

Article

Preparation and Screening of Ni-Based Catalysts for the Olive Oil Mill Wastewater Steam Reforming Process

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Abstract

Olive mill wastewater (OMW) is a highly polluting effluent rich in organic pollutant compounds derived from olive oil production. In this work, the steam reforming reaction of OMW (OMWSR) was performed in a traditional reactor at 400 °C and different pressures (1–4 bar) to treat and valorize this effluent. A commercial catalyst (Rh/Al₂O₃) was used as a reference sample and several new catalysts were prepared (Ni-Ru/Ce-SiO₂) using different preparation methods to study their effect on the activity and stability. The best-performing catalysts were also subjected to long-term operation experimental tests (24 h). It was observed that the preparation method used for the catalysts synthesis influenced the catalytic performance of the samples. In addition, temperature-programmed oxidation (TPO) analysis of the used catalyst showed the presence of carbon deposits: the results showed that periodic oxidative regeneration improved the catalyst stability and sustained H₂ production. Finally, it was verified that the Ni-Ru/Ce³ catalyst stood out during the experimental tests, exhibiting high catalytic activity along the stability test at 400 °C and 1 bar: H₂ yield always over 7 mol_{H₂}·mol_{OMW}^{−1} and total organic carbon (TOC) conversion always higher than 94%. Despite these promising results, further research is needed to assess the economic feasibility of scaling up the process. Additionally, future work could explore the development of catalysts with enhanced resistance to deactivation by carbon deposition.

Keywords: olive oil mill wastewater; steam reforming; catalyst preparation method; hydrogen; oxidative regeneration



Academic Editors: Mohamed Mokhtar M. Mostafa, Tamer S. Saleh and Nesreen S. Ahmed

Received: 10 April 2025

Revised: 11 June 2025

Accepted: 26 June 2025

Published: 4 July 2025

Citation: Rocha, C.; Soria, M.A.; Madeira, L.M. Preparation and Screening of Ni-Based Catalysts for the Olive Oil Mill Wastewater Steam Reforming Process. *Catalysts* **2025**, *15*, 654. <https://doi.org/10.3390/catal15070654>

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1. Introduction

Worldwide, in 2023, there were approximately 900 million olive trees covering a total area of 10 million hectares [1]. The world's olive oil production is mainly concentrated in Europe, with the Iberian Peninsula being a leader region—olive oil production in this region is estimated to reach 1485 tons in the 2024/25 crop year (there is no full report on this campaign yet) [1]. In this way, the olive oil industry is economically very important for Mediterranean countries; however, it is observed that all these producing countries are considerably affected by the high pollution resulting from the production of olive oil. The process generates large amounts of solid and liquid waste (the last one, called olive oil mill wastewater—OMW), raising serious disposal problems for the producers. This occurs because of the high values of the chemical oxygen demand (COD—60–185 g·L^{−1})

and biochemical oxygen demand (BOD—14–75 g·L^{−1}) present in the OMW [2]—these wide ranges are explained by the different compositions that OMW can present, which depend on many factors, like the olive species itself, the land, the local climate and the olive oil production process. Actually, the pollution from this stream was estimated to cause approximately 200 times more impact than that from urban wastewater due to its specific chemical composition [3]. The composition of OMW is highly variable and suggests that several substances can be present, depending on several factors (e.g., the surface of cultivation and the age of the olive tree) [4]. In general, the OMW effluent is composed of water (80–95 wt.% [2,5–7]), sugars (up to 20–30 g·L^{−1}), polyphenols (up to 8 g·L^{−1}) and fatty acids (5–10 g·L^{−1}) [2]. In this way, the uncontrolled disposal of OMW represents a social, economic, and environmental problem, which must be addressed.

In recent decades, several processes have been explored to reduce the OMW pollutant load. From this perspective, the possibility of waste treatment and valorization has been considered, namely through the steam reforming reaction process of the OMW (OMWSR) [8–10]. This process would eliminate the pollutant load present in the effluent while simultaneously producing H₂. The OMWSR reaction (Equation (1)) consists of the sum of two independent reactions: the thermal decomposition of high-molecular-weight molecules in the presence of steam (Equation (2)) and the water–gas shift (WGS—Equation (3)) reaction. The reaction enthalpy for each equation was taken from a previous work [11] and depends on the OMW composition.

	$\Delta H_r^{25^\circ\text{C}} \text{ (kJ}\cdot\text{mol}^{-1}\text{)}$	
$\text{C}_x\text{H}_y\text{O}_z + (2x - z) \text{H}_2\text{O} \rightarrow (2x - z + \frac{y}{2})\text{H}_2 + x\text{CO}_2$	Varies	(1)
$\text{C}_x\text{H}_y\text{O}_z + (x - z)\text{H}_2\text{O} \rightarrow (x - z + \frac{y}{2})\text{H}_2 + x\text{CO}$	Varies	(2)
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$	−41	(3)

This process can have side reactions, namely the following: Equation (4)—carbon monoxide methanation, Equation (5)—dry steam reforming of methane, Equation (6)—steam reforming of methane, and Equation (7)—cracking of the oxygenated molecules. Among the proposed reactions, Equations (4) and (7) are the most probable, as confirmed in previous studies [8,10].

	$\Delta H_r^{25^\circ\text{C}} \text{ (kJ}\cdot\text{mol}^{-1}\text{)}$	
$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CH}_4$	−206	(4)
$\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247	(5)
$2\text{H}_2\text{O} + \text{CH}_4 \rightleftharpoons \text{CO}_2 + 4\text{H}_2$	165	(6)
$\text{C}_x\text{H}_y\text{O}_z \rightarrow \text{C}_n\text{H}_m\text{O}_k + \text{gas}(\text{H}_2, \text{CO}_2, \text{CO}, \text{CH}_4, \text{CH}_n) + \text{C}$	Varies	(7)

Also, the formation of coke very often occurs in steam reforming processes (leading to pore blockage and active site coverage, thereby reducing the catalyst performance and accelerating its deactivation), particularly through the following reactions: Equation (7)—cracking of the oxygenated molecules, Equation (8)—cracking of hydrocarbons, Equation (9)—Boudouard reaction, Equation (10)—methane cracking, Equation (11)—carbon monoxide reduction, and Equation (12)—carbon dioxide reduction.

	$\Delta H_r^{25^\circ\text{C}} \text{ (kJ}\cdot\text{mol}^{-1}\text{)}$	
$\text{CH}_x \rightarrow \text{coke precursors (alofins + aromatics)} \rightarrow \frac{x}{2}\text{H}_2 + \text{C}$	Varies	(8)
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	−172	(9)
$\text{CH}_4 \rightleftharpoons 2\text{H}_2 + \text{C}$	74	(10)
$\text{CO} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{C}$	−131	(11)
$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{C}$	−90	(12)

Compared to conventional steam reforming feedstocks like ethanol or glycerol [12,13], OMW not only represents a low-cost and sustainable feedstock but also offers higher hydrogen yield potential per oxygenated molecule due to its rich and diverse organic composition.

The only authors who experimentally studied the OMWSR reaction were Tosti et al. [2,3,14], Casanovas et al. [15] and Alique et al. [16], apart from Rocha et al. [8–10]. Tosti et al. used a commercial Pt-based catalyst [2] and developed new noble-metal-based catalysts (with Pd, Rh and Pt supported on Al_2O_3 coated with $\text{CeO}_2\text{--ZrO}_2$) to compare them with a commercial material [14]. On the other hand, Casanovas et al. [15] prepared several catalytic honeycombs loaded with noble metals (Pt, Pd, Rh or Ru) or Ni over La-stabilized CeO_2 . It is important to highlight that the studies of Tosti et al. [2,3,14] were performed in a membrane reactor (MR) with the separation of H_2 , while the work of Casanovas et al. [2] was performed in a traditional reactor (TR) at high temperatures ($\geq 600^\circ\text{C}$). More recently, it was found by Rocha et al. [8–10] that commercial Rh-based catalysts and a prepared catalyst loaded with Ni and Ru presented high catalytic performance (in terms of the H_2 yield—maximum of $9\text{ mol}_{\text{H}_2}\cdot\text{mol}_{\text{OMW}}^{-1}$), H_2 selectivity, stability and total organic carbon (TOC) conversion. Nevertheless, until now, no studies have been found in the literature related to the effect of the preparation methods on the performance of the Ni-based catalysts. In particular, none of these previous studies focused on developing new Ni-based materials to improve the economic viability of the reaction under investigation. Moreover, limited attention was paid to carbon production on the catalysts, and the range of pressures explored was narrow, typically restricted to atmospheric pressure.

The present work aims to evaluate the performance of a TR at various pressures for the OMWSR process, using two types of catalysts: one commercial (material that presented the best catalytic performance in a previous scientific work [10] acting as a reference sample)—Rh/ Al_2O_3 —and five new samples prepared in the laboratory—a series of Ni-Ru/Ce-SiO₂ catalysts. The prepared catalysts were also doped with Ce, since it was observed that the addition of this promoter improved the stability of the materials [17–21].

