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Hydrogenolysis of glycerol to propanediols over a Pt/ASA catalyst: The role of acid and metal sites on product selectivity and the reaction mechanism

I. Gandarias[a,*], P.L. Arias[a], J. Requies[a], M.B. Güemez[a], J.L.G. Fierro[b]

[a] School of Engineering (UPV/EHU), c/Alameda Urquijo s/n, 48013 Bilbao, Spain
[b] Institute of Catalysis and Petrochemistry, c/Marie Curie s/n, 28049 Madrid, Spain

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ABSTRACT

Pt supported on amorphous silico alumina (Pt/ASA) was studied as a catalyst for glycerol hydrogenolysis (dehydration + hydrogenation) to 1,2-propanediol under mild operation conditions (493 K and 45 bar H_2 pressure). Glycerol hydrogenolysis also took place in experiments performed under N_2 pressure due to hydrogen available from glycerol aqueous phase reforming. As both acid and metallic sites are involved in this process a study including activity tests and different characterization techniques (TPR and FTIR of adsorbed pyridine, NH_3-TPD, XPS and TGA) were applied to this catalytic system (ASA support and Pt/ASA catalyst) in order to get a deeper understanding about their interactions.

1. Introduction

Nowadays large amounts of glycerol are generated as a by-product in biodiesel manufacture by transesterification of seed oils. Therefore, glycerol price experimented constant reduction during the last years, allowing new interesting applications like the production of high added value chemicals [1]. Among the different possible transformations of glycerol, the selective conversion to 1,2 and 1,3-propanediol (PDO), which are usually produced from petroleum derivates, presents a special interest [2]. 1,3-PDO is a starting material in the production of polytrimethylene terephthalate (PTT), which is used for the manufacture of fibers and resins [3], while 1,2-PDO is a commodity chemical widely used in the manufacture of a significant number of industrial and consumer products [4].

Propylene glycols can be produced through a two-step process: glycerol is first dehydrated to 1-hydroxypropan-2-one (acetol) and 3-hydroxypropanal (3-HPA), which are subsequently hydrogenated to 1,2- and 1,3-PDO respectively [5]. Various bi-functional metal-acid catalysts, which combine acid sites for dehydration reactions and metal sites for hydrogenation reactions, have been attempted for the conversion of glycerol to PDOs. Investigations on Pt [6], Ru [7], Ru + Re [8] and Rh [9] on different acid supports have been reported. The role of the acid function of the supports on glycerol hydrogenolysis with Cu catalysts has been also studied [10], even at ambient hydrogen pressure [11]. Miyazawa et al. developed an intense work with the aim to develop a Ru/C catalyst for glycerol hydrogenolysis in combination with an ion-exchange resin [12–14]. Besides dehydration and hydrogenation reactions, other unwanted side reactions such as cracking, addition and coking also occur simultaneously [10]. Scarce information has been reported about the role of acid and metallic sites, the acid–metal interaction, and H_2 availability effects on glycerol hydrogenolysis and side reactions. Accordingly, this work is focused on the hydrogenolysis of glycerol over Pt supported on an amorphous silica–alumina (Pt/ASA), analyzing the effect that the presence of Pt metallic sites and H_2 availability has on the catalyst performance. This will be discussed through the study of glycerol conversion, coke formation and selectivity to PDOs. The information regarding the structure of fresh and used catalysts was assessed using several physico-chemical techniques such as temperature-programmed reduction (TPR), FTIR spectroscopy of adsorbed pyridine, temperature-programmed desorption of ammonia (TPD-NH_3), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). All the data collected from the activity tests and catalysts characterization were utilized to gain a deeper understanding of this catalytic system and to formulate a reaction scheme of glycerol hydrogenolysis and degradation process.

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* Corresponding author at: Escuela Técnica Superior de Ingeniería, Alameda Urquijo s/n, P.C. 48013 Bilbao, Spain. Tel.: +34 946017297; fax: +34 946014179.
E-mail address: inaki_gandarias@ehu.es (I. Gandarias).

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Table 1
Characteristics of the catalysts.

Sample	Pt (wt.%)[a]	Al_2O_3 (wt.%)[a]	Pretreatment	I_{1543}/I_{1452} ratio[d]
ASA	–	15.7	Degassing[b]	0.058
			Reduction[c]	0.060
Pt/ASA	0.7	15.1	Degassing[b]	0.056
			Reduction[c]	0.092

[a] Chemical composition determined by ICP.

[b] Samples were degassed at 723 K for 1 h.

[c] Samples were reduced in a H_2 flow at 673 K during 1 h and then degassed at 723 K for 1 h.

[d] As determined by FTIR of adsorbed pyridine.

2. Experimental

2.1. Catalyst

Amorphous silica–alumina (ASA) (surface area 389 m^2/g, pore volume 0.63 mL/g) and ASA loaded with 1 wt.% of Pt (1% Pt/ASA) were kindly supplied by Shell. Table 1 lists the Pt and Al content of the catalyst. Catalyst samples for activity tests were used in powdered form with granule size between 320 and 500 μm. They were used without further pretreatment.

2.2. Activity test

The reaction of glycerol hydrogenolysis was carried out in a 50 mL stainless steel autoclave with a magnetic stirrer, using 41 mL glycerol aqueous solution. The standard activity test was conducted under the following conditions: 493 K reaction temperature, 45 bar hydrogen or nitrogen pressure, 24 h reaction time, 20 wt.% glycerol aqueous solution, and 166 mg of catalysts/g of reactant (Pt/ASA or ASA). The stirring speed was set constant at 550 rpm. Reaction temperature and reacting atmosphere were changed to investigate the dependence of conversion and selectivities on the operating conditions. In addition, to elucidate the reaction mechanism of glycerol hydrogenolysis and degradation, 1,3-PDO, 1,2-PDO, ethylene glycol (EG), acetol, and 2-propanol were also used as reactants. The concentration of these reactants on the aqueous solution fed is described when the corresponding results are discussed.

