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Hydrogen production from glycerol steam reforming over nickel catalysts supported on alumina and niobia: Deactivation process, effect of reaction conditions and kinetic modeling

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ABSTRACT

Ni catalysts were prepared by wet impregnation of three different supports: alumina, niobia and 10 wt.% niobia/alumina, prepared by (co)precipitation. The catalysts were evaluated on steam reforming of glycerol at 500 °C, for 30 h. The catalyst supported on Nb₂O₅/Al₂O₃ presented the best performance, with higher conversion into gas (80%) during all reaction time and hydrogen yield of 50%. Alumina supported catalyst showed higher deactivation and lower hydrogen yield. All catalysts showed coke formation, but it was formed in larger amount on the catalysts supported on single oxides. A depth study was conducted to evaluate the effect of reaction variables as space velocity, glycerol concentration in feed and temperature on the catalytic performance of the Nb₂O₅/Al₂O₃ catalyst. Kinetic study was also performed for this catalyst using two different approaches, obtaining glycerol and steam orders, as well as the apparent activation energy.

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Introduction

Currently, fossil fuels are responsible for the major energy supply in the world, playing an essential role in developing various sectors of the economy. However, these resources are non-renewable and related to emission of pollutant gases, especially those associated with global warming. These gases cause a disturbance in fauna and flora and can affect human health, as they are responsible for respiratory and skin diseases and may also affect the nervous system.

Thus, considering the increasing concern about environmental issues and the expected increase in energy demand,

the development of alternative fuels is urgent and essential [1]. Hydrogen is a potential alternative, because it can be produced from a variety of feedstocks and different processes and its use in fuel cells does not release significant amount of pollutant gases. Furthermore, hydrogen has a high calorific value (122 kJmol⁻¹), which is almost three times higher than the calorific value for hydrocarbons [2]. Hydrogen is also employed in a variety of chemical industry processes, as for the ammonia synthesis, oil refining and Fischer Tropsch reaction.

Most of the hydrogen production nowadays is through natural gas (48%), heavy oils (30%) and coal (17%). Only a small

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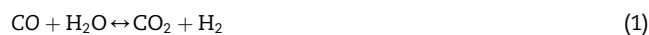
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part of the production is provided by water electrolysis (4%) or by biomass derivatives (1%) [2]. There are some routes for producing hydrogen from hydrocarbons as steam reforming, partial oxidation, autothermal reforming, and CO₂ reforming. However, steam reforming is the most dominant route, converting natural gas into hydrogen. Currently, 50% of the hydrogen supply is from steam reforming of hydrocarbons [3]. New methods to produce hydrogen with chemical looping reforming of ethanol with CO₂ capture has been studied [4,5].

The study of glycerol conversion into hydrogen intends to increase the participation of green resources in the hydrogen production matrix, because glycerol is the main byproduct in biodiesel production. Glycerol is a chemical commodity that has a large field of application; it can be used as feedstock by a variety of chemical industries, and also pharmaceutical, food and cleaning industries. However, currently, there is a large excess of this product in the market, due to the increased production of biodiesel in the world, because glycerol is a byproduct of transesterification of oils and fats, which is the main route for biodiesel production. Furthermore, the glycerol produced by transesterification has lots of impurities as the catalyst employed, alcohols, fatty acids, salts and water; thus, its use directly in usual applications that require a high level of purity is impracticable.

In Brazil, for example, the National Agency of Petroleum, Natural Gas and Biofuels (ANP) regulates the compulsory addition of 8% biodiesel to diesel since 2017, which contributed for increasing biodiesel production and therefore increasing glycerol amount in Brazilian market. According to ANP, the biodiesel (B100) production in 2016 was approximately 3.8 million m³, which corresponds to a production of 380,000 m³ of glycerin, as 1 m³ of biodiesel production generates approximately 100 L of glycerol [6]. Global biodiesel market is expected to reach 37 billion gallons by 2016, growing 42% per year and predicted to produce approximately 4 billion gallons of crude glycerol by 2016 [7]. In this context, there is an urgent demand in developing alternative routes for glycerol conversion into products with higher added values. Thus, glycerol reforming for hydrogen production is an attractive alternative.

