



Vapor phase hydrogenolysis of glycerol to 1,2-propanediol at atmospheric pressure over copper catalysts supported on mesoporous alumina

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ABSTRACT

The present work explores the hydrogenolysis of glycerol to produce 1,2-propanediol in vapor phase at atmospheric pressure over copper catalysts supported on mesoporous alumina. Catalysts were prepared by alumina impregnation varying CuO loading between 3 wt% and 30 wt%. The textural and structural characteristics of the catalysts were determined by N₂ sorptometry (BET), powder X-ray diffraction (PXRD), temperature programmed reduction (TPR) and N₂O chemisorption (copper metallic area). The characterization showed that all catalysts present textural properties characteristic of mesoporous solids, such as the adsorption isotherms which are type IV. Based both on characterization and activity results, it was possible to conclude that the yield to 1,2-propanediol presented a non-monotonic dependence on total copper metallic area. In addition, it was proved that 1,2-propanediol production is associated with the presence of highly dispersed CuO phase in the solids. Promising results were obtained with CuO(15)Al catalysts, taking into account that the performance can be improved by increasing residence time.

1. Introduction

During the last decade biodiesel has gained attention as a biofuel, in particular because it can replace significant fractions of petroleum-derived fuels, both for stationary and mobile applications. Its production has markedly increased worldwide in the last decade with a forecast production for 2020 of 36.9 million metric tons [1]; in Argentina, one of the world major biodiesel producers, biodiesel production in 2014 reached 2.50 million tons [2].

Biodiesel is mainly produced by transesterification of oils and fats, being glycerol the main by-product (10 wt% of production). Consequently, glycerol has become a low cost building block, with high potential to be transformed into chemicals of high added value [2,3]. Among them, the production of 1,2-propanediol (1,2-PDO) by glycerol hydrogenolysis is of great interest due to the renewable character of this route. Traditionally, 1,2-PDO is produced by hydration of propylene oxide or ethylene oxide derived from propylene or ethylene, respectively [4].

Some applications for 1,2-PDO are in unsaturated polyester resins, as functional fluids such as anti-freezing and de-icing, in pharmaceutical products, food, cosmetics, liquid detergents, humectants for tobacco, flavorings and scents, personal hygienic products and paints [4].

In particular, the market of anti-freezing and de-icing products derived from 1,2-PDO is growing, as a consequence of the concern over the toxicity of ethylene glycol [5].

In the presence of a metallic catalyst and hydrogen, depending mainly on the reaction conditions and on the characteristics of the catalysts, glycerol can be converted into 1,2-PDO, 1,3-propanediol and ethylene glycol [6,7].

It is widely accepted that when the hydrogenolysis of glycerol is performed in vapor phase the reaction pathway is the dehydration – hydrogenation through an intermediate reactive which is acetol. In the first stage glycerol is dehydrated to form the intermediate, acetol. The second stage, reversible and exothermic, involves the hydrogenation of the intermediate to form finally 1,2-PDO [8–10].

The production of 1,2-PDO by glycerol hydrogenolysis employs catalysts mainly based on noble metals such as Pt, Ru, Pd, and Rh, or based on transition metals like Cu, Ni, or Co [4–6,8,11–17], regardless if the reaction is performed in liquid or vapor phase. In contrast to catalysts based on novel metals, that present lower selectivity to 1,2-PDO as consequence of the cleavage of the bond C–C [4,17–20]; catalysts based on copper offer both high conversions of glycerol and high selectivity to 1,2-PDO [4,15,21].

