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New approaches to the $Pt/WO_x/Al_2O_3$ catalytic system behavior for the selective glycerol hydrogenolysis to 1,3-propanediol



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ABSTRACT

Although the hydrogenolysis of glycerol to 1,2-propanediol is already well developed, the production of the more valuable 1,3-propanediol is still a challenge. To achieve this aim, it is essential to design catalysts showing high selectivity toward the CO cleavage of the secondary hydroxyl group in glycerol. In this work, two different series of Pt/WO_x/Al₂O₃ catalytic systems were studied for the selective hydrogenolysis of glycerol to 1,3-propanediol. The results reveal the necessity to control the tungsten surface density in order to obtain highly dispersed polytungstate species, which are able to produce Brönsted acidity and are involved in the selective formation of 1,3-propanediol. After optimization of the tungsten surface density, the effect of platinum content was also studied. It was found that by improving the interactions between platinum and tungsten oxides, it is possible to increase the selectivity toward 1,3-propanediol. Under optimized conditions, a selectivity toward 1,3-PDO of 51.9% at 53.1% glycerol conversion was obtained. Based on the characterization and activity test results, a reaction mechanism for the Pt–WO_x catalytic system in glycerol hydrogenolysis to 1,3-propanediol was also proposed.

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1. Introduction

The development of new transformation processes to convert biomass into fuels and high added value chemicals is a real necessity in order to reduce the petroleum dependence and the carbon footprint of modern societies. In this respect, glycerol appears as one of the top 12 biomass-derived building blocks in the biorefinery industry for the production of a wide range of commodity chemicals [1]. In the last years, glycerol availability has immensely increased, promoted by the biodiesel production via transesterification of vegetable and animal oils which generates large amounts of glycerol as by-product (10.5 kg of glycerol for 100 kg biodiesel). The huge amount of glycerol placed in the market cannot be absorbed by its conventional uses and ends up becoming a residue. Therefore, there is a great interest in the valorization of the biomass-derived glycerol.

The hydrogenolysis of glycerol to obtain propanediols (PDOs), both 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), has attracted a great deal of attention in the recent years. 1,2-PDO is widely used in the manufacture of a broad array of industrial and consumer products, and it has become the

* Corresponding author. *E-mail address:* sara_garcia@ehu.es (S. García-Fernández). substitute of ethylene glycol as antifreeze fluid in food applications due to its non-toxicity [2]. Interestingly, 1,3-PDO compound has an even greater added value than 1,2-PDO, as it is used as a monomer together with terephthalic acid to produce polytrimethylene terephthalate (PTT), a polymer whose unique properties make it very attractive in a wide range of uses.

There is a considerable research dealing with the catalytic conversion of glycerol to PDOs in which high yields of 1,2-PDO have been reported, using typically bifunctional systems formed by a hydrogenation metal and an acid or base cocatalyst [3–7]. Nevertheless, the production of 1,3-PDO is more challenging. The control of the 1,2-PDO/1,3-PDO ratio, which requires highly selective C–O cleavage of the primary or secondary hydroxyl groups of glycerol, is strongly dependent on the catalyst used. Thus, there is a need for the development and understanding of new selective catalytic systems in order to obtain the more valuable 1,3-PDO.

Chaminand et al. [8] found that the addition of H_2WO_4 to the sulfolane media in the glycerol hydrogenolysis using Rh/SiO₂ enhanced the yield of 1,3-PDO (4%) at 200 °C and 80 bar and also in aqueous media (3%). However, from an industrial and environmental perspective, the use of heterogeneous catalysts is preferred. Kurosaka et al. [9] obtained a 24% yield of 1,3-PDO in 1,3-dimethyl-2-imidazolidinone (DMI) solvent over Pt/WO₃/ZrO₂ at 170 °C and 80 bar. Huang et al. [10] achieved a 27% yield of 1,3-PDO in vapor phase and aqueous media using Cu-H₄Si₁₂O₄₀SiW/SiO₂ catalyst at

5 bar and 210 °C. A significantly higher 1,3-PDO yield (56%) was attained by Oh et al. [11] with Pt deposited on the super-acid sulfated ZrO_2 support, in DMI solvent at 170 °C and 73 bar. All these previous works present some drawbacks, such as the use of organic solvents or the work in gas phase, which will greatly reduce the environmental and economic viability of the process. Water is the ideal solvent for the process as glycerol is obtained in aqueous phase after the transesterification reaction. [12].

Up to date, the most effective approach in the production of 1, 3-PDO in aqueous phase has shown to be the use of heterogeneous catalysts formed by a noble metal (Ir, Rh, or Pt) combined with oxophilic metals such as Mo, Re, and W [13]. In fact, one of the most complete works was carried out by Tomishige's group using ReO_x-modified Rh/SiO₂ [14] and Ir/SiO₂ [15–17] catalytic systems, obtaining with this last catalyst a 38% 1,3-PDO yield at 120 °C and 80 bar, using small amounts of H₂SO₄ as an additive. However, the weak interactions of ReOx species with the silica support and the high solubility of these species in water favor Re leaching under the reaction conditions, which compromises the stability of such catalysts [18]. Thus, more robust and stable tungsten Pt-WO₃ based catalytic systems appear as a better option. In 2010, Quin et al. [12] reported a high yield of 1,3-PDO (32%) using a Pt/ WO₃/ZrO₂ catalyst at 130 °C and 40 bar. Zhu et al. [19] investigated the performance of zirconia supported bifunctional catalysts containing Pt and heteropolyacids, obtaining 31% of 1,3-PDO yield with Pt-HSiW/SiO₂ catalyst at 180 °C and 50 bar. More recently, Arundhathi et al. [20] obtained the highest 1,3-PDO yield (66%) reported to date using Pt/WO3/"AlOOH" catalytic systems. The high yield obtained was attributed by these authors to the plentiful Al–OH groups in the boehmite support, but the high temperatures used in the catalyst pretreatment and the XRD results indicate a different alumina structure than boehmite (possibly γ -Al₂O₃) and therefore the absence of many hydroxyl groups. In spite of these previous works, the overall C-O hydrogenolysis mechanism as well as the role of tungsten and platinum still remains unclear [21].

