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Aqueous-phase reforming of glycerol using Ni–Cu catalysts prepared from hydrotalcite-like precursors

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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 aqueous-phase reforming of glycerol. The catalysts were characterized by chemical composition, textural analysis, crystalline structure, reducibility and acidity. The reaction was performed in a continuous flow reactor with a solution of 10 vol% glycerol, at 250 °C/35 atm and 270 °C/50 atm. The maximum glycerol conversion at 250 °C/35 atm was 70% and total conversion of glycerol was achieved at 270 °C/50 atm with Cu-containing catalysts. In the gas phase, the H_2 selectivity was around 40% and CO selectivity was very low at 250 °C/35 atm. The addition of Cu decreased the CH_4 formation. The main products formed in the liquid phase were acetol and lactic acid and a small quantity of propanoic acid. The Cu-containing catalysts showed higher formation of acetol, which was correlated with their higher acidity. Characterization of the spent catalysts revealed a sintering of the metal particles, although no deactivation was observed during 6 h of reaction.

1. Introduction

The search for alternative energy sources is increasing in the world motivated by predictions that point to a progressive decrease in the production of fossil fuels. Besides the shortage, another problem associated with the use of fossil fuels is the continuing increase in emissions of pollutants, especially those related to global warming. These greenhouse gases affect human health and also cause imbalance in fauna and flora. Therefore, there is a great necessity for alternative fuels that do not affect the environment. Nowadays several alternative fuels, such as hydrogen, ethanol and biodiesel, are being explored with the intention of developing a sustainable energy scenario.

Hydrogen is an attractive alternative fuel because it can be produced from a variety of feedstocks and utilized in different applications. The use of hydrogen as fuel could help reduce carbon emissions, if produced from renewable energy sources. Currently, the global production of hydrogen is divided as: 48% produced from natural gas, 30% from heavy oils and naphtha, 18% from coal, and 4% from the electrolysis of water.[1,2]

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Glycerol is a commodity chemical widely used by the pharmaceutical, food and cleaning industries. However, it is being overproduced as a result of biodiesel fuel production, as 1 L of glycerol is made for every 10 L of biodiesel.[3] In Brazil, according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP), the production of biodiesel (B100) in 2011 was approximately 2.6 million m^3, generating 260 000 m^3 of glycerin, creating a surplus of glycerin in the Brazilian market. Biodiesel production is largely increasing in Brazil because of the compulsory addition of biodiesel to diesel: the addition of 2% biodiesel (B2) in diesel has become mandatory since 2008, and this amount increased to 5% (B5) in 2010. 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.[4]

One alternative use of glycerol is hydrogen production by aqueous-phase reforming (APR). The APR process using glycerol for hydrogen production has been studied by various researchers.[5–9] This process operates at relatively higher pressures (∼40 atm) and lower temperatures (∼250 °C) in comparison to steam reforming, which is normally carried out at atmospheric pressure and temperatures higher than 500 °C. APR has several advantages as it can be carried out at low temperatures, reducing the cost of the process because it is not necessary to vaporize water, and minimizing undesirable

