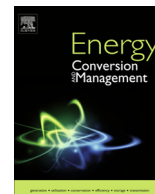




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Steam reforming of crude glycerol over nickel supported on activated carbon

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ABSTRACT

Steam reforming of crude glycerol, a side product of biodiesel industry, could be used to obtain H₂ and H₂/CO mixtures using Ni based catalysts. In this work, carbon supported nickel catalysts prepared by a simple impregnation technique were studied in the crude glycerol steam reforming at 650 °C to yield H₂ and CO₂ as the main products. Promotion with different metal oxides (MgO, La₂O₃, Y₂O₃) is effective to increase H₂ yield which attain more than 80% of the maximum theoretical amount with MgO. Rh promotion is also detected at the initial stages of the process although it is counteracted by the deleterious effect of carbon deposits on the active metal. Carbon deposits and sintering of the active metal are the main sources of deactivation.

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1. Introduction

Glycerol is the only by-product of the transesterification reaction which nowadays is the most widespread method for biodiesel production. It is produced in a ratio of 1:10 per weight and contains impurities such as methanol, inorganic salts and biodiesel making it a low value product. Because of that and also of the increasing worldwide biodiesel production this low grade crude glycerol (CG) has become a significant problem concerning its final disposal. Purified glycerol could be obtained for further production of many useful chemical products although refining costs are expensive and makes this alternative uninteresting mainly for small and medium scale biodiesel industries.

Conversion of glycerol in a rich hydrogen gas mixture is an alternative which has been explored by using catalytic steam reforming, partial oxidation, autothermal and aqueous reforming techniques [1]. Hydrogen and/or its mixtures with CO and CO₂ could be used to generate energy or to produce methanol thus improving economic and environmental aspects of the biodiesel plants [2]. Coupled to a CO₂ adsorption process the catalytic conversion can be efficiently performed at temperatures as low as 450 °C, thus enabling the use of low quality heat to operate the reactor and coupling with other processes such as Fischer–Tropsch and methanol synthesis [3,4].

When crude glycerol is used for these purposes, a product gas similar to the product gas produced by pure glycerol reforming is

obtained. Some of the impurities such water and methanol favor the production of hydrogen, so its removal step, which is often used for upgrading crude glycerol value, is avoided by using the reforming. Some other impurities such unreacted triglycerides, biodiesel catalyst contribute to increased deposit formation, pore clogging and catalyst deactivation [5,6]. Catalytic bed regeneration becomes thus a key aspect to be handled in this case in order to reduce energy consumption and to extent catalyst lifetime as much as possible.

Noble metals Rh, Pt, Pd display the best catalytic performance in steam reforming and in small amounts they are also effective to improve the performance of less active catalysts such as Ni and Co [7]. Different metal oxides (Al₂O₃, zeolites,) with high thermal stability and high specific surface area are used as supports in order to improve metal dispersion and provide suitable acid–base properties to enhance water reactivity and prevent carbon formation [8–10]. Steam reforming of different oxygenated hydrocarbons such ethanol and glycerol over nickel coprecipitated catalysts is also studied [11,12].

Carbon materials have been used as catalyst support due to its relatively inert chemistry in several reaction systems and low activity for H₂O activation, as well as high hydrothermal stability [13]. They also offer the possibility of modifying the pore size distribution, good reductive properties, easy recovery of the active metal from the spent catalyst by burning off the support and the possibility of modifying easily their surface chemistry to improve the interaction between the support and the catalytic metal during the impregnation step [14]. Different transition metals supported on carbon (Ni/C, Co/C and Pt/C) have shown to be active in the

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steam reforming of different oxygenated hydrocarbons at low temperature [4,15–18]. Addition of promoters has also shown to greatly increase C_1 product yield. ZnO addition to a Co/C catalyst introduced sites for water activation which favored C–C cleavage activity and oxidation of CH_x to CO and CO_2 [16]. Re addition to a Pt/C catalyst favored spillover of CO from neighboring Pt and facile desorption of CO, which could further react to form CO_2 . Such facile CO desorption leads to enhanced glycerol steam reforming and water–gas shift activities [19].

As far as we know this is the first work that shows carbon supported Ni as catalyst for steam reforming of glycerol and it could be useful to assess its potential under low temperature conditions which would avoid H_2O and O_2 activation of carbon. When used in CG conversion Ni and promoters could be easily recovered from the spent catalyst by simple procedures (burning, chemical separation of inorganic ashes by precipitation from an aqueous dissolution).

In the present work, the behavior of Ni/C catalysts is tested in the steam reforming of crude glycerol at 650 °C. MgO , Y_2O_3 and La_2O_3 promoters and two types of carbon with different surface properties are tested in order to detect their influence on the catalytic behavior. Rh addition is also tested as promoter.

