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Hydrogen production via the glycerol steam reforming reaction over nickel supported on alumina and lanthana-alumina catalysts

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ARTICLE INFO

Article history:

Received 5 January 2017

Received in revised form

31 March 2017

Accepted 9 April 2017

Available online xxx

Keywords:

Glycerol

Hydrogen

Steam reforming

Nickel supported catalysts

Alumina

Lanthana

ABSTRACT

In the present work, a comparative study of Ni catalysts supported on commercially available alumina and lanthana-alumina carriers was undertaken for the glycerol steam reforming reaction (GSR). The supports and/or catalysts were characterized by PZC, BET, ICP, XRD, NH₃-TPD, CO₂-TPD, TPR and SEM. Carbon deposited on the catalytic surface was characterized by SEM, TPO and Raman. Concerning the Ni/LaAl sample it can be concluded that the presence of lanthana by: (a) facilitating the active species dispersion, (b) strengthening the interactions between nickel species and support, (c) increasing of the basic sites' population and redistributing the acid ones in terms of strength and density, provides a catalyst with improved performance for the GSR reaction, in terms of activity, H₂ production and long term stability. TPO and Raman indicate that the carbon on the Ni/LaAl catalyst was mostly amorphous and was deposited mainly on the support surface. For the Ni/Al catalyst, graphitic carbon was prevalent and likely covered its active sites.

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Introduction

The development of the biodiesel industry, due to the need to move towards renewable transport fuels, has led to an increase in the production of crude glycerol, as 100 g of oil generate approximately 10 g of glycerol as byproduct. Thus,

finding ways to utilize glycerol is not only an environmental necessity, but it may also help this nascent industry (bio-diesel) to move away from subsidies and become more competitive.

One of the most interesting options is the production of hydrogen via catalytic steam reforming (GSR) [1–7], because as can be seen in Eq. (1), one mole of glycerol can produce

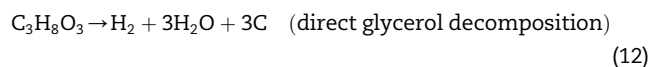
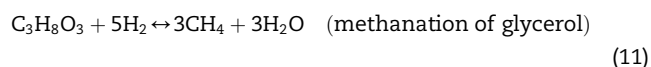
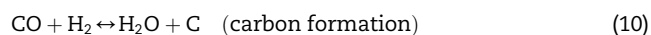
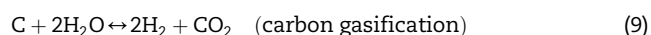
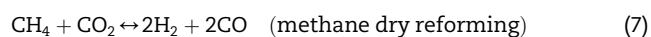
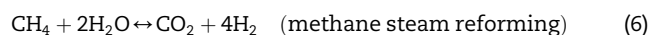
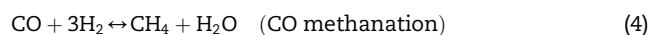
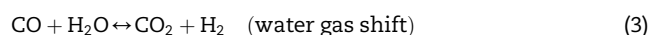
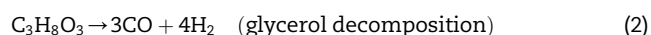
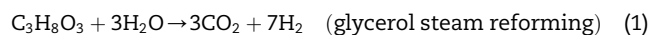
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<http://dx.doi.org/10.1016/j.ijhydene.2017.04.048>

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seven moles of hydrogen. Eq. (1) is in fact a combination of glycerol decomposition (Eq. (2)) and the water-gas shift reaction (Eq. (3)). The process is accompanied by a number of other reactions that depend on the operating conditions, as shown in Eqs. (4)–(12) [8–10].



Thermodynamics predict that three factors mainly impact on the glycerol steam reforming reaction namely, temperature, the water to glycerol feed ratio (WGFR) and pressure. In regards to temperature, the strong endothermic nature of the overall GSR reaction ($\Delta H^\circ = 123 \text{ kJ/mol}$) means that hydrogen production is favored by higher temperatures. The production of CO, which is also favored at high temperatures, is usually attributed to the reverse water gas shift (RWGS) reaction. In contrast, at low temperatures, the production of CO_2 and CH_4 is prevalent because of the exothermic water gas shift and methanation reactions. In regards to the WGFR, the Le Chatelier principle is prevalent, meaning hydrogen production is favored when water is in excess. However, it has been reported that when the WGFR exceeds 9:1 (molar) the H_2 production increases at slow rates. The Le Chatelier principle is also in play in regards to pressure, meaning that an increase in pressure favors the production of methane and inhibits that of hydrogen [11–17].