The main novelty of this work is the utilization of a series of Ni-Ru/Ce-SiO₂ catalysts prepared with different methods (namely, with different calcination programs and different impregnation steps) that have never been applied in the OMWSR reaction, and the study of the effect of the pressure and oxidative regeneration treatments on this process. To evaluate the performance of the catalysts, the results were analyzed in terms of the H_2 yield, H_2 selectivity, TOC conversion and stability of the catalysts. It was expected to obtain a TOC conversion close to 100% and an H_2 yield higher than $9\text{ mol}_{\text{H}_2}\cdot\text{mol}_{\text{OMW}}^{-1}$ (considering previous studies by the research group) [8,10].

2. Results and Discussion

2.1. Catalysts Characterization

2.1.1. TPR-H₂ and TPD-CO₂

Temperature-programmed reduction with hydrogen (TPR-H₂) analyses were performed with all the prepared catalysts to determine an adequate temperature for their reduction; the results are shown in Figure 1 (see more details in Section 3.3). The results indicated that, in a general way, the materials were reduced mostly at temperatures below 400°C (except Ni-Ru/Ce¹, which was attributed to the reduction of NiO species strongly interacting with the silica support, likely in the form of nickel silicates [22]). It was also observed that the TPR profiles present several peaks and/or broad peaks related to the reduction of oxide species with different interactions with the support, evidencing the inhomogeneity of the surface of these materials (for instance, for the Ni-Ru/Ce³ catalyst, it was possible to distinguish three different temperatures peaks between 200 and 450°C). In the profile of the Ni-Ru/Ce³ sample (catalyst with a higher content of Ce), a small peak

was present at 225 °C, which, according to the literature, can be related to the interaction of NiO with CeO₂ [23,24] and/or attributed to the partial reduction of the surface oxygen of the Ce species [25–27]. For the Ni-Ru/Ce⁴ and Ni-Ru/Ce⁵ catalysts, the consumption of H₂ in the temperature range considered was very low. So, considering the results of these TPR-H₂ analyses, all the materials in this work were reduced/activated at 400 °C during 2 h under a 10% H₂/N₂ stream—total flow rate of 100 mL_{NPT}·min^{−1}—before the catalytic tests. It was also verified that this temperature program allowed the complete reduction of all the samples (reduction tests were also carried out in which these materials, after undergoing this reduction program, were exposed to higher temperatures under a 10% H₂/N₂ stream, without showing any hydrogen consumption at that stage).

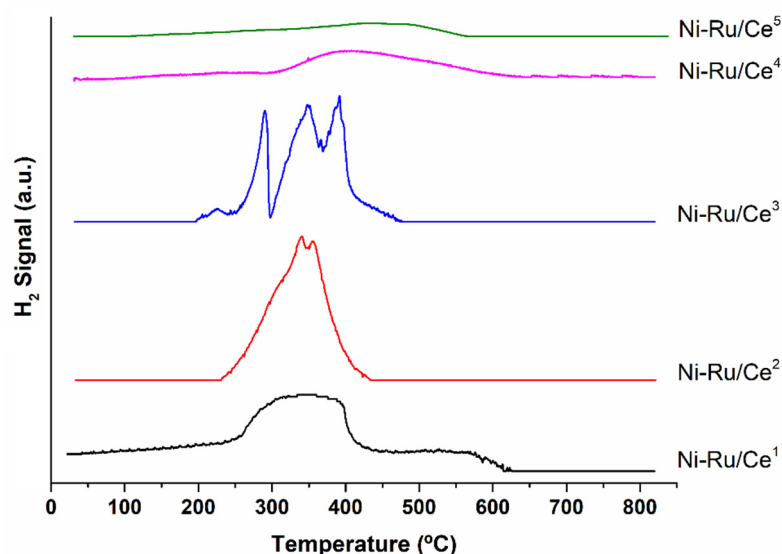


Figure 1. TPR analyses of all the Ni-Ru/Ce catalysts.

To determine and compare the basicity of the Ni-Ru/Ce² and Ni-Ru/Ce³ samples, temperature-programmed desorption with carbon dioxide (TPD-CO₂) analyses were performed—see Figure S1 in the Supporting Information (SI) and Table 1 (see more details in Section 3.3). These two specific samples were chosen to be analyzed because they were prepared with the same preparation method (but with different Ce contents). In this way, it is possible to verify only the effect of Ce addition on the basicity of the catalysts. In addition, these samples were characterized in more detail since the catalyst Ni-Ru/Ce³ presented the highest catalytic activity among all the materials tested in this work. According to the literature, the basic active sites can be classified as weak, medium, or strong: peaks in the range of 23–250 °C are attributed to weak basic sites, at 250–500 °C to medium basic sites and above 500 °C to strong basic sites [28]. The TPD results for the Ni-Ru/Ce² show three distinct peaks very well defined, with maxima at 95, 605 and 705 °C, associated with weak and strong basic sites. In the TPR profile of the Ni-Ru/Ce³ sample, it was possible to see three different peaks related to the different types of basic sites considered in this study (at 105, 300 and 560 °C). In contrast to the other samples, this material presents very well-defined different types of basic sites. In Table 1, it is possible to see the quantities of basic sites present in these two catalysts, obtained by integration of the TPD curves; for comparison purposes, it also presents the quantities of basic sites determined for the same catalyst without the Ce impregnation, prepared in a previous study [8]. Analyzing the values presented in Table 1, one can conclude that the impregnation with Ce increases the basicity of the materials and the number of basic sites was higher for the material impregnated with higher content of Ce (Ni-Ru/Ce³); still, the increase in Ce loading led to the formation of a higher number of basic sites with weak and medium strength.

Table 1. Quantities of basic sites in some selected catalysts.

Catalyst	Weak Basic Sites (mmol _{CO2} ·g _{catalyst} ^{−1})	Medium Basic Sites (mmol _{CO2} ·g _{catalyst} ^{−1})	Strong Basic Sites (mmol _{CO2} ·g _{catalyst} ^{−1})	Total Basic Sites (mmol _{CO2} ·g _{catalyst} ^{−1})
Ni-Ru ^(a)	0.18	0.10	0.04	0.32
Ni-Ru/Ce ²	0.21	0.07	0.19	0.47
Ni-Ru/Ce ³	0.42	0.13	0.03	0.58

^(a) Material prepared in a previous study using the same preparation method for the remaining catalysts (Ni-Ru/Ce^{2/3}). Reprinted with permission from Ref. [8]. 2022, Elsevier.

2.1.2. Metal Loading

The inductively coupled plasma–optical emission spectrometry (ICP-OES) technique was used to determine the real content of metals in the Ni-Ru/Ce catalysts (see more details in Section 3.3). It can be seen in Table 2 that the Ni loading determined in the samples was close to the nominal values, indicating a reasonable impregnation of this metal in the support. The content of Ru in the catalysts was low, probably due to the poor impregnation of the element in the SiO₂ support and/or due to the calcination program used (which promotes Ru evaporation), as verified in a previous study [8]. Additionally, it was possible to verify that the Ru content was higher in the samples prepared with larger support particles, allowing a higher content of this metal. Furthermore, as expected, since the materials Ni-Ru/Ce⁴ and Ni-Ru/Ce⁵ were calcined before Ru impregnation, there was a higher amount of Ru in these samples. About the Ce content achieved for the different materials, it was concluded that the preparation method influences the impregnation—for the Ni-Ru/Ce⁴ and Ni-Ru/Ce⁵ catalysts, the real content of Ce was well below the target value, explained by the different calcination temperature used in the preparation of these materials in comparison with the three remaining samples. This loss is often due to the decomposition of cerium compounds or the volatilization of cerium species at elevated temperatures, as previously reported [29,30]. Only the real values of the metals content will be considered in the discussion of the catalytic results.

Table 2. ICP-OES results of the Ni-Ru/Ce catalysts.

Catalyst	Theoretical Ni Loading (wt.%)	Real Ni Loading (wt.%)	Theoretical Ru Loading (wt.%)	Real Ru Loading (wt.%)	Theoretical Ce Loading (wt.%)	Real Ce Loading (wt.%)
Ni-Ru/Ce ¹	10	7.0	1	0.06	0.3	0.39
Ni-Ru/Ce ²	10	10.2	1	0.52	0.3	0.23
Ni-Ru/Ce ³	10	8.6	1	0.43	3	2.2
Ni-Ru/Ce ⁴	10	10.4	1	0.59	0.3	0.04
Ni-Ru/Ce ⁵	10	8.6	1	0.58	3	0.8

The characterization was performed by an external entity and no error margins were provided.

2.2. Catalytic Tests

2.2.1. Thermodynamic Simulation and Blank Tests (*Exp. 0*)

Before the catalytic experiments, blank experimental tests (*Exp. 0*) under different operation conditions were performed in the reactor packed with only SiC particles (inert). In addition, the production of H₂, CO₂, CO, CH₄ and coke and the conversion of the OMW (in terms of the TOC conversion) in the thermodynamic equilibrium for the operation conditions defined were determined in Aspen Plus V.9[®] software—see details elsewhere [31]. The maximum theoretical yield of H₂ for this OMW stream (considering the complete conversion of OMW and considering only the OMWSR reaction (Equation (1)) is 12.18 mol of H₂ per mol of OMW fed.

