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Hydrogen production by glycerol steam reforming: How Mg doping affects the catalytic behaviour of Ni/Al$_2$O$_3$ catalysts

M.L. Dieuzeide [a], M. Laborde [a], N. Amadeo [a,*], C. Cannilla [b], G. Bonura [b], F. Frusteri [b]

[a] ITHES – CONICET-Universidad de Buenos Aires-Pabellón de Industrias, Ciudad Universitaria, 1428, Buenos Aires, Argentina
[b] National Council of Research, CNR-ITAE – Via S. Lucia 5, 98126, Messina, Italy

ARTICLE INFO

ABSTRACT

Glycerol steam reforming, using Mg doped Ni/Al$_2$O$_3$ catalysts, was investigated with the aim to efficiently produce hydrogen. Catalyst containing different Mg loading were prepared by impregnation method maintaining constant the Ni loading (10 wt.%). Catalytic experiments were performed in fixed bed reactor operated at 500 and 600 °C. Characterization results revealed that Mg, further to infer a basic character to the carrier, promotes the Ni dispersion. In addition to observe that the catalytic activity was mainly dependent upon the Ni dispersion, the amount and morphology of coke formed during reaction was affected by Mg loading. In particular, the addition of 3wt% of Mg contributes to reduce the coke formation rate while a subsequent addition of Mg up to 10wt%, does not significantly affect neither the catalytic activity nor the carbon formation. By operating at 600 °C and with H$_2$O/Gly ratio of 6, low amount of coke, mainly of filamentous nature, was formed. The size and structure of carbon filaments changed as a function of Ni particle size and Mg loading.

Introduction

Vehicular transport is nowadays responsible for a large part of CO$_2$ emissions. Among the mitigation strategies, the Panel on Climate Change (IPPC) proposes the use of biofuels, electricity and hydrogen to reduce the transport greenhouse gases emissions [1].

Among the biofuels one of the most promising is biodiesel, which production has grown sharply in recent years. In biodiesel plants, around 10 wt.% of the vegetable oil or animal fat is converted to glycerol as a by-product [2]. Of course, the excess of glycerol production has led to a drastic decrease in its commercial value. Moreover, this non-toxic biomass has quite safe storage and handling policies. Such an integrated bioenergy production model may indeed allow a sustainable environmental local development [3].

Among different approaches proposed, the production of hydrogen by reforming processes has received particular attention [4–12].
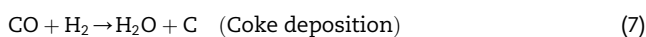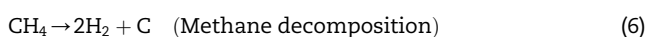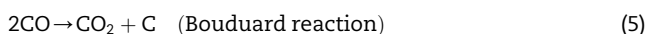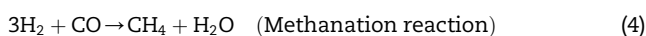
The steam reforming of glycerol (GSR) is an endothermic process that takes place according to the following main reaction scheme:

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad \text{(Glycerol steam reforming)}$$
(1)

$$C_3H_8O_3 \rightarrow 4H_2 + 3CO \quad \text{(Direct decomposition)}$$
(2)

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \text{(WGS)}$$
(3)

$$3H_2 + CO \rightarrow CH_4 + H_2O \quad \text{(Methanation reaction)}$$
(4)

$$2CO \rightarrow CO_2 + C \quad \text{(Bouduard reaction)}$$
(5)

$$CH_4 \rightarrow 2H_2 + C \quad \text{(Methane decomposition)}$$
(6)

$$CO + H_2 \rightarrow H_2O + C \quad \text{(Coke deposition)}$$
(7)
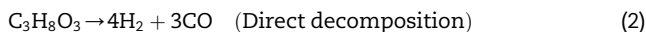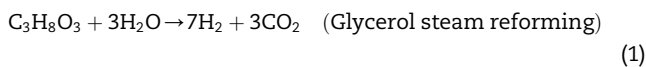
However, the GSR process involves multiple complex reactions, which lead to several intermediate by-products that strongly affect H_2 selectivity.

H_2 selectivity is mainly the result of simultaneous glycerol decomposition (Eq. (2)) and water-gas shift (Eq. (3)) reactions, methanation reaction (Eq. (4)), and a series of reactions that lead to carbon formation (Eqs. (5)–(7)). A previous thermodynamic study [5] concluded that, in order to both favour H_2 production and minimize carbon formation, the steam reforming of glycerol should be performed at high temperatures and at atmospheric pressure with high water to glycerol molar feed ratio.

