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## Nickel based monometallic and bimetallic catalysts for synthetic and real bio-oil steam reforming

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### ABSTRACT

Catalysts based on Ni supported on alumina were studied for steam reforming (SR) of a synthetic bio-oil/bio-glycerol mixture and a real bio-oil. Catalyst tests were carried out in a continuous fixed bed reactor at atmospheric pressure and steam to carbon (S/C) ratio of 5.0. In the case of experiments with the bio-oil/bio-glycerol mixture the initial temperature was 1073 K, then it was successively changed to 973 K and 1073 K again to assess catalyst deactivation. Experiments with the bio-oil sample were run at 1073 K. First, the effect of modifications to the alumina support with CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> was studied in monometallic catalysts. Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was identified as the catalyst more resistant to deactivation, likely due to its higher oxygen mobility, and selected for further tests. Then, bimetallic catalysts were produced by impregnation of noble metals (Pd, Pt or Rh) on the Ni catalyst supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Co-impregnation of Rh and Ni on the CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support represented a further improvement in the catalytic activity and stability respect to the monometallic catalyst, leading to stable gas compositions close to thermodynamic equilibrium due to the favourable Rh-Ni interactions. Rh-Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is therefore a promising catalyst to produce a hydrogen-rich gas from bio-oil SR.

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## Introduction

Global energy demand is increasing due to worldwide economic and industrial development [1]. However, the environmental issues associated to the use of fossil fuels, in which current energy systems are based, make the development of sustainable energy resources necessary. Hydrogen is recognized as an emerging energy carrier due to its clean combustion and high energy density [2]. Although, apart from the potential energetic applications of hydrogen, it currently plays

important roles in oil, chemical, metallurgical, petrochemical, food and fertilizer industries [3–5]. Nevertheless, in order for it to be carbon neutral, hydrogen needs to be produced from renewable resources, unlike the currently predominant hydrogen production processes based in the utilization of fossil fuels such as natural gas, heavy oil fractions and coal [6–8]. Biomass can be an alternative to overcome the above mentioned issues as it is widely available, carbon neutral and renewable [7]. The production of bio-oil by means of fast pyrolysis of biomass is a promising bio-fuel source, which can be

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used as a liquid fuel after upgrading or reformed to produce hydrogen or synthesis gas [9,10]. Additionally, bio-oils have higher energy densities than the original biomass and therefore bio-oil reforming may have certain advantages over direct gasification of biomass as a pathway towards hydrogen, in which smaller decentralized pyrolysis plants could feed larger central reforming units, decreasing the energy and emissions associated to transport of raw materials.

Bio-oils are complex mixtures of hundreds of organic compounds, including carboxylic acids, aldehydes, ketones, alcohols and phenols, among others. Bio-oil is a thermodynamically unstable product, and decomposition and coking reactions take place during its production and in downstream processes, giving rise to blockage of pipelines and reactor fouling. Therefore, physical and chemical bio-oil upgrading processes are needed and have been the subject of numerous studies [7,9–15]. Among various alternatives, bio-oil/bio-glycerol blends have been proposed as a stable liquid mixture with suitable rheological and fuel properties [13], which could solve above mentioned problems during catalytic bio-oil reforming.

For that process, a reforming catalyst must promote breaking of C–C, C–H and O–H bonds and production of H<sub>2</sub>, while being resistant to deactivation, which is typically due to carbon deposition [14,15]. Moreover, activity towards the water-gas shift reaction (WGS) contributes to increase H<sub>2</sub> selectivity. Therefore, a commercial reforming catalyst should present high and stable activity towards hydrogen; high ability to remove carbon and/or other carbonaceous species that cause deactivation from the catalyst surface; and should maintain those properties regardless of the variations on the reaction temperature that can take place in an industrial process. Thus, the most commonly used reforming catalysts are Ni-based, as Ni presents high activity in bond breaking and WGS, favouring hydrogen production [16,17]. In addition, Ni-based catalysts are cheaper than those containing noble metals [18]. However, Ni catalysts are prone to form carbon deposits and suffer from sintering during steam reforming (SR) reactions. Different alternatives such as changes in the preparation method, modification of the catalyst support or the addition of promoters have been studied as ways to address these drawbacks [18].

