

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.

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 ¼ 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 ¼ 4500 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, 2e3% 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

removal of the organic matter in OMW after reaction, which was related to the extension of the reforming process. In parallel, and for comparative purposes, gas chromatography analyses of the OMW distillate and the condensed liquids collected at the exit of the reactor were also used to quantify the consumption of organic matter during the reforming process (Shimadzu GC-2010b equipped with a TRB-1 column). The values obtained independently by both methods (COD vs. GC) were in agreement in all cases and within 5% error.

Catalyst characterization

X-Ray Diffraction (XRD) of the La-stabilized ceria support was conducted using a Bruker D8-advance instrument. The support was constituted by particles of about 23 nm with a fluorite structure. X-ray photoelectron spectroscopy (XPS) was used to characterize the catalytic honeycombs as synthesized and after the catalytic stability tests for 24 h. The monoliths were cut to study the catalytic layer on the channel walls. XP spectra were collected with a SPECS system using a Mg X-ray source (200 W) and a 9-channel Phoibos detector at a pressure below 5×10^{-7} Pa. XPS quantification of surface elements was carried out using Shirley baselines and Gaussian/Lorentzian (3e70) lineshapes.

Results and discussion

Effect of the active metal

Fig. 1 shows the production of hydrogen obtained over the catalytic monoliths 1Pt/CeLa, 1Pd/CeLa, 1Rh/CeLa, 1Ru/CeLa and 10Ni/CeLa as well as over a monolith loaded with the La-stabilized ceria support (CeLa) and over the empty reactor (blank test) at different reaction temperatures over time. The production of H_2 of the catalytic honeycombs followed the trend: Pt > Rh > Ni > Ru >> Pd. As it is shown in Fig. 1, Pt-, Rh- and Ni-based catalytic monoliths reached a maximum close to 11.8 mL min^{-1} at 873 K, whereas for the Ru-based sample more energetic conditions, 923 K, were needed to reach the same value of H_2 production. At higher temperature the amount of hydrogen produced was maintained approximately

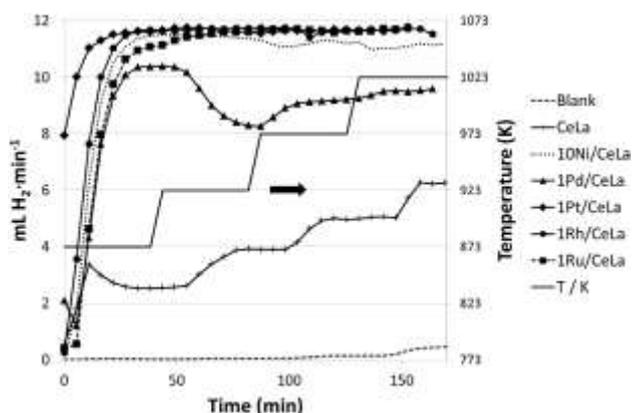


Fig. 1 e H_2 production at 873e1023 K, $F_{OMW} \text{ } \frac{1}{4} 0.3 \text{ mL min}^{-1}$, $GHSV \text{ } \frac{1}{4} 4500 \text{ h}^{-1}$.

constant, which means that the steam reforming of OMW was complete. However, a progressive deactivation was observed over the Ni-based sample. The Pd-based sample was significantly less active in the production of hydrogen; at 873 K, 10.4 mL min^{-1} of H_2 were obtained, and at 923 K this value decreased at about 8.3 mL min^{-1} , suggesting that a rapid deactivation of the catalyst occurred under these operational conditions. At higher temperatures, the amount of hydrogen produced over the Pd-based sample increased but the production of hydrogen was significantly lower than that obtained over the other catalytic honeycombs. As expected, the amount of hydrogen produced over the bare support was much lower, 2.5 mL min^{-1} at 873 K and a maximum of 6.2 mL min^{-1} at 1023 K. No significant H_2 production was found in the blank experiment (less than 0.5 mL min^{-1} were produced at 1023 K), which rules out any thermolysis effect of the reactor walls.

In addition to the production of hydrogen, it is interesting to discuss the selectivity towards the gaseous products obtained. Table 1 compiles the results on a dry basis. It is accepted that steam reforming processes over noble metal- and Ni-based catalysts at high temperatures operate through cracking of high molecular weight molecules to simple ones, followed by the steam reforming of these low molecular weight molecules and the water gas shift equilibrium [15] (Equations (1)e(3)).



