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HYDROGEN PRODUCTION THROUGH GLYCEROL STEAM REFORMING REACTION USING TRANSITION METALS ON ALUMINA CATALYSTS

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ABSTRACT

Hydrogen can be produced from a wide variety of primary energy sources and by applying quite different technologies. For a long period of time it has been considered as a sustainable and environmentally friendly alternative to conventional fossil fuels, with a large potential that can meet energy requirements, ensuring future supplies. At present, research is mainly focusing on biomass and biomass-derived fuels that can be used for the production of hydrogen through thermo-chemical or biological processes.

On the other hand, biodiesel production has recorded enormous growth in the last decade, which has led to a simultaneous co-production of glycerol. As a consequence, finding alternative feasible uses for glycerol has become imperative as such processes would not only solve the environmental problems associated with its disposal, but also, the discovery of new and innovative uses for glycerol would greatly increase its market demand. Thus, the development of new uses for glycerol is the subject of heightened research interest.

The production of hydrogen from biomass-model compounds including glycerol via low temperature catalytic aqueous phase and steam reforming has been investigated. Steam reforming (SR) is a highly energy efficient technology and can be carried out at atmospheric pressure. Glycerol steam reforming reaction (GSR) has intensively been studied experimentally using a variety of supported catalysts. Nickel (Ni) is the most investigated active metal in the GSR reaction, due to its well known property to promote the necessary C–C rupture. Nickel catalysts were shown to be active and selective with a strong dependence on the reaction temperature with glycerol conversion to gaseous products.

In this contribution a systematic study of supported on γ-alumina transition metals', catalytic performance is reported. Catalysts with active phase nickel (Ni), cobalt (Co) and copper (Cu) were synthesized via the incipient wetness impregnation method (dry impregnation) at a series of constant loading (8wt%). The synthesized samples, at their calcined or/and their reduced form, were characterized by the X-Ray Diffraction (XRD) and the N_2 adsorption-desorption techniques. The chemical composition of the catalysts was determined by inductively coupled plasma emission spectroscopy (ICP), while the deposited on their surface carbon during the reaction was measured by a CHN analyzer. Catalytic performance for the glycerol steam reforming reaction was studied in order to investigate the effect of reaction temperature on: (i) glycerol total conversion, (ii) glycerol conversion to gaseous products, (iii) hydrogen selectivity and yield, (iv) selectivity of gaseous products, (v) selectivity of liquid products.

It was concluded that all catalysts were active with glycerol conversion values ranging from 75% to 95% for the studied reaction temperatures. However, the Ni/Al catalyst reveals higher conversion to gaseous products, improved hydrogen yield and selectivity especially for T>500 and less carbon deposited on its surface compared with the Co/Al and Cu/Al catalysts.

Keywords: glycerol steam reforming, nickel, cobalt and copper catalysts, hydrogen production

1. Introduction

With an ever-increasing demand for energy and problems associated with global warming due to the use of fossil fuels, the quest for alternative and renewable fuels has become paramount. In this respect, biodiesel is being gradually accepted as a replacement for the mainstream diesel. A

major by-product of the biodiesel production through the trans-esterification reaction (approximately 10% w/w of the amount of biodiesel) is glycerol, an important feedstock in food, cosmetics, pharmaceuticals and other industries [1]. Among the possible uses of glycerol, the production of hydrogen by steam reforming (GSR) is considered attractive because it turns raw glycerol to a potential source for a renewable zero-emission fuel. In the present study, the catalytic performance of nickel (Ni), cobalt (Co) and copper (Cu) catalysts based on a commercial γ-Al$_2$O$_3$ support were synthesized, characterized and studied for the glycerol steam reforming reaction in order to investigate the effect of reaction temperature on: (i) glycerol total conversion, (ii) glycerol conversion to gaseous products, (iii) hydrogen selectivity and yield, (iv) selectivity of gaseous products, (v) selectivity of liquid products.

2. Materials and methods
2.1. Catalysts preparation
A commercial γ-Al$_2$O$_3$ (Akzo, 350-500μm, S$_{BET}$ =195m^{2}g^1) was used as the supporting material of the nickel (Ni), cobalt (Co) and copper (Cu) based catalysts. The samples were prepared using the incipient wetness (or dry) impregnation technique, by impregnating the γ-alumina with aqueous solutions of Ni(NO$_3$)$_2$6H$_2$O having the appropriate concentration, in order to obtain a nominal loading of 8wt % Ni, Co or Cu in the final catalysts. The total volume of the impregnation solutions was equal with the total pore volume of the alumina used. The impregnated samples were dried overnight and calcined at 800°C for 5 hours. The catalysts have been labelled herein as Ni/Al, Co/Al and Cu/Al.

