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Production of hydrogen from steam reforming of glycerol using nickel catalysts supported on Al_2O_3, CeO_2 and ZrO_2

Abstract

Nickel catalysts supported on Al_2O_3, CeO_2 and ZrO_2 were prepared by wet impregnation method and evaluated in steam reforming of glycerol. The catalysts were characterized by chemical composition, textural analysis, crystalline structure and reducibility. The structural characterization of the catalysts revealed a good dispersion of Ni particles using the Al_2O_3 support, needing higher reduction temperature. The reactions were performed at 500°C with 10 vol.% glycerol solution in a continuous flow reactor. All catalysts showed conversions close to 100%. The selectivity to gas products and formation of liquid by-products were found to be dependent on the type of support. The H_2 selectivity showed the following trend: $ZrO_2 > Al_2O_3 \approx CeO_2$. The catalyst supported on CeO_2 showed low activity for water-gas shift reaction, with the highest CO selectivity. All catalysts presented a low formation of CH_4. In the liquid phase some by-products were identified (hydroxyacetone, acetic acid, lactic acid, acetaldehyde, acrolein and ethanol) and secondary reaction routes were proposed. Coke formation was higher on Ni/Al_2O_3 catalyst, but no deactivation was observed during 8 h of reaction.

Keywords

Hydrogen • Glycerol • Steam reforming • Nickel • Catalysts

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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 imbalances in fauna and flora, such as acid rain. Therefore, there is a great necessity for alternative fuels that do not affect the environment [1].

Motivated by concerns about air pollution, energy security and climate change, the notion of "hydrogen economy" is moved beyond the area of the scientists and engineers, it is a matter of policy issues and treated by business leaders. The interest in hydrogen, the simplest element and most abundant in the universe, is increasing due to technological advances in fuel cells, a potential successor to batteries in portable electronics, power stations and the internal combustion engine [2]. For hydrogen to become a truly sustainable energy source, it should be promoted its production from renewable resources; more than 95 % of hydrogen produced today comes from nonrenewable resources, based on fossil fuels [3,4].

Glycerol is a chemical used for more than two centuries in a variety of applications, such as production of nitroglycerin and esters. Glycerol is also widely used in food, pharmaceutical, cosmetics, toiletries and cleaning industries. The demand and supply of glycerol in the world market was in equilibrium by the end of the 1990s. With the production of biofuels, especially biodiesel, this equilibrium has been completely changed. Biodiesel is produced by the transesterification of vegetable oils and animal fats, and glycerol is a byproduct of this reaction. One ton of biodiesel yields about 110 kg of crude glycerol (glycerin) or 100 kg of pure glycerol [3]. In Brazil, according to National Agency of Petroleum, Natural Gas and Biofuels (ANP), the production of biodiesel (B100) in 2010 was approximately 2.4 million m^3, generating 240,000 m^3 of glycerin, creating a surplus of glycerin in the Brazilian market. Thus, glycerol is a product that has a large potential market, however, with increasing biodiesel production, their supply has risen substantially and the price of glycerin has fallen to about U$ 0.11 kg^{-1} [5].

Dumesic et al. [6,7] have produced hydrogen from oxygenated biomass-derived compounds, including glycerol, through the aqueous phase reforming (APR). Although the catalyst has provided stability for a long period, the high pressure and low

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