



Efficient and stable Ni–Ce glycerol reforming catalysts: Chemical imaging using X-ray electron and scanning transmission microscopy



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ABSTRACT

Nickel–ceria composite catalysts prepared by a microemulsion method showed outstanding catalytic behavior in hydrogen production by glycerol steam reforming. Contrarily to usual Ni-based catalysts, the system allows long-term stability and nearly absence of by-products, particularly methane and carbon monoxide. With the help of scanning transmission electron microscopy and energy dispersive X-ray spectroscopy we confirmed the key role played by an intimate intermixing of Ni and Ceria components at reaction conditions. In addition, chemical imaging maps as well as more conventional techniques, such as Temperature Programmed Oxidation (TPO) and X-ray Photoelectron Spectroscopy (XPS) were used to identify the carbon containing (including coke) species nature and to establishing their chemical relevance. Combination of these techniques points out that the optimum interphase contact, reached for a specific 20:80 molar Ni:Ce formulation, allows: (i) to keep the Ni particle size controlled with absence of significant formation of coke and thus without deleterious effects on the long-term stability of the catalysts; and (ii) to eliminate undesirable side reactions such as methanation.

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1. Introduction

The settlement of a hydrogen economy derived from renewable energy sources may provide significant benefits by solving problems related to the energy crisis and environmental pollution [1,2]. Among numerous renewable candidates, glycerol seems to provide significant advantages. Being a biomass derivative, glycerol is currently produced in large quantities in the process of transesterification of fatty acids into biodiesel [3]. During this process glycerol is normally generated at a rate of 1 mol of glycerol for every 3 mol of methyl ester synthesized, which accounts for approximately 10 wt% of the total product [2,3]. Other bio-based processes also produce glycerol; for example, up to 4 wt% of this molecule (with respect to the initial sugar weight) is obtained in fermentation of sugars oriented to ethanol formation [2]. Due to constant increment of biodiesel production it is estimated that by 2015, 1.54 million tons of glycerol will be generated worldwide [3]. Thus, in order to make the chemicals obtained from the biomass

sector competitive with chemicals from fossil fuels, all of this glycerol should be efficiently processed.

Bio-oils including glycerol have numerous potential applications which includes its usage in boilers for heat and electricity, in engines and turbines for electricity, in chemicals production such as phenols, organic acids, and oxygenates or in transportation fuel production [1–3]. The latter would be the more important from an economic point of view, however bio-oil derived transportation fuels require expensive upgrading techniques, and this route is currently less attractive for motor fuels production. To alleviate this disadvantage, reforming of bio-oil has been proposed and employed to produce hydrogen, a key fuel for the future.

The steam reforming of glycerol appears thus as a potential alternative for producing hydrogen in the near future with significant impact in the viability of numerous bio-refining processes [1–4]. Steam reforming of glycerol is an endothermic process and the offgas composition is governed by the (formal) equilibrium between the decomposition, reaction (1), water gas shift (WGS), reaction (2), and methanation, reaction (3) [5]:



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The first two provide a H_2/CO_2 ratio of 7/3 which will render the maximum attainable hydrogen yield. The third, methanation, is an almost unavoidable reaction in Ni-based catalysts which can limit such hydrogen yield. High temperatures will shift the decomposition (reaction (1)) and methanation (reaction (3)) steps to enhance production of H_2 . This however has concomitant detrimental effects in catalyst lifetime due to the aggregation of the active metals and carbon deposition [2].

In this context the search of active and stable, low-temperature glycerol reforming catalysts is a field of intense research [2]. Ni-based catalysts are among the best choices for the reaction not only from a catalytic but also from an economic point of view, due to its significantly lower price than other, alternative active metal typically used in this reaction, i.e. Pt [1,2]. Both metals, Ni and Pt, are active in dehydrogenation and decarbonylation reactions to produce hydrogen although Ni shows enhanced activity toward methanation. Enormous efforts have been made in Ni-based systems to control activity/selectivity in reforming reactions to favor hydrogen production, and to increase the resistance to carbon formation and sintering of the metal phase. Strategies related to regulating surface composition, tuning particle sizes and shapes, metal “encapsulation” by rigid supports, enhancing metal–support interaction, and fabricating hierarchical structures within the catalysts has been essayed with partial success [6–24].

In this contribution we exploit the development of a Ni–CeO₂ catalyst system based in a single pot preparation method yielding a fluorite-based mixed oxide. This system has been shown high activity in the WGS and ethanol reforming reactions as it evolves in a “composite” metal–oxide (nickel–ceria) solid with high interaction area among components [8,25]. In this work, we subjected such system to the more thought glycerol reforming test and founded superior performance in terms of activity/selectivity and stability. Specific nickel–ceria formulations having certain Ni/Ce atomic ratios show activity at relatively low temperatures, e.g. well below 873 K, and presents significant stability under reaction conditions due to the control of the structure/morphology of the solid-state components of the system as well as of the carbon formation process. To interpret the scientific bases of these features at atomic scale we present a scanning transmission electron imaging study with the aim of “chemically” discriminating between elements of the samples [26]. To this end, energy dispersive X-ray maps were obtained for a series of catalysts to track the evolution of metal, oxide and carbon phases present in spent catalysts. Combined with more conventional techniques such as X-ray diffraction, X-ray photoelectron spectroscopy and temperature programmed oxidation reaction, we would provide evidence of the key issues leading to highly active and stable Ni-based glycerol reforming catalysts.

