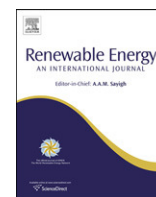


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Production of renewable hydrogen by aqueous-phase reforming of glycerol over Ni–Cu catalysts derived from hydrotalcite precursors

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ABSTRACT

Ni–Cu catalysts derived from hydrotalcite-like compounds were prepared and evaluated in aqueous-phase reforming of glycerol. The catalysts were characterized by chemical composition, textural analysis, crystalline structure and reducibility. The reaction was carried out in a batch reactor with solution of 10 wt.% glycerol, at 250 and 270 °C. A maximum glycerol conversion of 60% was achieved at 270 °C. In the gas phase, the H₂ selectivity was always higher than 80% and formation of CO was very low (<3%) at 250 °C. The addition of Cu decreased the formation of methane. H₂ is consumed during the reaction at 270 °C, mainly for Cu-containing catalysts, with simultaneous formation of propylene glycol in the liquid phase. Acetol, lactic acid and acetaldehyde were also formed in the liquid phase, at both temperatures.

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1. Introduction

Renewable energy sources are becoming increasingly important because of depleting of petroleum reserves and mounting environmental concerns associated with fossil fuel utilization. In this sense, the use of hydrogen as an alternative energy carrier has been largely encouraged over the last years. Nowadays nearly 95% of the world hydrogen is produced from fossil fuels [1], thus, it is necessary to find renewable sources to produce hydrogen. Biomass is a promising source for hydrogen production due to the carbon neutral nature with environmental benefits.

Gasification and steam reforming have been widely investigated for conversion of biomass to hydrogen, but these processes involve high temperatures and many side reactions, which decrease the hydrogen selectivity [2,3]. Aqueous-phase reforming (APR) for production of hydrogen, first developed by the Dumesic group [4], is an advantageous technology for feedstocks such as sugars, alcohols and polyols, because it is carried out at low temperatures, reducing the cost of the process and minimizing undesirable decomposition reactions. Moreover, it produces H₂ and CO₂ in a single reactor with low levels of CO, which is important for fuel cell applications [5].

Several biomass-derived oxygenated compounds have been used in APR process, such as methanol, sorbitol, glycerol, ethylene glycol, and ethanol [4–9]. Glycerol is of particular interest because

it is obtained as a by-product of biodiesel production by transesterification of vegetable oils or animal fats. The transesterification reaction produces approximately 110 kg of glycerol per ton of biodiesel [10]. With increase in production of biodiesel, an excess of glycerol is expected in the world market and therefore, it is essential to find useful applications for glycerol. One of the promising ways to utilize this diluted glycerol from biodiesel plants is to produce hydrogen. The hydrogen generation by APR of glycerol takes place according to the Eq. (1):



Noble metal catalysts are commonly used to carry out the APR at small scales because they are more active and less susceptible to carbon deposition than non noble metal catalysts [6–8]. However, large scale reforming processes use Ni-based catalysts that are far cheaper and more available than noble metals. A good catalyst for APR process has to be active in the cleavage of C–C bonds and water-gas shift reaction, but has to inhibit the cleavage of C–O bond and methanation reactions [4–6,11].

Ni shows a good activity for C–C scission, but it also exhibits high rates of methanation [5]. Cu, on the other hand, is inactive for C–C bond cleavage but has high activity for water-gas shift reaction, thus favoring the selectivity to hydrogen. In the present work Ni and Cu were selected to be included in catalyst formulations applied to glycerol reforming in order to obtain high activity and selectivity to hydrogen.

Hydrotalcite-like compounds (HTLCs) or layered double hydroxides, also known as anionic clays, have a lamellar structure

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