Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina

CrossMark

Esteban A. Sanchez, Raúl A. Comelli*

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ-UNL, CONICET), Santiago del Estero 2654, S3000AOJ Santa Fe, Argentina

ARTICLE INFO

ABSTRACT

Hydrogen is a clean energy carrier, and its utilization will reduce environmental problems related to fossil fuels one. Biomass is an inexhaustible renewable source to generate bio-compounds. Glycerol, obtained from a crescent biodiesel industry, is an abundant bio-substrate to produce hydrogen. The steam reforming of glycerol was studied employing $4Ni/Al_2O_3$, $4Co–4Ni/Al_2O_3$, and $12Co–4Ni/Al_2O_3$ catalysts at 300, 500, and 700 °C, 1 atm, 10 h^{-1} WHSV, 6:1 water:glycerol molar ratio (WGMR), 0.17 ml min^{-1} glycerol solution feed flow rate and time-on-stream 8 h. The main product obtained was H_2, followed by CO_2, CO, and CH_4 in smaller proportion. Co promotes H_2 production and unfavors CO_2 generation when temperature decreases; CH_4 formation is observed at higher temperature. A low Co loading produces the largest H_2 and CO_2 amounts at the lowest temperature. A high Co loading improves H_2 production at lower temperature, but this does not occur at high temperature.

1. Introduction

There is a growing interest to employ the hydrogen as an energy carrier, mainly by the possibility of improve the current energy scene, and to reduce the environmental problems related to greenhouse gas emissions from utilization of non-renewable fossil fuels [1]. Furthermore, the continuous decrease of fossil fuel reserves and the increment of crude oil prices promoted the necessity to obtain renewable raw materials to generate clean energy by a sustainable way [2], contributing to improve the actual environmental condition [3]. Most of new technologies applied to energy production in European Union countries, USA, and the Asia-Pacific region, are directed to develop processes to transform raw materials derived from biomass into chemicals with high added value and also more economical and clean fuels [4].

In recent years, significant advances were obtained in order to use biocompounds, obtained from renewable biomass sources, in different industrial processes. Biodiesel, a mixture of methyl esters of fatty acids is produced by trans-esterification of vegetable oils using simple alcohols such as methanol or ethanol [5]; glycerol is obtained as the main by-product. It was estimated that the glycerol amount obtained from biodiesel production will have a rapid increase in coming years in world, and it represents a problem because glycerol excess will not be easily absorbed by the future market with the increasing biodiesel demand [6]. There is a crescent

interest for glycerol transformation because it comes from renewable resources, it is abundant, and it will allow a sustainable environmental development. Glycerol is a very convenient bio-renewable substrate to produce hydrogen, which can be used as a renewable and clean fuel in fuel cell, as a raw material to obtain chemicals and food products, in industrial processes such as ammonia production and Fischer–Tropsch synthesis [5], and to produce electricity [7].

Current processes for hydrogen production are based on catalytic reforming of hydrocarbons. In recent years, the possibility to obtain H_2 by reforming of glycerol has been widely investigated, because they are efficient processes to employ the excess of glycerol coming from the biodiesel industry [8]. Steam reforming of glycerol shows a great interest due to its operational characteristics and it is possible to obtain adequate reaction efficiency.

The glycerol steam reforming has been extensively investigated using supported catalysts with transition metals of VIII group, such as Pt, Pd, Ru, Rh, Co, and Ni, showing the last one an adequate activity during reaction. Using monometallic and bimetallic catalysts of Pt and Ni impregnated on Al_2O_3–SiO_2, Ni reached the best performance at 900 °C and WGMR 9:1, with 80% H_2 selectivity [9]. With Ni on MgO–Al_2O_3, an adequate calcination temperature favored the interaction with metallic phase, increasing catalytic activity [10]. Using Ni/Al_2O_3, the H_2 selectivity was strongly affected by reaction temperature, increasing at high temperature [11]; the best H_2 yield was 65% of the maximum theoretical value [12]. Ni/Al_2O_3 catalysts are susceptible to deactivation by carbon deposition, but their low costs made interesting investigate the possibility to improve the catalytic properties by addition of a promoter. Only a few studies employed Co/Al_2O_3 catalysts to produce H_2 by steam reforming [5,13,14], whereas Co–Ni/Al_2O_3 bimetallic catalysts were used in processes such as methane dry reforming [15], glycerol aqueous phase reforming [16], glycerol steam reforming [2], and acetol steam reforming [17].

