INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 9234–9244

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Promoting effect of Sn on supported Ni catalyst during steam reforming of glycerol

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ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form
4 April 2016
Accepted 18 April 2016
Available online 10 May 2016

Keywords:
Hydrogen production
Sn-addition
Coke deposition

ABSTRACT

The promoting effect of Sn on the catalytic performance of supported Ni catalyst in the reaction of glycerol steam reforming was studied. The physico-chemical properties of the prepared samples were investigated by X-ray fluorescence (XRF), BET surface area, *in situ* X-ray diffraction (XRD), laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and temperature-programmed oxidation (TPO) techniques. The characterization results of the samples after reduction treatment (in the same conditions than the activation before catalytic activity measurements) revealed the formation of Ni–Sn alloy. The Sn-doped catalyst exhibited a high activity and it was demonstrated that the Sn addition increase the catalyst stability and durability by decreasing the coke deposition.

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Introduction

During the last decades important efforts are ongoing to reduce fossil fuel dependency and greenhouse gas emissions. Among the different possibilities to find a viable option, the use of hydrogen as an energy carrier is considered to be an interesting alternative for the future and could have a crucial role in reducing atmospheric pollution. Biomass is considered as one of the most attractive renewable source for hydrogen production and numerous studies are being directed toward the development of novel technologies to produce hydrogen from biomass [1–4]. Steam reforming of glycerol is an important approach for hydrogen production from biomass. Glycerol is the main by-product generated in the biodiesel production. Biodiesel is one renewable biofuel obtained by catalytic trans-esterification of triglycerides with methanol [5]. About 10 wt.% of glycerol can be produced during the conversion of vegetable oils into biodiesel. The use of glycerol for hydrogen generation is a very advantageous option since its use would decrease the price of biodiesel making it more competitive [6].

The overall reaction of glycerol steam reforming is given by the following equation:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad (1)$$

which can be expressed as a combination of glycerol decomposition (2) and the water-gas shift reaction (3):

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad (2)$$

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http://dx.doi.org/10.1016/j.ijhydene.2016.04.119
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$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

Theoretically, a maximum of 7 mol of H_2 per mol of glycerol can be produced, although this ratio depends on the reaction conditions such as temperature, pressure and steam-to-glycerol steam ratio.

Although the glycerol steam reforming process is very attractive and it could be developed on an industrial-scale, it has some challenges that must to be overcome in order to accomplish its effective commercialization. For example, the process is an endothermic reaction and requires high temperatures increasing the operation costs. Besides, the catalyst deactivation by coke deposition is also an issue since it affects hydrogen yield and long term operation. With the aim of overcoming these challenges, the development of active, stable and inexpensive catalytic materials is mandatory. Catalysts containing group 8–10 metals such as Ni [7–12], Co [13–16], Pt [17–21], Ru [22–24], Rh [25], Pd [26] or Ir [27] on different oxides have been largely investigated as active catalysts for glycerol steam reforming. Ni-supported is one of the most promising active metals for such an application because of its high activity, low cost and wide availability. However, Ni-based catalysts suffer deactivation by coke deposition on the catalyst surface that block active sites and favour side reactions. Deactivation of nickel-based catalysts by sintering of nickel crystallites is another important drawback. Promoting nickel catalysts with a second metal has been proven to be one of the most promising approach to obtain more stable and optimal catalysts [28]. Bimetallic catalysts comprising Sn as a Ni promoter have been proved to outperform Ni monometallic catalyst in steam reforming processes [29]. The coke deposition can be markedly reduced by using Sn-doped catalysts in the steam reforming reaction to generate hydrogen from hydrocarbons. Sn alloyed with nickel prevents the formation of nickel atom ensembles, which are the responsible of the coke formation, and avoids the diffusion of carbon to form larger coke agglomerates [30]. Therefore, NiSn-based catalysts have the potential to decrease the catalyst deactivation caused by coking maintaining its high specific activity. Sn-doped Ni catalysts have been reported for aqueous phase reforming [31,32] and methane steam reforming [33] where the formation Ni_xSn_y alloys play a key role to inhibit coke deposition. Pengpanich et al. [34] reported a clear example of this positive effect in the partial oxidation of iso-octane. These authors found that the addition of small amounts of tin decreased by more than 50% the formation of carbon deposits without changes in the conversion. This enhancement was ascribed to the ability of Sn to reduce the growth of carbon filament by retarding carbon solubility in the Ni particles [28]. Moreover, Saadi et al. [35] have demonstrated, using density functional theory (DFT) calculations, the ability of Ni–Sn to inhibit graphite formation during steam reforming reactions. They demonstrated that the presence of Sn increases the C–C bond formation barrier.