As observed in a previous work [10], due to the high quantity of H₂O present in the initial effluent, the thermodynamic equilibrium of the steam reforming process is shifted to the production of a high quantity of H₂ and CO₂; still, the methanation reaction (Equation (4)) is inhibited by the presence of such a high amount of H₂O. For the same reason, the H₂ yields obtained in the simulations for several pressures were nearly identical to the maximum theoretical yield of H₂ (see Table 3), and the TOC conversions were complete. Despite the low formation of CH₄, it is possible to verify that the CH₄ yield, as expected, is higher for higher pressures (the methanation reaction is favored at higher pressures—Equation (4)).

Table 3. Yields of gaseous products and OMW TOC conversion in the thermodynamic equilibrium (Aspen Plus simulation) and in the blank experiments (*Exp. 0*) at 400 °C.

Pressure (Bar)	H ₂ Yield	CO Yield	CH ₄ Yield	CO ₂ Yield	TOC Conversion (%)
Thermodynamic Equilibrium (Simulations in Aspen Plus V.9®)					
1	12.18(0)	1.4×10^{-3}	5.7×10^{-7}	6.0	100
2	12.18(0)	1.4×10^{-3}	2.3×10^{-6}	6.0	100
3	12.18(0)	1.4×10^{-3}	5.1×10^{-6}	6.0	100
4	12.18(0)	1.4×10^{-3}	9.1×10^{-6}	6.0	100
Blank Tests/Experimental results (<i>Exp. 0</i>)					
1	0.71	0.09	1.6×10^{-2}	0.70	51
2	0.83	0.18	5.0×10^{-3}	0.70	51
3	0.88	0.12	7.0×10^{-3}	0.67	49
4	0.83	0.10	9.0×10^{-3}	0.56	48
Maximum Theoretical Yield of H ₂	12.18(2)				

Table 3 also shows the results obtained in the blank tests—*Exp. 0*. Since the process was not catalyzed in these experimental tests, the H₂ and CO₂ yields were very low. The quantities of CH₄ and CO detected were also very low for all the pressures tested, but they were higher than those obtained in the thermodynamic simulations. The TOC conversions were low and all close to 50%, related to the absence of a catalyst and, in this way, very slow kinetics.

2.2.2. Effect of the Catalyst Mass (*Exp. 1*)

For the Rh catalyst, an initial experimental test (*Exp. 1*) was carried out with different catalyst masses (different weight hourly space velocity, WHSV) to define a proper quantity of material to be used in *Exp. 2* and *Exp. 3*. The results related to the production of H₂ and the TOC conversion are shown in Figure 2 for the catalytic tests performed at several pressures.

In this experimental run, as expected, it was possible to verify that the quantity of catalyst inside the reactor significantly affects the production of gases and the conversion of OMW: the increase in the catalyst mass allowed a higher formation of H₂ and a higher TOC conversion for all the pressures studied—see Figure 2. The yields of CO and CH₄ were very low in all the catalytic tests, in line with the predominance of the WGS reaction (Equation (3)) in the process—in this way, the main products were always H₂ and CO₂. However, the increase in the pressure leads to the formation of small quantities of CH₄: the increase in the total pressure in the reaction medium leads to a shift in the equilibrium to the side with the lesser number of moles to counter the pressure rise. In this way, the methanation reaction (Equation (4)), which is favored at high pressures, is responsible for

the increase in the CH_4 yield [31,32]. Taking these results into consideration, the twice amount of catalyst was used in the next experimental runs (a total of 7 g of material) to increase the yields of the gas products and to attempt to achieve a TOC conversion close to 100%.

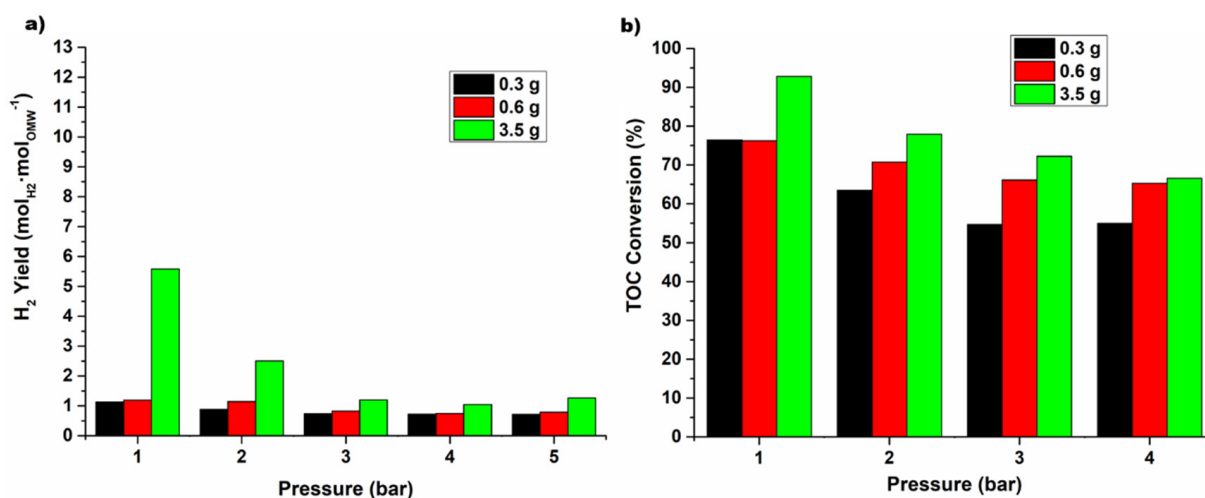


Figure 2. (a) H_2 yield and (b) TOC conversion as a function of the pressure, obtained in *Exp. 1* for the Rh catalyst at 400 °C, using different quantities of catalyst—0.3 g of catalyst corresponded to $\text{WSHV} = 100 \text{ h}^{-1}$, 0.6 g to $\text{WSHV} = 50 \text{ h}^{-1}$ and 3.5 g to $\text{WSHV} = 9 \text{ min}^{-1}$.

In these initial tests, the existence of catalyst deactivation was verified over the reaction time. The results indicated a decrease in the catalytic activity, mainly verified in the experimental test with 3.5 g of catalyst (green columns in Figure 2): taking into account that the formation of CH_4 is very low, the high decrease in the H_2 formation cannot be explained simply by favoring the methanation reaction at higher pressures; furthermore, the TOC conversion decreased along the experimental run (regardless of the catalyst mass used), indicating that the catalysts lose activity to crack the molecules of the OMW along the experimental run; finally, observing the results at the end of this experimental campaign—repetition of the catalytic test at 1 bar—it was concluded that the catalytic performance of the material was much lower at the end of the experiment. All these results strongly indicate that the catalyst undergoes several deactivation during the reaction.

After the catalytic test with 3.5 g of catalyst, a TPO analysis (see the temperature program used in Section 3.3) of the spent sample was carried out, since the decrease in the catalytic activity verified in the tests could be related to the formation of amorphous coke on the catalyst surface throughout the experimental test [33–38]. The results of this analysis confirm that the formation of carbon deposits on the catalyst occurred during OMWSR, which was oxidized up to CO_2 during the oxidative regeneration—CO and CH_4 were not detected in this analysis. In this manner, in the following experimental runs (*Exp. 2* and *Exp. 3*), the utilization of an oxidative regeneration program was considered before changing the system pressure to avoid the deactivation of the materials—the oxidative regeneration promotes the gasification of the carbon deposits present on the catalysts' surface, inhibiting the deactivation of the materials. Moreover, the quantity of coke produced at 1 bar (where a higher decline in H_2 production is observed over time) was determined for each catalyst.

2.2.3. Effect of Preparation Method (*Exp. 2*)

As already mentioned, the mass of catalysts used in this *Exp. 2* (7 g) was higher than that for *Exp. 1* to reach higher catalytic performances (closer to the thermodynamic equilibrium of the process) in the catalytic tests at several pressures (1, 2, 3 and 4 bar) with

the commercial and prepared catalysts. The mean of the results of these experimental tests can be seen in Figures 3 and S2 in the SI. It is possible to see more detailed information about all these results over time in Figure S3.