In all experiments, 20.5 mL of deionized water and the catalyst powder (inside a basket) were placed in the autoclave; then the reactor was purged with N_2 (99.999% Air Liquide). After purging, the reactor was heated to the required temperature and the N_2 or H_2 (99.999% Air Liquide) pressure was increased up to 45 bar. The temperature was monitored with a thermocouple that was inserted into the autoclave and connected to the thermo-controller. 20.5 mL of the aqueous solution of the reactant, having twice the desired concentration, was placed on a feed cylinder and heated to the reaction temperature. Reaction starting time was established when the line connecting the feed cylinder and the reactor was opened. H_2 or N_2 pressure was kept constant during the reaction, keeping the reactor connected to a H_2 or N_2 flowing line with constant 45 bar pressure. Along the reaction seven liquid samples (1.2–1.7 mL each) were taken in order to obtain the time evolution of reactant and product concentrations. These compounds were analyzed using a gas chromatograph (Agilent Technologies, 7890 A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A Meta-Wax capillary column (diameter 0.53 mm, length 30 m) was used for separation. After the reaction, the gas phase products were collected in a gas bag and analyzed with another GC-TCD-FID (Agilent Technologies, 7890 A) equipped with a molecular sieve column (HP-MOLESIEVE, diameter 0.535 mm, length 30 m) and a capillary column (HP-PLOT/Q, diameter 0.320 mm, length 30 m). Liquid products were identified using GC–MS (Agilent Technologies, 5973). Conversion of the reactants in all reaction tests were calculated based on the following equation:

$$\text{Conversion of react. (\%)} = \frac{\text{sum of C-based mol of all liquid prod. } t = t}{\text{C-based mol of react. } t = 0}$$

The conversions calculated by this method were compared with the conversions defined as (reactant $t = 0$ − reactant $t = t$)/(reactant $t = 0$), in order to determine the error that is made when the gas products formed during the process are not accounted in the conversion calculations. Selectivities were only calculated for liquid products using the following equation:

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

The yield was calculated using the firstly defined conversion:

$$\text{Yield} = \frac{\text{conversion (\%)} \times \text{selectivity (\%)}}{100}$$

2.3. Characterization

Chemical analysis of the catalysts was performed by Inductively Coupled Plasma Atomic Emission (ICP-AES) using a Perkin-Elmer Optima 2000 instrument. The solid samples where treated with a mixture of HF, HCl and HNO_3 at 453 K in a microwave oven. The metal content of the catalysts is summarized in Table 1. Fresh Pt/ASA and ASA catalysts (not used in the activity test) were characterized by temperature-programmed reduction (TPR) and FTIR spectra of adsorbed pyridine.

Temperature-programmed reduction (TPR) experiments were carried out on a Micromeritics 3000 analyzer interfaced to a data station. A 50 mg catalyst sample was reduced in flowing gas containing 10 vol.% H_2 in Ar at a total flow rate of 50 mL min^{-1}, and using a heating rate of 15 K min^{-1} up to a final temperature of 1273 K. The FTIR spectra of adsorbed pyridine were recorded to determine the relative Brønsted and Lewis acidity of the reduced Pt/ASA and ASA catalysts. Self-supporting wafers of the oxide catalysts with a thickness of 10–12 mg cm^{-2} were prepared by pressing the powdered samples at a pressure of 7×10^3 kg cm^{-2} for 10 min. The wafer was introduced into an IR cell fitted with greaseless stopcocks and KBr windows. The samples were first purged in a helium flow at 673 K for 0.5 h. Some samples were reduced in a H_2 flow at 673 K for 1 h, prior to degassing at 723 K for 1 h. Subsequently, samples were contacted with approximately 2 mbar of pyridine and then degassed at 393 K for 1 h to remove the physisorbed pyridine.

The acidity of fresh and spent Pt/ASA and ASA catalysts was determined by ammonia temperature-programmed desorption (TPD) measurements carried out with the same apparatus described for TPR. After loading, a sample of 0.050 g was pretreated in a He (99.996%, Air Liquide) stream at 773 K for 0.5 h. Following this, the sample was cooled to 373 K and ammonia-saturated in a stream of 5% NH_3/He (Air Liquide) flow (50 mL min^{-1}) for 0.5 h. Then, after catalyst equilibration in a helium flow at 373 K for 0.5 h, the ammonia was desorbed using a linear heating rate of 10 K min^{-1} to 1123 K. In order to determine the total acidity of the catalyst from its NH_3 desorption profile, the area under the curve was integrated. A semiquantitative comparison of the strength distribution was achieved by Gaussian deconvolution of the peaks. Weak, medium and strong acidities were defined as the areas under the peaks at the lowest, medium and highest temperatures respectively.

X-ray photoelectron spectra were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Mg Kα ($h\nu = 1253.6$ eV) X-ray source. The energy regions of Al 2p, Si 2p, O 1s, C 1s and Pt $4d_{5/2}$ core levels for ASA and Pt/ASA fresh and spent samples were recorded. Although the most intense photoemission lines of platinum were those arising from the Pt 4f levels, this energy region was overshadowed by the presence of a very strong Al 2p peak, and thus the Pt 4d lines were