2.2. Catalysts characterization
Catalysts' specific surface area (SSA) was measured by applying the BET method from the N$_2$ adsorption-desorption isotherms. Total metal loading (wt%) of the final catalysts' was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The catalysts' crystalline structure was determined by applying the X-ray diffraction (XRD) technique, using ThermoAl diffractometer (40kV, 30mA, CuK$_α$ radiation, λ=1.54178 nm). The percentile concentration of deposited carbon in used catalysts was measured by quantitative infrared spectroscopy performed with a Leco CHN-200 analyser.

2.3. Catalysts testing
The glycerol steam reforming (GSR) reaction was carried out at atmospheric pressure, in a continuous flow, fixed-bed, single pass, tubular stainless steel reactor, with an inner diameter of 14 mm, at temperature ranging from 400-750°C. The experimental set up used allowed the feeding of both liquid and gaseous streams, having two vaporizers and a pre-heater before the reactor and a condenser after it. The vaporizers, pre-heater and reactor are placed into electrical ovens and regulated with programmed-temperature controllers. The liquid stream consisted of C$_3$H$_8$O$_3$ (20%v/v.) and H$_2$O (total liquid flow rate = 0.12 ml/min). The glycerol/ water mixture was fed with a HPLC pump (Series I) and was first vaporized at 350°C before it was mixed with He (He flow rate = 38 ml/min). Prior to catalytic testing, 200 mg of catalyst (350-500 μm) was reduced in situ in a hydrogen flow (100 ml/min) at 800°C for 1 hour. The gaseous products were analyzed on-line by a gas chromatographer (Agilent 7890A), with two columns in parallel, HP-Plot-Q (19095-Q04, 30m length, 0.530mm I.D.) and HP-Molesieve (19095P-MSO, 30m length, 0.530mm I.D.), equipped with TCD and FID detectors. Liquid products were analyzed via a combined system of a Gas Chromatographer (Agilent 7890A, with a 5MS column, equipped with an FID detector) and a Mass Spectrometer (Agilent 5975C).

3. Results and discussion
3.1. Physicochemical properties
In Table 1 the physicochemical properties of all samples are presented. As can be observed, the specific surface area (SSA) for all the supported on Al$_2$O$_3$ catalysts are significantly lower than the one of the support (γ-Al$_2$O$_3$, 195 m^2 g^{-1}, after calcination at 800°C), whereas the pore volume was not significantly altered. The lower surface area can be attributed to the fact that the internal surface area of the support pore system is probably progressively covered by nickel, cobalt and copper species forming a layer. Moreover, it should also be noted that all catalyst samples have comparable SSA's. The ICP results (metal loading, wt%) indicate that the desired metal level was

achieved in all samples. Carbon deposition is less for the Ni/Al catalyst in comparison to the Co/Al, Cu/Al

Table 1: Characterization techniques results of the support (γ-Al$_2$O$_3$) and the catalysts (Ni/Al, Co/Al, Cu/Al) after calcination (S$_{BET}$, V$_p$, loading) or after reaction (carbon, wt%)

Catalyst/ Support	S$_{BET}$ (m^{2}g^{-1})	V$_p$ (ml g^{-1})	Metal loading (wt%)	Carbon, (wt%)
Al	195.00	0.65	-	n/a
Ni/Al	158.32	0.57	7.88	15.80
Co/Al	154.31	0.58	7.42	19.26
Cu/Al	142.01	0.58	7.35	18.36
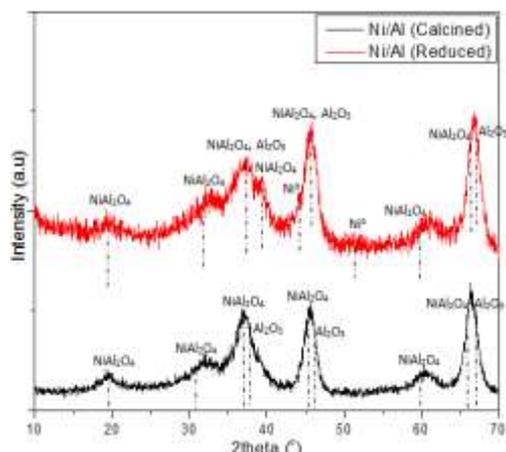
Figure 1: XRD patterns of calcined and reduced (at 800°C) Ni/Al catalysts
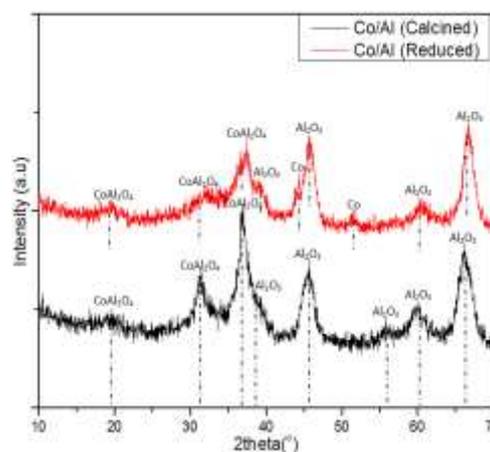
Figure 2: XRD patterns of calcined and reduced (at 800°C) Co/Al catalysts