In the present paper, the H_2 production by glycerol steam reforming was evaluated using Ni catalysts impregnated on Al_2O_3, adding Co as a promoter in order to analyze the catalytic performance under standardized operating conditions. Characterization of materials was performed by N_2 adsorption, X-ray diffraction (XRD), and Fourier-Transform infrared spectroscopy (FTIR).

2. Experimental

2.1. Catalyst preparation

Catalysts containing either Ni or Co–Ni on alumina were prepared following the incipient wetness impregnation technique. The base material was a commercial sample of γ-Al_2O_3 (CK-300 Akzo Nobel, 199 m^2 g^{-1}, 0.51 cm^3 g^{-1}, and 35–80 mesh), which was calcined at 600 °C for 3 h in 50 ml min^{-1} air. Different solutions were prepared using nickel nitrate hexahydrate (Anedra) and sodium cobaltonitrite (Sigma) as precursors of Ni and Co species, respectively; concentrations were adequate to obtain 4 wt% Ni, and 4 and 12 wt% Co loadings. Impregnated samples were placed in a desiccator at room temperature for 4 h and then were dried in an oven at 110 °C for 12 h. Samples were identified as yCo-xNi/Al_2O_3, being "x" and "y" the Ni and Co loadings, respectively. Finally, catalysts were calcined at 500 °C for 3 h in 50 ml min^{-1} air.

2.2. Catalyst characterization

Prepared catalysts were characterized by N_2 adsorption, XRD, and FTIR being equipments and conditions previously reported [18]. Previous characterization, samples were reduced for 3 h in 100 ml min^{-1} H_2 at 300 and 400 °C for Ni and Co containing catalysts, respectively.

2.3. Catalytic measurements

Catalytic behavior of prepared materials was evaluated during the glycerol steam reforming using a system previously described [18]. A 50 wt% glycerol (Cicarelli) aqueous solution fed by a Cole Parmer 74900 syringe pump, and He as carrier gas were fed to the vaporizer. For catalytic test, 500 mg of reduced catalyst were placed into quartz reactor, being operating conditions 300, 500, and 700 °C, atmospheric pressure, 10 h^{-1} WHSV, 6:1 WGMR, 0.17 ml min^{-1} glycerol solution flow rate, and total time of 8 h.

Reaction was monitored by gas chromatography, being details of equipments, columns, temperature programs, and detectors previously reported [19]. Non-condensable products were on-line analyzed by gas chromatography using a 1.9 m
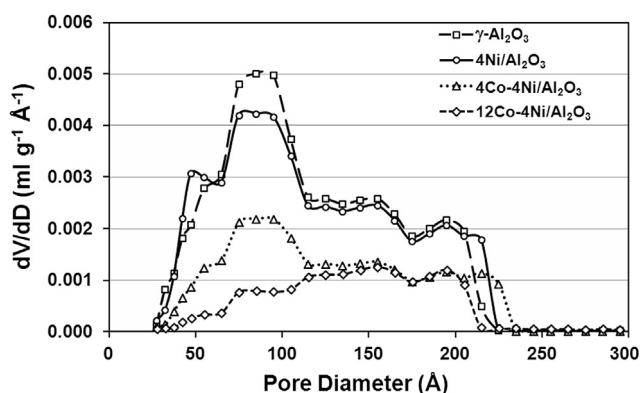
Fig. 1 – Pore-size distribution for Ni and Co–Ni catalysts, and γ-Al_2O_3 support. Samples calcined at 500 °C for 3 h in 50 ml min^{-1} air flow and reduced at 300 °C (Ni) and 400 °C (Co) for 3 h in 100 ml min^{-1} H_2 flow.

Table 1 – Textural properties for γ-Al_2O_3 support, and Ni and Co–Ni impregnated catalysts.

Materials	S_{BET} (m^2 $g^{-1}_{support}$)	PV (ml $g^{-1}_{support}$)	PD_M (Å)
γ-Al_2O_3	195.1	0.4771	97.8
4Ni/Al_2O_3	182.5	0.4776	104.7
4Co–4Ni/Al_2O_3	85.7	0.2527	118.0
12Co–4Ni/Al_2O_3	59.3	0.1592	107.4

Pretreatment conditions: samples calcined at 500 °C for 3 h in 50 ml min^{-1} air flow, and reduced at 300 °C (Ni) and 400 °C (Co) for 3 h in 100 ml min^{-1} H_2 flow.