2. Experimental

2.1. Catalysts preparation

The activated carbon (AC) was provided by Brascarbo Agroindustrial, Brazil and it was produced by water vapor activation of a mineral carbon (lignite). The carbon was washed, dried and ground to sizes between 40 and 50 mesh. Surface oxidation of AC was performed by its immersion into a water solution containing HNO_3 30% by weight followed by vigorous stirring during 5 h. After filtration the solid was washed repeatedly with distilled water until neutral pH was attained. The carbon material was finally dried in an oven at 110 °C for 24 h (AC-OX). Supported catalysts were prepared by a wet impregnation technique using an ethanolic solution of the metal nitrate salts. The solid was poured into the solution and kept in suspension under stirring during 5 h. Then, the solvent was eliminated by rotary evaporation and the solid thus obtained was dried in an oven at 110 °C during 24 h and then heat treated at 700 °C under argon (20 mL min^{-1}) during 6 h. All catalysts contain 10 wt% of nickel and 10 wt% of Y_2O_3 , La_2O_3 or MgO and for its identification in the rest of the manuscript they will be cited as NiMe/AC with Me: Y, La or Mg. 0.5% of Rh was introduced by impregnation to the NiMg/AC catalyst, starting from an ethanolic solution of $RhCl_3$. This catalyst will be denoted as Rh/NiMg/AC.

2.2. Catalysts characterization

Nitrogen physisorption measurements were conducted on a Beckman Coulter surface area analyzer (Coulter SA model 3100). The catalyst was degassed at 100 °C for 10 h prior to N_2 adsorption–desorption measurements. The specific surface area was calculated from the BET model, the pore size distribution was

obtained through the BJH approach and the total pore volume was estimated at a relative pressure of 0.98.

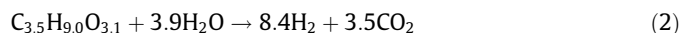
The crystalline phases of the reduced catalysts were characterized by a Rigaku Ultima IV diffractometer (XRD), using Cu $K\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation and coupled to a data acquisition system. The morphology and structure of the catalysts were observed using a JEOL JEM-1010 transmission electron microscope (TEM). Mean nickel particle size (\overline{d}_{Ni}) was calculated according to:

$$\overline{d}_{Ni} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where n_i represents the number of particles with diameter d_i ($\sum n_i \geq 100$).

Nickel content in the catalysts was determined by atomic absorption spectrometry with a Perkin Elmer AAnalyst 200.

The CG used in the present work mainly consists of 64 wt% glycerol, inorganic salts 5.7 wt%, methanol and water lower than 5 wt% and polyglycerol impurities up to 26 wt%, provided by the manufacturer. Potassium methylate was used as transesterification catalyst. CG composition was determined by elemental analysis (Thermo Scientific Flash 2000) and it is shown in Table 1. The calculated average elemental molar formula for CG determined from these results was $C_{3.5}H_{9.0}O_{3.1}$ and subsequently used to calculate conversion and yield parameters. According to this results steam reforming equation was:



2.3. Catalytic tests

Steam reforming tests were performed with a continuous down-flow fixed-bed stainless steel tubular reactor (12 mm i.d.) operated at atmospheric pressure and heated by a temperature-controlled electrical furnace. The catalyst bed configuration consists in a 5 g SiC bed placed above 0.200 g of the catalyst. The catalyst was first subject to in situ reduction under a 20 mL min^{-1} pure H_2 flow by heating from room temperature to 650 °C, at a rate of 10 °C min^{-1} and keeping the final temperature for 1 h. Following reduction, the H_2 flow was stopped and the reactor purged with argon. Then the water:CG solution (30% by weight of CG) was fed at 2.0 mL h^{-1} with a peristaltic pump (Cole Parmer 74900 Series) through a device consisting of two concentric tubes. Water:CG solution was injected into the internal tube (0.02 mm i.d.) and argon through the external one (2.1 mm i.d.). With this device the solution was sprayed into the catalyst bed. Partial vaporization of glycerol and other compounds in the CG would occur in the sprayed liquid solution along with water. The steam-to-carbon (S/C) molar ratio was equal to 3.7. Unreacted glycerol, some of the reaction products and excess water, were retained in a cold trap (-10 °C) at the exit replacing the trap every 2 h of reaction time. Carbon containing, determined by elemental analysis, of this liquid effluent was below 1% in all the experiments. Non-condensable products, mainly H_2 , CO, CO_2 , CH_4 , C_2 (ethane and ethylene) and C_3 (propane and propylene) hydrocarbons, were analyzed with a gas-chromatograph (Shimadzu GC-14B) equipped with FID and TCD detectors in series and columns Supelco

Table 1
Crude glycerol characterization.

Composition elemental (% p/p)					Water (% p/p)	Ash (% p/p)	Density (kg m^{-3})	pH
C	H	N	S	O (dif)				
41.97	9.08	n.d ^a	n.d	48.95	1.1	5.7	1049	11.4

^a Not detected.

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