Fig. 1 & 2 depict the XRD patterns of the calcined and reduced Ni/Al and Co/Al catalysts, respectively. Characteristic peaks at 2θ= 37.19°, 38.74°, 45.28°, 47.09°, 66.62° and 66.92° (for the Ni/Al), 2θ= 37.24°, 38.53°, 45.62°, 45.8°, 56.27°, 60.07° 60.28°, 67.38°, and 68.52° (for the Co/Al) assigned to poorly crystalline γ-Al$_2$O$_3$. Peaks of the spinel nickel aluminate phase (NiAl$_2$O$_4$), indicated by the diffraction lines at 2θ=19.18°, 19.24°, 30.96°, 31.34°, 36.92° 37.19°, 39°, 45.28°, 45.54°, 59.63°, 59.79° 65.16°, 65.95° can be observed for the nickel based catalyst. The formation of NiAl$_2$O$_4$ is caused by the reaction of NiO and Al$_2$O$_3$ due to the high calcination temperature, i.e., T=800°C [2]. For the case of Ni/Al-reduced catalyst the appearance of two small peaks at 2θ=44.10° and 51.26° indicate the presence of metallic Ni°. Peaks of the cobalt aluminate spinel phase (CoAl$_2$O$_4$), indicated by the intensity of diffraction lines at 2θ=18.86°, 18.97°, 31.35°, 31.36°, 36.95° and 37.24° can be observed for the cobalt based catalyst. For the case of Co/Al-reduced catalyst two small peaks at 2θ= 44.31° and 51.61° indicate the presence of metallic Co. As for the XRD pattern of Cu/Al-calcined catalyst no peaks indicating the presence of CuO have been detected, in accordance to the literature [3,4]. On the other hand, in the case of Cu/Al-reduced catalyst additional peak associated with metallic copper was indentified.

3.2. Catalytic performance
Thermodynamic studies for the steam reforming of glycerol reaction predict that high temperatures, low pressures and high H$_2$O/C molar ratio favor hydrogen production [5]. Catalytic testing experiments were carried out in a temperature range of 400-750°C, at atmospheric pressure and for a water to glycerol molar ratio of 20/1. The influence or reaction temperature to total glycerol conversion and glycerol conversion into gaseous products is presented in Figure 3a. All catalysts reveal improved activity with increased temperature (a consequence of the endothermic nature of the overall steam reforming reaction) however, the Ni/Al catalyst exhibits higher conversion into gaseous products (H$_2$, CO$_2$, CO, CH$_4$) for the whole temperature range (450-750°C).
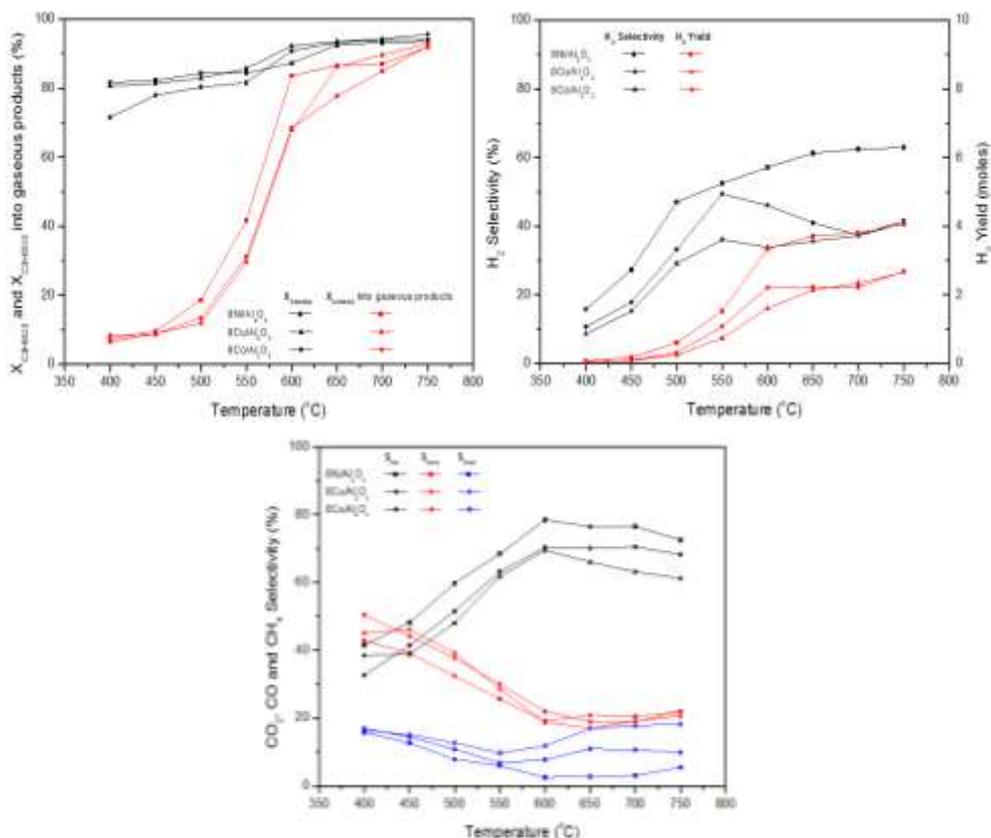
Figure 3: (a) Total glycerol conversion and glycerol conversion into gaseous products, (b) H_2 selectivity and H_2 yield, (c) CO_2, CO, CH_4 selectivity for Ni/Al, Co/Al, Cu/Al catalysts.

