



Hydrogenolysis of glycerol to propylene glycol in continuous system without hydrogen addition over Cu-Ni catalysts



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ABSTRACT

A series of Cu, Ni and Cu-Ni catalysts with 20 wt% of each metal, supported on Al_2O_3 and ZSM-5, was prepared by wet impregnation method and tested in glycerol hydrogenolysis to 1,2-propanediol (propylene glycol) using a WHSV of 2 h^{-1} at 250°C , and pressure of 40 bar for 6 h. Without external hydrogen, the reaction pathway involves glycerol dehydration to acetol, with simultaneous reforming to H_2 and CO_2 ; this hydrogen generated *in situ* is used for the hydrogenation of acetol to propylene glycol. Under these conditions, the CuNi/ Al_2O_3 and CuNi/ZSM-5 catalysts exhibited the highest glycerol conversion, 80% and 85%, respectively, with propylene glycol yield around 25%. With external hydrogen, all catalysts showed higher glycerol conversion (>90%) and the monometallic Cu catalysts presented higher conversion to liquid and propylene glycol yield than the bimetallic ones; the Cu/ Al_2O_3 showed the highest yield to propylene glycol (70%). The activity of the catalysts was correlated with their metallic dispersion and also the support acidity.

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1. Introduction

Fossil fuels are currently the largest source of energy in the world; however, their extensive use leads to the increase of carbon dioxide concentration in the atmosphere. Due to this fact, concern about the environment has been growing and the environmental laws are becoming more stringent. Besides the environmental issue, another serious problem is the reduction of oil reserves. Despite the discovery of new oil fields, this is a source of finite energy. For these reasons, researchers are looking for alternative energy sources. One of the alternatives to fossil fuels is biomass that could eventually replace oil.

Several high value-added products and fuels can be obtained from biomass: biogas that is obtained from the waste, bio-oil obtained from the pyrolysis reaction, bioethanol from lignocellulosic material, as well as biodiesel, the most popular among others, which is obtained by transesterification reaction of vegetal oils or animal fats. In the production of biodiesel, glycerol is obtained as a byproduct of the transesterification reaction: one ton of biodiesel results in around 110 kg of crude glycerol, or 100 kg of pure glycerol [1].

The use of glycerol as a feedstock for the production of high value-added products is very interesting due to its high availability and low price in the market. Several products can be obtained from glycerol, such as 1,3-propanediol, 1,2-propanediol, β -carotene, propionic acid, epichlorohydrin, ethanol, syngas, and hydrogen [2]. 1,2-propanediol or propylene glycol has an average value in the market of 1.0–2.2 \$/kg and has an annual growth of 4% [3,4]. Propylene glycol is used as feedstock to produce polyester resin, liquid detergent, pharmaceuticals, cosmetics, and paints [4]. Traditionally it is obtained by hydration of propylene oxide [3].

Propylene glycol is obtained from glycerol by hydrogenolysis reaction that involves breaking of C=O chemical bond and the simultaneous addition of hydrogen [3]. The most commonly used heterogeneous catalysts for the hydrogenolysis reaction are the noble metals, such as Pt, Rh, Ru, Pd, Ir, and Re, because they exhibit high selectivity to propylene glycol and a high conversion of glycerol [3–6]. However, non-noble metals, such as Cu, Co, and Ni, can present catalytic activity as high as noble metal catalysts, besides having lower cost [1,7–10].

Nickel-based catalysts have high activity for producing hydrogen since they are typical catalysts for glycerol reforming, which is an advantage for the hydrogenolysis reaction, because there is no need for external addition of hydrogen to the system [1,4]. As hydrogen is usually derived from fossil fuels, the use of hydrogen generated *in situ* from glycerol reforming turns hydrogenolysis into a more “green” process.

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In the literature there are few studies on the glycerol hydrogenolysis without using external hydrogen; most of them with batch reactors. D'Hondt [11] reported that Pt/Al₂O₃ catalyst exhibited 99.9% of glycerol conversion and 19.1% of propylene glycol selectivity at 230 °C, in a batch reactor, under inert atmosphere. Roy et al. [12] tested a mixture of Ru and Pt catalyst supported on alumina, also using a batch reactor, and obtained 50% of glycerol conversion and 47% of propylene glycol selectivity, at 220 °C, under 14 bar of N₂ pressure. Yun et al. [13] studied bimetallic Cu-Ni catalysts supported on mesoporous alumina for glycerol hydrogenolysis in a batch reactor, obtaining 60% of glycerol conversion and 20% of propylene glycol yield at 220 °C, under atmospheric pressure. More recently, Seretis and Tsiakaras [14] studied aqueous phase reforming and hydrogenolysis of glycerol in a batch reactor, using 65%Ni catalyst supported on SiO₂/Al₂O₃; the maximum propylene glycol yield was 22% after 4 h of reaction at 240 °C, under autogenous pressure. The only report of continuous operation, without H₂ addition, was that of Mane and Rode [15], using Cu-Al catalyst prepared by co-precipitation, obtaining 90% of glycerol conversion, 25% of propylene glycol and 55% of acetol selectivities, at 220 °C under 20 bar of N₂ pressure. Rajkhowa et al. [16] studied glycerol hydrogenolysis with Cu/Al₂O₃ catalyst in an isothermal trickle-bed reactor at 230 °C, with very high selectivity to propylene glycol (94.7%), but using high hydrogen pressures (80 bar).