In addition, other reactions such as dehydrogenation, dehydration, carbon formation etc, take place, resulting in a production of undesired products, which is detrimental for the production of hydrogen. As expected, a low selectivity towards the reforming products, H_2 and CO_x , was obtained in the blank test, where large amounts of undesirable products such as $C_{1e}C_3$ hydrocarbons were produced. The reaction over the bare support yielded better selectivity values with respect to the blank test, but large quantities of methane were obtained in all the temperatures tested. In contrast, a remarkable improvement of selectivity values towards the reforming products was obtained over the catalytic monoliths loaded with metals supported on the La-stabilized ceria support. In all cases, the main products were H_2 and CO_2 . In the case of 1Pt/CeLa, 1Rh/CeLa, 1Ru/CeLa and 10Ni/CeLa, the amount of H_2 and CO_2 accounted for nearly 99% of all products present in the gas phase in the range of temperatures tested. The 1Pd/CeLa sample was less selective and higher amounts of methane and CO were obtained along with minor $C_{2e}C_3$ hydrocarbons. This is explained taking into account that Pd has a lower capacity for C-C bond cleavage compared to the other metals tested [16]. On the other hand, the higher amount of $C_{2e}C_3$ hydrocarbons obtained over the 1Pd/CeLa sample (ca. 1% C_2H_4) was likely responsible for the fast deactivation of

Table 1 e Selectivity on a dry basis for gaseous products obtained at $F_{\text{OMW}} \text{ } \frac{1}{4} 0.3 \text{ mL min}^{-1}$, $\text{GHSV} \text{ } \frac{1}{4} 4500 \text{ h}^{-1}$. (C2 and C3 refer to hydrocarbons of 2 and 3 carbons, respectively).

Sample	Temperature/K	Selectivity/% (dry basis)					
		H ₂	CH ₄	CO	CO ₂	C2	C3
Blank	873	37.0	4.2	0.0	33.8	5.1	19.9
	923	34.1	11.8	0.0	25.1	7.7	21.3
	973	33.0	12.3	6.7	16.8	10.2	21.0
	1023	34.6	12.6	10.2	13.2	11.6	17.8
CeLa	873	52.7	8.2	3.4	23.5	6.1	6.1
	923	49.9	14.1	4.7	22.7	4.1	4.5
	973	53.6	12.0	2.6	23.8	3.8	4.2
	1023	59.6	7.8	0.8	24.6	3.7	3.5
10Ni/CeLa	873	73.0	0.4	0.2	26.4	0.0	0.0
	923	72.9	0.6	0.2	26.3	0.0	0.0
	973	72.6	0.7	0.3	26.4	0.0	0.0
	1023	72.6	0.8	0.4	26.2	0.0	0.0
1Pd/CeLa	873	72.1	1.7	0.3	25.8	0.0	0.1
	923	67.3	2.6	3.4	23.5	1.1	2.1
	973	68.6	2.2	1.9	24.5	1.1	1.7
	1023	69.3	2.7	0.9	25.2	1.0	0.6
1Pt/CeLa	873	73.2	0.4	0.2	26.2	0.0	0.0
	923	73.5	0.2	0.3	25.9	0.0	0.1
	973	73.6	0.2	0.3	25.9	0.0	0.0
	1023	73.6	0.1	0.4	25.9	0.0	0.0
1Rh/CeLa	873	73.3	0.2	0.2	26.3	0.0	0.0
	923	73.5	0.0	0.2	26.3	0.0	0.0
	973	73.5	0.0	0.3	26.2	0.0	0.0
	1023	73.4	0.0	0.4	26.2	0.0	0.0
1Ru/CeLa	873	72.2	1.2	0.2	26.3	0.0	0.1
	923	72.9	0.5	0.2	26.4	0.0	0.0
	973	73.2	0.3	0.3	26.2	0.0	0.0
	1023	73.3	0.2	0.4	26.1	0.0	0.0

this sample, since it is well known that ethylene is an efficient coke precursor [17,18]. It merits to be highlighted the low amount of methane obtained over the catalytic monoliths 1Pt/CeLa, 1Rh/CeLa, 1Ru/CeLa and 10Ni/CeLa as well as the nearly absence of C2eC3 hydrocarbons. This is in accordance to the results obtained in methane steam reforming (Equation (3)) studies, where Rh has shown to be the most active metal [19]. A progressive decrease of CH₄ selectivity with increasing reaction temperature was found for both Rh-, Pt- and Ru-based catalysts according to thermodynamics of methane steam reforming, but not for 10Ni/CeLa. Finally, for these samples, the CO/CO₂ ratio increased with increasing temperature, according to the thermodynamics of the water gas shift equilibrium.