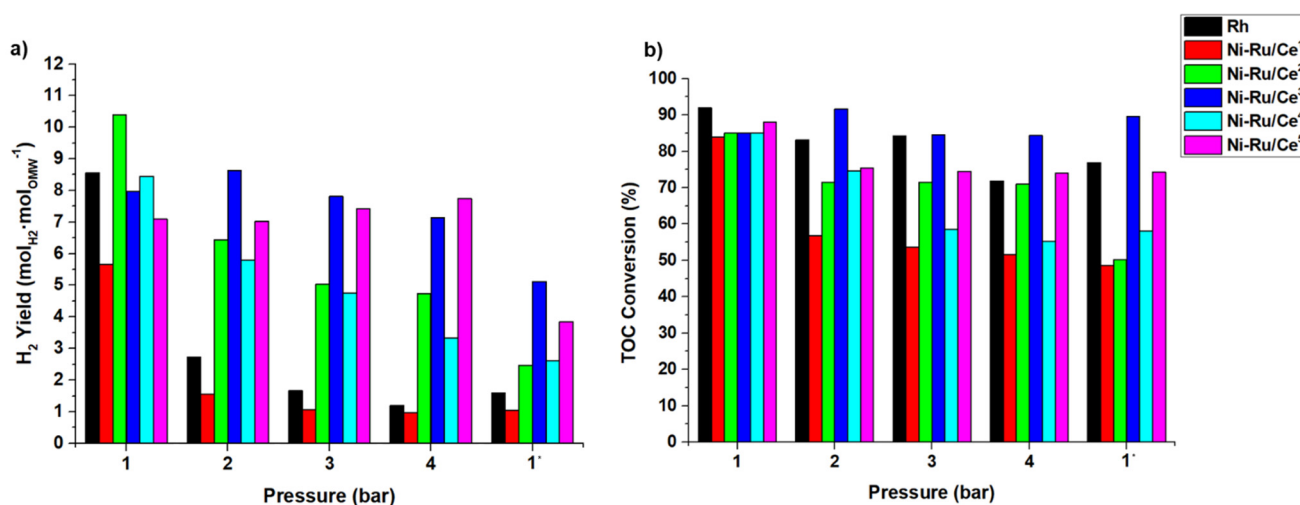


Figure 3. (a) H₂ yield and (b) TOC conversion as a function of the pressure, obtained in *Exp. 2* for all the catalysts at 400 °C (* repetition of the experimental test at 1 bar for comparison purposes) and WHSV = 18 min⁻¹.

For most catalysts used, the productions of CO and CH₄ were very low in all the tests, in line with the predominance of the WGS Equation (3) in the process; still, the behavior of the production of H₂ and CO₂ was very similar. For all the materials, the performance at the end of the experiment campaign (repetition of the experimental test at 1 bar for comparison purposes) was lower than at the beginning of the reaction—showing catalyst deactivation phenomena—despite the utilization of an oxidative regeneration program always operating before changing the pressure system. This deactivation of the samples was verified in detail in the results over time obtained at 1 bar—the H₂ yield and TOC conversion decreased in all the materials over time (see Figure S3 in the SI).

Nevertheless, the Ni-Ru/Ce³ and Ni-Ru/Ce⁵ catalyst samples stood out during these catalytic tests, exhibiting higher catalytic activity (Figure 3a), except in terms of H₂ yield at 1 bar. Looking at the overall results, the TOC conversion using these two materials was high at all the pressures, indicating that it is possible to reduce the enormous quantity of organic load from the effluent with these catalysts. The Ni-Ru/Ce⁵ material was also the material that better promoted the methanation reaction (Equation (4))—higher production of CH₄ in all the operating conditions). However, it is important to highlight that the TOC conversion was much higher using the Ni-Ru/Ce³ catalyst and close to 100%—see Figure 3b.

In opposition, the Rh and Ni-Ru/Ce¹ catalysts presented the worst performance in this study: the H₂ yield decreased drastically for higher pressures (>1 bar) using both materials and the production of CO was higher in the experiment with the Ni-Ru/Ce¹ sample. However, for the Rh catalyst, the TOC conversion was high for all the pressures, in contrast with the results obtained for Ni-Ru/Ce¹ (also decreased at higher pressures).

In this study, it was verified that the difference in the performance between the catalysts, namely the decrease in the H₂ yield along the experimental campaign at 1 bar, is related to the coke formation on the materials' surface (Equations (7)–(12)) [33–38]. In several previous studies [38–43], the existence of two different combustion peaks was noticed during the oxidation of spent catalysts, below and above 500/550 °C [44], related to the formation of amorphous and graphitic carbon, respectively. In this way, as already

mentioned, oxidative regeneration programs with air at 400 °C and 500 °C were carried out (before modifying the pressure of the system) in all the experimental tests—see an example in Figure 4. It was possible to distinguish the oxidation of the two types of coke (amorphous and graphitic) in all the experiments, which were quantified and are reported in Table 4 for the experimental tests conducted at 1 bar with fresh catalysts (and when it was possible to see a more pronounced deactivation over time—c.f. Figure S3 in the SI).

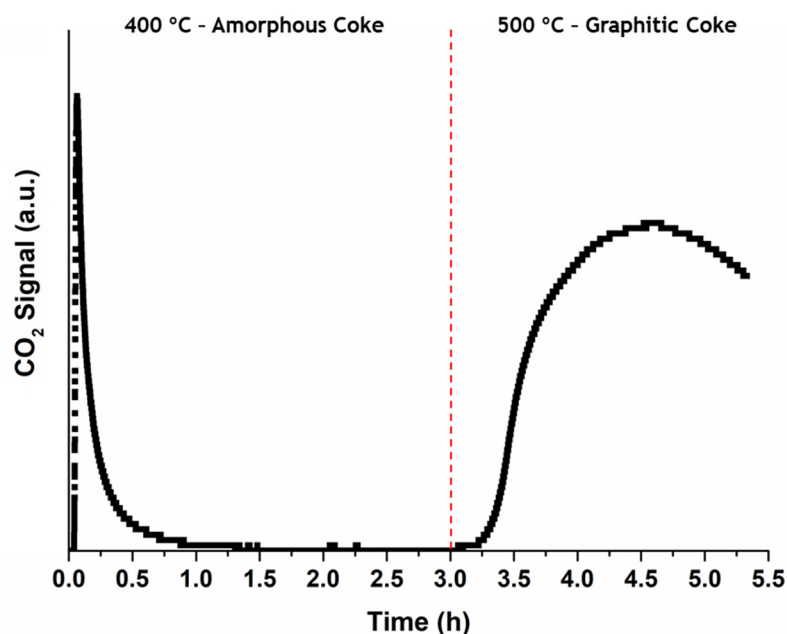


Figure 4. TPO profile of the Ni-Ru/Ce³ catalyst after a catalytic test at 400 °C and 1 bar in *Exp. 2*.

By comparing the coke content in the spent catalysts (see Table 4), it was observed that higher amounts of amorphous carbon were formed in the Rh and Ni-Ru/Ce¹ catalysts in comparison with the remaining prepared catalysts. Amorphous coke is reported to be the type of coke most detrimental to the performance of the materials [33,35–38], explaining the highest decrease in the catalytic performance along the experimental campaign (particularly evident in the repetition of the catalytic test at 1 bar at the end of the experimental run). Despite the high production of total coke in the Ni-Ru/Ce³ and Ni-Ru/Ce⁵ samples, the performance of the materials was high, in contrast with the other samples, since a high percentage of the coke produced had a graphitic nature—which has been shown to have a minor effect on the catalytic activity of materials.

On the other hand, it was possible to verify that the use of a higher content of cerium (using the same preparation method—Ni-Ru/Ce² vs. Ni-Ru/Ce³) allows a decrease in the amorphous coke production due to the good properties of the promoter for oxidizing dehydrogenated carbon species deposited on the catalyst surface in the steam reforming reaction [17–21,45–47]. In this way, the deactivation was much lower in the catalyst with a higher quantity of basic sites, which are the materials with a higher content of Ce (see Section 2.1.1).

Table 4. Quantities of coke produced with all the catalysts at 1 bar (values between brackets represent the fraction of total carbon).

Catalyst	Amorphous Coke ($\text{mmol}_\text{C} \cdot \text{g}_{\text{catalyst}}^{-1}$)
Rh	0.29 (62%)
Ni-Ru/Ce ¹	0.20 (51%)
Ni-Ru/Ce ²	0.15 (33%)
Ni-Ru/Ce ³	0.04 (10%)
Ni-Ru/Ce ⁴	0.13 (33%)
Ni-Ru/Ce ⁵	0.09 (21%)
	Graphitic Coke ($\text{mmol}_\text{C} \cdot \text{g}_{\text{catalyst}}^{-1}$)
Rh	0.18 (38%)
Ni-Ru/Ce ¹	0.19 (49%)
Ni-Ru/Ce ²	0.30 (67%)
Ni-Ru/Ce ³	0.36 (90%)
Ni-Ru/Ce ⁴	0.26 (67%)
Ni-Ru/Ce ⁵	0.34 (79%)
	Total Coke ($\text{mmol}_\text{C} \cdot \text{g}_{\text{catalyst}}^{-1}$)
Rh	0.47
Ni-Ru/Ce ¹	0.39
Ni-Ru/Ce ²	0.45
Ni-Ru/Ce ³	0.40
Ni-Ru/Ce ⁴	0.39
Ni-Ru/Ce ⁵	0.43

For the stability tests, the Ni-Ru/Ce³ catalyst was selected (together with the commercial Rh catalyst, for comparison purposes), which presented a high H₂ yield and TOC conversion in the range of pressures studied, presenting also the highest content of Ce among all the prepared materials. The Ni-Ru/Ce⁵ catalyst, although also exhibiting high catalytic activity, showed higher coke formation, possibly due to its lower Ce content in the structure (see Section 2.1.2—Table 2), making it a less suitable candidate for stability tests in comparison with the Ni-Ru/Ce³ catalyst. Its higher tendency to deactivate over time is attributed to the increased formation of carbon deposits on its surface (see Table 4). As already mentioned, the Ce content specifically affects coke formation and catalyst stability, reducing coke formation by enhancing the oxygen storage capacity and redox properties, which promote the oxidation of carbon deposits and maintain metal dispersion, thus limiting the deactivation over time [48].