Different catalyst supports have been proposed for the

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hydrogenolysis of glycerol, some of them are Al_2O_3 [8,14,15,18,22–25]; SiO_2 [9,10,13,26,27]; $\text{ZnO}/\text{Al}_2\text{O}_3$, ZnO/TiO_2 , ZnO/ZrO_2 [13,28], ZnO [29] and MgO [16]. The role of the support on the hydrogenolysis of glycerol to 1,2-PDO has been extensively discussed. Some authors have proposed that the acid or basic character of the support determine the reaction mechanism, when the reaction is carried out in liquid phase, and affects 1,2-PDO selectivity [4,6,17]. On the other hand, it has been proposed that, when the reaction is performed in vapor phase, metal-support interactions must be considered and the support has an important role in promoting the dispersion of the metallic phase [4]. In fact, in a previous study of our group it was proved that Al_2O_3 has no activity in vapor phase hydrogenolysis of glycerol [25].

Considering, as mentioned before, that the catalyst support has a great influence on the metal-support interaction as well as on metal dispersion [4], we have considered employing mesoporous alumina as support for copper based catalysts. Yuan et al. [30] proposed a facile synthesis of highly ordered mesoporous alumina with high thermal stability and tunable pore size by self-assembly of Pluronic 123, $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$, triblock copolymer and alumina precursors in ethanolic solutions in the presence of additives such as nitric acid. This synthesis was then extended to obtain mesoporous alumina-supported noble metals or metal oxides [31–34]. Nevertheless there are few studies considering the impregnation of CuO over mesoporous alumina [35,36], these studies concluded that the textural and structural characteristic of mesoporous alumina have great influence both on copper metallic dispersion and on copper-support interactions.

Therefore, the aim of the present work is to analyse the effect of copper loading on catalytic activity in the hydrogenolysis of glycerol in vapor phase at atmospheric pressure, and its correlation with metallic copper dispersion.

2. Experimental

2.1. Catalyst preparation

Mesoporous alumina was prepared following a similar procedure to that reported by Yuan et al. [30] and Morris et al. [31]. For this synthesis, 25 g of $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ (Pluronic 123 of Sigma Aldrich) triblock copolymer were dissolved in 100 mL of anhydrous ethanol (99.5% Cicarelli). Then, 50 g of aluminum isopropoxide (98% Sigma Aldrich) were dissolved in 40 mL of nitric acid (65 v/v% Cicarelli) and 460 mL of ethanol. Once both solutions were dissolved they were combined, employing additionally 20 mL of ethanol, in order to transfer the solution of aluminum isopropoxide. The combined solution was kept under stirring for 24 h. Solvent evaporation was done at 60 °C for 48 h under air without stirring. Finally mesoporous alumina was obtained after calcining the precursor at 600 °C for 5 h.

Copper impregnation was performed by incipient wetness impregnation method with aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5% Merck), with concentrations ranging between 0.06 M and 6.3 M. Previously to impregnation, mesoporous alumina was ground and sieved, in order to obtain particles with diameters between $44 \mu\text{m} < dp < 88 \mu\text{m}$. After impregnation with copper solutions, samples were dried at 120 °C for 6 h and then calcined at 400 °C for another 6 h. Both drying and calcination of impregnated samples were carried on in a stove under air atmosphere, with a temperature ramp of 10 °C/min. Fresh alumina is denoted as m- Al_2O_3 and the catalysts were denoted as: $\text{CuO}(x)\text{Al}$, being x the nominal CuO (wt%) loading, between 3 wt% and 30 wt%.

2.2. Catalyst characterization

Catalysts were characterized by several techniques.

Textural characterization was performed by N_2 sorptometry in a Micromeritics equipment ASAP 2020, employing 20 mg of sample.

Characterization by powder X-ray diffraction (PXRD) was

performed with Siemens D5000 equipment, employing $\text{Cu K}\alpha$ radiation.

Temperature programmed reduction (TPR) of fresh samples (after calcination) were performed in a Micromeritics Autochem II 2920, with a thermic conductivity detector (TCD). The samples (100 mg) were placed in a quartz U-shaped reactor. Previously to temperature programmed reduction, samples were pre-treated under a flow of Ar (50 mL/min) at 200 °C for 1 h. TPR was performed from 50 °C to 800 °C at a heating rate of 10 °C/min, under a flow of 100 mL/min of a mixture 2% H_2/Ar . Hydrogen consumption was determined by a TCD detector.