In this study, two different series of $Pt/WO_x/Al_2O_3$ catalysts were prepared, with different WO_x and Pt contents, in order to understand the role of each active phase. The obtained glycerol conversion and PDOs selectivity values were related to the physicochemical properties of the catalysts measured by N₂ physisorption, H₂ temperature programmed reduction (H₂-TPR), Fourier transform infrared spectroscopy (FTIR) of adsorbed pyridine, Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectronic spectroscopy (XPS), NH₃ adsorption calorimetry, transmission electron microscopy (TEM), and CO chemisorption techniques. The results from this research allow a better understanding of the behavior of $Pt/WO_x/Al_2O_3$ catalytic systems in glycerol hydrogenolysis.

2. Experimental

2.1. Catalyst preparation

Pt/WO_x/Al₂O₃ catalysts were prepared by sequential wetness impregnation method. The typical procedure followed for the preparation of the catalysts is detailed below. γ-Al₂O₃ (Sigma–Aldrich, ≥99.9%) was used as support, and it was impregnated using the appropriate amounts of ammonium metatungstate ((NH₄)₆(H₂W₁₂O₄₀)·nH₂O, Sigma–Aldrich, ≥99.99%)) dissolved in deionized water.

Impregnated samples were dried at 110 °C overnight and subsequently calcined in air from room temperature up to 450 °C at a heating rate of 2 °C min⁻¹, maintaining this temperature for 4 h. Pt was then loaded on supported tungsten oxide catalysts by wetness impregnation using tetraammineplatinum(II) nitrate ((Pt(NH₃)₄(NO₃)₂, Sigma–Aldrich, \ge 99.995%)) as precursor. The resulting catalysts were dried and calcined as above. These Pt/WO₃/Al₂O₃ samples are denoted as *x*PtyW, where *x* refers to the platinum content in weight percent (wt%) in the final catalyst and y to the tungsten content related to the alumina support (in terms of wt% of W/ γ -Al₂O₃), both of them measured by ICP. The tungsten surface density (expressed in W atoms nm⁻² of support) was calculated based on the following equation,

$$\rho_{\rm W}[{\rm W \ atoms/nm^2 \ of \ support}] = \frac{\left(\frac{x_{\rm W}}{M_{\rm W}}\right){\rm NA}}{{\rm SA}_{\rm Al_2O_3}\left[1 - (x_{\rm WO_3} + x_{\rm PtO})\right]}$$

where x_W is the mass fraction of the W species in the final catalyst, NA is the Avogadro number, M_W is the W atomic weight, and $SA_{Al_2O_3}$ is the initial BET surface area of the calcined γ -alumina support used. In this case, it was assumed that all the tungsten oxide species presented in the catalyst were WO₃ and the platinum oxides were PtO.

2.2. Catalyst characterization

2.2.1. Chemical analysis

The chemical analysis of the catalyst was carried out by inductively coupled plasma atomic emission (ICP-AES) using a Perkin– Elmer Optima 2000 instrument. Previously to the analysis, the solid samples were digested in a microwave oven in a mixture of HF, HCl, and HNO₃ heating from room temperature up to 180 °C during 30 min.

2.2.2. N₂ physisorption

Textural properties (surface area, pore volume, and pore size distributions) were obtained by N₂ physisorption at -196 °C using a Quantachrome AUTOSORB-1C-TCD instrument. All samples were dried at 300 °C overnight under high vacuum prior to the physisorption measurements. The surface area was calculated using the Brunauer, Emmett, and Teller (BET) method, and the pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the isotherms.

2.2.3. CO chemisorption

The measurements were performed in an AUTOSORB-iQ equipment. Prior to adsorption, all samples were outgassed in He flow at 120 °C for 3 h and subsequently reduced at 450 °C under a stream of pure H₂ for 1 h (reaction conditions). The samples were cooled down to room temperature and evacuated under He flow for 2 h. After that, CO chemisorption uptakes were measured by pulses of pure CO at 40 °C.

2.2.4. TEM

TEM images were obtained in a Philips SuperTwin CM200 apparatus operated at 200 kV and equipped with LaB_6 filament and EDAX EDS microanalysis system. The reduced samples (at reaction conditions) were prepared via dispersion into ethanol solvent and placed on a carbon-coated copper grid (300 Mesh) followed by drying under vacuum.

2.2.5. XRD

XRD studies of the reduced catalyst were recorded on an Xpert-Pro instrument with a PW3050/60 goniometer and a Cu anode at current of 40 mA and voltage of 40 kV, in a 2θ range from 10° to 90° with a 0.026° step size. The patterns were compared with the power diffraction files (PDF) by Xpert-Pro High Score tool.

2.2.6. Raman spectroscopy

The Raman spectra of the calcined catalysts were determined at ambient conditions using samples in powder form, using a

Renishaw InVia microscope with Ar ion laser (Modu-Laser) employing 514 nm laser excitation, in order to determine the species present in the samples and the interaction between the platinum and tungsten species. The spectra were recorded at ambient temperature within the $150-1500 \text{ cm}^{-1}$ region.

2.2.7. XPS

XPS spectra of the reduced samples (fresh and some after use) were obtained on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer an Mg K α (hv = 1253.6 eV) X-ray source. Binding energy ($E_{\rm b}$) values were referred to the C1s peak at 284.6 eV. The recorded XPS signals were analyzed using a nonlinear Shirley-type background and decomposed into subcomponents by Gaussian–Lorentzian functions.

2.2.8. H₂-TPR

The reducibility study of the surface species was carried out on a Quantachrome AUTOSORB-1C-TCD apparatus. TPR profiles were obtained using a catalyst powder amount of 0.3 g. The samples were reduced in a flowing gas of 5 vol% H₂ in Ar (50 mL min⁻¹ of total flow rate) increasing the temperature from 40 °C up to 1100 °C at 10 °C min⁻¹. A TCD detector downstream of the sample monitored changes in the concentration of H₂.

2.2.9. NH₃ adsorption microcalorimetry

Adsorption microcalorimetry measurements were performed at 80 °C in a volumetric line linked to a heat-flow microcalorimeter (Tian-Calvet type, C80 from Setaram) in order to measure the whole acidity as well as the strength of the catalytic sites present in the samples. Ammonia (NH₃) was used as a basic probe molecule to titrate the surface acid sites. An amount of 0.1 g of powder calcined sample was pretreated under vacuum at 250 °C overnight (about 12 h) and subsequently evacuated at the same temperature for 1 h prior to the measurements. Small successive NH₃ injections were sent onto the sample until a final NH₃ equilibrium pressure of about 67 Pa. For each dose, the adsorption heat and the pressure of the adsorbate, this last measured by means of a differential Barocel capacitance manometer (Datametrics), were recorded by a computer. Following the first adsorption isotherm, the sample was outgassed under vacuum for 30 min at the same temperature and a second adsorption isotherm was performed until the equilibrium pressure of 27 Pa was attained. The irreversible volume of NH₃ $(V_{\rm irr})$, associated with the strongly chemisorbed NH₃, was calculated from the difference between the first and second volumetric isotherms at 27 Pa.