Finally, it was observed that the reducibility of the materials (see Section 2.1.1) did not influence the catalytic activity of the materials, since the TPR-H₂ profiles are very similar, in contrast to the H₂ yields obtained in the experimental results.

2.2.4. Stability Tests (Exp. 3)

The catalysts used in the stability tests (Exp. 3; time-on-stream = 24 h) were the commercial Rh-based and the Ni-Ru/Ce³ catalysts. As expected, in all the catalytic tests, the CO and CH₄ yields were always very low.

The two catalysts exhibited a high-level loss of catalytic activity during the time-on-stream, as verified by the decrease in the H₂ yield (drop close to 50% for the Ru catalyst and close to 33% to the Ni-Ru/Ce³ catalyst) and TOC conversion, even when the oxidative regeneration was performed over 5 h (2 h at 400 °C and 3 h at 500 °C)—see Figure 5a,b. The catalytic activity was partially recovered over a small period after oxidation of the catalyst and continued to deactivate markedly after that—this indicates, again, that the catalyst deactivation was connected to the coke formation on the materials. It was also verified for both catalysts that after 14 h, the production of H₂ and TOC conversion remained constant

until the end of the catalytic tests. Also, in both materials, when the oxidative regeneration was not fully executed, a significant decline in performance was observed until the end of the experimental test, with the H_2 yield decreasing by approximately 90%.

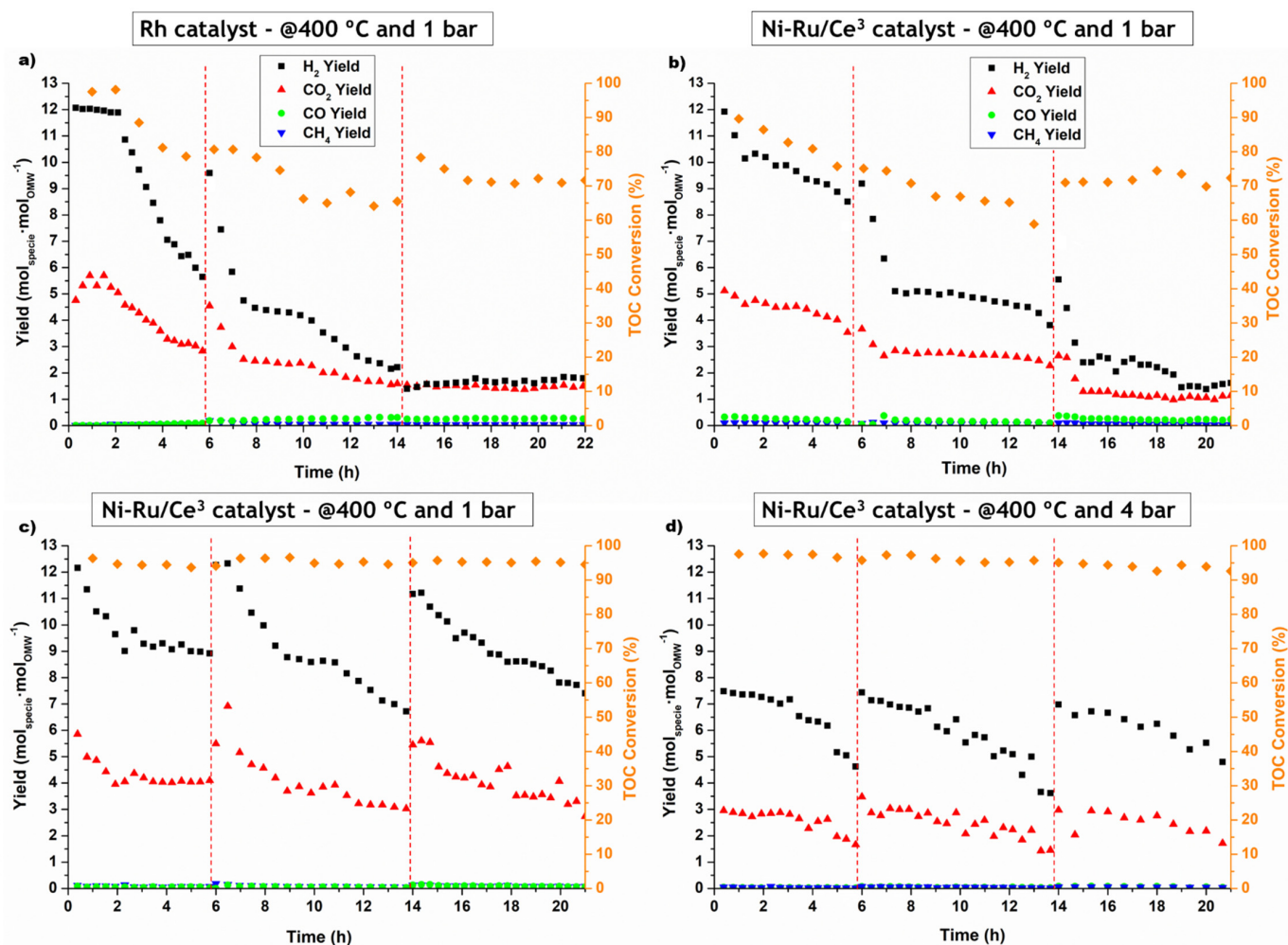


Figure 5. Gaseous species yield and TOC conversion during *Exp. 3* for the catalyst Rh and for the catalyst Ni-Ru/Ce³ (oxidative regeneration represented by the dashed red lines) with WHSV = 18 min^{−1}. In the first experimental tests (a,b), the coke was not fully oxidized in the oxidative regeneration program; in the catalytic tests (c,d), the coke was fully oxidized. The symbols used in figures (c,d) have the same meaning as those shown in figures (a,b).

It is important to take into consideration that Ni-based catalysts may suffer high deactivation by carbon accumulation [20,21]. The differences in the catalysts' stability are related to the formation of coke on their surface throughout the experimental tests, as verified in Section 2.2.3 [33,35–38]. In this way, and to recover the catalytic activity of the Ni-Ru/Ce³ catalyst, the oxidative program was changed in the following experimental tests: the oxidation of the catalyst was only stopped when the concentrations of CO₂ and CO in the outlet stream were equal to zero (at 400 °C and 500 °C) to achieve complete oxidation of the coke—in the previous tests, the time for this regeneration program was fixed and the graphitic coke was not full oxidized (c.f. Figure 4).

Stability tests at 400 °C and 1 or 4 bar, with the new oxidative regeneration step, were performed with the Ni-Ru/Ce³ catalyst; the data are shown in Figure 5c,d, respectively. The deactivation of the catalyst was much lower in comparison with the stability test with incomplete oxidation—higher and more stable H_2 production was obtained, so that after the oxidative regeneration the production of H_2 was similar to the initial performance

with the fresh material at both pressures (not verified in the previous experiments). These results indicate that the formation of graphitic coke, despite having a lower effect on the activity of the catalyst as compared to the amorphous coke (as verified in Section 2.2.3), has also impacted the decrease in the catalyst performance. This more organized carbon also influences the stability of the material, making it necessary to completely oxidize it to fully recover the activity of the catalyst. Still, the decrease in the H_2 yield was much lower at 4 bar, in line with the results obtained in Section 2.2.3—the amorphous and graphitic coke productions were much lower, inducing less inhibition of the catalyst and increasing the stability. In this way, it was possible to conclude that the formation of coke is the main route for the deactivation of the Ni-Ru/Ce³ catalyst, as verified in a previous work for a similar catalyst [8]. In addition, it was observed that the TOC conversion remained practically constant along the time-on-stream for both pressures (≈ 95 —see Figure 5) when the oxidative regeneration step was properly/completely performed. The H_2 yield observed was always between 12 and 6.5 mol_{H₂}·mol_{OMW}^{−1} at 1 bar and always between 7 and 3.5 mol_{H₂}·mol_{OMW}^{−1} at 4 bar. So, the lower H_2 yield verified at 4 bar in Section 2.2.3, for this catalyst, was not related to the deactivation of the catalyst but explained by the fact that H_2 production was not favored at this pressure.

3. Materials and Methods

3.1. Chemicals and Gases

Nitrogen ($\geq 99.999\%$ —used as the carrier gas in the catalytic experimental tests and the makeup gas for the gas chromatograph (GC Agilent 7820A—Santa Clara, CA, USA), respectively), reconstituted air ($\geq 99.999\%$ —used as the oxidant agent during the catalyst regeneration program of the catalyst), argon ($\geq 99.999\%$ —the makeup gas for the GC) and hydrogen ($\geq 99.999\%$ —for the GC and catalyst activation) were supplied by Linde (Dublin, Ireland).