The dissociative N_2O adsorption method was performed in a Micromeritics Autochem II 2920 in order to determine copper metallic area and dispersion. The catalysts sample (100 mg) was placed in a U-shaped quartz reactor and was pre-treated in flowing Ar (50 mL/min) at 100 °C for 30 min, followed by cooling at room temperature. The catalyst pre-reduction, was performed increasing the temperature to 500 °C with a ramp of 10 °C/min under a 2% H_2/Ar (100 mL/min) flow for 30 min. Then the sample was cooled to 50 ± 5 °C in Ar flow (50 mL/min) and sequentially was exposed to a 50% $\text{N}_2\text{O}/\text{Ar}$ flow (100 mL/min) for 1 h, in order to oxidize the Cu^0 to Cu_2O by dissociative adsorption of N_2O . Finally, after the purge of the sample under Ar flow (50 mL/min) at 50 °C for 15 min, the TPR was carried out, in order to reduce the Cu_2O species to metallic copper. This stage was performed in a 2% H_2/Ar flow (100 mL/min) and temperature was increased to 500 °C with a 10 °C/min ramp. The copper metallic area and dispersion, were calculated based on bibliography [37,38], considering that the number of superficial copper atoms per unit surface area is 1.47×10^{19} atoms/ m^2 and the density of copper is 8.92 g/ cm^3 .

2.3. Catalytic activity

The hydrogenolysis of glycerol was carried out at atmospheric pressure in a stainless-steel continuous flow fixed bed reactor ($\varnothing = 12$ mm) placed in an electric furnace equipped with temperature controllers. Reaction temperature was measured with a k-type thermocouple, placed in the middle of the catalytic bed. For all catalytic tests, the liquid stream was fed with an HPLC bomb (Eldex 1HM) and vaporized in the initial third of the reactor. The liquid stream consisted of a water glycerol solution with a molar ratio ($R = n_{\text{H}_2\text{O}}/n_{\text{C}_3\text{H}_8\text{O}_3}$) $R = 9:1$ (35 wt% glycerol); with a liquid feed rate of 2.4 mL/h. The catalytic runs were performed isothermally at 240 °C, 0.5 g of catalyst were employed. Catalyst was diluted within an inert material in a ratio 1:5, in order to avoid temperature gradients. The hydrogen-glycerol molar ratio was 65:1. The feed stream was completed with Ar, as carrier. Both hydrogen and argon were fed to the reaction system by mass flow controllers (Brooks 0254), being the gaseous feed rate 360 mL/min.

The total flow rate and particle diameter were chosen in order to guarantee the absence of diffusional resistance during reaction tests.

Catalysts are reduced in situ at 500 °C (heating ramp of 10 °C/min) under a flow of 50% H_2/Ar (100 mL) during 30 min and under a flow of pure hydrogen (100 mL) for another 30 min. Then the catalytic bed temperature was set at reaction temperature (240 °C) under an Ar flow.

Both liquid feed samples and condensed samples were analysed by a GC (Agilent Technologies 7890A, DB-5, 30 m \times 0.320 mm \times 0.5 μm). Liquid samples were collected every hour during reaction. The internal standard method was used for the quantification of the results, being *n*-butanol the standard. The liquid products analysed were: 1,2-propanediol (propylene glycol), 1,3-propanediol, ethylene glycol and hydroxyacetone (acetol); no propanol was detected in the condensed stream. Gas stream was analysed by a GC (Agilent Technologies 6890N, Carboxen™ 1010 Plot, 30 m \times 0.53 mm), however no gaseous products were detected except for non-reacted hydrogen. Since hydrogen is in excess respect to glycerol, it was not possible to estimate its consumption by chromatography.

In order to analyse the catalytic results, the following parameters were considered:

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