Production of Renewable Hydrogen by Glycerol Steam Reforming Using Ni–Cu–Mg–Al Mixed Oxides Obtained from Hydrotalcite-like Compounds

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Abstract Ni-Cu catalysts derived from hydrotalcite-like compounds were prepared with 20 wt% of NiO and 0, 5, and 10 wt% of CuO, and evaluated in the steam reforming of glycerol. The reaction was performed in a continuous flow reactor with a solution of 10 and 20 vol.% glycerol, at 500 °C and atmospheric pressure. The highest conversion of glycerol (around 100 %) was obtained with Ni catalyst in both solutions. In the gas phase, the higher H₂ selectivities were obtained with Cu-containing catalysts: 71 % (Ni5Cu/10 vol.%) and 68 % (Ni10Cu/20 vol.%). The main products formed in the liquid phase were lactic acid, acetol, acetaldehyde and acrolein and a small quantity of acetic acid. Characterization of the spent catalysts revealed that Cu-containing catalysts have greater resistance to carbon formation and the sintering process is not significant, showing that the catalysts prepared exhibit good catalytic stability.

Keywords Steam reforming · Glycerol · Hydrogen · Nickel · Copper

1 Introduction

After the energy crisis in the 1970s, significant attention was given on the development of alternate energy resources. Currently, biomass has received much interest as an alternate energy source because it is renewable and, theoretically, does not increase the levels of carbon in

Escola de Química, Universidade Federal do Rio de Janeiro - UFRJ, Centro de Tecnologia, Bloco E, sala 206, Rio de Janeiro/RJ CEP 21941-909, Brazil e-mail: mmattos@eq.ufrj.br atmosphere. Although the use of liquid fuels produced from biomass is very small in the total energy supply, their production and demand is increasing worldwide. Biodiesel production, for example, has increased from 700 m³ in 2005 to 2.7 million m³ in 2012 in Brazil, according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP). In converting vegetable oils into biodiesel, approximately 10 % (w/w) of glycerol is produced as a byproduct [1]. With the increase in production of biodiesel, a glut of glycerol is expected in the world market. It is beneficial to find alternative uses for this excess glycerol.

Glycerol is a commodity chemical widely used by the pharmaceutical, personal care, food and cleaning industries. Currently, glycerol is used to produce a variety of products chemical, such as 1,3 propanediol, 1,2 propanediol, succinic acid, polyesters, lactic acid, and polyglycerols [2]. A detailed review on glycerol utilization can be found elsewhere [3, 4]. With the fast increase of glycerol supply in the world market the price of glycerol dropped from \$0.43 per kg in 2003 to \$0.18 per kg in 2010 for pure glycerol, and to only \$0.02 per kg for crude glycerol [5].

One possible option for using of glycerol is in hydrogen production. Demand for hydrogen, the simplest and most abundant element, is growing due to the technical advancements in fuel cell industry [6]. Hydrogen is an attractive alternative fuel because it can be produced from a variety of feedstocks and utilized in different applications; furthermore, the use of hydrogen as fuel could help reduce carbon emissions. In order to produce a clean source of energy, such as hydrogen, it is necessary to promote their production from renewable sources, such as glycerol, for example. However, almost 95 % of the hydrogen is being produced from fossil fuel-based feedstocks [7], which are non-renewable.

Dumesic et al. [8, 9] were the first to produce hydrogen from biomass-derived oxygenated hydrocarbons, including

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