Effect of reactant load

A set of experiments aimed to evaluate the effect of reactant load was performed over 1Pt/CeLa, 1Rh/CeLa, 1Ru/CeLa and 10Ni/CeLa at 973 K (1Pd/CeLa was discharged since it showed strong deactivation as discussed above). Weight-to-flow (W/F) values ranging from 0.4 to 1.6 g min mL⁻¹_{OMW} (from 0.3 to 1.2 mL_{OMW} min⁻¹) were selected. Fig. 2 shows the production of hydrogen obtained for each catalytic honeycomb at each OMW load tested. At low W/F values (high OMW loads) the production of H₂ became different for the various samples. The reforming activity of the 1Pt/CeLa catalytic monolith was higher than that of Ru- and Rh-based samples. The activity of

the 10Ni/CeLa catalytic monolith was the lowest, even with a metal loading 10-fold higher than that of the noble metal-based samples. The catalytic activity followed the trend: 1Pt/CeLa > 1Ru/CeLa > 1Rh/CeLa >> 10Ni/CeLa. For the 1Pt/CeLa catalytic monolith, a linear correlation was found between the production of hydrogen and the F_{OMW} in the range studied, thus demonstrating the high capacity of this catalytic honeycomb sample for OMW steam reforming, with a constant hydrogen production rate of about 35 mL_{H₂}=mL_{OMW}.

The selectivities of the gaseous products are compiled in Table 2. As a general rule, the amount of the reforming

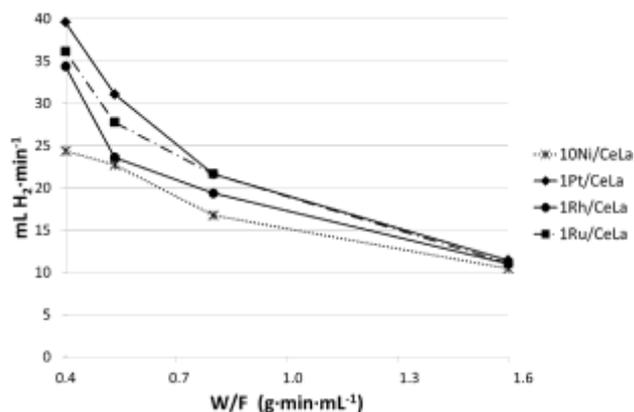


Fig. 2 e H₂ production at 973 K, $F_{\text{OMW}} \text{ } \frac{1}{4} 0.3 \text{ e } 1.2 \text{ mL min}^{-1}$, $\text{GHSV} \text{ } \frac{1}{4} 4500 \text{ e } 16,000 \text{ h}^{-1}$.

Table 2 e Selectivity on a dry basis for gaseous products obtained at 973 K, $F_{\text{OMW}} \frac{1}{4} 0.3\text{e}1.2 \text{ mL min}^{-1}$, GHSV $\frac{1}{4} 4500\text{e}16,000 \text{ h}^{-1}$. (C2 and C3 refer to hydrocarbons of 2 and 3 carbons, respectively).

Sample	OMW flow/ mL min^{-1}	Selectivity/% (dry basis)					
		H ₂	CH ₄	CO	CO ₂	C2	C3
10Ni/CeLa	0.3	71.3	1.7	0.3	26.2	0.3	0.2
	0.6	68.9	2.8	0.6	26.0	0.9	0.8
	0.9	65.0	5.3	1.9	25.1	1.3	1.4
1Pt/CeLa	1.2	63.0	6.3	3.2	24.1	1.6	1.8
	0.3	73.3	0.2	0.3	26.2	0.0	0.0
	0.6	72.9	0.2	0.4	26.5	0.0	0.0
	0.9	72.4	0.4	0.5	26.4	0.2	0.1
1Rh/CeLa	1.2	72.0	0.8	0.8	25.9	0.3	0.2
	0.3	73.2	0.0	0.3	26.5	0.0	0.0
	0.6	73.1	0.2	0.3	26.4	0.0	0.0
	0.9	72.6	0.3	0.4	26.6	0.0	0.1
1Ru/CeLa	1.2	72.9	0.5	0.6	25.9	0.0	0.1
	0.3	72.9	0.3	0.3	26.5	0.0	0.0
	0.6	72.4	0.4	0.5	26.2	0.3	0.2
	0.9	71.5	0.8	0.8	26.2	0.3	0.4
	1.2	70.1	1.9	1.7	25.3	0.4	0.6

