Applied Catalysis B: Environmental 220 (2018) 31–41

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

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

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ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form 2 August 2017
Accepted 8 August 2017
Available online 12 August 2017

Keywords:
Glycerol
Hydrogenolysis
Propylene glycol
Nickel
Copper

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.

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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http://dx.doi.org/10.1016/j.apcatb.2017.08.030
0926-3373/