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Steam reforming of ethanol over Ni-based catalysts obtained from $LaNiO_3$ and $LaNiO_3/CeSiO_2$ perovskite-type oxides for the production of hydrogen

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ABSTRACT

This work studied the performance of Ni-based catalysts derived from $LaNiO_3$ and $CeSiO_2$ supported $LaNiO_3$ perovskite-type oxides for the steam reforming of ethanol. In situ XRD and TPR revealed the presence of different Ni species on both calcined samples: $LaNiO_3$, La_2NiO_4 and NiO phases. Both catalysts deactivated during the reaction. Ni sintering was ruled out based on the in situ XRD experiments under reaction conditions. For $LaNiO_3$, metallic Ni particles were partially oxidized by the water present in the feed at the beginning of the reaction. Then, NiO particles formed were reduced again by the syngas produced during the reaction. TG analysis showed significant carbon formation on $LaNiO_3$ catalyst. However, carbon formation was significantly decreased over $LaNiO_3/CeSiO_2$ catalyst, which was due to the important role of the support on the mechanism of carbon removal for steam reforming of ethanol.

1. Introduction

Recently, ethanol has been claimed to be an attractive fuel for hydrogen production, since it can be manufactured from biomass and thus not contribute to net CO_2 emissions. Moreover, in countries like Brazil and the USA, ethanol production and distribution infrastructure is already established [1].

Hydrogen may be generated from ethanol by steam reforming (SR) (Eq. (1)) [2–8]. However, one of the main barriers of the SR of ethanol technology is the catalyst deactivation that occurs mainly due to carbon deposition on catalyst surface, which may lead to a decrease in catalytic activity and selectivity toward hydrogen [2–8].

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (1)$$

Carbon formation may take place via several reactions, such as ethanol dehydration to ethylene (Eq. (2)), followed by polymerization to coke (Eq. (3)); the “Boudouard” reaction (Eq. (4)); the decomposition of methane (Eq. (5)) [6,7]. The extent of each reaction depends on both reaction conditions and catalyst used. Therefore, the development of a catalyst resistant to carbon deposition during SR of ethanol is one of the main issues of this technology.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (2)$$

$$C_2H_4 \rightarrow \text{polymers} \rightarrow \text{coke} \quad (3)$$

$$2CO \leftrightarrow CO_2 + C \quad (4)$$

$$CH_4 \leftrightarrow 2H_2 + C \quad (5)$$

Ni-based catalysts have been extensively studied for the SR of ethanol due to their low cost and high activity but this metal is prone to coking [9–11].

In order to suppress carbon deposition, different approaches have been used, such as: (i) controlling the nickel crystallite size and (ii) using redox supports [6].

The nickel particle size significantly influences the nucleation rate of carbon. The initiation step for carbon formation is more difficult for smaller particle sizes [12]. A critical ensemble size (ensembles of 6–7 atoms) was proposed, below which carbon formation does not occur.

Several works in the literature [11,13–19] reported that perovskite-type oxides are promising precursor catalyst for SR of ethanol. The reduction of this mixed oxide produces thermally

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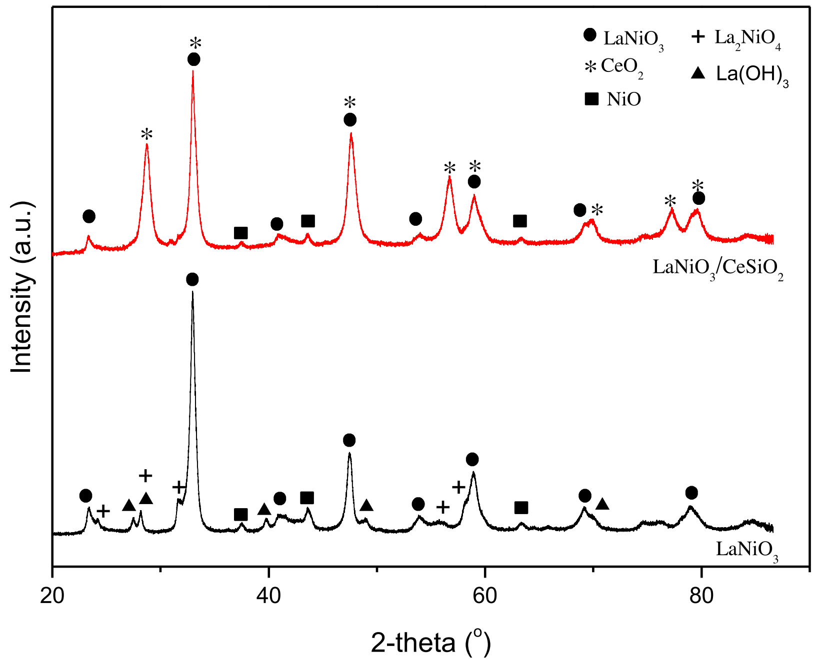

