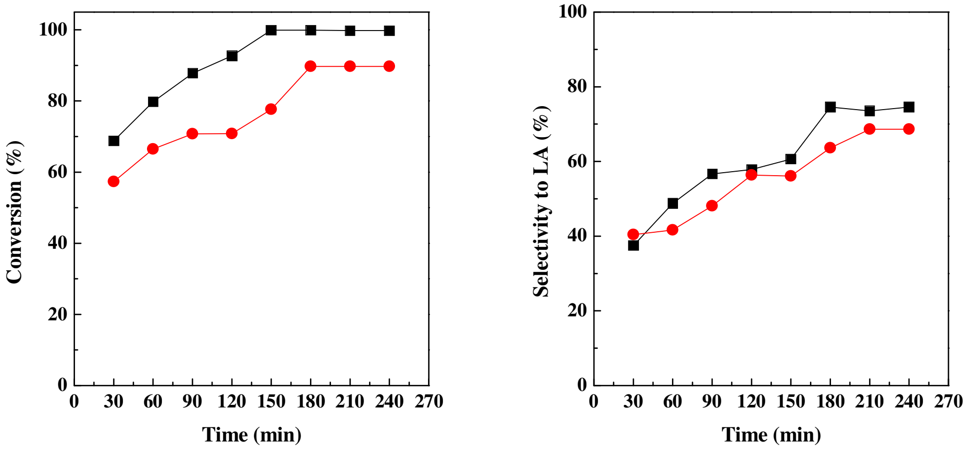

Fig. 11. Effect of reaction temperature 200 °C (●), 230 °C (■) and reaction time on: Glycerol conversion and selectivity to LA for 5% Pt/C catalyst. Reaction conditions: 100 mL of 0.5 mol L^{-1} glycerol solution, 0.55 mol L^{-1} of NaOH, 0.4 g of catalyst.

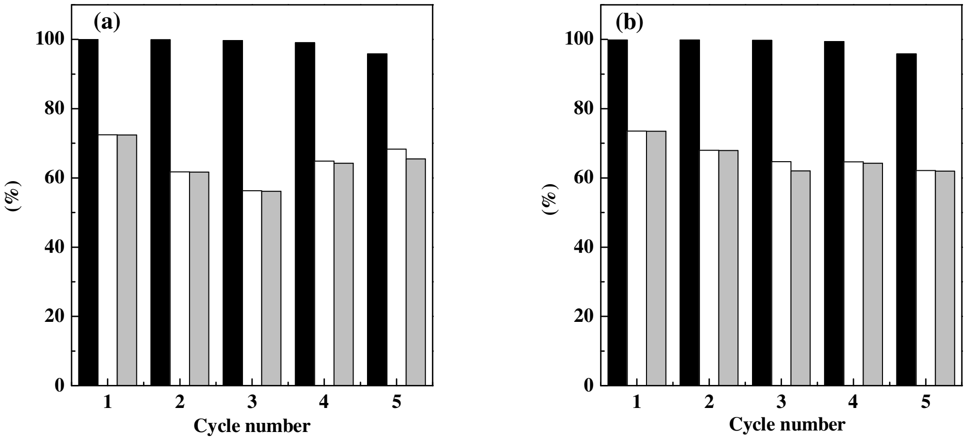

Fig. 12. Effect of repeated use of catalyst on reaction performance. Reaction conditions: (a) 100 mL of 0.5 mol L^{-1} glycerol solution, 0.2 g of catalyst 10% Pd/C, 230 °C, 3 h. (b) 100 mL of 0.5 mol L^{-1} glycerol solution, 0.4 g of catalyst 5% Pt/C, 230 °C, 3 h. Conversion% (■), selectivity% (□) and Yield% (▨).

since that temperature used was 230 °C, which probably was not favorable to the production of other compounds in addition to lactic acid. Ramirez-Lopez et al. showed that elevated temperatures (>277 °C) are required in the hydrothermal process for converting glycerol to lactic acid. However, the decomposition of lactic acid and pyruvaldehyde is significant at this temperature, negatively affecting the selectivity to lactic acid.

With regard to the reaction time, both samples, at both reaction temperatures studied, showed an increased conversion and selectivity to LA. According to Perosa and Tundo [35], such behavior is related to the disposition of the interfacial area of the catalyst in the reaction medium, directly affecting the overall mass transfer coefficient of the system and consequently the reaction rate. The glycerol consumption is also accelerated by increasing the temperature, since this is an endothermic reaction and therefore favored at high reaction temperatures, because under mild conditions there is a difficulty to remove the OH groups of glycerol and oxidize the glycerol to glyceraldehyde (or dihydroxyacetone) [19] in the first reaction step according to reaction mechanism suggested in Fig. 6.

After the completion of the reaction, the catalysts could be easily recovered by filtration followed by washing with water and reused for subsequent runs. The recovered catalysts showed an efficient recycling ability without giving any change in the reaction time and the yield of the product. Suggesting an efficient stability of the catalytic structure with values of glycerol conversion and lactic acid selectivity, no significant differences in five consecutive cycles (Fig. 12).

ICP analyses were carried out to determine the Pd and Pt amount content in the fluid phase, after glycerol reaction. These analyses were performed in order to investigate if the leaching process occurred. The Pd and Pt content in fluid phase after the glycerol (230 °C, 3 h) was 0.822 ± 0.0003 mg/L (which corresponds to 0.05% (w/w) of Pd charged in the catalyst) and 0.117 ± 0.0007 mg/L (corresponds to 0.002% (w/w) of Pt charged in the catalyst).

5. Conclusions

Palladium and platinum-based catalysts supported on activated carbon are efficient catalysts for the conversion of glycerol into lactic acid in aqueous solution in the presence of a base and at a temperature of 230 °C. The catalytic results have revealed that Pd and Pt content and reaction conditions have significant effects on the catalytic performance; meanwhile the catalyst weight only influenced the selectivity to LA in the case of Pt catalysts. Thus only 0.2 g of Pd/C and 0.4 g of Pt/C were enough to achieve high level of Glycerol conversion and selectivity to LA. Thus, LA selectivity of up to 68% and 74% were obtained under the optimum conditions for 10% Pd/C and 5% Pt/C, respectively, with glycerol conversions of about 99%. The reusability of the prepared samples was also high since they hardly lost activity after 5 cycles. Compared to the hydrothermal

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process, this catalytic process requires of lower temperature, lower glycerol/alkali ratios and no need of oxygen or hydrogen addition.

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