In this work, Cu, Ni and Cu-Ni catalysts supported on Al₂O₃ and ZSM-5 were employed for glycerol hydrogenolysis in continuous reactor, using hydrogen generated *in situ* and also with the addition of external hydrogen. The continuous operation of hydrogenolysis reactor is not common in the literature, and most of the works only use external hydrogen. Therefore, our goal here is to investigate the influence of the metal, the support nature and the effect of hydrogen in the catalytic performance for glycerol hydrogenolysis to propylene glycol.

2. Experimental

2.1. Catalyst preparation

Cu, Ni and Cu-Ni catalysts supported on HZSM-5 (FCC) and Al₂O₃ (BASF) were prepared using the wet impregnation method, with CuO and NiO loading of 20 wt%. In a typical preparation, Cu(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O (Sigma-Aldrich) were dissolved in deionized water, and a known amount of powdered support was added afterward. After 2 h of rotation for homogenization, the water was removed by evaporation at 80 °C under vacuum. Finally, the obtained material was dried at 110 °C for 12 h, and calcined at 500 °C for 3 h under air flow (60 mL min⁻¹). The prepared catalysts will be referred to as Cu/Al₂O₃, Ni/Al₂O₃, CuNi/Al₂O₃, Cu/ZSM-5, Ni/ZSM-5 and CuNi/ZSM-5.

2.2. Catalyst characterization

The chemical composition of the catalysts after calcination was determined by X-ray fluorescence (XRF) using a Rigaku Primus spectrometer, with X-ray generator tube of palladium.

X-ray diffraction (XRD) was carried out on a Rigaku Miniflex II diffractometer with CuKα radiation (30 kV and 15 mA). The measurements were performed with steps of 0.05° using a counting time of 1 s per step and over the 2θ range of 5°–90°. Reduced catalysts were analyzed after *ex situ* reduction under the same conditions used before the catalytic tests and spent catalysts were analyzed without any other treatment after reaction. The average diameter of the Cu, Ni and Cu-Ni crystals was calculated by the

Scherrer equation (Eq. (1)), using the diffraction peak correspondent to (111) plane:

$$d = \frac{k\lambda}{\beta \cdot \cos\theta} \quad (1)$$

where *d* is the average diameter of the crystals (Å), *k* is a constant that depends on the particle shape (for sphere, *k* = 0.94), *λ* is the wavelength of the X-ray source (for CuKα, *λ* = 1.5488 Å), *β* is the full width at half maximum (FWHM) in radians and *θ* is the diffraction angle. The corresponding metallic dispersion (*D*) was estimated according to Anderson [17] (Eq. (2)):

$$D = \frac{6V_m}{d \cdot A_m} \quad (2)$$

where *V_m* is the atomic volume (0.0118 nm³ for Cu and 0.0109 nm³ for Ni), *d* is the crystallite size (in nm) and *A_m* is the surface area of a single atom (0.068 nm² for Cu and 0.0649 nm² for Ni).

X-ray photoelectron spectra (XPS) were recorded using a hemispherical spectrometer (PHOIBOS 150 – SPECS) equipped with an X-ray Gun (XR-50) and an Al Kα source (soft X-ray source at 1486.6 eV, which is non-monochromatic). The binding energy shifts due to surface charging were corrected using the C 1s level at 284.6 eV, as an internal standard. The spectra were fitted using CasaXPS Version 2.3.16. The base pressure in the analysis chamber was maintained at 5 × 10⁻¹⁰–1 × 10⁻⁹ mbar. Reduced catalysts were analyzed after *ex situ* reduction under the same conditions used before the catalytic tests.

Absorption spectra were obtained by Fourier transform infrared spectroscopy (FTIR) in order to verify the changes in the structure of HZSM-5. A Shimadzu spectrometer, PRESTIGE-21 model, was used to obtain infrared spectra in the region 4000–400 cm⁻¹. The samples were prepared by diluting 3 wt% of the zeolite in KBr (dispersing agent).

N₂ adsorption-desorption experiment was carried out at –196 °C using a Micromeritics TriStar 3000 equipment. The samples were outgassed for 24 h at 300 °C. The specific surface area was obtained using the BET method and pore volume by the BJH method.

The reduction profiles of the catalysts were obtained by temperature-programmed reduction (TPR). The analysis was performed in a conventional apparatus equipped with a thermal conductivity detector (TCD). All samples were pre-treated for 30 min at 150 °C under Argon flow (30 mL min⁻¹). After cooling, they were heated from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹ and a flow rate of 30 mL min⁻¹ of 1.8% H₂/Ar.

The catalyst acidity was investigated by temperature-programmed desorption of ammonia (NH₃-TPD), which was performed using a mass spectrometer QMG-200 Prisma Plus (Pfeiffer). The samples were firstly reduced *in situ* using a mixture of 1.8% H₂/Ar (30 mL min⁻¹) and heating up to 1000 °C (10 °C min⁻¹) for 30 min. Then, the samples were cooled down to room temperature using He. The ammonia adsorption was carried out at 70 °C using a mixture of 4% NH₃/He with a flow rate of 30 mL min⁻¹ for 30 min. After the adsorption, the sample was purged with flowing He at 70 °C for 1 h. The desorption of the chemisorbed ammonia was carried out by heating the samples up to 800 °C at a rate of 20 °C min⁻¹. The ratio *m/z* = 15 was used for quantification of ammonia.

2.3. Hydrogenolysis of glycerol

The glycerol hydrogenolysis was carried out in a fixed bed reactor of Inconel 625, with internal diameter of 0.5 cm. The catalysts in the form of pellets were reduced *in situ* at temperature determined by TPR analysis (550 °C, for Cu-containing catalysts, or 850 °C), for 1 h. The aqueous solution of glycerol (10 vol%) was injected to

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