Glycerol oxidation in liquid phase: Highly stable Pt catalysts supported on ion exchange resins

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ABSTRACT

The glycerol oxidation reaction in liquid phase was studied using platinum supported on ion exchange resin as catalysts, with the objective of obtaining glyceric acid. In particular, the effect of the competitor anion, which is the ion used during the support pre-treatment, was addressed. It was found that the competitor ion affects the radial distribution of the active metal in the resin sphere. As the adsorption equilibrium constant of the competitor ion increases, the penetration of platinum in the resin particle also increases. Nevertheless, this difference did not affect the catalytic performance. However, the presence of iodide as competitor ion affected the platinum chemical environment, thus modifying the platinum active sites in this catalyst. Such effect was not observed when chloride or citrate ions were used for the resin pretreatment. Therefore, the competitor ion effect on the platinum catalysts performance is related with the ion nature more than with its affinity for the resin exchange sites. Iodide is adsorbed by platinum, and consequently, it affects its electronic state improving the selectivity. These catalysts showed very good activity, and what is also very important, very good stability, being possible to maintain the conversion and selectivity for many reaction cycles.

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1. Introduction

The growing production of biodiesel by triglycerides transesterification has generated an excess of glycerol in the world market, since approximately 100 kg of glycerol is produced for each ton of biodiesel. This led to a decrease in the price of glycerol, and in some cases it has been disposed by incineration [1–3]. Therefore, it is important to develop new applications for glycerol in order to obtain chemicals with added value, what would significantly improve the profitability of the biodiesel production process.

Glycerol is a highly functionalized molecule which could be used to obtain many useful compounds through oxidation, hydrogenolysis, dehydration, esterification, and/or polymerization [4,5]. One of the routes that have been most intensively studied over the past few years is the oxidation. Selective oxidation of glycerol leads to many valuable oxygenated compounds such as glyceric, tartronic, glycolic and hydroxypyruvic acids and dihydroxyacetone.

The oxidation products of glycerol are actually synthesized from chemical processes [6] or through low-productivity fermentation processes [7,8]. In the first method, oxidation of glycerol with inorganic compounds (such as potassium permanganate, chromic acid or nitric acid) is a known process but it has negative effects on the environment due to the formation of undesired waste [6]. Therefore, heterogeneous catalytic oxidation of glycerol is a high potential and environmentally friendly alternative for producing these compounds of high economic value. Among them, the glyceric acid (2,3-dihydroxypropanoic acid) is widely used in medicine since it acts as glucose metabolite. It is also used as precursor for aminoacids synthesis, such as serine.

The catalytic oxidation of glycerol in liquid phase has been extensively studied in the last years, using both mono and bimetallic catalysts on different supports. The metals used in these studies included Pt [6,9–11], Au [6,12–17], Pd [6,18–21], Pt-Bi [22–25], Au-Pd [20,21,26–30] and Au-Pt [12,31] supported on carbonaceous materials (carbon black, graphite, activated carbon, carbon nanotubes) and oxides (TiO_2, CeO_2, Al_2O_3). It has been demonstrated that the activity and selectivity of the reaction strongly depend on the reaction conditions (temperature, pH, metal/glycerol ratio).

The pH of the reaction media plays a key role during glycerol oxidation. It is generally accepted that the presence of a base is beneficial, because higher reaction rates are obtained in this condition [11]. It has been reasonably established that in basic media, a proton is removed from the glycerol primary hydroxyl groups, as the first step of the reaction mechanism [6,9]. Nevertheless, other

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authors have succeeded in performing the glycerol oxidation in a non-basic media. Au-Pt nanoparticles supported on H-mordenite [32], MgO [33] or carbonaceous materials [34] were found to be active for glycerol oxidation in the absence of a base. More recently, Tongsakul et al. [35] also reported that Pt and Pt-Au nanoparticles supported on hydrotalcites were able to oxidize glycerol to glyceric acid without the use of a basic medium.
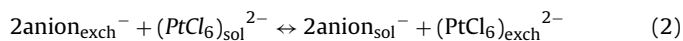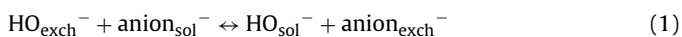
As regards the support, most authors agree that carbon-supported catalysts are more active than most oxide-supported catalysts [36,37]. Ion exchange resins offer extensive possibilities for the deposition of metals in a controlled manner both for monometallic and bimetallic catalysts. Moreover, this support has the advantage of allowing the use of fixed bed reactor configuration, which is of particular interest for the possible industrial application of the process. In addition, the ion exchange resin is highly stable in a wide range of pH. However, there is only one article in the literature in which this support was employed for the catalytic oxidation of glycerol [12].

