Hydrogen production by steam reforming of m-cresol, a bio-oil model compound, using catalysts supported on conventional and unconventional supports

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ABSTRACT

The steam-reforming of a bio-oil model compound, like m-cresol, was performed in order to produce renewable hydrogen. Different nickel based catalysts supported on both conventional and unconventional supports, which had also been modified, were tested. Fresh and used catalysts were characterized using different techniques and this characterization was correlated with the reforming experiments results. The highest hydrogen yield was obtained with the catalyst supported on alumina modified with ceria, due to its high dispersion. The use of ceria as a support modifier promoted coke gasification and avoided catalytic deactivation through coking. The catalyst supported on olivine sand presented, among the unconventional supports, the highest hydrogen yield as a result of a recrystallization process that enhanced metal dispersion at high temperatures.

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Introduction

In view of the growing environmental concerns about global warming and fossil fuels depletion, major efforts are being dedicated to developing and using alternative energy sources. Hydrogen is considered an emerging energy carrier with significant environmental benefits, due to the fact that its combustion is free of pollutants [1]. Hydrogen can play a key role in the near future, due to its use not only as energy carrier but also in different industries (chemical, petrochemical and refining).

It can be produced from different sources through different processes, but it can be only considered a sustainable energy vector when produced from renewable sources. Nowadays most of the hydrogen produced worldwide is produced from fossil fuels via catalytic reforming processes or via partial oxidation.

One of the forthcoming sustainable pathways for producing hydrogen is steam-reforming of bio-oils derived from biomass, e.g. via fast pyrolysis. Bio-oils are a mixture of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, multifunctional compounds and also up to a 30 wt% of water [2].

One of the limits of hydrogen production via steam-reforming of the bio-oil is catalyst deactivation caused by carbon deposition. Hydrocarbons are adsorbed on catalyst surface and coke can be formed, blocking metal atoms. The parameter which influences most the coke formation rate is temperature, higher temperatures enhance coke formation rate.

In recent years, significant research has been performed on the steam-reforming of bio-oil and bio-oil derived model compounds [3–6].

Ni has been extensively used as an active metal for the steam reforming of oxygenates due to its high activity for C–C bond rupture and H_2. The conversion of the oxygenates has been found to increase with the increasing metal content in the catalytic system but a 10–15% Ni loading is generally preferred as higher loading has been reported to cause significant catalyst deactivation due to sintering [7].

The main goal of this study was the development of new catalytic systems to produce hydrogen via steam reforming of m-cresol ($T_{boil} = 475.2 \pm 0.9$ K), a bio-oil model compound. Steam reforming of m-cresol can be described by the following reaction:

$$C_7H_8O + 6H_2O \leftrightarrow 7CO + 10H_2 \quad \Delta H° = 810.85 \text{ kJ/mol}$$
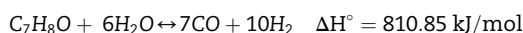
Another important reaction that occurs during the steam reforming process is water-gas shift (WGS).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H° = -41.15 \text{ kJ/mol}$$
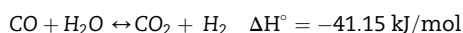
Assuming that both reactions go to completion, the overall reaction can be presented as follows [8]:

$$C_7H_8O + 13H_2O \leftrightarrow 7CO_2 + 17H_2 \quad \Delta H° = 522.77 \text{ kJ/mol}$$
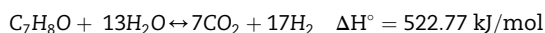
Different catalytic systems were tested in a bench scale plant, performing the steam reforming of m-cresol. The catalysts were based on nickel supported on different supports: I) conventional supports such as γ-Al_2O_3, α-Al_2O_3 II) conventional supports modified with CeO_2 and La_2O_3; III) unconventional supports such as olivine sand or zircon sand. These unconventional supports, which are one of the main innovations of the present work, are widely available and much cheaper than alumina. Nickel was selected as active metal, due to its high activity, high hydrogen selectivity and low cost compared to noble metals [9].

Materials and methods

Catalysts preparation

Catalysts were prepared by wet impregnation method. Supports were calcined, before the catalyst preparation, at 973 K during 4 h in air atmosphere in order to avoid structural changes after the impregnation. Different supports were employed for the catalysts preparation:

- γ-Al_2O_3 (Alfa-Aesar)
- α-Al_2O_3 (Alfa-Aesar)
- Olivine sand (48 wt% MgO, 41 wt% SiO_2, 8 wt% Fe_2O_3), provided by a casting company "Ilarduya y Cía"

- Zircon sand ($ZrSiO_4$), provided by a casting company "Ilarduya y Cía"

The metallic precursors employed for catalysts' preparation were the following:

- Nickel (II) nitrate hexahydrate (99.999 wt%, Sigma–Aldrich)
- Lanthanum (III) nitrate hexahydrate (99.9 wt%, Sigma–Aldrich)
- Cerium (III) nitrate hexahydrate (99.5 wt%, Sigma–Aldrich)

An appropriate amount of support and metallic precursor were mixed, with 10 ml of distilled water per gram of support, in order to prepare the catalysts with the desired composition (13 wt% nickel, 10 wt% CeO_2 or 6 wt% La_2O_3, depending on the catalyst). The composition of the catalyst was chosen taking into account results obtained in previous studies [10]. The suspension containing the support and the metallic precursor was mixed overnight, in order to obtain a homogeneous mixture of the two compounds. The excess of solvent was evaporated to dryness in a rotary evaporator; model Heidolph Laborota 4000. This rotary evaporator is equipped with a vacuum pump, used for reducing the boiling temperature of the solution. The evaporation of the excess of solvent was performed at 338 K and 40–100 mbar.

Once the solvent was evaporated, the resulting solid was introduced in an oven at 373 K during 1 h in order to ensure a complete drying. After this, the catalysts were calcined in air atmosphere at 973 K during 4 h. Finally, the calcined catalysts were pressed and sieved to the desired particle size: 0.42 mm < d_p < 0.50 mm. This particle size was selected in order to maintain a internal pipe diameter-to-particle diameter higher than 10 in order to avoid bypassing near the wall [11].

The prepared catalysts were named as: 13Ni/Al_2O_3 (γ), 13Ni/Al_2O_3 (α), 13Ni/olivine sand, 13Ni/zircon sand, 13Ni/10CeO_2–Al_2O_3 (γ) and 13Ni/6La_2O_3–Al_2O_3 (γ).

Catalyst characterization

Different characterization techniques were employed to determine the physicochemical properties of the fresh-reduced and used (after the reforming experiments) materials: hydrogen chemisorption, inductively coupled plasma-optical emission spectroscopy (ICP-OES), N_2 adsorption–desorption isotherms at 77 K, temperature-programmed reduction (TPR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS).

Hydrogen chemisorption: Autosorb 1C-TCD was employed for the determination of the nickel dispersion, active surface area and average crystallite size of the previously reduced nickel catalysts (under pure hydrogen flow of 40 Nml/min for 4 h at 973 K) by H_2-pulse chemisorption at 373 K. Metal dispersion was determined by assuming a stoichiometric ratio of H/Ni = 2.

ICP-OES: this technique was employed to determine the Ni, Ce and La contents in the catalysts. The solid samples were firstly disaggregated in acid solutions (mixture of HF, HNO_3