Besides reaction conditions, the catalyst also plays a key role on determining the reaction pathway and product distribution. In this sense, the fundamental steps involving the catalyst are the cleavage of C−C, O−H and C−H bonds of glycerol molecule while keeping the C−O ones [6−8].

Noble metal based catalysts are commonly used for the steam reforming reaction of hydrocarbons or alcohols [9−11] since they are highly active, and less susceptible to promote undesired carbon formation. On the other hand, catalysts based on non-noble transition metals are far cheaper, present higher availability than the former, but they are affected by coke formation. Among them, Ni based catalysts, in particular, are known to be active for the cleavage of C−C, O−H and C−H hydrocarbon bonds, while they also catalyse water gas shift reaction to remove CO adsorbed on metallic surface [6,12,13].

Several studies have been published regarding steam reforming of glycerol over Ni based catalysts [6,12,14−19]. Adhikari et al. [6] reported a glycerol conversion of 100% and a hydrogen yield of 57% over Ni/MgO catalysts at 650 °C. Additionally Thyssen et al. [18] obtained a glycerol conversion of 100% and a hydrogen yield of 54% referred to the stoichiometric one at 600 °C, over NiLaSi catalysts. Finally, Bobadilla et al. [19] studied glycerol steam reforming over NiSn/MgAl catalysts at 650 °C, they reported a glycerol conversion of 90% with a hydrogen yield of 45% of the stoichiometric one.

Regarding the catalyst support, it has been observed that supports featuring a basic character provide both higher activity and deactivation resistance [14−17,20−24]. The nature of the support influences the catalytic performance of supported Ni catalyst for the hydrocarbon reactions [25], since it affects metallic dispersion and stability.

Alumina-based support is normally used to prepare steam reforming catalyst due to its mechanical and chemical resistance. Nevertheless, the acid sites of alumina promote the deposition of carbon with negative consequence on catalyst stability and reaction pressure. One possible strategy to avoid carbon deposition is to favour its gasification by modifying the support with alkaline earth oxides such as MgO or CaO [25,26]. These additives favour water adsorption and OH surface mobility, decreasing the rate of coke deposition on catalyst surface [24].

It is known that hydrocarbons dissociate on the metal surface producing adsorbed carbon than can be either gasified to produce carbon oxides or polymerised to give rise to the formation of carbon species that accumulate on the metallic surface. Elementary carbon can also dissolve inside metal particle; in such case the carbon dissolution can lead to the formation of carbon with filamentous nature (whiskers). Or it can encapsulate the metallic particle and hence deactivates the catalyst [27].

In this paper the influence of Mg(II) doping on performance of Ni/Al$_2$O$_3$ catalyst in glycerol steam reforming reaction is investigated over a wide range of reaction conditions. Furthermore it is an aim of this work to understand the effect of Mg doping over carbon formation rate and carbon morphology.

Experimental

Catalysts preparation

The catalysts were prepared by the incipient wetness impregnation method. Aqueous solutions of Mg(NO$_3$)$_2$·6H$_2$O (99% Merck), with concentrations between 2.8 M and 14.0 M, and Ni(NO$_3$)$_2$·6H$_2$O (99% Merck) 3.9 M were prepared.

As elsewhere reported [28−30], bare γ-alumina (Rhône Poulenc, 200 m^2/g) was impregnated with increasing contents of Mg(II); the samples were dried in a furnace at 120 °C for 6 h, following by calcination at 900 °C for 6 h.

Then, each Mg(II)−Al(III) modified support and γ-Al$_2$O$_3$ calcined at 900 °C for 6 h, were impregnated with Ni(II) in order to reach a final loading of Ni(II) of 10wt.%. After impregnation with Ni(II) solution, the samples were dried at 120 °C for 6 h and calcined at 500 °C for 6 h.

Catalysts were identified as Ni(10)Mg(x)Al, being x the nominal content of Mg (wt.%) (0 wt.%, 3 wt.%, 5 wt.%, 10 wt.%).

Prior to impregnation with Mg(II) or Ni(II) solutions, bare γ-Al$_2$O$_3$ was crushed and sieved in order to obtain particles with diameters ranging between 44 and 125 μm.

Catalyst characterization

Fresh catalysts samples were characterized by N$_2$ adsorption − BET analysis, powder X-ray diffraction (PXRD), temperature programmed reduction (TPR), H$_2$ chemisorption and temperature programmed desorption of CO$_2$ (CO$_2$-TPD).

Used catalysts were characterized by temperature programmed oxidation (TPO), thermogravimetric analysis (TGA/