products decreased as the OMW load increased (short contact times). Concomitantly, the selectivities towards C1eC3 hydrocarbons increased at the expense of H₂ and CO₂ and the amount of CO increased at the expense of CO₂ due the reaction scheme, where the water gas shift reaction follows the CeC bond breakage steps. These trends were particularly more pronounced over the Ni/CeLa catalytic honeycomb, which was the less active sample. The Pt- and Rh-based catalytic monoliths exhibited the best catalytic performance in terms of selectivity with practically constant percentages of products in the effluent gas, being the most significant a slight increase of the amount of CH₄ (from 0.0 to 0.8%) and CO (from 0.3 to 0.8%) when increasing the reactant flow from 0.3 to 1.2 mL min⁻¹. The amount of C2eC3 hydrocarbons was maintained low at 0.0e0.3%.

Effect of active metal loading

The effect of metal load was evaluated over catalytic honeycombs loaded with 0.5, 1 and 2% w/w Pt/CeLa at 973 K and $F_{\text{OMW}} \frac{1}{4} 0.3\text{e}1.2 \text{ mL min}^{-1}$ (W/F $\frac{1}{4} 0.4\text{e}1.6 \text{ g min mL}^{-1}_{\text{OMW}}$). The

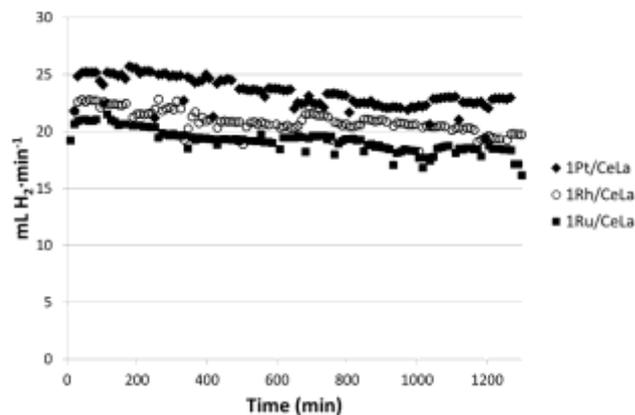


Fig. 3 e H₂ production at 973 K over time on stream, $F_{\text{OMW}} \frac{1}{4} 0.6 \text{ mL min}^{-1}$, GHSV $\frac{1}{4} 9000 \text{ h}^{-1}$.

OMW distillate used to carry out these catalytic tests came from a different batch and had a TOC value of 3.8 g_C L⁻¹. Results are shown in Table 3. Selectivity trends were similar for all samples (the amount of H₂ and CO₂ decreased at short contact times and that of CO and hydrocarbons increased as discussed above), but an increase of the metal loading resulted in a progressively slightly better hydrogen yield and selectivity to the reforming products. For the same OMW load, a decrease in selectivity towards CH₄, CO, C2 and C3 was found when the Pt load was increased from 0.5 to 2% w/w. For instance, at $F_{\text{OMW}} \frac{1}{4} 1.2 \text{ mL min}^{-1}$ (GHSV $\frac{1}{4} 16,000 \text{ h}^{-1}$), the selectivity towards methane was 0.6% for 0.5Pt/CeLa whereas for 1Pt/CeLa and 2Pt/CeLa it decreased to 0.3 and 0.2%, respectively. Similarly, for C2eC3 the selectivity decreased from 0.6% for the 0.5Pt/CeLa catalytic honeycomb down to 0.3% for the 1Pt/CeLa and 0.1% for the 2Pt/CeLa. This behavior had a direct effect on the production of H₂, being the 2Pt/CeLa catalytic honeycomb more efficient. An increase of the OMW load from 0.3 to 1.2 mL min⁻¹ resulted in an increase of the H₂ production in 2.9, 3.0 and 3.2 times for 0.5Pt/CeLa, 1Pt/CeLa and 2Pt/CeLa, respectively.

Stability tests

Finally, a series of stability tests (973 K, $F_{\text{OMW}} \frac{1}{4} 0.6 \text{ mL min}^{-1}$) were conducted over 1Pt/CeLa, 1Rh/CeLa, and 1Ru/CeLa

Table 3 e Production of hydrogen and selectivity on a dry basis for gaseous products obtained at 973 K, $F_{\text{OMW}} \frac{1}{4} 0.3\text{e}1.2 \text{ mL min}^{-1}$, GHSV $\frac{1}{4} 4500\text{e}16,000 \text{ h}^{-1}$. (C2 and C3 refer to hydrocarbons of 2 and 3 carbons, respectively).

