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Glycerol steam reforming on bimetallic NiSn/CeO_2–MgO–Al_2O_3 catalysts: Influence of the support, reaction parameters and deactivation/regeneration processes

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ABSTRACT

NiSn bimetallic catalysts supported over Al_2O_3 modified with different promoter (Mg and/or Ce) were prepared and characterized by powder X-ray diffraction (XRD), N_2 sorptometry, and temperature programmed reduction (TPR). Hydrogen production by glycerol steam reforming over these catalysts was investigated. Among the catalysts, NiSn/AlMgCe catalyst shows the highest hydrogen yield as well as the best stability during the reaction. The effect of reaction temperature, water/glycerol molar ratio and space velocity on the glycerol steam reforming over NiSn/AlMgCe were also investigated. Finally, it was verified that the catalyst can be regenerated by oxidation of carbonaceous deposits.

1. Introduction

With the depletion of fossil fuels and the environmental problems resulting from their combustion, it is urgent to find new energetic alternatives replacing the fossil fuels [1]. Hydrogen produced from renewable resources such as biomass appear to be one of the most effective solutions for the future due to the carbon neutral emissions and their lesser effects on the environment [2]. Among the products that may be considered as derivative of the biomass, biodiesel takes a special importance. Biodiesel is produced *via* transesterification of vegetable oil or animal fat reacted with methanol or ethanol generating about 10 wt.% of glycerol as by-product. The growing production of biodiesel expected for the next years implies that a high quantity of glycerol will be generated in the future as a waste of biodiesel production and the current market for glycerol will not be able to absorb the expected quantities of this by-product [3–5]. In this respect, the search of alternative uses of glycerol becomes an essential and the hydrogen production from glycerol is among the most attractive.

Hydrogen can be produced from glycerol by catalytic steam reforming [6], oxidative steam [7], and autothermal method [8] or by aqueous phase reforming (APR) [9]. Steam reforming is one of the most used reactions since although is highly endothermic the low pressure favors the selectivity to hydrogen.

Different catalyst formulations have been proposed for the glycerol steam reforming using metals having the ability to cleavage of C—C, O—H and C—H bonds of the hydrocarbon. In comparison with noble metal-based catalysts, nickel is one of the most promising active phases because of its low cost and wide availability, especially if it was highly dispersed over the support. However, its higher tendency to deactivation by coking and sintering are the main causes of catalyst failure. In previous studies devoted to improve the stability of Ni-based catalysts, Dumesic's group [9] have proposed that addition of Sn results in an increased selectivity to hydrogen production by decreasing the selectivity toward the formation of alkanes (precursors of the coke formation) of these catalysts.

The nature of the support strongly influences the catalytic performance of Ni supported catalysts in the steam reforming of alcohols: (i) it activates the dissociation of water into hydroxyl groups and promotes the migration of these species toward the metal particles, where formation of CO_x and hydrogen takes place; and (ii) it contributes to the stabilization of the metal particles at high temperature under steam [10–13]. Among the metallic oxides, alumina-based supports are often used in reforming

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processes because of their mechanical and chemical resistance under reaction conditions. Nevertheless the acidic site of the alumina surface favors the alcohols dehydration generating ethylene and/or other coke precursors. Thus, basic additives or promoters that favor water adsorption and OH surface mobility are typically added to the Al_2O_3 in order to neutralize its acidity, so lowering the rate of coke deposition on catalyst surfaces [14]. Alternatively, coking may be reduced by gasification of the deposited carbon species [15–17]. The addition of alkaline components such as MgO, K_2O [18] or lanthanide oxides [19–21] is usually used to favors the gasification of coke. The combination of adding a basic promoter and an alloying element like Sn must result in active and coke-resistant Ni catalysts, adequate to be used in hydrocarbons reforming reactions.

In this work both strategies have been used in order to obtain active and stable catalysts for glycerol steam reforming reaction. A series of catalysts formulations based on NiSn as active phase and γ-Al_2O_3 modified with MgO and/or CeO_2 as support were tested under the most optimal conditions predicted from the thermodynamic analysis to maximize the hydrogen production (650 °C, water/glycerol molar ratio = 12 and atmospheric pressure). The effect of the operating conditions (temperature, space velocity and molar composition feed) and the catalytic stability were investigated on the most optimal catalyst. Finally, deactivation/regeneration processes were analyzed in successive cycles of reaction with longer time of reaction.

2. Experimental

2.1. Preparation and characterization

Spherical pellets of γ-Al_2O_3 (*Spheralite SCS505*) with 2.5 mm diameter were milled in a high-energy ball milling with stainless steel ball (22 balls, 15 mm diameter). Besides, ethanol was added to avoid the agglomeration of particles. The alumina to ethanol weight ratio was 2.5:1. In a typical experiment, alumina and ethanol were mixed and then milled for 2 h at 300 rpm. This method permitted to obtain Al_2O_3 with a particle size of 7–8 µm, which was used to prepare all the materials used in this study.

A series of catalysts supported on milled γ-Al_2O_3 having a 26 wt.% NiSn loading with a 17:9 Ni:Sn weight ratio and variable loading of MgO and/or CeO_2 (Table 1) were prepared by the impregnation method. All the precursors were impregnated simultaneously with an aqueous solution of the required concentrations of $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich) and $SnCl_2$ anhydrous (Sigma Aldrich) to achieve a Ni/Sn = 1.88 weight ratio and the corresponding precursor promoter $Ce(NO_3)_3{\cdot}6H_2O$ (Sigma–Aldrich) and/or $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich). The concentrations of all the precursors were adjusted to generate the loads indicated in Table 1. The solids were dried at 100 °C overnight, and then calcined at 700 °C for 12 h in flowing 0.1%NO_x/He/10%H_2O/synthetic air. The calcination process is performed in NO_x atmosphere in order to obtain better dispersion of Ni particles [22]. Catalysts were designated as NiSn–Al, NiSn–AlMg, NiSn–AlCe, and NiSn–AlMgCe. In order to compare the supports and catalysts, the solids without nickel and tin were prepared following the same methodology and named in a similar manner but without NiSn.

BET specific surface areas, pore sizes and pore volume were measured through nitrogen adsorption–desorption isotherms at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. Before analysis, the samples were outgassed for 2 h at 150 °C in vacuum.

X-ray diffraction (XRD) analysis was performed in a Siemens D-500 diffractometer. Diffraction patterns were recorded 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 temperature programmed reduction (TPR) experiments were carried out in a conventional quartz reactor coupled to a thermal conductivity detector (TCD). The reactive gas stream (5%, v/v H_2/Ar) with a flow rate of 50 mL min^{-1} was flown through 50 mg of sample and the temperature rose at 10 °C min^{-1} from room temperature to 900 °C. A molecular sieve 13× was used to retain the H_2O produced during the reduction.

The surface acidity of the catalysts and supports was investigated by means of a Fourier transform infrared spectroscopic (FT-IR) study of pyridine adsorption. Spectra of adsorbed pyridine were recorded on a Nicolet Avatar 380 FTIR spectrometer equipped with a DTGS detector. The samples were pressed into self-supporting disks, placed in a quartz IR cell and treated under vacuum (10–6 Torr) at 600 °C for 1 h. After cooling at room temperature, the samples were exposed to subsequent doses of pyridine until surface saturation and spectra (128 scans, 2 cm^{-1} resolution) were recorded after addition of each one of the doses. The thermal stability of the species formed on the surface was also studied.

FT-IR spectra of the fresh and spent catalysts were collected in self-supporting disks of KBr diluted samples using a Thermo Nicolet Nexus infrared spectrometer equipped with KBr optics and a MCT/B detector working at liquid nitrogen temperature. Spectra were recorded at 4 cm^{-1} resolution in the 400–4000 cm^{-1} range accumulating 32 scans.

2.2. Catalyst performance testing

The catalytic glycerol steam reforming was carried out in a commercial computerized Microactivity Reference Catalytic Reactor from PiD Eng&Tech, employing a Hastelloy C-276 tubular reactor (Autoclave Engineers) with 9 mm internal diameter. Prior to reaction, the catalyst was reduced at 750 °C for 1 h passing 100 mL min^{-1} of H_2 (50%, v/v in inert). In all the catalytic tests, catalysts were ground and sieved in the size range 100–200 µm. Besides, catalysts (100 mg) were diluted with quartz (100 mg) of the same particle size. Gas products were analyzed on line using a microGC (Varian 4900) equipped with Porapak Q and MS-5A columns and nitrogen as internal standard. Condensable products and glycerol not transformed were analyzed by HPLC (Varian 356-LC) equipped with a Refractive Index Detector and a *Hi-Plex H* column with deionized water as eluent.

In order to evaluate the recovery of catalytic activity were performed three reaction cycles of 18 h making intermediates states of regeneration between each one. Reaction conditions were 750 °C, water-to-glycerol molar ratio equal to 12 and space velocity 100 L g^{-1} h^{-1}. The catalyst regeneration was performed at 750 °C flowing 100 mL min^{-1} of nitrogen during 1 h to remove the most unstable species and subsequently passing 100 mL min^{-1} of air during 1 h to oxidize the possible coke deposited. After oxidation, the catalyst was activated during 1 h flowing 100 mL min^{-1} of H_2 (50%, v/v in inert).

The performance of the catalysts was evaluated in terms of glycerol total conversion, X (Eq. (1)), glycerol conversion into gaseous products, $X_{\text{gas phase}}$ (Eq. (2)), and glycerol conversion into condensable products, $X_{\text{liquid phase}}$ (Eq. (3)). These parameters were calculated based on the following equations:

$$X(\%) = \frac{n_{\text{glycerol in}} - n_{\text{glycerol out}}}{n_{\text{glycerol in}}} \times 100 \quad (1)$$

$$X_{\text{gas phase}}(\%) = \frac{n_{CO} + n_{CO_2} + 2 \times n_{C_2H_4} + n_{CH_4}}{3 \times n_{\text{glycerol in}}} \times 100 \quad (2)$$

$$X_{\text{liquid phase}}(\%) = \frac{\sum\limits_{i=1} x_i \times n_i}{3 \times n_{\text{glycerol in}}} \times 100 \quad (3)$$