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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 $Pt/WO_x/Al_2O_3$ 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.

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 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/SiO_2 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 $Pt/WO_3/ZrO_2$ 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 $Cu–H_4Si_{12}O_{40}SiW/SiO_2$ catalyst at

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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/SiO_2 [14] and Ir/SiO_2 [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 H_2SO_4 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–WO_3 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 $Pt/WO_3/ZrO_2$ 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 $Pt–HSiW/SiO_2$ 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/WO_3/"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-Al_2O_3) 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 N_2 physisorption, H_2 temperature programmed reduction (H_2-TPR), Fourier transform infrared spectroscopy (FTIR) of adsorbed pyridine, Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectronic spectroscopy (XPS), NH_3 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

$Pt/WO_x/Al_2O_3$ catalysts were prepared by sequential wetness impregnation method. The typical procedure followed for the preparation of the catalysts is detailed below. γ-Al_2O_3 (Sigma–Aldrich, ⩾99.9%) was used as support, and it was impregnated using the appropriate amounts of ammonium metatungstate ($(NH_4)_6(H_2W_{12}O_{40})\cdot nH_2O$, 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 ($(Pt(NH_3)_4(NO_3)_2$, Sigma–Aldrich, ⩾99.995%)) as precursor. The resulting catalysts were dried and calcined as above. These $Pt/WO_3/Al_2O_3$ 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-Al_2O_3), 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,

$$\rho_W[\text{W atoms/nm}^2 \text{ of support}] = \frac{\left(\frac{x_W}{M_W}\right)NA}{SA_{Al_2O_3}\left[1-\left(x_{WO_3}+x_{PtO}\right)\right]}$$

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 WO_3 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 HNO_3 heating from room temperature up to 180 °C during 30 min.

2.2.2. N_2 physisorption

Textural properties (surface area, pore volume, and pore size distributions) were obtained by N_2 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 H_2 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