All the components present in the synthetic OMW effluent (vanillic, gallic, cinnamic, 4-hydroxybenzoic and syringic acids, L-arabinose and D-galactose) were purchased from Alfa Aesar (Waltham, MA, USA), except the veratric and protocatechuic acids, obtained from Acros Organics, and tyrosol, obtained from Sigma-Aldrich (St. Louis, MO, USA). An aqueous solution of HCl (Sigma-Aldrich, ≥ 37 wt.%) and an aqueous solution of HNO₃ (JMGS, Odivelas, Portugal, ≥ 65 wt.%) were used in the ICP-OES technique analyses.

3.2. Catalysts and OMW Preparation

One commercial catalyst—Rh/Al₂O₃ promoted with an alkaline earth metal, manufactured by Johnson Matthey (herein called by Rh)—and five prepared catalysts—Ni-Ru-based catalysts supported on SiO₂ and doped with CeO₂ (herein called Ni-Ru/Ce^x, with x varying from 1 to 5)—were used in this work. All the precursors of the metals and the support were obtained from Sigma-Aldrich.

A series of Ni-Ru/Ce catalysts were synthesized using different preparation methods using SiO₂ as support and CeO₂ as promoter—see Table 5. First, before the metal loading, SiO₂ was calcined during 5 h at 500 °C (heating rate of 5 °C·min^{−1}) to activate the support, as mentioned in previous works [49,50]. Then, in order to prepare the Ni-Ru/Ce¹ (Figure 6a) and Ni-Ru/Ce² (Figure 6b) samples (see the methodology in Figure 6 and Table 5), the activated support was impregnated (wet impregnation) with an aqueous solution of Ni(NO₃)₂·6H₂O, RuCl₃·H₂O and Ce(NO₃)₃·6H₂O dissolved simultaneously in water, with the aim of achieving a final Ni content of 10 wt.%, Ru content of 1 wt.% and Ce content of 0.3 wt.%. The Ni-Ru/Ce³ (Figure 6b) sample was prepared using the same procedure (cf. Figure 6 and Table 5), however with the aim of achieving a final Ce content of 3 wt.%. These three catalysts were dried at 60 °C (during 24 h) and calcined at

250 °C (during 5 h—heating rate of 5 °C·min^{−1}) in the final preparation procedures. The calcination temperature of these catalysts was chosen considering the TGA results obtained in a previous work [8]; particularly, it was possible to verify that at high temperatures (>270 °C), the catalyst decomposed due to the volatilization of Ru, as also verified in other studies [51–55].

Table 5. Preparation conditions considered in the production of the series of Ni-Ru/Ce catalysts.

Catalyst	SiO ₂ Particles Size (μm)	Stirring Temperature (°C)	Ni (wt.%)	Ru (wt.%)	Ce (wt.%)	Calcination Temperature (°C)
Ni-Ru/Ce ¹	210–500	Room temperature	10	1	0.3	250
Ni-Ru/Ce ²	1410–3360	55			3	
Ni-Ru/Ce ³					0.3	250 and 550
Ni-Ru/Ce ⁴					3	
Ni-Ru/Ce ⁵						

The preparation of the Ni-Ru/Ce⁴ (Figure 6c) and Ni-Ru/Ce⁵ (Figure 6d) samples followed a distinct preparation method (see Figure 6 and Table 5). In the production of the Ni-Ru/Ce⁴ catalyst, the activated support was, firstly, impregnated (wet impregnation) only with an aqueous solution of Ce(NO₃)₃·6H₂O dissolved in water; then, the sample was dried at 60 °C (during 24 h) and calcined at 250 °C (during 5 h—heating rate of 5 °C·min^{−1})—higher temperatures are not required to form CeO₂ [56,57]. At that point, the sample was impregnated again (wet impregnation) with an aqueous solution of Ni(NO₃)₂·6H₂O, dried again at 60 °C (during 24 h) and calcined at 550 °C (during 5 h, 5 °C·min^{−1}). Lastly, the sample was impregnated (wet impregnation) with an aqueous solution of RuCl₃·H₂O and, finally, only dried at 60 °C (during 24 h) to avoid Ru evaporation. To produce the Ni-Ru/Ce⁵ catalyst, the activated support was, firstly, impregnated with an aqueous solution of Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O dissolved simultaneously in water, dried at 60 °C (24 h) and calcined at 550 °C (during 5 h, 5 °C·min^{−1}). Then, the sample was impregnated with an aqueous solution of RuCl₃·H₂O and only dried at 60 °C (during 24 h).

In addition, the aqueous solution prepared for the production of the Ni-Ru/Ce¹ catalyst was stirred at a lower temperature (room temperature) than the other aqueous solutions considered in this work (stirred at 55 °C)—see Table 5. The calcination treatments applied for all the materials were performed with the purpose of removing volatile species (e.g., H₂O and NO₃^{2−}) and promoting the formation of metal oxides (e.g., NiO). The calcination temperatures used in the treatment of these catalysts was similar to the ones selected for identical materials prepared in previous works [58–60]. The size of the support particles (SiO₂—between 210 and 500 or 1410 and 3360 μm) was controlled before the impregnation of the metals, using a sieve.

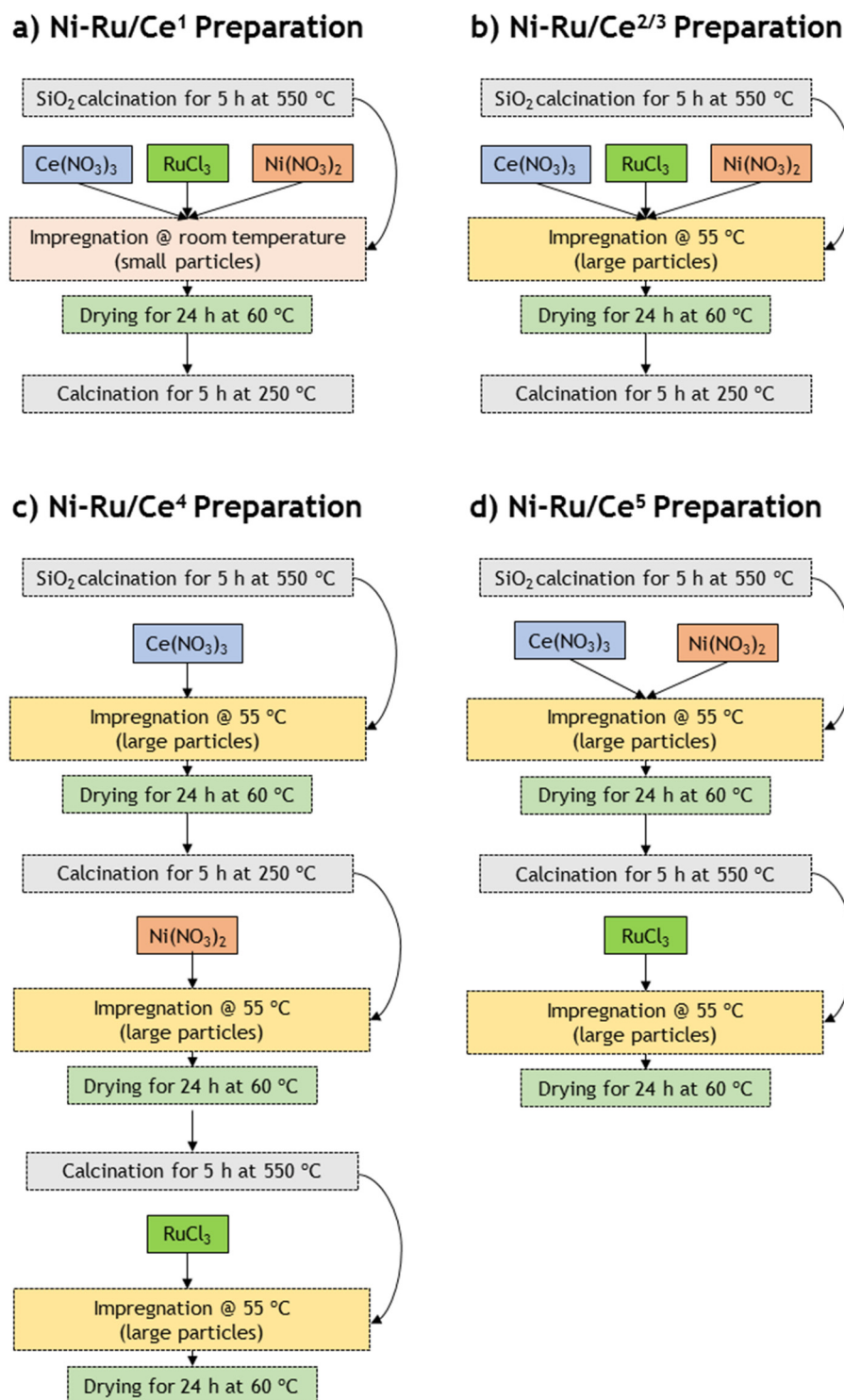


Figure 6. The schematic flowchart illustrates the preparation steps for the series of Ni-Ru/Ce catalysts used in this work.