In this work, we studied platinum catalysts supported on weak anion-exchange resin (Mitsubishi, WA-30) for the liquid phase oxidation of glycerol to obtain glyceric acid. In a previous work [38] it was reported that the concentration of the ion used during the support treatment, previous to the exchange step, affects the metal dispersion and its radial distribution along the resin particle. Such ion is known as the competitor ion, since it competes with the anion containing the active metal for the ion-exchange sites. Besides the concentration, the type of competitor anion modifies the metal distribution on the resin sphere, due to a different adsorption constant of each anion. In this work, the effect of the competitor anion as well as the reaction conditions in the catalytic performance of Pt(1%)/WA30 catalysts for glycerol oxidation reaction, was studied.
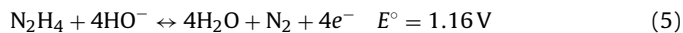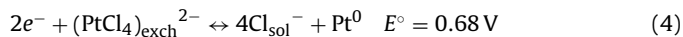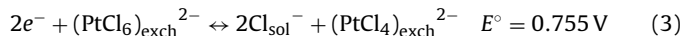
2. Experimental

2.1. Catalyst preparation

Platinum supported on ion exchange resin, prepared using hexachloroplatinic acid (H_2PtCl_6), was used as catalyst for glycerol oxidation. The resin used in this work was Mitsubishi WA-30, which is a macroporous weak anion exchange resin, with tertiary amine functional groups. The nominal platinum loading was 1 wt%, based on the mass of wet resin. The resin is provided in a basic form, i.e. with HO^- ions in the exchange sites. Before adding the metal, the resin was pretreated with different competitor anions in order to replace the hydroxyl anion. This step is represented by Eq. (1), which shows the equilibrium between the anions present in the resin (HO_{exch}^-) and those present in the liquid media ($anion_{sol}^-$), which are the competitor anion. It has already been reported that the type and concentration of the anion used in the pretreatment influence the radial distribution of the metal in the catalyst [38,39], this being the main reason for this step. The anions used as competitor in this study were chloride (hydrochloric acid), iodide (potassium iodide) and citrate (citric acid). The concentrations of all these solutions were 1.4 M, using one volume of solution per volume of treated resin. This concentration was chosen according to the results previously obtained when the effect of the competitor ion concentration was studied [38]. These anions incorporated into the resin, were then exchanged in a second step by the anion containing the noble metal ($PtCl_6$)$^{2-}$. Before adding the solution containing the metal precursor, the resin was drained and two volumes of deionized water per volume of resin were added. Eq. (2) describes the equilibrium condition between the competitor anion in the resin and the precursor anion present in the liquid phase.

$$HO_{exch}^- + anion_{sol}^- \leftrightarrow HO_{sol}^- + anion_{exch}^- \quad (1)$$

$$2anion_{exch}^- + (PtCl_6)_{sol}^{2-} \leftrightarrow 2anion_{sol}^- + (PtCl_6)_{exch}^{2-} \quad (2)$$

During the exchange step, that takes 30 min, it is important to maintain the system agitated to assure homogeneity in the catalyst particles. After this step, the metal was reduced with hydrazine (N_2H_4) in the presence of NaOH at a pH of 14. The reactions that take place during this step and the standard potentials of each of them are the following:

$$2e^- + (PtCl_6)_{exch}^{2-} \leftrightarrow 2Cl_{sol}^- + (PtCl_4)_{exch}^{2-} \quad E^\circ = 0.755\,V \quad (3)$$

$$2e^- + (PtCl_4)_{exch}^{2-} \leftrightarrow 4Cl_{sol}^- + Pt^0 \quad E^\circ = 0.68\,V \quad (4)$$

$$N_2H_4 + 4HO^- \leftrightarrow 4H_2O + N_2 + 4e^- \quad E^\circ = 1.16\,V \quad (5)$$

According to the potential values in Eqs. (3)–(5), it can be inferred that the reduction of platinum with hydrazine is spontaneous.

Finally, after the reduction step, the catalyst was rinsed with distilled water until neutral pH of the eluted solution.

2.2. Support and catalysts characterization

Total exchange capacity. It is the number of exchange sites present in the resin. The determination was performed using two different methods: (a) following the methodology described in ASTM D-2187 standard. This test method consists of converting the sample to the chloride form, elution of chloride with sodium nitrate, followed by determination of chloride ion in the eluted solution; (b) by titration of the resins in the HO^- form with hydrochloric acid.

Water retention capacity. It corresponds to the amount of water retained in the interstices of the polymer network. The determination was carried out following the methodology described in ASTM D-2187. It consists in the determination of the mass lost during drying at $377 \pm 2\,K$ for $18 \pm 2\,h$.

Metal loading. The metal content in the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) after digesting the samples with a mixture of nitric and perchloric acids. Measurements were performed with a PerkinElmer Optima 2100 DV equipment. In addition, the metal content of the aqueous solution at the end of the exchange step was also determined using the ICP technique, in order to verify the effectiveness of the ion exchange step.

Microscopic analysis. The catalysts were analyzed using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The optical microscope used was a Leica, model DM2500M. The electron microscope was a JEOL JSM 35C model. The observation was made in the mode of secondary electron images using an accelerating voltage of 20 kV. Elemental chemical analyses were also carried out by X-ray, using an electron probe micro-analysis (EPMA) technique with energy-dispersive system (EDAX), attached to the scanning electron microscope. With this technique it was possible to determine the radial profile of the metal concentration in the catalyst, taking a measurement every $10\,\mu m$ starting from the edge of the particle. The TEM analyses were carried out with a JEOL microscope model 100CXII operated at 100 kV. The Pt dispersion was calculated applying the equation [40]:

$$D_{Pt} = \frac{0.821}{D_{va}} \quad (6)$$

where D_{Pt} is the dispersion of platinum particles and D_{va} is a volume–area average size defined as follows:

$$D_{va} = \frac{\sum_i n_i \cdot d_i^3}{\sum_i n_i \cdot d_i^2} \quad (7)$$

being n_i the number of particles with diameter d_i.