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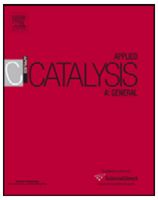

Review

Catalytic features of Rh and Ni supported catalysts in the steam reforming of glycerol to produce hydrogen

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ABSTRACT

Glycerol steam reforming on Rh and Ni supported catalyst was investigate in view to produce syn-gas to feed a high temperature fuel cell system (SOFC-MCFC). Results obtained revealed that glycerol is subjected to pyrolysis phenomena and at temperature higher than 720 K drastically decomposes before to reach the catalyst surface. Rh/Al_2O_3 catalyst resulted to be more active and stable than Ni supported catalysts but independently from the catalyst used (Rh or Ni) and temperature investigated, the reaction is affected by coke formation mainly promoted by the large presence of olefins formed by glycerol thermal decomposition. Even if for thermodynamic reasons the hydrogen production should be favored by operating at high temperature, results obtained demonstrate that it is more convenient to operate at temperature not higher than 923 K, since higher reaction temperature promotes the formation of encapsulated carbon which negatively reflects on catalyst stability.

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1. Introduction

The increasing commercial interest on diesel production by transesterification of vegetable oil aimed several research groups to investigate innovative routes to improve the economic balance of the overall process. For this purpose, most emphasis has been also addressed towards the development of processes that can convert the glycerol, the main by-product of FAME process, into added value chemicals like bio-fuels or hydrogen.

The amount of glycerol produced in the bio-fuel production process, which use vegetable oil as renewable source, is about the 17 wt% of the bio-diesel mass produced. The glycerol separated from bio-fuel contain about 20 wt% of water.

One promising way to use glycerol as carbon source is the production of hydrogen or syn-gas by steam reforming (SR) process in order to supply a solid oxide or molten carbonate fuel cells to produce electricity and heat [1,2].

Theoretical feasibility of the steam reforming process of glycerol has been demonstrated by different authors [3,4] in terms of hydrogen yield as a function of process temperature, pressure and steam/carbon ratio.

Steam reforming process of hydrocarbons is, as well known, a strongly endothermic reaction usually performed on Ni based catalysts that allow to obtain a hydrogen rich gas mixture containing H_2, CO_2, CH_4, CO and H_2O. However, the composition of reformed gas change as a function of operative conditions (temperature, pressure

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and steam/carbon ratio), while catalyst life is depending upon several deactivation phenomena that usually affect steam reforming reaction [5–7].

Ni/based catalysts, typically used for methane SR have been recently investigated to produce H_2 by SR of glycerol. In particular, Ni based catalysts investigated in aqueous phase reforming (AFR) of glycerol resulted to be affected by significant deactivation phenomena [5]. Ni appear more suitable for application on steam reforming of glycerol if supported on bare alumina [6] or modified with promoters [5,7]. These studies indicate that Ni catalysts are sufficiently active and selective to syn-gas production but coke formation represents a serious problem to overcame since glycerol give rise to the formation of several intermediate products that promote coke formation. Pt/alumina catalysts were also investigated in SR of glycerol [8] but, even if, higher reaction temperature enhances the overall reforming process, reaction pathways is characterized by several side reactions (like dehydration) that leads to carbon formation that negatively affects catalyst stability. Carbon formation has been also observed on La_2O_3 supported Ru catalysts [9].

On the basis of a preliminary experience acquired in the use of Rh and Ni catalysts to produce syn-gas by ethanol steam reforming [10,11], in this paper we have focused our attention to evaluate the behavior of such catalysts in the glycerol steam reforming. The study was focused to investigate the deactivation phenomena occurring on such systems with the objective to find technological solutions to design an active and stable catalyst for glycerol conversion into syn-gas.

2. Experimental

2.1. Catalyst preparation and characterization

Catalyst were prepared by impregnation (incipient wetness) using γ-Al_2O_3 AKZO-NOBEL 001-3P (SA (BET) 260 $m^2\,g^{-1}$), MgO Martin Marietta (SA (BET) 120 $m^2\,g^{-1}$) and CeO_2 ("*smoke powder*"; SA (BET): 27 $m^2\,g^{-1}$) as carriers. Before impregnation MgO was stabilized in steam atmosphere at 973 K for 12 h. Using a $RhCl_2$ aqueous solution for the preparation of 5% Rh/Al_2O_3 and Ni-acetate for the synthesis of 21% Ni/MgO. An aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ was used to synthesize 30% Ni/CeO_2 and 30% Ni/Al_2O_3 catalysts. All samples were dried at 353 K for 24 h and then air calcined at 673 K for 12 h. Catalysts were pressed at 400 bar, crushed and sieved and the 40–70 mesh fraction was used for the catalytic tests.