2.2.10. FTIR of adsorbed pyridine

FTIR of adsorbed pyridine analysis was carried out in order to study the nature (type and strength) of acid sites on the surface of different WO_x/Al₂O₃ and Pt/WO_x/Al₂O₃ samples. Infrared transmission spectra were recorded on Nicolet 8700 FTIR spectrometer equipped with an extended KBr beam splitter and a mercury cadmium telluride (MCT) detector. The samples were pressed into a 30-35 mg of self-supporting wafers, having a surface area of about 2 cm², which were placed into an infrared quartz cell, with CaF₂ windows, connected to a vacuum line. Pellets were pretreated under vacuum (about 10^{-5} Pa) with an oxygen flow and by a slow heating of 2 °C min⁻¹ up to 350 °C. Then, they were outgassed at the same temperature for 1 h. A known amount of pyridine was introduced into the cell at room temperature. Spectra were recorded after pyridine desorption by evacuation for 15 min under vacuum at different temperatures (200 °C and 300 °C) with a spectral resolution of 2 cm⁻¹ and 32 scans per spectra. All reported spectra were obtained by subtracting the spectrum of the activated catalyst (after pretreatment but before pyridine adsorption) from those after pyridine adsorption.

2.3. Activity test

Activity tests were carried out in a 50-mL stainless steel autoclave with a magnetic stirrer at 550 rpm. Typically, 0.35 g of catalyst powder (300–500 μ m) was introduced into a catalytic basket inside the autoclave. Prior to the activity test, the catalyst was in situ reduced under a stream of pure H₂ (100 mL/min) at 450 °C for 1 h. After reduction, the reactor was cooled down to the reaction temperature (200–220 °C) and the H₂ pressure was increased up to 20 bar. The reactant solution (42 mL of 5 wt% glycerol aqueous solution), placed into a feed cylinder at 50 bar H₂ pressure, was fed into the reactor taking advantage of the pressure difference and by circulating a continuous flow of H₂ from the cylinder to the reactor for about 5 min. Thereafter, the pressure was increased up to the 45 bar operation pressure.

Along the first 7 h of reaction time, 4 liquid samples were taken and a last sample was taken at 24 h reaction time. These samples were analyzed using 1,4-butanediol (Sigma–Aldrich, 99.99%) as internal standard with a gas chromatograph (Agilent Technologies, 7890 A) equipped with a Meta-Wax capillary column (diameter 0.53 mm, length 30 m), a flame ionization detector (FID), and a thermal conductivity detector (TCD). After 24 h of reaction, the gas phase was collected in a gas bag and analyzed with another GC-TCD-FID equipped with a molecular sieve column (HP-MOLESI-EVE, diameter 0.535 mm, length 30 m) and a capillary column (HPPLOT/Q, diameter 0.320 mm, length 30 m).

The conversion of glycerol and the selectivity of liquid products were calculated based on the following equations:

Conversion of glycerol (%) =
$$\frac{\sum \text{C-based mol of all liquid product}_{t=t}}{\text{C-based mol of glycerol}_{t=0}}$$

Selectivity of liquid product (%) = $\frac{\text{C-based mol of the product}}{\sum \text{C-based mol of all liquid products}}$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. N₂-physisorption

The textural properties of the calcined catalysts are shown in Table 1. The catalysts surface area was reduced in all the catalysts as compared to the γ -alumina support (SA_{BET} of 140 m² g⁻¹) as the tungsten surface density increased. This could be due to the blocking or filling of γ -alumina pores when the tungsten oxide species were added. The reduction in pore volume of the catalysts in comparison with the bulk support (pore volume of 0.23 cm³ g⁻¹) can be explained through the same assumption. The incorporation of the platinum oxide on the tungstated support had the same effect.

3.1.2. CO chemisorption

The tungsten oxides present in the $Pt/WO_x/Al_2O_3$ catalysts do not adsorb CO [22]; therefore, CO chemisorption was used to measure the platinum particle size and metal dispersion on platinum loaded samples. Depending on the type of adsorption sites, the average of CO/Pt adsorption stoichiometry usually varies from 1 to 2 because CO chemisorbs in various forms [23]. The most widely CO/Pt adsorption stoichiometry used for the calculation of platinum size and metal dispersion is a ratio of 1 [24,25]. In order to facilitate the comparison with other works, the same value was assumed in this article. The results are shown in Table S1. It can be noted that increasing the platinum loading, the metal size notably increased, from 4 to 26 nm for 2Pt8W and 9Pt8W catalyst, respectively, and with the resultant decline in platinum dispersion (from 27% to 4%, respectively).

Catalyst ^a	SA_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Glycerol conversion (%)	Product selectivity (%)			
				1,3-PDO	1,2-PDO	1-PO	Degradation products ^b
1Pt1W (0.2)	128	0.24	25.6	0.0	78.2	1.9	19.9
1Pt5W (1.0)	111	0.22	22.2	3.1	76.3	3.5	17.2
1Pt9W (2.4)	104	0.19	16.7	16.4	57.5	12.4	11.3
1Pt14W (3.9)	96	0.18	11.6	10.9	60.9	20.7	7.5
1Pt19W (5.9)	79	0.15	5.5	11.2	59.5	29.3	0.0
2Pt8W (2.2)	105	0.19	25.6	25.7	39.3	21.5	6.1
4Pt8W (2.2)	-	-	42.1	27.8	25.9	25.9	7.8
9Pt8W (2.2)	81	0.15	60.3	31.2	11.0	35.6	12.0
9Pt8W (2.2) ^c	81	0.15	53.1°	51.9°	9.5 ^c	24.8 ^c	1.2 ^c

Table 1		
Textural properties of the catalyst and its activity	y results obtained after 24 h reaction time,	220 °C, and 45 bar pressure.

^a Tungsten surface density in brackets (W at. nm⁻²).

^b Main degradation products: ethylene glycol, ethanol, methane.

^c Results obtained for 9Pt8W (2.2) catalyst at 200 °C reaction temperature.



Fig. 1. TEM images of fresh reduced (a) 1Pt9W and (b) 9Pt8W catalysts.

3.1.3. TEM

Fig. 1(a) and (b) shows the TEM images of 1Pt9W and 9Pt8W catalysts. Although the TEM images do not allow a visual clear discrimination among platinum and tungsten oxide clusters (neither by shape nor contrast), it is interesting to note that only particles with diameters \leqslant 5 nm were found. EDS microanalysis on different specific particles allowed to differentiate certain platinum particles from the tungsten oxides at low platinum content. In Fig. 1(a), a platinum particle (circle) of a diameter lower than 1 nm surrounded by tungsten oxides well dispersed in the catalyst surface can be seen. For 9Pt8W sample, the differentiation was absolutely impossible even by EDS microanalysis, which reveals the closer proximity between these species at higher platinum contents. Both, platinum and tungsten, characteristic X-ray peaks were obtained around throughout the sample investigated (Fig. 1(b)).

The particle sizes obtained by TEM are commonly smaller than those from chemisorption uptakes as Iglesia et al. reported [26]. In this case, the platinum particle size estimated from TEM (5 nm) and CO chemisorption (26 nm) measurements is significantly different for the 9Pt8W catalyst.

3.1.4. XRD

The structure of the reduced (at reaction conditions) fresh Pt/ WO_x/Al₂O₃ catalysts was analyzed by XRD (Fig. S1). The XRD patterns of the catalysts with a constant Pt content (1 wt%) and different WO_x loading reveal that only diffraction peaks related to crystalline γ -alumina (2θ = 37.5°, 45.4°, 66.9°) [27] were observed for catalyst with a tungsten surface density lower than 2.4 W at. nm⁻². However, diffraction peaks' characteristic of monoclinic-WO₃ phase (m-WO₃) (2θ = 23.5, 33.3) were observed for a tungsten surface density of 3.9 W at. nm⁻² [28]. This indicates the formation of WO₃ crystalline nanoparticles (WO₃ NPs) of around 5 nm at high tungsten surface density values. These results are in good agreement with the Raman spectroscopy and XPS results. The absence of platinum diffraction peaks revealed the homogeneous dispersion of this metal on the catalyst.

As it can be observed in the XRD patterns of the catalysts with a constant tungsten surface density of about 2.2–2.4 W at. nm⁻², for platinum loadings higher than 2 wt%, large and narrow peaks' characteristics of metallic platinum $(2\theta = 39.9^\circ, 46.4^\circ, 67.6^\circ)$ [29] started to be observed. There was no evidence of the presence of platinum oxides, which means that the complete reduction of the catalyst was attained at the reduction conditions used. As the platinum content raised from 2 wt% to 4 wt%, the platinum crystallite size also increased considerably but remained almost constant for higher platinum contents (9 wt%). This trend was supported by CO chemisorption and TEM technique results. However, the platinum particle size values obtained by XRD are considerably higher, probably due to the most dominant contribution of some big platinum particles formed on this bulk type analysis and to the very small clusters being undetectable because of the detection limit of this technique was 3 nm.

3.1.5. Raman spectroscopy

Tungsten surface density determines the different types of tungsten oxides species that are deposited on the surface of the catalyst, namely surface monotungstate species (coordinated structure: WO_4), polytungstates (coordinated structure: WO_5 / WO_6), and WO_3 crystalline nanoparticles (NPs) [30].

Raman spectroscopy was used to differentiate the species present on the catalysts surface, and the spectra of calcined catalysts are shown in Fig. 2. The γ -alumina support has no Raman active modes [30]. The Raman bands of Pt/WO_x/Al₂O₃ catalysts appearing in the 970–1008 cm⁻¹ region can be attributed to W=O vibration



Fig. 2. Raman spectra of the calcined catalysts. Tungsten surface density (W at. $nm^{-2})$ in brackets.

bands of mono- and polytungstate species [30]. The progressive shift of the position of this band to higher wavenumbers, from 971 cm⁻¹ to 1008 cm⁻¹, as the tungsten density increases from 0.2 W at. nm^{-2} up to 3.9 W at. nm^{-2} , can be ascribed to an increase of the polytungstates to monotungstates ratio [31]. Typical WO₃ NP bands at 800, 700, and 250 cm⁻¹ could be observed at densities \geq 3.9 W at. nm⁻², which are assigned to W–O stretching, W–O bending, and W-O-W deformation modes of octahedrally coordinated WO₃ crystals [32]. These NPs correspond to m-WO₃ phase as the XRD results revealed. The formation of WO₃ NPs on the catalyst surface is due to the aggregation and sintering of tungsten oxides before reaching the theoretical γ -alumina monolayer coverage (7 W at. nm⁻²). This value was calculated by Barton et al. at [33] assuming corner sharing WO_x octahedra with bond distances derived from m-WO₃. These data suggest that there are a fixed number of binding sites for tungsten oxides on γ -alumina surface. It is widely suggested this species anchor to the γ -alumina support by titrating the surface hydroxyls [34]. One possible assumption is that WO₃ NPs start forming once all the surface hydroxyls are titrated. However, we cannot exclude the possibility that the formation of NPs starts before all the anchoring sites are occupied. At the highest tungsten surface density of 5.9 W at. nm⁻², the m-WO₃ is the predominant phase detected by Raman spectroscopy.

For the 9W catalyst, the band corresponding to polytungstates appears at 973 cm⁻¹. When 1 wt% of platinum was incorporated into WO_x/Al₂O₃ (1Pt9W), a shift to a higher wavenumber occurred (from 973 cm⁻¹ to 1003 cm⁻¹). This shift might be due to the interaction between platinum and surface tungsten oxides that affects the distortion of the oxotungsten species. This approach was also found over Pd–WO_x/TiO₂ system by Taylor et al. [35]. In Pt/WO_x/Al₂O₃ catalytic systems, it appears that the transfer of electrons from the metallic platinum to the WO_x increases the W=O bond strength.

3.1.6. XPS

XPS measurements were carried out to identify the surface chemical species, its oxidation state and to estimate the metal dispersion on the catalyst surface for WO_x/Al_2O_3 and $Pt/WO_x/Al_2O_3$ reduced samples.