Sample	OMW flow/ mL min^{-1}	mL H ₂ min^{-1}	Selectivity/% (dry basis)					
			H ₂	CH ₄	CO	CO ₂	C2	C3
0.5Pt/CeLa	0.3	7.8	73.0	0.2	0.4	26.4	0.0	0.0
	0.6	15.8	73.2	0.2	0.4	26.2	0.0	0.0
	0.9	19.6	72.4	0.4	0.8	26.0	0.0	0.4
1Pt/CeLa	1.2	22.7	72.0	0.6	1.1	25.7	0.3	0.3
	0.3	7.7	73.2	0.0	0.4	26.4	0.0	0.0
	0.6	14.9	73.2	0.1	0.4	26.3	0.0	0.0
	0.9	21.2	73.1	0.2	0.7	25.9	0.0	0.1
2Pt/CeLa	1.2	23.3	72.3	0.3	0.9	26.2	0.1	0.2
	0.3	8.2	73.0	0.0	0.4	26.5	0.0	0.1
	0.9	23.6	72.8	0.1	0.7	26.3	0.0	0.1
	1.2	26.3	72.6	0.2	0.8	26.3	0.0	0.1

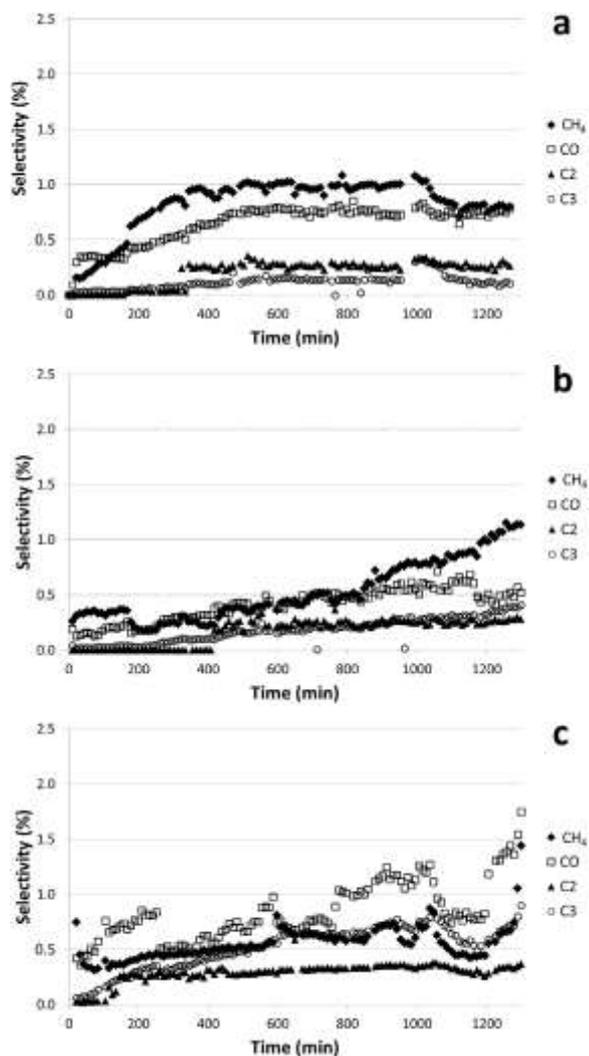


Fig. 4 e Selectivity values on a dry basis at 973 K over time on stream, $F_{\text{OMW}} \frac{1}{4} 0.6 \text{ mL min}^{-1}$, $\text{GHSV} \frac{1}{4} 9000 \text{ h}^{-1}$. a) 1Pt/CeLa, b) 1Rh/CeLa, c) 1Ru/CeLa.

catalytic monoliths. Fig. 3 shows the production of hydrogen over time on stream. At any time, the production of H_2 was higher over the Pt-based sample. At the end of the stability tests, a decrease in the production of H_2 of about 10% was observed in all samples. The deactivation was apparently more severe over the catalytic honeycomb 1Ru/CeLa. The analyses of the condensed liquid collected at the outlet of the reactor after 24 h on stream revealed that the consumption of carbon was 90e95% for all samples.