The selected metal loadings were based on previous studies that employed similar compositions [8,61]. A relatively low Ru content (1 wt.%) was chosen due to its high cost, while still being sufficient to promote catalytic activity. The Ni loading of 10 wt.% is commonly used in the literature to ensure adequate active phase dispersion, and the Ce content was varied (0.3–3 wt.%) to evaluate its effect on the catalyst performance. Summing up, and considering the description of the preparation methods utilized (see Figure 6), it was possible to observe that the preparation parameters studied in this work were

the particles size, temperature of the impregnation, content of Ce, order of the metal's impregnation and calcination programs. It is important to emphasize that careful control of the stirring temperature during catalyst preparation is very important to control the morphology of the material, which in turn influences the catalyst's efficiency and longevity in steam reforming reactions.

The synthetic OMW was composed of a mixture of six different phenolic acids and two sugars typically present in real OMW streams (see Table 6). The concentrations of the components were adjusted according to several reports in the literature, namely they were based on the compositions defined with OMW real streams [4,62–65]. The compounds were dissolved in distilled water and then the solution was submitted to ultrasound (Sonorex Super RK255H from Bandelin Electronic GmbH & Co. KG [Berlin, Germany]) for 15 min to ensure full dissolution (the steam to carbon feed ratio was equal to 694).

Table 6. OMW composition.

Chemical Compound	Concentration (mg·L ^{−1})
Vanillic acid	50
Gallic acid	50
Cinnamic acid	50
Syringic acid	50
Tyrosol	100
Veratric acid	100
4-hydroxybenzoic acid	100
Protocatechuic acid	100
L-arabinose	1050
D-galactose	450

3.3. OMW and Catalysts Characterization

The total organic carbon (TOC) was determined by catalytic oxidation at 698 °C (method 5310 D [66]) with a TC/TOC analyzer (Shimadzu TOC-L apparatus equipped with an auto-sampler, which was operated at a maximum coefficient of variation $\leq 2\%$). A TOC of 972 ppm was observed for the initial effluent of OMW used in this research work.

In situ temperature-programmed reduction (TPR-H₂), in a custom-built facility, of all the Ni-Ru/Ce catalysts (around 1 g) was carried out after thermal treatment at 150 °C for 1.5 h under N₂ flow (100 mL_N·min^{−1}) to remove the water. Thereafter, the sample was cooled down to room temperature and then heated up to 820 °C (10 °C·min^{−1}) under a flow rate of 10 mL_N·min^{−1} of H₂ diluted with 90 mL_N·min^{−1} of N₂ (10 vol.% H₂ in N₂). For the in situ temperature-programmed desorption (TPD-CO₂) of the Ni-Ru/Ce samples, the fresh catalysts (around 200 mg) were first reduced (see in Section 3.4 the activation program applied in this work, based on the TPR-H₂ results). Then, the methodology was analogous to the one reported elsewhere [67]: the catalysts were fully saturated with CO₂ at room temperature for 1 h under CO₂ flow (30 mL_N·min^{−1}). The setup was flushed with N₂ for 30 min and the catalyst was heated up to 820 °C at 10 °C·min^{−1} (under a flow of 30 mL_N·min^{−1} of pure N₂).

For the in situ temperature-programmed oxidation (TPO) analyses/oxidative regeneration of the catalysts, the samples of spent catalysts were treated with a flow of 25 mL_N·min^{−1} of reconstituted air (20 vol.% O₂/N₂ stream; similar to air composition, thus cheaper in industrial practice) diluted in 75 mL_N·min^{−1} of N₂, first at 400 °C and then at 500 °C—the duration of this program at both temperatures was object of study in

this work. Air was diluted in nitrogen during the TPO to avoid the temperature gradients observed in previous works [43]. The amount of carbon gasified in the form of CO₂ and CO was measured with an online infrared-based analyzer (Servomex, model 4210). The CO and CO₂ outlet concentrations obtained in the TPR-H₂ runs were also monitored with this analyzer.

The metal contents of the Ni-Ru/Ce catalysts were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES) using an iCAP 7000 spectrophotometer from Thermo Scientific. Prior to the analysis, the samples were digested in a mixture of HCl and HNO₃ (10:1) at 250 °C using a Start D Microwave Digestion System from Milestone. Then, 10 mg of each sample was digested and then diluted with ultrapure water until reaching 50 mL. Any possible support residues remaining after digestion were eliminated by filtration.

3.4. Catalytic Experiments and Performance Indicators

The experimental tests were performed in a custom-built stainless-steel module that consists of two concentric tubes with different diameters: a stainless-steel module shell with 32 cm of length and 4 cm i.d. and a stainless-steel tube closed at both ends with 30 cm of length and 12.7 mm o.d. The packed-bed with the catalyst and inert is localized between these 2 tubes (reaction medium with 12 cm of length) and, in this way, the feed stream flows through the annular section during the reaction (see the detail in Figure 7)—this configuration was considered since it is expected to use the best material in multifunctional reactors (namely in a membrane reactor). At the bottom and upper parts of the module, a layer of SiC smooths the flow of the reaction mixture. The module was placed inside a tubular oven (model Split from Termolab, Fornos Eléctricos, Lda., Águeda, Portugal) equipped with a 3-zone PID temperature controller (model MR13 from Shimaden, Nerima City, Japan). The thermocouples used to evaluate and control the oven temperature were placed in the same radial position in the oven and very close to the column wall. In addition, a thermocouple recorded the temperature inside the module (inside the reaction medium). N₂ was fed into the reactor using a mass flow controller (model F201 from Bronkhorst-High Tech, Ruurlo, The Netherlands), while the OMW solution was fed by an HPLC pump (Eldex, 1LMP) and forced to pass through an evaporation/mixing zone at 400 °C before entering the reactor. The pressure in the system was measured by means of two pressure transducers (model PMP 4010 from Druck) placed before and after the packed-bed unit. The liquid phase produced during the course of the reaction was condensed in a home-assembled Peltier cold trap located after the reactor (cf. Figure 7). The tube and fittings between the module outlet and the first Peltier condenser were kept at 150 °C to avoid condensation. A system of two Peltier-based cold traps, a coalescence filter and a filter were used between the reactor and the analysis system to retain all the condensable species.

A gas chromatograph (GC-Agilent 7820A) equipped with a thermal conductivity detector (TCD using N₂ as makeup gas) and a flame ionization detector (FID—with a methanizer and using He as makeup gas) was used to analyze the gaseous products. The chromatograph is also equipped with two columns (Plot Q (30 m × 0.32 mm) and Plot 5A (30 m × 0.32 mm)). The H₂ was analyzed by TCD with Ar as a carrier gas to achieve a better response owing to the higher difference in thermal conductivity.

An oxidative regeneration program was considered in the catalytic experiments because it was previously observed that this treatment (promoting the coke deposits' gasification) for several catalysts used in the OMWSR process allowed the recovery of the catalytic performance [9,43].

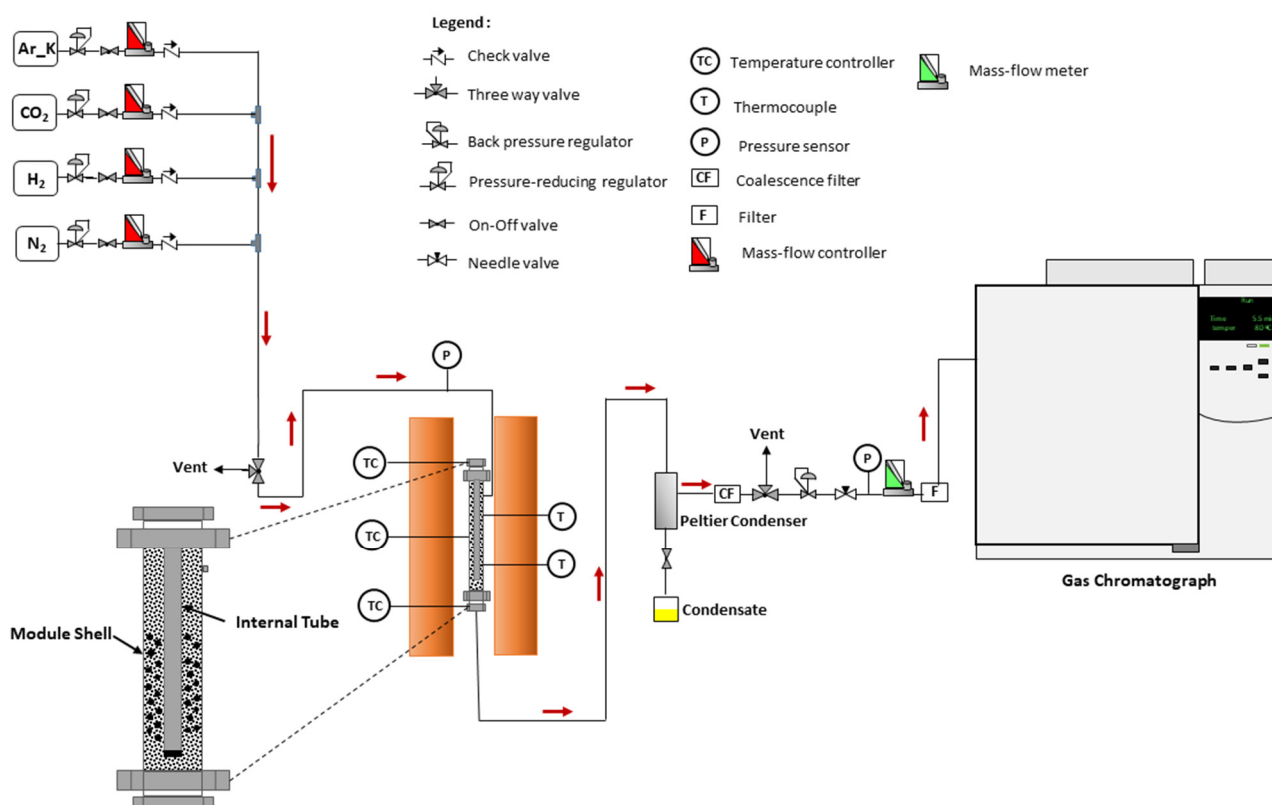


Figure 7. Scheme of the set-up and detail of the stainless-steel module used for the experimental tests.

The catalysts were crushed, sieved (350–600 μm) and mixed with inert silicon carbide particles with the same particle size. Using this range of particle sizes, it is possible to neglect the gas–solid wall effects and the pressure drop in the reactor. Before the OMW steam reforming catalytic tests (also before the TPD- CO_2 analyses), the catalysts were activated (@ 400 $^\circ\text{C}$ during 2 h under a 10% H_2/N_2 stream—total flow rate of 100 $\text{mL}_{\text{NPT}}\cdot\text{min}^{-1}$), taking into account the results of the TPR- H_2 analyses (see more details in Section 2.1.1).

The operating conditions used in this work are shown in Table 7. The blank tests, herein called *Exp. 0*, in which the packed-bed reactor was filled only with inert SiC , was carried out for all the operation conditions studied in this work. In addition, two other different experimental runs were carried out. For the Rh-based catalyst, preliminary experimental tests (*Exp. 1*) were carried out with different catalyst masses, from 0.3 to 3.5 g, to see the effect of the quantity of catalyst on the OMW conversion and H_2 production and to define the catalyst mass for the *Exp. 2*. In *Exp. 2*, a high quantity of catalysts was used (7 g) and, besides that, oxidative regeneration was always performed before changing the system pressure. Finally, in *Exp. 3*, stability tests were performed during 24 h with the two catalysts with better performance in *Exp. 2*. The catalyst oxidative regeneration was employed in *Exps. 2* and 3, since it was verified in a previous work that this treatment allowed almost complete recovery of the catalytic performance [9]. In this work, the occurrence of two different combustion peaks was observed during the oxidative regeneration of the spent samples, below and above 500 $^\circ\text{C}$, which were connected to the oxidation of amorphous and graphitic carbon deposits, respectively. In this work, for the in situ oxidative regeneration program used in *Exps. 2* and 3, the sample of spent catalyst was treated with a flow rate of 25 $\text{mL}_{\text{N}}\cdot\text{min}^{-1}$ of reconstituted air (20 vol.% O_2 in N_2) diluted with 75 $\text{mL}_{\text{N}}\cdot\text{min}^{-1}$ of N_2 , first at 400 $^\circ\text{C}$ and then at 500 $^\circ\text{C}$. The coke produced during the experimental tests of the *Exp. 3* runs was fully oxidized (the concentration of CO_2 measured

at the reactor outlet was equal to zero at the end of the program). After this procedure, the catalyst was exposed to a reducing atmosphere (H_2), as described in this section.

Table 7. Operational conditions for the different experimental tests.

Experimental Runs	Catalyst (s)	Temperature (°C)	Pressure (Bar)	Catalyst Mass (g)	Oxidative Regeneration Program
Exp. 0	-			-	-
Exp. 1	Rh	400	1/2/3/4	0.3/0.6/3.5	3 h at 400 °C and 2 h at 500 °C *
Exp. 2	Rh and Ni-Ru/Ce ^x			7	3 h at 400 °C and 2 h at 500 °C
Exp. 3	Rh and Ni-Ru/Ce ³		1/4		Full oxidation at 400 and 500 °C

* Only used in one particular experimental test.

Samples of the condensable phase were collected during all the experimental tests and analyzed in terms of the TOC. The system was always flushed with N_2 ($100 \text{ mL}_{\text{NPT}} \cdot \text{min}^{-1}$) for 20 min between the treatment programs and before and after the catalytic tests in all the experimental runs.

In all the experimental runs, the OMW was fed into the evaporation system at a constant flow rate of $0.5 \text{ mL} \cdot \text{min}^{-1}$. Then, the vaporized OMW was carried into the reactor by the carrier gas ($25 \text{ mL}_{\text{NPT}} \cdot \text{min}^{-1}$ of N_2).

The conversion of OMW during the reaction was analyzed by the TOC conversion—Equation (13):

$$\eta(\%) = \left(1 - \frac{\text{TOC}_{\text{outlet}}}{\text{TOC}_{\text{inlet}}}\right) \times 100 \quad (13)$$

where the subscripts “inlet” and “outlet” stand for the feed and outlet condensate streams, respectively. The yield of the reaction products was calculated by Equation (14), where F_i is the molar flow rate of component i (H_2 , CO_2 , CO and CH_4) at the outlet stream and F_{OMW} is the molar flow rate of compounds present in the OMW flowing into the system.

$$\text{Yield}_i = \frac{F_i}{F_{\text{OMW}}} \quad (14)$$

4. Conclusions

Among the synthesized catalysts, Ni-Ru/Ce³ showed the best results upon a comparison of the performance of a series of Ni-Ru/Ce-SiO₂ catalysts prepared by different methods. The Ni-Ru/Ce³ was prepared through a straightforward and reproducible method. All the catalysts tested in *Exp. 2* presented deactivation over the experimental campaign, especially at 1 bar.

In the stability tests, it was confirmed that the catalysts suffer from pronounced deactivation at 1 bar when oxidative regeneration with a fixed time was employed. However, after total oxidative regeneration, complete recovery of the catalytic performance was observed in the stability tests at 1 and 4 bar and the stability of the catalyst increased.

Moreover, with complete oxidation of the coke, it was observed that the TOC conversion remains stable at approximately 95% over 24 h time-on-stream for both pressures and the H_2 yield observed was always between 12 and $6.5 \text{ mol}_{H_2} \cdot \text{mol}_{\text{OMW}}^{-1}$ and 7 and $3.5 \text{ mol}_{H_2} \cdot \text{mol}_{\text{OMW}}^{-1}$ at 1 and 4 bar, respectively. With this study, it was concluded that this type of catalyst was significantly deactivated due mostly to the coke produced.

For future work, testing the best material with real OMW effluents and considering new oxidative regeneration program strategies are proposed.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15070654/s1>, Figure S1: TPD-CO₂ profile of some selected Ni-Ru/Ce catalysts; Figure S2: Carbon gas products yields as a function of pressure, obtained in Exp.2 for all the catalysts at 400 °C (* repetition of the experimental condition for comparison purposes); Figure S3: Yields of H₂, CO₂, CH₄ and CO and TOC conversion in Exp.2 for all the catalysts as a function of time on stream at different pressures (* repetition of the experimental condition for comparison purposes).

Author Contributions: Conceptualization, C.R.; methodology, C.R.; validation, C.R. and M.A.S.; investigation, C.R.; resources, L.M.M.; writing—original draft preparation, C.R.; writing—review and editing, M.A.S. and L.M.M.; supervision, M.A.S. and L.M.M.; funding acquisition, L.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by national funds through FCT/MCTES (PIDDAC): LEPABE, UIDB/00511/2020 (DOI: 10.54499/UIDB/00511/2020) and UIDP/00511/2020 (DOI: 10.54499/UIDP/00511/2020), and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020). This work was also financially supported by national funds through the FCT/MCTES (PIDDAC), under the project DRI/India/0504/2020-WASTENERGY –Distillery WASTes Valorisation into renewables ENERGY, with DOI 10.54499/DRI/India/0504/2020. This work is also financially supported by the HYDROAZEITE project, funded by U. Porto Innovation through the BIP PROOF 2023 program.

Data Availability Statement: No research data available for this work.

Conflicts of Interest: The authors declare no conflicts of interest.

Notation and Glossary

List of Variables

F_i	Molar flow rate of component i at the reactor outlet (mol·min ^{−1})
F_{OMW}	Molar flow rate of OMW fed to the reactor (mol·min ^{−1})
η	TOC conversion (dimensionless)

List of Acronyms

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
FID	Flame ionization detector
OMW	Olive mill wastewater
OMWSR	Olive mill wastewater steam reforming
TCD	Thermal conductivity detector
TOC	Total organic carbon
TPO	Temperature programmed oxidation
WGS	Water–gas shift

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