Glycerol reforming consists in the reaction of glycerol with steam for producing synthesis gas (hydrogen and carbon monoxide) at atmospheric pressure and temperatures normally above 500 °C. Shift reaction (Eq. (1)) occurs next and consists in the reaction of carbon monoxide with steam for producing more hydrogen and carbon dioxide. The shift reaction is exothermic, however the global reforming reaction (Eq. (2)) is highly endothermic [8].



One advantage of glycerol reforming over methane reforming is the higher hydrogen molar flow with the same molar feed of reagent. For one mole feed of glycerol, 7 mol of hydrogen can be produced, while only 3 mol of hydrogen for 1 mol feed of methane [9]. Furthermore, another advantage is the lower temperature of operation: methane reforming takes place at 700–1000 °C.

Glycerol reforming has some challenges that still need to be overcome, as glycerol conversion by dehydration and other

reactions, decreasing hydrogen yield, methane formation, which reduces the rate and purity of generated hydrogen, and coke formation, which leads to catalyst deactivation during reaction time [3,9]. Furthermore, the effect of impurities of crude glycerol as salts, metal alkaline and methanol should be also investigated on steam reforming performance, including catalyst deactivation, in order to reduce the cost with glycerol purification [7].

A good catalyst for glycerol reforming has to be active for the cleavage of C–C bonds and water gas shift reaction. However, it has to inhibit the cleavage of C–O bonds and inhibit the methane formation [10–13]. Catalysts based on noble metals are less susceptible to deactivation through coke deposition and more active for reforming reaction. However, these catalysts are expensive and their availability is limited, thus it is more economical the development of catalysts based on non-noble metals, as nickel, which presents high activity for C–C bond scission and selectivity for synthesis gas production [13].

The use of different supports for nickel-based catalysts changes significantly the catalytic performance. Many authors have verified the formation of coke deposits over Ni/Al₂O₃ catalysts, causing their deactivation [14–17]. Usually, coke formation is associated with reactions as dehydration, cracking and polymerization, occurring in acid sites [18].

The employment of niobia as support for nickel catalysts in glycerol reforming was not found in the literature. It is known that Brazil is the major niobia producer; moreover, niobia presents some interesting properties as catalyst support, for example, strong metal-support interaction (SMSI) and oxygen mobility, which is also observed in other supports, like titania and ceria [19,20]. When niobia-supported catalysts are reduced at high temperature, it promotes the migration of the support over the surface of the metal particles, which is known as decoration effect. This greatly affects the properties of the dispersed metal phase, both by geometric and electronic factors. Geometric effects refer to the partial covering of active sites by reducible oxide species, while electronic effects can affect the adsorption strength, changing the catalytic activity and resistance to coke formation [19,20]. Because of these properties, niobia has been used as catalytic support or promoter in several different reactions [21,22].

Adhikari et al. [23] compared catalytic performance of nickel catalysts supported on MgO, CeO₂ and TiO₂ for glycerol steam reforming and verified that ceria catalyst presented the highest selectivity to hydrogen (70%) at 600 °C, and the lowest coke deposition. Pant et al. [16] and Shao et al. [24] verified that ceria reduces coke formation because of oxygen release by ceria reduction during reaction. They also concluded that the ceria support improves nickel dispersion, reduces sintering, and increases thermal stability and oxygen storage capacity. It is supposed that niobia has similar properties to ceria when used as catalytic support in reforming reactions.

This work aims the development of nickel catalysts supported on alumina, niobia and niobia/alumina, where the supports were prepared by (co)precipitation method, for glycerol steam reforming. The effect of the support on glycerol conversion, hydrogen yield and catalytic stability was evaluated and the catalytic performance was correlated with structural and morphological properties of the catalysts.

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