As expected, all the samples showed good selectivity values at initial reaction time, with values below 0.5% for light hydrocarbons (C1eC3) and CO (Fig. 4). However, the amount of non-reforming products rapidly increased over 1Ru/CeLa, achieving selectivity values of 0.3 and 0.4% for C2 and C3 compounds, respectively, after only 5 h on stream (after 24 h under reaction selectivity values increased up to 2% CO , 2% CH_4 , 0.4% C2 and 1% C3). It should be noted the unstable selectivity values recorded over the 1Ru/CeLa catalytic honeycomb on time on stream. The 1Rh/CeLa catalytic monolith showed a progressive increase of non-reforming products

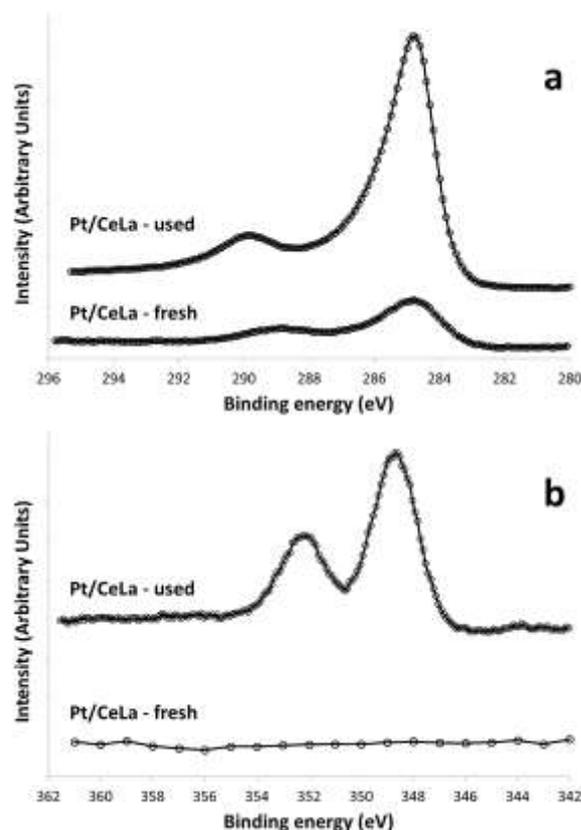


Fig. 5 e XPS spectra of fresh and used Pt/CeLa samples. a) C 1s region, b) Ca 2p region.

during the stability test, reaching selectivity values of 1.2% CH_4 , 0.7% CO , 0.3% C2 and 0.4% C3 after 24 h on stream. In contrast, over the 1Pt/CeLa catalytic honeycomb, a rapid increase of the amount of non-reforming products was observed during the first 7 h on stream (1% CH_4 , 0.7% CO , 0.1% C2 and 0.1% C3) but, after this period of time, the distribution of products remained essentially constant, resulting in a very stable catalytic behavior. Therefore, Pt-based catalysts are robust and capable to reform the different molecules present in OMW.

At the end of the stability tests, the catalytic honeycombs were analyzed by XPS. In all cases there was an increase of the amount of carbon deposited on the surface with respect to the fresh samples (from 2.6 to 4.5 fold increase with respect to adventitious carbon). The trend of carbon accumulation on the surface was: 1Ru/CeLa > 1Rh/CeLa > 1Pt/CeLa, which is exactly the opposite to that of the catalytic performance for the production of H_2 , strongly suggesting that carbon deposition was likely the cause of catalyst deactivation during OMW steam reforming. In addition, calcium deposition (6e9% of atomic surface concentration) was also observed after the stability test in all samples (Fig. 5). Calcium comes from OMW and its possible effect on the long term catalytic performance must be further investigated.

Conclusions

Several catalytic honeycombs loaded with noble metals (Pt, Pd, Rh or Ru) or Ni over La-stabilized CeO_2 were prepared and

tested in the steam reforming of distilled olive mill wastewater (OMW) at different temperatures and OMW loads. Their catalytic performance in terms of H₂ production, selectivity towards reforming products and stability followed the trend Pt/CeLa > Rh/CeLa > Ru/CeLa >> Ni/CeLa > Pd/CeLa. Up to 40 STP mL of H₂ per mL of distilled OMW were obtained over the catalytic honeycomb Pt/CeLa (1% Pt w/w) at 973 K and 16,000 h⁻¹, which showed a very stable distribution of products in long term runs. An increase of the Pt load up to 2% w/w had a positive effect on product distribution, particularly on the suppression of CH₄ and C₂H₆ hydrocarbons. Independent carbon mass balances obtained by COD and gas chromatography analyses showed 90–96% of reduction of the organic carbon present in distilled OMW. Deactivation of the catalysts was ascribed to carbon deposition, as deduced from XPS analysis.

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