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Hydrogen production by crude glycerol steam reforming over Ni–La–Ti mixed oxide catalysts

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ABSTRACT

The production of H₂-rich gaseous mixtures from steam reforming of crude glycerol was investigated on ternary Ni–La–Ti catalysts. Ni–La–Ti mixed oxides containing 15 wt% of Ni and a La/Ti atomic ratio of 1 were prepared by a coprecipitation method and characterized by a variety of physical and spectroscopic techniques. Samples were calcined in air at 700 °C or 850 °C for 2 h. Ni–La–Ti samples calcined at 700 °C (NiLaTi700) showed a well-defined NiO phase and an amorphous La–Ti mixed oxide, while those calcined at 850 °C (NiLaTi850), exhibited two well defined phases of NiO and LaTiO₃ perovskite, respectively. NiO was completely reduced to metallic Ni on both solids under pure H₂ at 650 °C and the resulting Ni⁰ phase remained as a separate phase under the steam reforming conditions. Standard catalytic tests for the steam reforming of glycerol were performed at 500 °C or 650 °C by feeding the fixed-bed tubular reactor with a crude glycerol:water solution containing 30 wt% glycerol. The best results were achieved on NiLaTi700 at 650 °C, obtaining H₂ yields and H₂/CO₂ molar ratios close to the theoretical values predicted by the steam reforming reaction stoichiometry. A slight activity decay was observed on NiLaTi700 with the progress of the reaction, probably reflecting the formation of small amounts of coke.

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Introduction

Glycerol is the main by-product of the vegetable oils transesterification with methanol which is nowadays the most widespread method for biodiesel production. At industrial level, crude glycerol (CG) is a low-value product that is obtained in a glycerol:biodiesel = 1:10 per weight ratio and

contains impurities such as methanol, solvents and inorganic salts [1]. Because of the increasing worldwide biodiesel production, the development of efficient technologies to convert crude glycerol into more valuable products has been widely investigated in order to offset the cost in biodiesel production [2,3]. In particular, steam reforming is an attractive method to process glycerol because hydrogen-rich gas mixtures that can

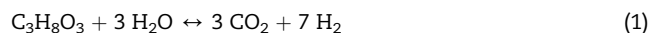
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be used to generate electricity directly in either a fuel cell or a gas turbine are obtained [4,5]. Several research groups have paid attention to the catalytic steam reforming (SR) of pure glycerol [6–11]. The gas-phase reaction takes place according to the following stoichiometry [8,10]:



In contrast, very few studies have been performed using CG as carbon source [11–13], probably because the catalyst is often rapidly deactivated by the CG impurities. Table 1 summarizes the results reported in the literature.

Some of the impurities, such as methanol, are easily decomposed, so its removal step, which is required to upgrade crude glycerol to value-added products, is avoided by using the steam reforming process. Other impurities, such as unreacted triglycerides and biodiesel catalyst residues, are undesirable to the reforming process since they contribute to increase deposit formation, pore clogging and catalyst deactivation. Catalytic bed regeneration becomes thus a key aspect to be handled in this case in order to extend catalyst lifetime and reduce energy consumption as much as possible. Nickel catalysts are particularly attractive for promoting the CG steam reforming because of the high activity of Ni and its lower cost compared with noble metals (Ru, Rh, Pt) [8,15,16]. Different oxides like SiO₂, Al₂O₃, MgO, La₂O₃, CeO₂, ZrO₂, TiO₂ or their mixtures are used to provide high Ni dispersion as well as suitable thermal, mechanical and chemical properties [17,18]. Several deactivation phenomena may take place in steam reforming reactions. On one hand, carbon deposits are formed by side reactions involving the formation of non-volatile compounds by polymerization of CH_x species and/or CO dissociation. The tendency to carbon deposition depends on the atomic ratio O/C and H/C in the feed gas. Lower H₂O/HC and H₂/CO ratios correspond to higher tendency toward coke formation. On the other hand, metal sintering, and consequently the loss of active sites, is favored under steam reforming conditions [17,19–21]. The support properties play a significant role regarding catalyst deactivation; for example, in the case of Ni-based catalysts the following decreasing stability order was observed for glycerol steam reforming: Ni/SiO₂ > Ni/ZrO₂ > Ni/Al₂O₃ [17]. Catalyst stability and activity also depends on the preparation method. It has been reported that Ni catalysts prepared by solid phase extraction (SFE) techniques display well stabilized Ni species and are very active and selective in steam reforming reactions [22–25]. Ni crystallites highly dispersed into a suitable oxide support are obtained after a thermal and/or reducing treatment of a mixed

oxide precursor. In previous works [26–28] we have studied the steam reforming of ethanol and glycerol on ternary Ni–La–Zr mixed oxides containing 5 wt% and 10 wt% of Ni. Nanosized crystallites of metallic Ni and a pyrochlore compound La₂Zr₂O₇ remained as the unique phases under typical reforming conditions. High conversion to gas phase products and H₂ yields close to the thermodynamic limits were achieved. Good stability was also observed and ascribed to very low carbon formation. Other metals commonly used in the preparation of conventional supported catalysts can be used for the preparation of Ni catalysts with the same techniques. In this sense, the ternary Ni–La–Ti system was selected as a starting material on the basis of its properties to yield metallic Ni and a lanthanum titanate compound under typical reforming experimental conditions [29]. Additionally, lanthanum titanates are known by their high thermal stability and chemical resistance against typical corrosion agents including alkaline metal compounds [30]. Chemical inertness could contribute to preserve not only textural and structural properties of the catalyst but also the properties (amount and intrinsic activity) of the different active sites involved in the whole reaction mechanism.

The aim of the present work is to study the ternary Ni–La–Ti mixed oxide system for the preparation of Ni catalysts by a SFC method and their behavior in the steam reforming of glycerol. Crude glycerol without any process of purification was used in the reforming tests.

Materials and methods

Materials

Nickel nitrate Ni(NO₃)₂·6H₂O, lanthanum nitrate La(NO₃)₃·6H₂O, titanium isopropoxide (Ti(OCH(CH₃)₂)₄) and oxalic acid (HO₂CCO₂H) were purchased from Sigma–Aldrich. Ethanol was purchased from Carlo Erba. All chemicals were reagent-grade and were used as received. The CG used in the present work mainly consists of 64 wt% glycerol, inorganic salts 5.7 wt%, methanol and water lower than 5 wt% and polyglycerol impurities up to 26 wt%, provided by the manufacturer. Potassium methylate was used as transesterification catalyst. CG composition was determined by elemental analysis (Thermo Scientific Flash 2000). Other CG characterizations were reported elsewhere [14]. The calculated average elemental molar formula for CG determined from these results was C_{3.5}H_{9.0}O_{3.1} and was used to calculate conversion and yield parameters.

Table 1 – Studies of CG steam reforming.

| Method | Catalyst | Reaction conditions | | | Stability | Reference |
|-------------------|---|---------------------|---------|--|-----------|-----------|
| | | S/C | T (°C) | WHSV _{GC} ^b (h ⁻¹) | | |
| SR | Pt (0, 5%)/Al ₂ O ₃ | 1.35 | 800 | 0.79–1.58 | 10 h | [11] |
| SESR ^a | 20%Ni–20%Co/HT | 3.0 | 525–600 | 0.9 | 150 min | [12] |
| SESR | 18%NiO/Al ₂ O ₃ | 3.0 | 400–700 | 0.34 | 15 min | [13] |
| SR | Ni10%Mg10%/AC | 3.7 | 650 | 3 | 6 h | [14] |

^a Sorption enhanced steam reforming.

^b WHSV_{GC} defined as the ratio between the mass flow rate of crude glycerol fed and the mass of catalyst.

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