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Hydrogen production by aqueous-phase reforming of glycerol over nickel catalysts supported on CeO₂

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ABSTRACT

Nickel catalysts supported on CeO₂ were prepared and evaluated in aqueous-phase reforming of glycerol. Three different methodologies of synthesis were used: wet impregnation, co-precipitation and combustion, and 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 1 and 10 wt.% glycerol, at 523 and 543 K. A maximum glycerol conversion of 30% was achieved by the catalyst prepared by combustion at 543 K using solution 1% glycerol. In the gas phase, the molar fraction of H₂ was always higher than 70% and formation of CH₄ was very low (<1%). The increase in glycerol concentration decreases the conversion and H₂ formation.

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1. Introduction

Renewable energy sources are highly desirable in this era of diminishing fossil fuels reserves and increasing environmental concerns. Several alternatives of renewable fuels, such as hydrogen, ethanol and biodiesel, are currently being exploited in order to promote a more sustainable development.

Hydrogen is an attractive alternative fuel because of its availability (the most abundant element in the universe), it can be utilized in different applications and produced from a variety of feedstocks. At present, almost 95% of the world's hydrogen is produced from fossil fuels [1]. Renewable biomass is a promising source for hydrogen production due to its environmental benefits since the produced CO₂ is consumed during biomass growth providing a carbon neutral cycle.

Current processes for conversion of biomass to hydrogen, such as gasification and steam reforming, involve high temperatures and many side reactions, which decrease hydrogen selectivity [2,3]. Glycerol reforming for hydrogen production has been recently reviewed by Vaidya and Rodrigues [4]. Aqueous-phase reforming (APR) of oxygenated compounds derived from biomass to produce hydrogen, first developed by Dumesic et al., has several advantages [5]. 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 decomposition reactions. Furthermore, it is possible to

generate H₂ and CO₂ in a single step with low levels of CO, which is important for fuel cell applications [6].

Many oxygenated compounds, such as methanol, sorbitol, glycerol, ethyleneglycol and ethanol, have been used in APR process [5,7–9]. Glycerol is produced as a by-product during biodiesel production by transesterification of vegetable oils or animal fats. One ton of biodiesel yields about 110 kg of crude glycerol or about 100 kg of pure glycerol [10]. As biodiesel production increases exponentially, the crude glycerol is also produced in a large amount. One of the promising ways to utilize this diluted crude glycerol is to produce hydrogen by APR.

Supported Pt, Ru, Rh, Pd, Ir and Ni catalysts have been tested in APR process and have shown good activity and selectivity for hydrogen production. The mechanism of H₂ production by APR was described by Dumesic group [5,7,11]. The process involves the cleavage of C–C bonds as well as C–H bonds to form adsorbed species (especially CO) on the catalyst surface (Eq. (1)); then CO is converted in H₂ and CO₂ by the water–gas shift reaction (Eq. (2)):



Thus, 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. Ni shows a good activity for C–C scission followed by water–gas shift reaction, but it also exhibits high rates of methanation [6].

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