The metal that has been most extensively tested in the GSR is nickel (Ni), because it is known to have good intrinsic activity in reforming reactions, especially when Ni is highly dispersed over the support [e.g. Refs. [18–23]]. The main disadvantages of Ni-based catalysts are deactivation due to carbon formation and sintering of the metal particles [24–26]. Sintering further provokes carbon deposition, as large metal aggregates encourage coke formation [27–30]. Alumina-based supports have attracted interest in the GSR because alumina possesses high surface area (which improves metal

dispersion) and mechanical and chemical resistance under reaction conditions [31–33]. However, alumina is also known to help deposition of carbon and sintering. The formation of coke deposits has been associated with dehydration, cracking and polymerization reactions, which take place on the acid sites of alumina, while sintering has been associated with a transition of alumina to crystalline phase during reaction [34,35]. The efforts to overcome the problems associated with the use of alumina, focus on basic additives or promoters that favor water adsorption and O–H surface mobility; the aim is the neutralization of the acidity of Al_2O_3 supports and the decrease in the rate of coke deposition on catalysts surfaces [36–48].

The contributions that have investigated the use of lanthanum oxide (La_2O_3) as promoter on alumina supporting nickel catalysts for the GSR are few in number. Iriondo et al. [49] focused on the investigation of the effect of different concentrations of La (3, 6 and 15%) on alumina for a catalyst that contained 16 wt. % Ni. The tests were conducted between 500 and 600 °C with 10 wt. % glycerol diluted in water and the results indicated that the addition of lanthana favored glycerol conversion into gaseous products (and thus inhibiting production of liquid effluents), with the best activity exhibited by the catalyst containing 6% La_2O_3 . Liquid products were not analyzed. Iriondo et al. [50] also studied the effect of the addition of different modifiers on the alumina support (Ce, Zr, La and Mg), again using catalysts that contained 16 wt. % Ni (and in the case of the Ni/LaAl catalysts 5 wt. % La). The tests were conducted at 600 °C with 1 wt. % glycerol diluted in water and the conclusion was that lanthanum increases hydrogen selectivity in comparison to the catalyst supported on bare alumina and explained this result by correlating it to the stability of the nickel phases under reaction conditions. Analysis of liquid effluents revealed the presence of mainly propylenglycol and ethylenglycol; acetol and ethanol were also identified but in much smaller quantities. Siew et al. investigated the syngas production from glycerol-dry(CO_2) reforming over La-promoted Ni/ Al_2O_3 catalyst and concluded that the addition of lanthana was responsible for improved metal dispersion. Moreover, their longevity run revealed that the promoted catalyst gave a stable performance [51,52]. In a more recent study, Kousi et al. [53] examined the effects on the physicochemical characteristics and catalytic performance of the addition of lanthanum on Ni/Al catalysts (the Ni/LaAl catalyst contained 10 and 17 wt. % Ni and La, respectively). Catalytic performance was investigated in the temperature range of 400–800 °C for a WGFR of 20:1 (molar) and the conclusion drawn was that conversion to gas-phase products and hydrogen yield are enhanced by the addition of La_2O_3 to the support.

As has been reported by a number of researchers, the addition of lanthanide oxides (an alkaline component) may help with coke reduction by favoring the gasification of the deposited carbon species [54–58]. In fact, for nickel catalysts used in the traditional dry methane reforming (DMR) reaction, reports suggest that the basic character of La_2O_3 results in promotional effects, as it was found to favor CO_2 adsorption and dissociation, contributing to deposited carbon gasification and thus preventing deactivation [59–64]. Moreover, Martinez et al. [65] has reported an increase in Ni dispersion in samples

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