2. Experimental

The Ce–Ni composite catalysts were prepared by employing reverse microemulsions following using *n*-heptane (Scharlau) as organic media, Triton X-100 (Aldrich) as surfactant and hexanol (Aldrich) as cosurfactant. Ce and Ni nitrates (Aldrich) were used as metal precursors [25]. Water/M (M = Ce + Ni) and water/surfactant molar ratios were, respectively, 110 and 18 for all Ce–Ni samples as well as a CeO₂ support reference. Systems are called Ni20 and Ni30 in correspondence of the molar percentage of Ni on cationic basis (equivalent to a 7.7 and 12.3 wt% of metallic Ni, respectively) as measured by X-ray Total Reflection Fluorescence (error below 3%). For the Ni20/CeO₂, the nickel nitrate has been used to impregnate the ceria support with the same loading as the Ni20 sample. Samples were dried overnight as subsequently calcined at 773 K during 2 h. Prior to reaction, samples were pre-reduced in 10%

H_2/He at 773 K during 2 h. For analysis (see below) of samples after reduction, they were transferred to the characterization technique cells in contact with air.

The BET surface area and average pore volume values were measured by nitrogen physisorption (Micromeritics ASAP 2010). XRD profiles were obtained with a Seifert D-500 diffractometer using Ni-filtered Cu K α radiation with a 0.02° step and fitted using the Von Dreele approach to the Le Bail method [27]; particle sizes and microstrain were measured with XRD using the Williamson–Hall formalism [28].

TEM analyses were done using a JEOL 2100F field emission electron gun microscope operated at 200 kV and equipped with an Energy-Dispersive X-Ray detector. The sample was ground until powder and a small amount was suspended in ethanol solution using an ultrasonic bath. Some drops were added to the copper grid (Aname, Lacey carbon 200 mesh) and the ethanol was evaporated at room temperature before introduce in the microscope. The Scanning Transmission Electron Microscopy (STEM) was done using a spot size of 1 nm.

The Temperature Programme Oxidation (TPO) analyses were done in a SDTQ600 5200 Thermogravimetric Analysis system. In this latter, the samples were heated from room temperature to 1173 K, with a heating rate of 8 K/min under pure air.

X-ray photoelectron spectra of the used samples were recorded with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyser and X-ray source (Mg K α) operated at 150 W, with pass energy of 50 eV. Each sample was pressed into a small pellet of 15 mm diameter and placed in the sample holder and fixed with a gold grid. The sample was degassed in the chamber for 6–8 h to achieve a dynamic vacuum below 10–8 Pa before analysis. The spectral data for each sample was analyzed using CASA XPS software. The Au 4f7/2 peak at 83.4 eV was used as an internal standard.

The glycerol steam reforming was conducted in a stainless steel fix-bed reactor (Length: 47 cm; inner diameter: 0.95 cm), operating at atmospheric pressure. The reactor was filled with 30 mg of catalyst and SiC was added to obtain 4 cm length. Prior to the catalytic test, the catalyst was reduced over 1 h with H_2 flow at 673 K increasing the temperature at 5 K/min. When the catalyst was reduced 50 mL/min of N_2 flow through the reactor and a mixture of 10 wt% (2.1 mol%) of glycerol in water (1 g/h) was added using a Controller Evaporator Mixture (CEM) (Bronkhorst) working at 473 K. After the CEM, all the system was heated to prevent condensation until the cooling system situated in the reactor exit. The outlet gas was analysed online with a GC equipped with two thermal conductivity detectors and one flame ionization detector (Bruker GC-450). The reaction test with water was done using the same experimental conditions and after reaction, the feed was changed to introduce 1 g/h of pure water.

For thermodynamic equilibrium calculations we used the Aspen-Hysys software. The Gibbs reactor was used to calculate the product composition behavior vs. temperature and other experimental variables using the condition of minimization of Gibbs free energy and the Peng–Robinson state equation due to its largest applicability range in terms of temperature, pressure and also because its suitability for systems containing hydrocarbons, water, air and combustion gases [29].

3. Results and discussion

The glycerol steam reforming activity of the Ni–Ce composite catalysts having 20 and 30 mol. Ni % on cation basis (called Ni20 and Ni30) and a reference Ni supported on CeO₂ (called Ni20/CeO₂) having the exact molar composition of the Ni20 catalyst were tested at 773 K. After stabilization on stream, the H_2/CO_2 ratio is 7/3 (within $\pm 8\%$) for the two composite materials indicating that

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