For tungstated samples (without platinum), Al2p and W4f were used to study the Al and W elements, respectively. Fig. 3 shows the intensity ratio of the W4f and Al2p photoelectrons, $(I_W/I_{Al})_{XPS}$, compared to the bulk W/Al atomic ratio, (W/Al)_{bulk}. The Kerkhof-Moulijn model (K-M model) has been used mainly to estimate the maximum concentration of tungsten at which a deviation from monolayer deposition occurs [36]. It can be observed that experimental and predicted by K-M model (black straight line) values almost match for tungsten surface density values below 2.4 W at. nm^{-2} . The fact that the sample with 14 wt% W $(3.9 \text{ W at. nm}^{-2})$ slightly deviates from the linearity reveals that the WO₃ is not only forming a two-dimensional phase in the catalyst surface, but also a small fraction of WO₃ begins to form three-dimensional clusters (WO₃ NPs). These results agree with previously shown XRD results and show that WO₃ NPs are formed at tungsten surface density values below the theoretical monolaver content of 7 W at. nm^{-2} [33]).

For Pt/WO_x/Al₂O₃ samples, due to the overlapping of Al2p and Pt4f lines, the Pt4d lines were used to study the platinum species on the catalyst surface, although this line is weaker. The E_b obtained in the Pt4d_{5/2} (314.8–315.9 eV) spectral region for the investigated samples (see Table 2) shows that the platinum species are completely reduced under the reduction conditions used [37]. Moreover, the E_b of W4f_{7/2} peaks can be associated with the existence of both WO₃ [38] and aluminum tungstates (Al₂(WO₄)₃) [39]. However, due to the relative low calcination temperature used in catalyst preparation (450 °C), it can be assumed that aluminum tungstates were not formed or in negligible proportion.

The XPS peak intensities were used to calculate the atomic relative contents of the $Pt/WO_x/Al_2O_3$ reduced samples, which are given in Table 2. These surface atomic ratios of Pt and W related to Al were there compared with the bulk ratios obtained from ICP-AES. For fresh reduced catalysts with low platinum contents of 1 wt%, it can be observed that Pt/Al surface ratios are rather similar to the bulk ratios, which suggests a good platinum dispersion, even at high tungsten oxide contents (1Pt14W sample). For higher platinum loadings, considerably smaller atomic surface ratios than bulk ratios were obtained, which might be a consequence of a worse platinum dispersion.

XPS can provide further information about the metal anchoring sites. Kwak et al. [40] observed that when platinum was supported



Fig. 3. Intensity ratio, $(I_{W4f}/I_{Al2p})_{XPS}$, of the W4f and Al2p photoelectrons against the bulk atomic ratio, $(W/Al)_{bulk}$. The black line corresponds to Kerkhof–Moulijn model. Tungsten surface density (W at. nm⁻²) in brackets.

Table 2

Bulk atomic ratio obtained from ICP-AES, surface atomic ratio obtained from XPS and BE of the Pt and W elements.

Catalyst ^a	Pt/Al		W/Al		E _b	
	Bulk	Surface	Bulk	Surface	Pt 4d _{5/2}	W 4f _{7/2}
1Pt4W (1.0)	0.003	0.003	0.011	0.029	315.0	35.5
1Pt9W (2.4)	0.004	0.003	0.027	0.056	314.9	35.6
1Pt14W (3.9)	0.004	0.003	0.045	0.080	315.0	35.8
4Pt8W (2.2)	0.012	0.007	0.026	0.032	314.9	35.9
4Pt8W (2.2) ^b	0.012	0.004	0.026	0.052	314.9	35.8
9Pt8W (2.2)	0.028	0.010	0.023	0.028	314.8	35.9
9Pt8W (2.2) ^b	0.028	0.007	0.023	0.041	315.9	35.9

^a Tungsten surface density in brackets (W at. nm⁻²).

^b Catalyst after use in glycerol hydrogenolysis reaction at 220 °C.

on bare γ -alumina, it was anchored at specific Al³⁺ sites. In the case of WO_x species, it is widely suggested that they anchor to the γ alumina support by titrating the surface hydroxyls [34]. However, we are not aware of studies concerning the sites where platinum is incorporated on the WO_x/Al₂O₃ surface. The W/Al surface ratio results of the investigated samples can reveal further information about these sites. A remarkable decrease in W/Al surface ratio was found as the platinum loading increased from 1 wt% to 10 wt% (0.056 to 0.028) for the fresh reduced samples. This may be an indication that the platinum could partially be anchored at the WO_x sites at high platinum loadings, in addition being anchored to the Al³⁺ sites. Nevertheless, further research is required to corroborate this hypothesis. Interestingly, XPS results of used catalysts (reaction at 220 °C) revealed an important decline in Pt/Al and an increase in W/Al surface ratios comparing to the ones of the fresh catalysts, which suggests a potential dispersion loss of the platinum on the tungsten oxide sites under the hydrothermal reaction conditions employed. These reaction conditions might also affect the oxidation state of Pt species, as the shift of the $E_{\rm b}$ of Pt 4d_{5/2} for the used catalyst with the highest Pt content (9Pt8W) suggests.

3.1.7. H₂-TPR

The H₂-TPR profiles of the catalysts are shown in Fig. 4. In the temperature range studied (40–1100 °C), the γ -alumina support cannot be reduced (not shown). Although the complete reduction of WO_x/Al₂O₃ catalysts requires temperatures higher than 1100 °C, it is possible to verify that the initial reduction temperature decreases as the tungsten surface density increases. This could indicate that the interaction between WO_x species and the support is stronger at low tungsten surface densities. The appearance of a peak at 780 °C for the 14 W (3.9 W at. nm⁻²) catalyst may be related to the presence of WO_3 NPs as Raman spectroscopy and XPS, among other techniques, revealed. The 4Pt catalyst TPR profile shows two main peaks at 133 and 260 °C, which are attributed to the reduction of platinum oxides [41]. The appearance of small reduction peaks between 400 and 600 °C is probably due to platinum species highly interacting with the support. The tungsten oxides incorporation (4Pt8W catalyst) notably reduced the platinum reduction peaks, which were detected with the maxima at 120, 230, and 470 °C. This decrease in the reduction temperature of platinum oxides indicates an interaction between platinum and tungsten oxides, which generates more reducible platinum species.

Concerning the reduction of WO_x species in the catalysts containing platinum, it started at a temperature around 550 °C, in contrast to the catalyst without Pt (9W), for which higher temperatures were required. The spillover of the H₂ molecules on the platinum sites seems to facilitate WO_x reduction. It has to be noticed that this effect is more noticeable as the platinum content



Fig. 4. H_2 -TPR of the calcined fresh catalysts. Tungsten surface density (W at. nm^{-2}) in brackets.

increases, which reveals that Pt and W phases are in closer proximity, which was also observed by XPS and TEM analysis.

3.1.8. NH₃ adsorption microcalorimetry

The amounts of NH₃ adsorbed at 80 °C and the corresponding interaction energies with the catalysts were determined by means of a volumetry–calorimetry coupled technique. Table 3 gives the total number of acid sites (estimated by V_{tot}), the number of strong acid sites (V_{irr}) as well as the initial differential heat of NH₃ adsorption (Q_{init}).

The volumetric adsorption isotherms (NH₃ uptake vs. equilibrium pressure) and differential heats of NH₃ adsorption (differential heats vs. NH₃ uptake) are reported in Fig. 5(a) and (b), respectively. The volumetric isotherms of the studied samples displayed in all cases an initial vertical section proportional to the amount of strongly chemisorbed NH₃ [42]. The incorporation of tungsten oxide to the γ -alumina support increases the total acidity, as it is indicated by the total amount of NH₃ retained at 27 Pa of equilibrium pressure (*V*_{tot}), as it can be observed in Fig. 5(a) and Table 3. It has to be noticed that the catalysts with tungsten (with and without platinum) presented similar capacity to adsorb the NH₃ probe. The small variations might be due to differences in

Table 3

Initial heats of adsorption, total, and irreversible amounts of $\rm NH_3$ adsorbed at an equilibrium pressure of 27 Pa, measured by $\rm NH_3$ adsorption microcalorimetry.

Catalyst ^a	Acidity				
	Q_{init}^{b} (kJ mol ⁻¹)	$V_{\rm tot}^{\rm c}$ (µmol NH ₃ g ⁻¹)	$V_{\rm irr}^{\rm d}$ (µmol NH ₃ g ⁻¹)		
γ -Al ₂ O ₃	179	219	120		
9W (2.4)	235	287	153		
2Pt8W (2.2)	222	260	147		
4Pt8W (2.2)	224	278	161		
4Pt	178	235	129		

^a Tungsten surface density in brackets (W at. nm⁻²).

^b Initial heat evolved in the first dose of NH₃.

 c Total amount of NH_3 retained as determined at 27 Pa of equilibrium pressure. d Irreversibly adsorbed amount of NH_3 as determined from the difference

between the amounts adsorbed in the first and second adsorptions isotherms at 27 Pa.



Fig. 5. (a) Volumetric adsorption isotherms, NH₃ uptake in μ mol g⁻¹ vs. equilibrium pressure and (b) differential heats of NH₃ adsorption, differential heats in kJ mol⁻¹ vs. NH₃ uptake in μ mol g⁻¹. Tungsten surface density (W at. nm⁻²) in brackets.

the real tungsten content. The non-tungstated catalyst (4Pt) presented a whole acidity similar to the one showed by the γ -alumina support, which indicates that the tungsten had the most remarkable impact on the total acidity of the catalyst.

Slight changes can be observed in the differential heats profiles as it is shown in Fig. 5(b). In all cases, the heats of adsorption showed a decreasing trend upon increasing coverage, as usually observed for heterogeneous surfaces. The heterogeneity of the studied samples is due to the presence of acidic sites of different nature and strengths [43–46]. All the tungstated alumina investigated samples exhibited high initial Q_{init} (>200 kJ mol⁻¹) and V_{irr} , very similar to each other, which are characteristic of the strongest acid sites, whereas lower values were presented by the γ -alumina support and the catalysts without tungsten.

It can also be seen in Fig. 5(b) that the presence of relatively high amounts of platinum (4 wt%) enhanced the content of medium strength acid sites, which seems to be independent of the presence of tungsten.

3.1.9. FTIR of adsorbed pyridine

The effect of the tungsten oxide content (and tungsten surface density) and the effect of the incorporation of platinum on WO_x/Al_2O_3 were studied by FTIR of adsorbed pyridine on the samples after successive heating at 200 and 300 °C (Fig. S2). Brönsted and Lewis acid sites are easily identified and distinguished by examination of the 1700–1400 cm⁻¹ range [47].

The type and strength of acidity on γ -Al₂O₃ has been a matter of controversy for some time. In this work, the pyridine adsorbed on the γ -Al₂O₃ support led to the following main bands at 200 °C in this frequency range: 1614 (ν_{8a}) cm⁻¹, 1578 (ν_{8b}) cm⁻¹, and 1450 (ν_{19b}) cm⁻¹, which can be assigned to coordinately bonded pyridine on Lewis acid sites [47]. Another band at 1493 (ν_{19a}) cm⁻¹ was found, which is common of both vibrations due to pyridinium ion (PyH⁺), produced by the reaction of pyridine with Brönsted sites, and coordinately bonded pyridine on Lewis sites. However, the non-appearance of another PyH⁺ bands seems to indicate the exclusive Lewis character of the γ -Al₂O₃ support acid sites.

The three characteristic bands of Lewis sites present on γ -alumina and the band at about 1490 cm⁻¹ have also been observed for all the samples studied. Tungsten surface density plays a key role in the formation of the Brönsted acid sites on the catalyst

surface. No evidence of Brönsted characteristic bands was found at low densities of 1.0 W at. nm⁻², so the acidity appears to be almost solely due to Lewis acid sites. On γ -Al₂O₃ tungstated samples, common bands related to PyH⁺ began to appear at densities ≥ 2.4 W at. nm⁻². On 9W (2.4 W at. nm⁻²) catalyst at 200 °C, these bands were found at 1540 cm⁻¹ and 1638 cm⁻¹, supporting the presence of Brönsted sites [48]. The isolated tungsten oxide species, observed by Raman spectroscopy at low tungsten surface densities (<2.4 W at. nm⁻²), cannot delocalize the negative charge required for the formation of Brönsted acid sites. However, at higher densities, polytungstates started to be formed resulting in the formation of an extended network of tungsten oxide species, over which an excess negative charge may be delocalized [33,49].

Qualitatively, the intensities of the IR bands of Lewis sites progressively decreased as the desorption temperature increased and shifted toward higher wavenumbers, which confirms the high strength of the Lewis sites. The same trend was observed for Brönsted sites.

In order to make a semi-quantitatively study of the samples acidity, the area of 1450 cm^{-1} peak for Lewis sites and the area of 1540 cm^{-1} peak for Brönsted sites were used. In Table 4, the results of the Brönsted to Lewis ratio (B/L) at the different pyridine desorption temperatures are shown. It can be noticed that WO₃ NPs formed at high tungsten surface densities (>3.9 W at. nm⁻²) had not a contribution to the catalyst acidity, displaying slightly lower B/L ratio than the sample with 2.4 W at. nm⁻².

On the other hand, for 9W and 4Pt8W, samples with a close tungsten surface density (2.4 and 2.2 W at. nm^{-2} , respectively), the decrease of the Lewis acidity was more noticeable than the Brönsted acidity decrease after desorption at 200 °C; therefore,

Table 4	
Brönsted to Lewis acid sites ratio (B/L) obtained from the FTIR of ad	sorbed pyridine.

Catalyst ^a	B/L ratio at 200 °C	B/L ratio at 300 °C
γ -Al ₂ O ₃	0.00	0.00
4W (1.0)	0.00	0.00
9W (2.4)	0.25	0.19
14W (3.9)	0.23	0.15
4Pt8W (2.2)	0.28	b

^a Tungsten surface density in brackets (W at. nm⁻²).

^b The area was too low to be integrated but not equal to zero.

the B/L ratio increased. However, Brönsted sites were hardly observed at 300 °C for the catalyst containing platinum (4Pt8W). This could mean that the presence of platinum reduced the strength of Brönsted acid sites.

It is worth adding that the hydrogen atoms forming by H_2 dissociation, during the catalyst pretreatment and along the reaction, could be involved in the generation and maintenance of Brönsted sites [32].

3.2. Effect of tungsten surface density on glycerol conversion and selectivity to PDOs

The effect of tungsten surface density was investigated in the aqueous phase glycerol hydrogenolysis. It is widely suggested that the production of 1,3-PDO from glycerol requires the presence of Brönsted acid sites [12] but also a hydrogenation metal able to activate the molecular H₂ present in the reactive atmosphere. As we have shown above, an interesting feature of the supported WO_x/Al_2O_3 catalysts is that their B/L acidity can be tuned as a function of the tungsten surface density. The activity test results are presented in Fig. 6(a) and (b) obtained at 24 h reaction time, 220 °C and 45 bar with the catalyst containing 1 wt% of Pt and different tungsten surface density values.

Glycerol conversion diminished with increasing tungsten surface density as it is shown in Fig. 6(a). On the other hand, it can be observed a different trend in the PDO yields. Whereas 1,2-PDO yield decreased as the tungsten density increased, the 1,3-PDO production was increased to a maximum value and then decreased as it can be seen in Fig. 6(b). The progressive coverage of the hydroxyl groups of the γ -alumina by the tungsten oxides, as the tungsten surface density increases [31], may explain the observed decrease in the glycerol conversion. It seems that tungsten oxide sites are less active than those of the γ -alumina support for the hydrogenolysis reaction of glycerol. This feature was not observed when other supports such as silica or zirconia were used [12,50]. The strong interaction between the γ -alumina support and tungsten oxide and therefore the low interaction between platinum and tungsten oxides, at low platinum loadings, could be the reason for this poor glycerol conversion.

The incorporation of the tungsten oxide enhances the total acidity of the catalyst, as observed from the NH₃ adsorption calorimetry results. B/L ratio also increased with increasing the tungsten surface density due to the generation of polytungstate species, as the FTIR of adsorbed pyridine (Table 4) and the Raman spectroscopy (Fig. 2) analysis showed. This fact causes a decrease in the 1,2-PDO yield and an increase in the 1,3-PDO yield until a density of 2.4 W at. nm⁻² was reached. For higher tungsten surface densities, the formation of crystalline WO₃ NPs has a negative effect on the 1,3-PDO yield due to the over-hydrogenolysis reactions obtaining 1-PO as the main by-product. This effect cannot be just related to the catalyst acidity, because small acidity differences were found between WO_x/Al_2O_3 containing WO_3 NPs and the sample with the maximum polytungstate content and without these WO_3 NPs (see Table 4 entries 3 and 4). This aspect is later discussed with the proposed reaction mechanism.

Therefore, it seems that the presence of highly dispersed polytungstate species in the catalyst surface, which provide Brönsted acid sites, is necessary in order to produce 1,3-PDO by hydrogenolysis of glycerol. It was found that the optimum surface density of tungsten that maximizes the production of 1,3-PDO at these conditions is 2.4 W at. nm⁻², obtaining a maximum 1,3-PDO selectivity of 16.4% (2.7% yield).

3.3. Effect of platinum metal content on glycerol conversion and selectivity to PDOs

The effect of platinum content was also studied on the $Pt/WO_x/Al_2O_3$ catalytic systems in the glycerol hydrogenolysis reaction. A series of catalysts with different platinum content and similar tungsten surface density, nearly the optimum value previously obtained (2.2 W at. nm⁻²), were prepared and tested.

The activity results are represented in Fig. 7(a) and (b), and the values are given in Table 1. As expected, when the platinum content increased, the glycerol conversion also increased, from 25.6% for 1 wt% Pt to 60.3% for 9 wt% Pt. The hydrogen molecules present in the reactive atmosphere might be dissociatively adsorbed on platinum metal giving rise to hydrogen atoms that are subsequently involved in the activation of the adsorbed glycerol molecule and in the later transformation to the products. The electronic interactions, observed by TPR and Raman spectroscopy, between platinum and the highly dispersed polytungstates could also contribute to increasing the activation of H₂ molecules on the platinum active sites. These interactions were more pronounced as the platinum content increased. On the other hand, glycerol conversion does not seem to be clearly correlated to the platinum dispersion, because the highest values were obtained at the lowest platinum dispersions.

More interestingly, the platinum content had not only an effect on glycerol conversion but it also affected PDOs selectivity. It must be added that the most remarkable effect of platinum loading was found in the 1,2-PDO selectivity: It decreased from 57.2% for 1 wt% platinum catalyst to 11.0% for 9 wt% platinum content catalyst, as it can be observed in Fig. 7(b). The 1,3-PDO selectivity increased slightly and progressively with the platinum content increase.