The influence of reaction temperature on H_2 yield and selectivity is depicted in Figure 3b. It can be observed that their values are increased with increasing temperature, while H_2 selectivity was found to be 63, 42 and 41% at 750 °C for the catalysts Ni/Al, Co/Al and Cu/Al, respectively. On the other hand, H_2 yield corresponds to 4.1, 2.7 and 2.66 moles of H_2 out of 7 for Ni/Al, Co/Al and Cu/Al, respectively.Generally, it was observed significantly higher H_2 selectivity and yield values for the Ni/Al compared to the ones for the Co/Al and Cu/Al catalysts.

Table 2: Selectivity values (S%) of liquid products for the Ni/Al, Co/Al, Cu/Al catalysts at various reaction temperatures (400 – 750 °C).

Ni/Al							
Product	**Reaction temperature (°C)**						
	400	**450**	**500**	**550**	**600**	**650**	**700**
Acetol	30.30	31.63	34.69	31.97	38.68	6.06	0.00
Acetone	19.23	19.33	18.06	18.02	15.96	28.58	71.97
Allyl alcohol	18.14	19.12	21.19	22.97	19.52	26.79	0.00
Acetaldehyde	24.30	22.35	17.84	18.36	15.52	20.72	0.00
Acetic acid	8.03	7.57	8.22	8.69	10.33	17.85	28.02
Co/Al							
Acetol	25.86	30.75	41.13	43.02	43.44	1.19	0.00
Acetone	14.49	14.96	19.48	19.27	19.68	30.19	42.07
Allyl alcohol	37.10	30.58	14.49	13.52	13.72	25.79	0.00
Acetaldehyde	14.47	14.31	12.16	11.98	11.24	21.14	25.86
Acetic acid	8.08	9.40	12.73	12.21	11.93	21.69	32.07
Cu/Al							
Acetol	30.64	40.85	42.35	37.81	32.58	11.04	0.00
Acetone	16.15	18.14	17.30	19.79	19.09	28.13	60.43
Allyl alcohol	22.36	16.54	15.62	16.70	18.15	8.15	0.00
Acetaldehyde	22.23	12.58	13.94	13.01	15.48	25.70	19.52
Acetic acid	8.63	11.89	10.80	12.69	14.68	26.99	20.05

The analysis of liquid products showed the same reaction intermediates over Ni/Al, Co/Al and Cu/Al catalysts. The main products were acetol, acetone, allyl alcohol, acetaldehyde and acetic acid. Table 1 displays the selectivity of liquid products at temperature range 400–750°C. It can observed that the selectivity values of acetol, acetone, allyl alcohol, acetaldehyde and acetic acid showed no significant differences for the catalysts Ni/Al, Co/Al and Cu/Al for the whole temperature range.

4. Conclusions

In concluding, all the catalysts were active with glycerol conversion values ranging from 75% to 95% for the studied reaction temperatures. However, the Ni/Al catalyst reveals higher conversion to gaseous products, improved H_2 yield and selectivity especially for T>500 and less carbon deposited on its surface compared with the Co/Al and Cu/Al.

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