We have investigated previously the effect of the nature of the support (acidity, basicity and redox properties) in the catalytic performance of Sn-doped Ni catalysts during the steam reforming of alcohols [36–38]. The objective of the present work is to investigate the effect of tin on the catalytic performance of Ni-supported catalysts in terms of activity, selectivity and durability in the steam reforming of glycerol.

Experimental

Catalysts preparation

The alumina support was obtained by ball milling spherical alumina pellets (*SASOL*, 1.78 mm diameter), by using a PM4 Retsch instrument particle sizes in 7–8 μm range were achieved. A monometallic Ni-based catalyst was prepared by impregnating the alumina with an aqueous solution of all the inorganic precursors with the desired concentrations of cerium (III) nitrate hexahydrate (*Sigma–Aldrich*), magnesium nitrate hexahydrate (*Sigma–Aldrich*), and nickel (II) nitrate hexahydrate (*Sigma–Aldrich*). Then, the sample was dried overnight at 100 °C and calcined at 700 °C for 12 h in flowing air using a heating rate of 10 C min^{-1} to obtain 20 wt.%Ni, 12 wt.% CeO_2, 8 wt.%MgO, and 60 wt.%Al_2O_3. The bimetallic NiSn catalyst was prepared following the same procedure but substituting a fraction of the nickel salt by the adequate amount of anhydrous tin chloride (*Fluka*) in order to obtain 17 wt.%Ni, 3 wt.%Sn, 12 wt.%CeO_2, 8 wt.%MgO, and 60 wt.%Al_2O_3. The resulting catalysts were labelled as Ni/CeMgAl and Ni–Sn/CeMgAl, respectively.

Materials characterization

The chemical composition of the samples was determined by X-ray fluorescence (XRF) spectroscopy in a Panalytical AXIOS PW4400 sequential spectrometer with Rh tube as source of radiation. The analysis were carried out onto pressed wafers containing 6 wt.% of wax. The textural properties (BET surface, pore size and pore volume) were studied by nitrogen physical adsorption–desorption isotherms at 77 K with Micromeritics ASAP 2010 equipment. Before each measurement, the samples were outgassed for 2 h at 150 °C in vacuum to remove the adsorbed impurities. X-ray diffraction (XRD) analysis was performed on a Siemens D-500 diffractometer using Cu Kα radiation (40 mA, 40 kV) and a position-sensitive detector using a step size of 0.05° and a step time of 1 s. The reducibility of the catalysts was investigated by *in situ* XRD analysis using a high temperature camera Anton Paar HTK 1200 coupled with an X'Pert Pro Philips diffractometer. The system was equipped with X'Celerator detector with a step of 0.05° and an equivalent time acquisition of 30 s. The diffractograms were recorded in the 25–900 °C temperature range under a flow of 100 mL min^{-1} (5% H_2 in Ar). Surface characterization was carried out by X-ray photoelectron microscopy (XPS) on a Leybold-Heraeus spectrometer (LHS-10/20), working with a constant pass energy of 50 eV and vacuum of 5×10^{-9} Torr. The system was equipped with an EA-200 MCD hemispherical electron analyser with a dual X-ray source working with Al Kα radiation (1486.6 eV) at 120 W and 30 mA. Binding energies were referenced to the spurious C (1s) signal at 284.6 eV and the atomic composition was estimated by the elemental sensitivity factor of each atom. Before each analysis, the sample was reduced in an external tube furnace for 1 h at 750 °C under a total flow of 100 mL min^{-1} (50% H_2 in

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