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Catalytic steam reforming of olive mill wastewater for hydrogen production

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ABSTRACT

Catalytic honeycombs functionalized with lanthanum-stabilized ceria as catalytic support and impregnated with different metals (Rh, Ru, Pt, Pd and Ni) were prepared and tested for hydrogen production through the steam reforming of distilled, three-phase olive mill wastewater (OMW). Tests were carried out at atmospheric pressure, different temperatures (873–1023 K), and space velocities (4500–16,000 h⁻¹) over catalytic honeycombs loaded with ca. 3 mg cm⁻² of catalyst. The catalytic performance was evaluated in terms of hydrogen production, selectivity of gaseous products and stability for 24 h. The best results were obtained over Pt- and Rh-based catalytic systems. Chemical oxygen demand values were determined to quantify the total organic content of OMW and post-reaction condensate to quantify the extension of the reaction. Total organic contents were found to be 5.4 mg L⁻¹ and 0.2–0.5 mg L⁻¹ in OMW distillate and post-reaction condensate, respectively, which leads to a 90–96 % of organic content removal during the steam reforming process. Up to 40 STP mL of pure hydrogen per mL of distilled olive mill wastewater were produced over Pt/CeLa at 973 K and 16,000 h⁻¹. X-ray photoelectron spectroscopy analyses revealed carbon and calcium deposition during catalytic reaction. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen will likely play an important role in near future energetic scenarios as a versatile energy vector. It is actually mainly produced from fossil fuels and steam reforming processes are the most common production methods to generate it. Approximately 50% of world's hydrogen production comes from the steam reforming of natural gas [1]. In recent years, many studies have been developed to produce hydrogen from renewable sources, like ethanol, bio-oil, acetic acid, glycerol,

etc. using steam reforming processes [2–6]. In this work, we investigate the steam reforming of olive mill wastewater (OMW) to produce hydrogen over different catalytic honeycombs for practical application. Olive mill wastewater is an environmental problem due to its high organic content [7], it is produced in large quantities, short period of time and has a variable composition depending on the olive type, weather conditions, and olive oil production method (two-phase centrifugation vs. three-phase centrifugation). The two-phase centrifugation method is gaining quote in the market rapidly due to its simplicity and less water demand.

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Phenolic compounds, fatty acids, lipids and sugars are the main components present in OMW, both in the two- and three-phase centrifugation methods. They are highly phytotoxic and their transformation may result in a great environmental problem that can negatively affect soils, aquatic ecosystems and even air medium [8]. This environmental issue is particularly appealing in Mediterranean countries. Currently, OMW is usually disposed in artificial ponds where warm temperatures favor evaporation. The remaining solid (sludge) can be then used as a fertilizer or as a heat source or just disposed on specific landfill. However, even if the sludge is a source of nutrients, the resulting phytotoxicity and acidification of the soil are unacceptable for agricultural purposes. Several physical, chemical and biological treatments like coagulation, precipitation, catalytic oxidation or digestion with microorganisms to produce biogas have been proposed in order to transform OMW to a less contaminant waste [9]. More recently, some methods have also been proposed to obtain hydrogen from OMW, such as dark fermentation and photofermentation [10,11] as well as electrohydrolysis [12].

In this context, Tosti et al. have recently proposed the use of the steam reforming of OMW to obtain hydrogen, facing two issues at the same time: the wastewater treatment and the hydrogen production. These authors used an unknown Pt-based catalyst in a Pd-membrane reactor (catalytic membrane reactor) and obtained up to 2 kg of H₂ per ton of OMW processed (distillate) at 723 K and 300 kPa [13]. To the best of our knowledge, this is the only work reporting the steam reforming of OMW. Here we attempt to study the catalytic performance of various catalytic honeycombs in the steam reforming of distilled three-phase OMW provided by “Cooperativa La Fatarella” under several operational reaction conditions, with special attention to the hydrogen yield, reduction of total organic content and stability (reduction of coke formation). The development of a robust catalyst capable to reform the different molecules present in OMW is a great challenge. We have focused on the study and comparison of different metals as active phases supported on lanthanum-stabilized ceria. We used ceramic monoliths (400 cpsi) as a structural support to allow an easier transfer of the obtained results to industry.