Fig. 6. (a) Glycerol conversion values and (b) PDO yields obtained for Pt/WO_x/Al₂O₃ catalysts with 1 wt% Pt as a function of the tungsten surface density, in the hydrogenolysis of glycerol at 220 °C, 45 bar H₂ pressure, and 24 h reaction time.



Fig. 7. (a) Glycerol conversion values and (b) product selectivities obtained for Pt/WO_x/Al₂O₃ catalysts with a constant tungsten surface density as a function of the platinum content, in the hydrogenolysis of glycerol at 220 °C (200 °C for 9Pt8W* catalyst), 45 bar H₂ pressure, and 24 h reaction time.



Fig. 8. Reaction mechanism proposed for glycerol hydrogenolysis to 1,3-PDO.

For the catalyst with 1 wt% of platinum, the 1,3-PDO selectivity was only of 16.4%, whereas the platinum content increases up to 9 wt% enhanced this value until 31.2%.

The amount of platinum does not significantly contribute neither to the total acidity nor to the relative B/L ratio, as it was observed by NH₃ adsorption calorimetry, and FTIR of the absorbed pyridine techniques. Therefore, the effect of the platinum loading on the PDOs relative formation must be related to other factors. The XPS results suggested that for high platinum contents (>5 wt%), it anchors to the tungsten oxides sites (in addition to the Al³⁺ preferential anchoring sites). Although this hypothesis must be confirmed by other techniques, it is clear that the closer proximity between the Pt and WO_x active sites seems to enhance the selectivity toward 1,3-PDO while decreasing the selectivity of 1,2-PDO. The main drawback is that the formation of 1,3-PDO seems to be accompanied by the over-hydrogenolysis to 1-PO. In order to avoid the undesirable reactions, the reaction temperature was decreased to 200 °C for the 9Pt8W catalyst. The results, shown in Table 1, indicate that the over-hydrogenolysis of 1,3-PDO to 1-PO was partially avoided at 200 °C, enhancing the 1,3-PDO selectivity up to 51.9% (27.6% yield).

3.4. Proposed reaction mechanism

The most accepted mechanism for the formation of PDOs from glycerol hydrogenolysis is the dehydration–hydrogenation route. In the first step, glycerol is dehydrated to acetol or 3-hydroxypropanal (3-HPA), while in the second step, these intermediates are hydrogenated to 1,2 and 1,3-PDO, respectively. The formation of acetol is thermodynamically favoured due to its higher stability as compared to 3-HPA, which explains why normally 1,2-PDO is the major product on glycerol hydrogenolysis. Our activity tests and characterization results match with previously reported studies that indicate that Bronsted acidity is required for the production of 1,3-PDO: The maximum selectivity toward 1,3-PDO was obtained at the tungstate surface density showing the highest B/L ratio (at 2.4 W at. nm⁻²). However, there are some important evidences suggesting that the formation of 1,3-PDO cannot be only related to the amount of Bronsted acid sites.

Recently, Tomishige's group [16] studied the influence that adding different concentrations of H_2SO_4 as acid co-catalyst had on the glycerol hydrogenolysis reaction, over another noble metal–oxophilic metal catalytic system (Ir–ReO_x/SiO₂).

Interestingly, the positive effect of H_2SO_4 on the production of 1,3-PDO formation over the Ir-ReO_x/SiO₂ catalyst was saturated at H⁺/ Re = 1. Both activity and selectivity were almost unchanged between H⁺/Ir = 1 and 12.4. Similarly, in our results, the yield of 1,3-PDO was more than two times higher with the 1Pt9W catalyst compared with the 1Pt14W catalyst even though both catalysts presented similar B/L ratios. In addition to this, it was observed that the amount of Pt and the interaction between Pt and WO_x active sites also affect the selectivity toward 1,3-PDO.

For Pt–W–Al catalysts, Kaneda et al. proposed a mechanism [12, 51] which involved an initial glycerol adsorption on Al–OH site forming an alkoxide specie. As it has been mentioned above, the tungsten oxide species anchor to the γ -Al₂O₃ support at its surface hydroxyls [40], and therefore, an increase in tungsten surface density should imply a decrease in Al-OH sites. We suggest that glycerol is adsorbed on tungsten active sites forming an alkoxide (see reaction scheme in Fig. 8). Next, a proton, coming from a Brönsted acid site provided by polytungstate species, protonates the secondary hydroxyl group of the alkoxide. After dehydration, a secondary carbocation is formed. The adsorbed carbocation is attacked by a hydride specie generated on the Pt active sites. Further hydrolysis yields 1,3-PDO. The key step in this reaction seems to be the fast hydrogenation of the secondary carbocation in order to avoid its conversion into acrolein (precursor of 1-PO). The stabilization of the carbocation might be crucial at this point. It was suggested that only the polytungstate species are able to delocalize the negative charge required for the carbocation intermediate stabilization, instead of the monotungstate and WO₃ NPs species [32]. This explains well the reason why the best results (at similar platinum content of 1 wt%) were obtained for the catalyst in which more polytungstate species are generated before the WO₃ NPs formation. These WO₃ NPs are not only inactive for the carbocation stabilization, but they also are tridimensional structures that limit the accessibility of the glycerol to the polytungstate acid sites. Another important factor is the close proximity between the Pt and the WO_x active sites, which might facilitate the attack of the hydride species for the fast hydrogenation of the secondary carbocation. This explains the higher selectivities toward 1,3-PDO that are obtained at higher Pt contents.

4. Conclusions

In this work, it has been demonstrated that the bimetallic Pt/ WO_x/Al_2O_3 catalytic system is effective for the selective hydrogenolysis of glycerol to 1,3-PDO. This study proved that 1,3-PDO selectivity depends on the tungsten surface density that controls the kind of tungsten oxide species deposited on the catalyst surface. The maximum selectivity was achieved when the highest content of polytungstate species are formed but before the appearance of WO₃ NPs, concluding that in order to selectively obtain 1,3-PDO, the presence of highly dispersed polytungstate species is required. These species are able to delocalize the negative charge required for the formation of Brönsted acid sites. However, the results from this work also indicate that not only acidity plays a role in the selective hydrogenolysis of glycerol to 1,3-PDO, but also the platinum and tungsten oxides sites interactions may be involved. The closer proximity between platinum and tungsten oxides at high platinum content and the electronic interactions between acid and metallic sites could be the responsible for the enhancement of the 1,3-PDO yields. Further research should allow improving Pt–WO_x synergies and as a result the yield to 1,3-PDO.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.12.028.

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