Table 1

	Metal loading (wt%)	MSA ($m^2{}_{Me/gcai}$)	BET_{SA} (m^2/g)	ds (nm)
Rh/Al_2O_3	5	8.1	163	2.1
Ni/Al_2O_3	30	12	44	7
Ni/MgO	21	6.3	45	8.1
Ni/CeO_2	30	6.2	27.2	22.8

The BET surface area and porosity of carriers have been determined in a conventional volumetric apparatus at 77 K with Carlo Erba Sorptomatic 1990 series instrument.

The metal particle size distribution of catalyst was evaluated by TEM analysis, using a Philips CM12 instrument provided with a high resolution camera which allow acquisition and elaboration of images. The samples were ultrasonically dispersed in isopropyl alcohol and deposited on a carbon supported film.

Carbon deposed during reaction was evaluated using a CHNS ThermoFlash EA 1112 Series instrument. Catalyst samples were treated at high temperature in air and the CO_2 produced by oxidation with oxygen was determined by a high sensitivity TC detector.

The main chemical–physical properties of the catalyst prepared according to the above procedure are reported in Table 1.

2.2. Catalytic measurements

The flow-sheet of glycerol steam reforming process is shown Fig. 1. Catalytic experiments were performed at atmospheric

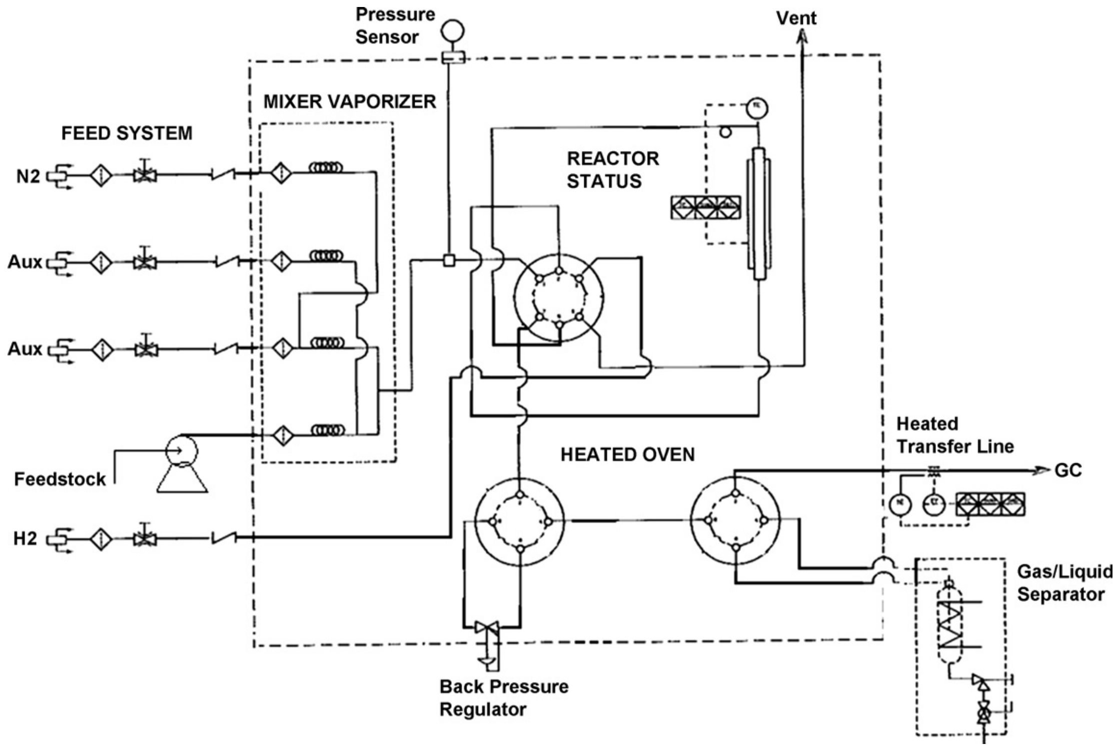

Fig. 1. Experimental set up used to perform the glycerol steam reforming reaction.