Experimental

Preparation of the catalytic honeycombs

Lanthanum-stabilized ceria (ca. 20% La₂O₃ w/w) was prepared by co-precipitation from a La(NO₃)₃·6H₂O and CeCl₃·7H₂O (Alfa Aesar) aqueous solution using NH₄OH (28% v/v Alfa Aesar) as a precipitating agent. The resulting catalyst support was dried at 383 K for 12 h and calcined in air at 873 K for 6 h. Cordierite monoliths (Celcor 400 cpsi from Corning) were sized to 20 mm long and 18 mm diameter pieces. The La-stabilized ceria support was loaded onto the channel walls of the honeycombs by the washcoating method under continuous rotation until a weight gain of about 500 mg (approximately 25% w/w) using a gel of polyvinyl alcohol (PVA). Rh, Pd, Ru and Ni were added by incipient wetness impregnation from RhCl₃, PdCl₂, RuCl₃ and Ni(CH₃COO)₂·4H₂O aqueous solutions,

respectively, and Pt was impregnated using an acidic acetone–water solution of PtCl₂. The load of Rh, Ru and Pd was kept at 1% w/w with respect to the catalytic support whereas the Ni load was 10% w/w. On the other hand, monoliths with different loads of Pt, 0.5, 1 and 2% w/w, were also prepared. Finally, the catalytic honeycombs were calcined in air at 673 K for 4 h. Monoliths were named as xM/CeLa, where x is the load in % w/w and M is the symbol of the metal.

Catalytic tests

Prior to the catalytic tests, catalytic honeycombs were activated for 1 h with a 10% H₂:N₂ mixture (50 mL min⁻¹) at 550 K for noble metal-based monoliths and at 923 K for Ni-based monolith. Tests were conducted at atmospheric pressure in a stainless steel reactor using a mixture of distilled OMW and 50 mL min⁻¹ of N₂ as diluent gas and analytical standard. The distilled OMW was introduced into the reaction system with a syringe pump (Kent Scientific Genie Plus) and the N₂ flow was introduced via a mass flow controller (Mass Stream). Four separated series of experiments were carried out. First, the effect of temperature was investigated at 873, 923, 973 and 1023 K (45 min at each temperature) with a distilled OMW load of 0.3 mL_{liq} min⁻¹ (GHSV = 4500 h⁻¹). For comparison purposes, blank experiments were also carried out under the same conditions over a naked ceramic monolith and a ceramic monolith loaded with the La-stabilized ceria catalyst support only. Second, the effect of the load of distilled OMW was studied at 973 K using 0.3, 0.6, 0.9 and 1.2 mL_{liq} min⁻¹ of distilled OMW (GHSV = 4500–16,000 h⁻¹, 1 h at each condition). Third, the effect of the metal load was studied using 0.5, 1 and 2% w/w Pt/CeLa catalytic honeycombs and exposing them to 0.3, 0.6, 0.9 and 1.2 mL_{liq} min⁻¹ of distilled OMW at 973 K. Finally, stability tests were conducted for 24 h at 973 K using a distilled OMW load of 0.6 mL_{liq} min⁻¹. The effluent of the reactor was connected to a condenser at 273 K and the dry gas was analyzed on-line (5 analyses for each experiment, 2–3% uncertainty) with a micro-gas chromatograph (Agilent 3000A) equipped with molecular sieve, plot-U and stabilwax columns.

Analysis of the organic content

Total organic carbon (TOC) analyses were conducted with a Shimadzu TOC-V CSN over OMW samples directly collected at the waste generation point without any previous treatment, after centrifugation (6000 rpm for 30 min), after filtration, and after distillation. Values of 28.1, 14.0, 12.5 and 5.4 g_C L⁻¹ were obtained, respectively. Catalytic tests were conducted with OMW distillate. The OMW distillate was analyzed by gas chromatography-mass spectrometry (Agilent GC7820A equipped with a Plot Q column) and the main components present in the reactant liquid were carboxylic acids and polyphenolic compounds.

The chemical oxygen demand (COD) was determined for the OMW distillate and the reaction condensed effluents by the dichromate titration method. The samples were oxidized with K₂Cr₂O₇ in the presence of H₂SO₄ under reflux for 3 h. Then, excess of K₂Cr₂O₇ was back titrated with Fe(NH₄)(SO₄)₂·6H₂O [14]. COD values were used to evaluate the

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