Regarding catalyst supports, reforming catalysts are usually supported on high surface area materials, such as alumina. The main role of the support is to prepare and preserve thermally-stable and well-dispersed catalysts during the reaction [16,19]. Support modification with CeO<sub>2</sub> provides the catalyst with ability for oxygen storage and release, reducing the amount of carbon formed on the catalyst surface, and produces a better metal dispersion [20]. Similarly, lanthanum oxides improve the metal dispersion and sintering resistance, enhancing catalyst stability [21]. Noble metals have been widely reported due to their high catalytic activity, efficiency and selectivity [22]. In addition, they are also used in other applications such as electronics, optics or anti corrosion materials because of their chemical and physical properties [23]. However, noble metals natural resources are characterized by their low availability and high cost, which makes them uneconomic and obstructs their promotion and practical applications [22–26]. Therefore, the development of catalysts

with low noble metal content became important for their use [26]. Accordingly, the incorporation of a small amount of a noble metal (Pd, Pt or Rh) has been observed to result in an improvement in the activity of the Ni-based catalyst and in an increase in its resistance to deactivation by coke deposition [27,28], while enhancing the selectivity to the desired compounds [29]. Thus, inexpensive but highly active bimetallic catalysts can be produced [29,30].

In this work, Ni-based catalysts supported on alumina were prepared. Firstly, the effect of the modification of the alumina support with CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> was tested in SR using both a mixture of model compounds (n-butanol, m-xylene, furfural, m-cresol, syringol and glycerol) simulating bio-oil/bio-glycerol blends and a real bio-oil as feedstock. Then, the effect of a noble metal incorporation in those SR processes was studied. Due to the large number of compounds present in the bio-oil, model compounds are commonly used in order to get a better understanding of the reactions taking place [12] and simplify the tests and computational modelling [31]. Thus, the main reactions with the model compounds used in this work are:

Eq.	Reaction	$\Delta H^0$ (KJ/mol)
(1)	n-butanol SR: $C_4H_{10}O + 3H_2O \leftrightarrow 4CO + 8H_2$	558
(2)	m-xylene SR: $C_8H_{10} + 8H_2O \leftrightarrow 8CO + 13H_2$	1031
(3)	Furfural SR: $C_5H_4O_2 + 3H_2O \leftrightarrow 5CO + 5H_2$	322
(4)	m-cresol SR: $C_7H_8O + 6H_2O \leftrightarrow 7CO + 10H_2$	808
(5)	Syringol SR: $C_8H_{10}O_3 + 5H_2O \leftrightarrow 8CO + 10H_2$	>0
(6)	Glycerol cracking: $C_3H_8O_3 \rightarrow 3CO + 4H_2$	244
(7)	Water Gas Shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$	-41

However, although the use of model compounds is common, there is a lack in the comparison of the catalytic activities in model compounds SR and real bio-oils SR. This paper tries to fill this gap and gain further insight on the matter. The most active formulation among those tested was used to prepare bimetallic Ni-noble metal catalysts by impregnation with Pd, Pt or Rh. These noble metals are known to be highly active, thermally stable and coke resistant [32–35]. A series of SR experiments were carried out to assess these bimetallic catalysts in bio-oil reforming under the same conditions in which monometallic catalysts were tested.

## Experimental procedure

### Catalyst preparation

Catalysts were prepared using the wet impregnation method as follows. First, alumina used as support was sieved to obtain a particle size in the range of 0.42–0.50 mm. Afterwards, it was heated up from 473 to 973 K in 3 h, calcined at 973 K for 4 h and cooled down to room temperature. CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> supports were prepared by weighting the desired amounts of cerium or lanthanum precursor salts (Cerium (III) nitrate hexahydrate, Alfa Aesar, or Lanthanum (III) nitrate

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