Fig. 1. X-ray diffraction patterns obtained for calcined samples.

stable and highly dispersed metallic particles [20]. However, the high reduction temperatures required for the removal of metal from the perovskite structure leads to the generation of large metallic Ni particles, which limits the effectiveness of this strategy [21]. One alternative is to deposit the perovskite-type oxides over a high surface area support. Different supported perovskite-type oxides have been reported in the literature for several reactions such as CO oxidation ($LaCoO_3/Al_2O_3$ [21]; $LaMO_3/ZrO_2$, M = Ni, Co, Fe [22]; $LaCo_{0.5}M_{0.5}O_3$/cordierite [23] $LaCoO_3/ZrO_2$ [24]), hydrocarbon combustion ($LaMnO_3/MgO$ [25]; $LaMnO_3/ZrO_2$ [26]; $LaMnO_3/Al_2O_3$ [27]; $LaFeO_3/Al_2O_3$ [28]), steam reforming of methane ($LaNiO_3/Al_2O_3$ and $LaNiO_3/ZrO_2$ [29]), conversion of tar ($LaCoO_3/Al_2O_3$ [30]), NO_x reduction ($LaCoO_3/K_2CO_3/CeO_2$ [31]). However, there is no work in the literature that studies the performance of supported perovskite-type oxides for SR of ethanol.

The type of support affects the product distribution and catalyst stability during ethanol conversion reactions since it also exhibits activity for this reaction. In the case of redox supports like ceria or ceria-mixed oxides, their high oxygen mobility promotes the mechanism of carbon removal, which in turn contributes to the high stability of the catalysts on ethanol conversion reactions [6,32]. Doping ceria with silica not only improves oxygen mobility but also inhibits the sintering of CeO_2 crystallites [33].

Therefore, the aim of this work is to study the performance of Ni-based catalysts prepared from $LaNiO_3$ and $CeSiO_2$ supported $LaNiO_3$ perovskite-type oxide for the production of hydrogen through SR of ethanol at different temperatures. In situ X-ray diffraction analyses (XRD) were also performed, which allowed to monitor changes on the catalyst structure during the reduction and SR of ethanol reaction.

2. Experimental

2.1. Catalysts preparation

The perovskite-type oxide was prepared by combustion method, using a fuel-to-oxidizers ratio (φ) of 0.7, which was defined as the ratio of the total valences of fuel (urea) to the total valence of oxidizers (nitrates of nickel and lanthanum) [10]. The combustion method exhibits several advantages such as low processing cost, simplicity and high production rate. Furthermore, this method is appropriated for the preparation of monolithic catalysts by dip-coating. The aqueous suspension containing the adequate amount of urea and nitrate precursors was stirred on a heating plate until spontaneous ignition. The resulting samples were calcined in a muffle at 1073 K for 1 h and designated as $LaNiO_3$.

The preparation of CeO_2-SiO_2 support ($CeSiO_2$) followed the method described by Ribeiro et al. [34]. Initially, SiO_2 (Aerosil 200 – Degussa) was dissolved in a solution containing potassium hydroxide and thus, it was added to a solution of ammonium hydroxide. Then, a solution of $(NH_4)_2Ce(NO_3)_6{\cdot}6H_2O$ (Aldrich 98%) was added to the solution containing silica and maintained under stirring for 30 min. The precipitate was washed until pH = 7 and dried at 383 K for 12 h. The samples were calcined at 1073 K for 5 h under air flow.

For the $CeSiO_2$ supported $LaNiO_3$, the perovskite and the support powders were added to an ethanol solution that was left in an ultrasonic bath for 20 min. Subsequently, the material was kept under stirring for 30 min, and then the ethanol was removed using a rotary evaporator. The sample was dried at 383 K and calcined at 1073 K (10 K/min) for 5 h. The catalyst prepared contained 30 wt.% of perovskite over $CeSiO_2$ and it was named as $LaNiO_3/CeSiO_2$.

2.2. X-ray fluorescence (XRF)

The chemical composition of each sample was determined on a Bruker Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD-XRF) S8 Tiger with a rhodium tube operated at 4 kW. The analyses were performed with the samples (300 mg) in powder form using a semi-quantitative method (QUANT-EXPRES/Bruker).

2.3. BET surface area

The BET surface areas of the samples were measured using a Micromeritics ASAP 2020 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen.