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Rh-perovskite catalysts for conversion of tar from biomass pyrolysis

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ABSTRACT

Alumina supported Rh-$LaCoO_3$ has been investigated for the catalytic conversion of tar produced by biomass pyrolysis into hydrogen-rich gas. A double fixed bed reactor system, equipped with a micro-chromatograph for the analysis of permanent gases and a chromatograph for the analysis of condensable species, has been developed to perform a preliminary screening of catalysts with different compositions by contacting them at 700 °C with a real mixture of gas and volatiles produced by biomass decomposition.

Biomass has been characterized by elemental, proximate and thermal analysis. Redox properties of catalysts, estimated with H_2 Temperature Programmed Reduction (TPR) analysis, have been correlated to the catalytic performance towards tar conversion. All catalysts completely convert tars into syngas with small quantities of CH_4 and CO_2, more reducible catalysts also strongly improve tar reforming and inhibit coke deposition.

1. Introduction

Biomass conversion to a hydrogen-rich gas is attracting an increasing interest because of depletion of fossil fuel, being an abundant and renewable energy source with a CO_2 neutral effect on the environment [1].

Biomass undergoes an easy decomposition process at quite low temperature (150–350 °C) producing a wide range of species [2]. A fast heat transfer, temperatures higher than 600 °C and the presence of an oxidant agent (steam, O_2, air, CO_2) promote the production of gas with respect to solid and liquid phases [3]. These conditions can be easily reached in a fluidized bed reactor [4]. Nevertheless, in a gasification process formation of tars represents a severe limitation and conversion of these products into permanent gases is required to transform biomass into a suitable fuel for internal combustion engines, fuel cells or feedstock for chemical synthesis [1].

Both mechanical methods and thermal cracking have been proposed for tars removal [5]. Mechanical methods do not allow energy recovering from tars which are just removed from product gases, while thermal cracking requires temperature higher than 1100 °C to convert them. The catalytic tar decomposition has been proposed to overcome these drawbacks [5]. In addition, the use of a catalyst can enhance the gas formation and modify the gas composition promoting the reforming reactions of hydrocarbons [6].

Different catalysts, such as nickel-based catalysts [7], dolomites [8], olivine [9] and zeolites [10], have been investigated for the catalytic tar decomposition, mostly used in a secondary reactor where the volatile tar, generated from the thermal decomposition of the biomass in the primary gasifier, cracks down to the product gas on the catalyst surface in the presence of gasifying agents such as steam, oxygen or air. Dolomites and nickel-based catalysts are the most conventional catalysts for tar decomposition in the secondary reactor at 800–900 °C and 700–800 °C, respectively [5]. Nevertheless, dolomites suffer from low mechanical strength and poor activity in the modification of gaseous hydrocarbon concentrations. On the other hand, although both a tar conversion higher than 99% and an effective reforming of light hydrocarbons in the gaseous products can be obtained using Ni based catalysts, they have a short life-time due to the large amounts of carbon deposited on the surface [5].

Recently, catalysts containing transition metals different from nickel (Co, Fe, etc.), supported (Al_2O_3, MgO, etc.) or not, have been also studied in order to improve the activity and the stability of catalysts [11–14]. Moreover, the introduction of Ni in a perovskite matrix together with other transition metals has been suggested to depress coke formation [13]. The use of noble metals has also been proposed [15–18]. 100% C-conversion to gas and high tar reforming ability have been reported for Rh/CeO_2 in cellulose gasification even if catalyst deactivation was observed due to a decrease in surface area [16]. More recently the use of SiO_2 has been suggested to inhibit the aggregation of CeO_2 and maintain the catalytic activity [16–17], whereas the use of Al_2O_3 increases the reforming activity of the catalyst and the effectiveness in coke suppression [18].

Primary catalysts are usually used in fluidized beds and consist of natural materials (dolomite or olivine) because of their low cost and large availability, which make possible a direct use in biomass fluidized bed gasifiers. As far as the development of a more active synthetic catalyst is concerned, it is not reasonable to perform a

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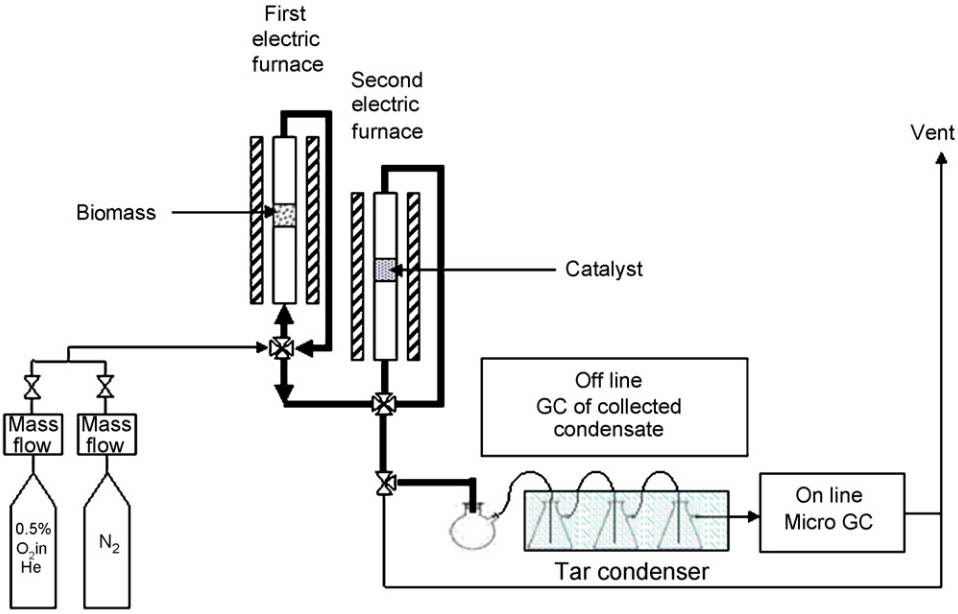

Fig. 1. Scheme of the catalytic screening plant.

preliminary screening at the typical scale of fluidized bed gasifiers, which implies the loading of large amounts of catalyst. In order to carry out a catalytic study a more sensible approach is a lab-scale fixed bed [10,11,14]. This system allows an easier evaluation of the catalytic performances using small quantities of material, generally investigating the catalysts effectiveness in the conversion of tar model compounds [10,14].

In the present work a double fixed bed reactor experimental plant has been developed to carry out a preliminary screening of novel noble metal based catalysts by contacting the catalyst kept at a constant operating temperature with a real mixture of products coming from the biomass decomposition. This system represents an alternative and more complete solution to a single bed catalytic reactor operating with one or more model compounds.

A Rh-$LaCoO_3$ supported on γ-alumina catalyst has been proposed for tar conversion due to the reforming and oxidation properties of noble metal and perovskite, respectively, which can potentially improve hydrocarbons conversion and avoid coke formation. Moreover, the introduction of the noble metal into the perovskite matrix improves its thermal stability by hindering sintering phenomena [19–21], which can take place at the typical temperatures of biomass gasification processes (up to 900 °C [22]).

2. Experimental

2.1. Biomass

Maple wood chips were used as biomass. The proximate analysis, performed with a TGA 701 LECO thermogravimetric analyzer, gave the following composition: moisture (8.9 wt.%), volatiles (74.6 wt.%), fixed carbon (15.9 wt.%) and ash (0.6 wt.%). The chemical composition, estimated on dry basis by elemental analysis, using a CHN 2000 LECO analyzer, was found to be: 46.28 wt.% C, 5.56 wt.% H, 47.52 wt.% O, 0 wt.% N. The thermogravimetric analysis of biomass and the evaluation of its thermal behaviour were also performed using a Perkin Elmer TGA7 balance. The thermo-balance was connected to a gas cell of a FTIR spectrometer (Perkin Elmer Spectrum GX) for the analysis of released products. Both FTIR cell and transfer line were heated at 200 °C in order to avoid tar condensation. During the experiment, about 25 mg of maple wood chips were heated under a constant nitrogen (99.998%) flow rate of 25 ml min^{-1}. The sample was firstly heated up to 100 °C at 2 °C min^{-1} and this temperature was kept for about 15 min in order to completely remove water; then the sample was heated at 5 °C min^{-1} up to 800 °C. In order to burn the fixed carbon after total devolatilization of the sample, kept at 800 °C, oxygen (2 vol.%) was added to the gas stream. During the heating ramp single scan FTIR spectra were collected each 12 s with 4 cm^{-1} resolution. The TG/FTIR experiment has been repeated several times obtaining the same weight loss and the same profiles of released species.

2.2. Catalyst

2.2.1. Preparation

The catalyst consists of a rhodium promoted $LaCoO_3$ perovskite supported on a commercial La stabilized (3 wt.% La_2O_3) γ-Al_2O_3 (Puralox SCF140-L3, SASOL) prepared by wet impregnation. Stoichiometric amounts of $La(NO_3)_3 \cdot xH_2O$ (Aldrich, >99.9%) and $Co(NO_3)_2 \cdot 6H_2O$ (Fluka, ≥99%) were dissolved in a water solution containing alumina adding few drops of nitric acid. The target amount of perovskite was 20 wt.%, corresponding to the theoretical monolayer coverage of the γ-Al_2O_3 (surface area = 140 $m^2\,g^{-1}$). The solution was completely evaporated and then the powder dried for 2 h at 120 °C.

A calcination treatment (3 h, flowing air: 150 ml min^{-1}, heating rate: 10 °C min^{-1}) at two different temperatures (800 or 900 °C) was performed. The calcined $LaCoO_3/Al_2O_3$ powder was impregnated with a $Rh(NO_3)_3 \cdot xH_2O$ (Riedel-de-Haën) solution using an amount of rhodium corresponding to 1 wt.%, then drying and calcination were repeated.

Catalysts containing 20 wt.% $LaCoO_3$ or 1 wt.% Rh only were also prepared for comparison with the bi-functional sample.

The catalysts will be referred to according to the following notation: *T*/p/Rh, where *T* is the calcination temperature and p and Rh indicates the presence of the perovskite or noble metal, respectively.

2.2.2. Characterization

Rhodium and cobalt contents were quantitatively determined using a ICP-MS Agilent 7500 instrument. Catalyst surface area measurements were carried out according to the BET method by N_2 adsorption at 77 K with a Quantachrome Autosorb 1-C analyzer.

Table 1
Rh and Co contents, BET surface areas, H_2 uptakes and H_2/metal ratios evaluated from TPR experiments of catalysts calcined at 800 and 900 °C.

Catalyst	Rh content (wt.%)	Co content (wt.%)	Surface area (BET) ($m^2\ g^{-1}$)	Total H_2 uptake ($mmol\ g^{-1}$)	H_2/Co ($mol\ mol^{-1}$)	H_2/Rh ($mol\ mol^{-1}$)
800/Rh	0.84	–	134	0.14	–	1.77
800/p	–	4.70	101	0.41	0.52	–
800/p/Rh	0.80	4.72	104	0.73	0.74[a]	1.77[b]
900/Rh	0.80	–	139	0.16	–	2.08
900/p	–	4.60	117	0.08	0.10	–
900/p/Rh	0.75	4.30	100	0.53	0.52[a]	2.08[b]

[a] Calculated by subtracting the H_2/Rh ratio of the corresponding *T*/Rh sample.
[b] Assigned on the basis of the H_2/Rh ratio of the corresponding *T*/Rh sample.

A Micromeritics 2900 TPD\TPR analyzer was used for H_2 Temperature Programmed Reduction (TPR) measurements reducing the catalyst with a 2% H_2/Ar mixture (25 ml min^{-1}) at 10 °C min^{-1} up to 800 or 900 °C depending on the calcination temperature. The catalyst was pre-treated for 1 h in air (100 ml min^{-1}) at the calcination temperature before the experiment.

2.3. Experimental rig

Fig. 1 shows the scheme of the catalytic screening plant. Two fixed bed quartz reactor (ID = 1 cm, length = 60 cm) were heated independently in two different electric furnaces. The dried biomass sample (500 mg, particle size range: 800–900 μm) was heated at 5 °C min^{-1} up to 800 °C in the first furnace under pure N_2 (99.998%) constant flow rate (12 N l h^{-1}) regulated with a Brooks mass flow controller (SLA 5850). The gaseous and condensable products formed in the first reactor by biomass pyrolysis passed through a second reactor containing the catalyst (500 mg, particle size range: 200–400 μm) kept at a fixed temperature (700 °C). Then the stream was sent to a two stage-condenser, in the first stage (a pear-shaped flask of 75 ml at room temperature) heavier tars were collected, whereas the second one (three Erlenmeyer of 50 ml) was used to collect lighter ones at −20 °C, following the CEN/TS 15439 (2006) procedure for sampling and analysis of tars. Finally, the permanent gases were sent to a micro gas chromatograph (Agilent 3000A), equipped with four different independent channels (with the following four columns: OV-1, Alumina, PLOT-U and MS5A), and a TCD detector. Helium was generally used as carrier gas for the analysis of O_2, CO, CO_2, CH_4 and C_2–C_6 hydrocarbons for all channels, however the most significant experiments were repeated under the same conditions using argon as carrier gas for the MS5A column in order to evaluate the H_2 concentration, although lowering the sensitivity of the measurement of other permanent gases.

The lines between the first and second reactor as well as between the second reactor and the first stage of the tar condensation train were heated between 300 and 400 °C to avoid the condensation of tarry compounds. The sampling train was weighted before and after the experiment for the quantitative evaluation of the condensable tars yield. The analysis of the condensed tars, after diluting with isopropanol, was performed off line in a gas chromatograph (HP 9600 series), equipped with a HP 35 PhenylEthylMethyl Siloxane column and a FID detector. As a measure of the catalysts performance, the difference between the yields and type of gas, liquid and solid products with and without catalyst, according to the method reported in [8,23], was used.

At the end of each experiment the amount of coke deposited on the secondary bed catalyst was determined by oxidation of the material after cooling down under inert atmosphere. The oxidation was performed following a heating ramp of 5 °C min^{-1} from ambient temperature up to 800 °C under O_2/He mixture (0.5 vol.%) constant flow rate (17 N l h^{-1}). The concentration of released carbon dioxide was measured using the micro GC. The numerical integration of the signal provided the stoichiometric amount of coke formed during the previous catalytic tar conversion experiment.

For all experiments the mass balance was closed with a maximum error of ±10 wt.%.

The good reproducibility of catalytic tests was verified by performing more than one experiment for each set of operating conditions. The obtained data were found to be reproducible.

Finally, the H_2/C ratio evaluated in the experiments with the most active catalysts (100% tar conversion) is very close to that expected from the biomass elemental composition by subtracting the carbon amount in the residual char.

3. Result and discussion

3.1. Catalyst characterization

In Table 1 the actual Rh and Co contents, the values of surface area of the catalysts calcined at both 800 and 900 °C, the H_2 uptakes

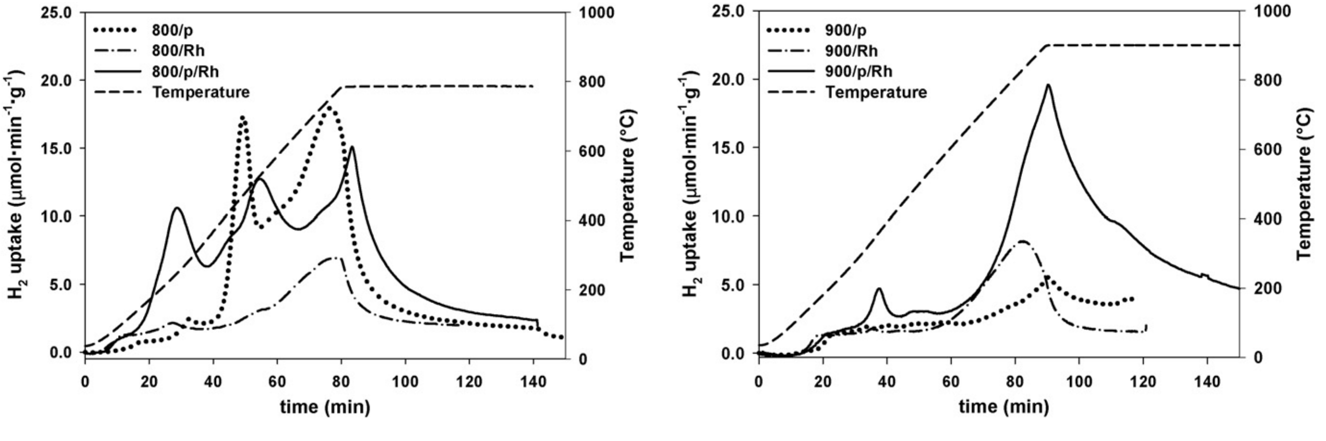

Fig. 2. Temperature Programmed Reduction test. H_2 uptake and temperature profiles as a function of time of catalysts calcined at 800 °C (left) and 900 °C (right).

and the H_2/metal ratios evaluated from integration of TPR profiles are reported.

The actual Rh content is always lower than the nominal one likely due to the undefined hydration of the Rh precursor salt. On the other hand the actual Co content is quite close to the nominal value (4.8 wt.%). Quite high values of surface area are maintained even upon calcination at 900 °C and, as expected, for both calcination temperatures the surface area decreases as the active phase loading increases.

In Fig. 2 the TPR profiles of catalysts calcined at 800 and 900 °C are reported.

The TPR profile of 800/Rh shows a lower temperature peak (250 °C) attributed to the reduction of rhodium oxide particles (RhO_x) having no interaction with the support, and a higher temperature peak (760 °C), accounting for a significantly greater hydrogen uptake, related to the reduction of Rh strongly interacting with the alumina to form spinel-type compounds ($Rh(AlO_2)_y$) [24]. In the TPR of 800/p sample the typical two stages reduction of cobalt from Co^{3+} to Co^{2+} and from Co^{2+} to Co^0, respectively, can be detected. The presence of those two peaks is characteristic of the $LaCoO_3$ bulk compound [25]. When 1 wt.% rhodium is added to the perovskite (800/p/Rh), the two peaks of cobalt reduction are still detectable and the low temperature signal of rhodium is more intense than for 800/Rh, suggesting that the perovskite layer has a barrier effect preventing or limiting the interaction between rhodium and alumina.

The H_2/Co ratio evaluated for 800/p catalyst, lower than the stoichiometric one (1.5), indicates that the interaction probably occurring between cobalt and alumina, leading to the formation of surface cobalt aluminate, limits the complete reduction of Co. On the other hand, rhodium is completely reduced to the metallic state in the 800/Rh sample, as shown by H_2/Rh ratio even exceeding the theoretical one (1.5) likely due to a not perfect recovery of TPR baseline which affects the signal integration or to the presence of some metal impurities. If a rhodium reduction occurring in the corresponding Rh/Al_2O_3 sample is assumed also for the bifunctional catalyst 800/p/Rh, the difference between the H_2 uptake of 800/p/Rh catalyst and the one due to the total Rh reduction can be attributed to the reduction of Co; the resulting H_2/Co ratio, lower than the stoichiometric one (1.5), is in agreement with the value obtained for the 800/p catalyst.

The TPR profiles of 900/Rh catalyst shows two peaks as for 800/Rh, however the low temperature signal, assigned to rhodium oxide, is smaller than that of 800/Rh suggesting that the higher calcination temperature promotes the formation of spinel-type compounds $Rh(AlO_2)_y$ due to the interaction of rhodium with the support. The same effect, even more pronounced, was observed for the 900/p catalyst. The perovskite-type phase, present in the sample calcined at 800 °C, has almost totally disappeared and a not easily reducible cobalt aluminate phase is formed due to the diffusion of cobalt in the alumina matrix. The signal starting just before the isothermal step of the experiment can be, in fact, attributed to the reduction of $CoAl_2O_4$ spinel [24,26]. Nevertheless, in the mixed sample 900/p/Rh, a greater amount of cobalt can be reduced at high temperature together with $Rh(AlO_2)_y$ species, as also shown by the greater amount of H_2 consumed. Furthermore, also in that case the lanthanum-cobalt mixed oxide layer partially inhibits the migration of rhodium into the alumina lattice, as shown by the peak of RhO_x at low temperature.

3.2. Catalytic tests

Before catalytic tests a preliminary analysis of the thermal behaviour of the biomass was performed using the TG-FTIR apparatus. The weight loss of the biomass and the corresponding IR spectra of the produced gaseous and volatile species are reported in Fig. 3.

Mainly water is released up to 100 °C (8.7 wt.%). However, a peak of CO_2 is detectable in this temperature range as also reported by Bassilakis et al. [27] which can be reasonably attributed to physically adsorbed CO_2. Then the decomposition of the biomass takes place mainly in the temperature range 150–350 °C, producing volatiles (75.8 wt.%). The two slopes detectable in the weight loss assigned to volatiles are attributed to hemicellulose (150–250 °C) and cellulose components (250–330 °C), respectively, whereas lignine decomposition takes place in a wider range of temperature superimposing to that of the other two components [2]. During the whole devolatilization phase the following species were detected by IR analysis: H_2O, CO, CO_2, alkanes (C–H bonds), aldehydes and acids (C=O bonds) and esters and formic acid (C–O–bonds). H_2 is not IR-detectable. Burning of fixed carbon takes place when oxygen is introduced in the flow at 800 °C, releasing CO_2. The amount of fixed carbon is 14.9 wt.%. The residual weight of the sample (0.6 wt.%) corresponds to ash. These values of weight loss are in good agreement with the results of proximate analysis reported in Section 2.1.

A further TG-FTIR experiment carried out by mixing the biomass with an equal amount of catalyst under the same conditions did not show any appreciable differences with the experiment without catalyst. Therefore, it was concluded that the TG-FTIR apparatus was not suitable to evaluate the performance of the catalysts since biomass decomposition takes place in a temperature range (150–350 °C) below that necessary to activate the catalyst (400–500 °C) [26]. As a consequence, the catalytic tests were carried out in the experimental rig, described in Section 2.3. This set-up

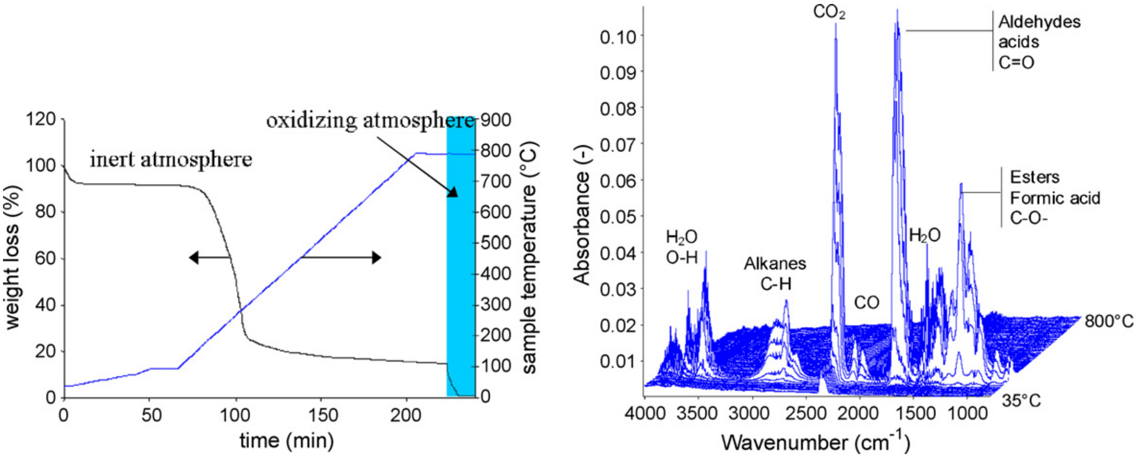

Fig. 3. Thermogravimetric analysis of biomass. Left: maple wood chips weight loss and sample temperature as functions of time. Right: infrared stack plot of volatile products emitted during the biomass decomposition.

Table 2
Solid, liquid and gas yields on dry basis obtained for the different materials loaded in the second reactor.

Material of the second reactor	Solid yield (wt.%)		Liquid yield (wt.%)	Gas yield (wt.%)	
	Char	Coke		Without H_2	With H_2
–	16.6	–	74.6	7.8	–
Sand	17.6	–	48.3	32.3	–
Alumina	16.8	5.1	29.2	51.5	53.2
800/Rh	16.5	2	–	71.9	77.5
800/p	18.3	3.5	–	72.0	75.9
800/p/Rh	18.0	1.1	–	72.5	77.6
900/Rh	17.3	2.6	–	73.5	–
900/p	18.3	5.6	11.0[a]	55.3	57.4
900/p/Rh	18.0	1.0	–	73.0	77.9

[a] Mainly water was found as liquid product.

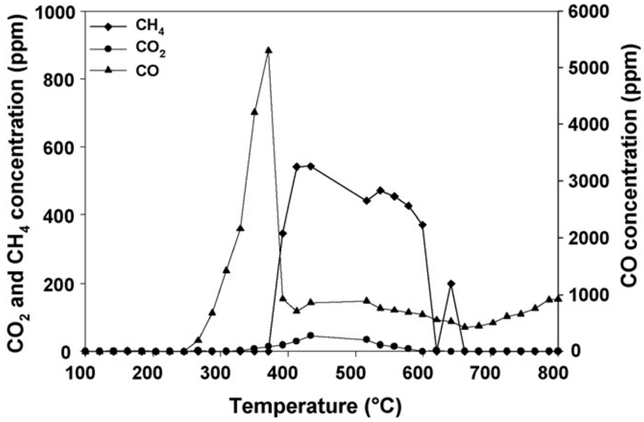

Fig. 4. Concentration profiles of the main gaseous products of maple wood pyrolysis as a function of sample temperature.

allows the catalyst to be kept at a given temperature being in contact with the gaseous and volatile products coming from biomass slowly decomposed in another furnace.

Three blank runs were carried out before catalytic tests. In the first one the second reactor was excluded and the quantitative and qualitative analysis of the biomass pyrolysis products was done. In the second one the second reactor was loaded with inert sand in order to verify the occurrence of thermal cracking reactions at high temperature (700 °C) and evaluate their effect. In the third one the La stabilized γ-Al_2O_3, used as catalytic support, calcined at 800 °C, was loaded in the second reactor in order to evaluate its possible contribution.

The products of the biomass pyrolysis were mainly constituted of gaseous species, condensable hydrocarbons and char. Their yields are reported in Table 2 on dry basis. Both char yield and total yield of liquid and gas (corresponding to volatiles species) are in agreement with the results of TG analysis.

Fig. 4 shows the profiles of detected gaseous species obtained from biomass pyrolysis as functions of sample temperature analyzed with the MS5A columns using He as carrier gas (no measure of produced H_2 is available in this run). They mainly consist of carbon oxides and methane, whereas light hydrocarbons (acetylene, ethylene, ethane, propane, propene, nC_4, nC_5, 1-pentene, 1-hexene) are emitted at very low concentration (<50 ppm) at about 370 °C. The amounts of light hydrocarbons are reported in Table 3. CO is the first compound to be released at about 270 °C, with a maximum concentration value of 5300 ppm at 370 °C (same peak temperature as light hydrocarbons), then its concentration sharply decreases down to 400 °C. The emission of CO continues at a lower extent until the end of the experiment. CO_2 starts being released at 330 °C and completely stops at 620 °C, its concentration being always less than 50 ppm. Methane starts to be released at about 390 °C with a maximum concentration of 540 ppm at 430 °C. A second peak of 200 ppm of methane is observed between 620 and 660 °C.

The chromatographic analysis of condensed tar highlighted the presence of different compounds. The identified peaks correspond to phenols, PAHs and guaiacols, characteristic of biomass decomposition. The identification of other species (acids, aldehydes, etc.) is still in progress.

In the blank run with sand the gaseous yield increases up to 32.3 wt.% with respect to the 7.8 wt.% obtained in the absence of the secondary reactor. Accordingly, the condensable tars are 48.3 wt.% compared to the 74.6 wt.%. The presence of the second reactor does not affect, as expected, the char yield (Table 2). The main components of the gas phase are again CO, CO_2 and CH_4, analyzed with the MS5A columns using He as carrier gas (no measure of produced H_2 is available). However, their concentration is about one order of magnitude higher than in the absence of the second reactor. Their profiles are reported in Fig. 5b–d, respectively, as functions of the temperature of the biomass sample. CO_2 is the first compound to be released at about 150 °C, with a maximum concentration value of about 5700 ppm at 350 °C; traces of CO_2 are observed also at higher temperature. CO starts to be released at 250 °C up to 400 °C, its concentration reaching a maximum value of about 27000 ppm at 350 °C. Methane starts to be released at about 300 °C up to 370 °C, with a maximum concentration of about 3200 ppm at 350 °C. The amounts of light hydrocarbons produced are reported in Table 3. In the case of sand the amounts of light hydrocarbons significantly increases with respect to the test carried out in the absence of the second reactor. They are emitted at different concentrations in the temperature range 170–560 °C; in particular, maximum concentration values of about 2500 ppm for ethylene and hundreds of ppm for nC_4, ethane, acetylene, propane and propene have been observed at 350 °C, the maximum concentration of remaining species being lower than 50 ppm.

Table 3
Amounts of gaseous light hydrocarbons produced during the biomass decomposition tests (μmol).

Sample in the second reactor	C_2H_2	C_2H_4	C_2H_6	C_3H_6/C_3H_8	nC_4	nC_5	1-Pentene	1-Hexene
–	1.3	0.7	0.6	0	1.1	0.2	1.3	1.6
Sand	50	307	42	56	38	2.7	6.7	1.3
Alumina	0	441	52	82	37	2.3	0	0
800/p	0	2.1	2.8	0	0	0	0	0
900/p	3.5	401	50	85	38	3.2	1.4	0.3

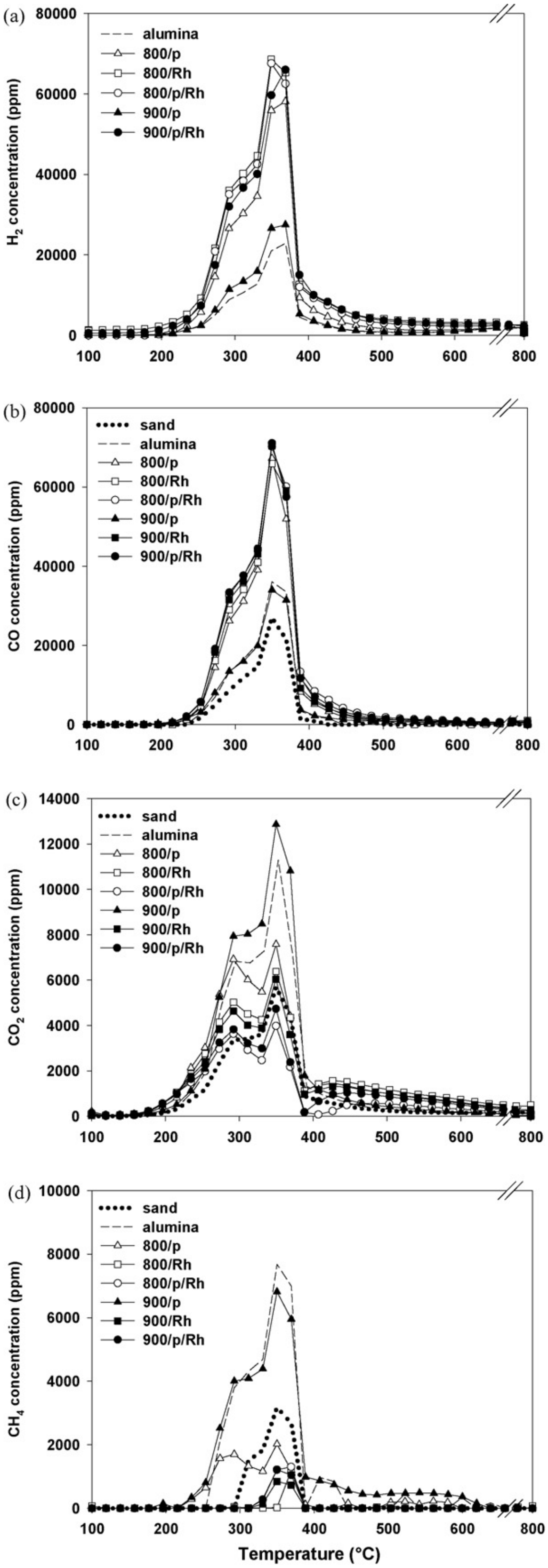

Fig. 5. Catalytic tar conversion tests. H_2 (a), CO (b), CO_2 (c) and CH_4 (d) concentration profiles as a function of biomass decomposition temperature.

Many compounds have been detected by the chromatographic analysis of condensed tar, with a qualitatively different products distribution if compared to that obtained in the absence of the second reactor. In particular, the oxygenated compounds (phenols and guaiacols) disappeared, whereas PAHs species were still detectable together with aromatic compounds. Moreover, a shift towards heavier polycyclic compounds has been observed. These findings suggest the occurrence of cracking phenomena followed by secondary reactions of polycondensation.

On the basis of these results, it can be concluded that the increase in the total gas yield can be explained by the thermal decomposition of part of the vaporized tarry species over the hot surface (700 °C) of the inert fixed bed material.

In the blank test with calcined alumina the gaseous yield increases up to 51.5 wt.% (53.2% including H_2) with respect to the 32.3 wt.% obtained with sand. Accordingly, the condensable tars decreases down to 29.2 wt.% compared to the 48.3 wt.% (Table 2). The concentration profiles of H_2, CO, CO_2 and CH_4 are reported in Fig. 5a–d, respectively, as functions of the temperature of the biomass sample. The carbon oxides profiles are qualitatively similar to those observed for sand, but with a significant yield increase. The hydrogen profile follows that of CO with a peak maximum of about 23000 ppm at 370 °C. Methane starts to be released at about 250 °C with a maximum concentration of about 7700 ppm at 350 °C. The emission of CH_4 continues at a lower extent up to 640 °C. Light hydrocarbons were produced in the temperature range 200–600 °C in similar amounts with respect to the test with sand (Table 3).

The chromatographic analysis of condensed tar showed a qualitatively similar products distribution to that obtained with sand, but with lower intensities.

On the basis of these results, it can be concluded that the presence of alumina in the second reactor further increases the gas yield (to the detriment of liquid phase), due to a stronger cracking activity related to its higher surface area and acidity.

The presence of a catalyst in the second reactor at 700 °C led to a large increase in gas yield due to the total conversion of tars, as reported in Table 2. In this table the gas yield both excluding or including H_2 has been reported for the catalysts which were also tested by changing the analysis conditions. Except for 900/p which favoured liquid formation (mainly water), no liquid condensation was observed in the flasks, neither at room temperature or at −20 °C. The char yield was in the range 16.5–18.3 wt.% for all the experiments, in good agreement with the data of TG analysis. All catalysts tested showed a gas yield higher than 72 wt.% (excluding H_2), except for the 900/p sample, which provided a lower gas yield (similar to calcined alumina).

As concerns the gaseous product distribution, no light hydrocarbons were found when rhodium was present in the catalyst also in combination with $LaCoO_3$ while the light hydrocarbons formed with the 900/p catalyst were qualitatively and quantitatively similar to those found with alumina whilst only ethane and ethylene, in small amount, were produced on 800/p, as reported in Table 3. H_2, CO, CO_2 and CH_4 were the main detected gas products for all samples. Their concentration profiles are also reported in Fig. 5a–d, respectively.

All samples showed two main CO_2 peaks at 290 and 350 °C. A broad peak extending from 390 °C to the end of the experiment was present for all catalysts except for sand, alumina and 900/p sample, the latter providing the highest total CO_2 concentration. As noted for the test with alumina the H_2 profiles qualitatively followed those of CO for all catalysts. As for light hydrocarbons the amounts of CO and H_2 produced on the 900/p was comparable to that found using alumina. All the other samples showed similar H_2 and CO yields, significantly higher than that observed for sand, alumina and 900/p sample. The highest concentration of methane in the gaseous products was found for calcined alumina and the 900/p

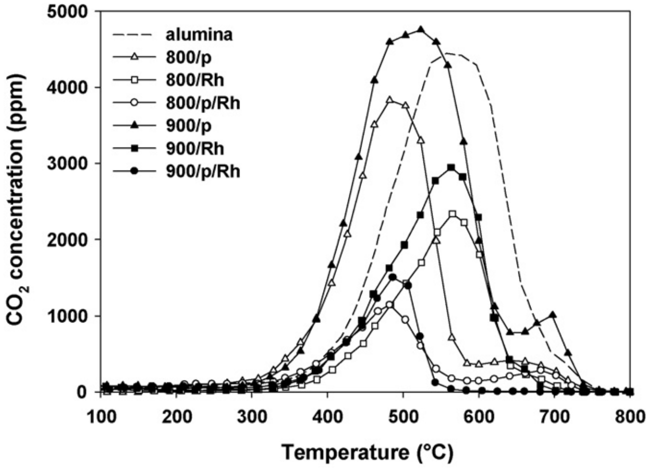

Fig. 6. CO_2 profiles obtained in coke oxidation experiments.

catalyst, followed by sand and 800/p. In the presence of the second reactor methane was produced at temperatures (215–390 °C) at which it was not present for simple pyrolysis and thus it should be the product of further conversion of species coming from the biomass decomposition. On the contrary, the methane released by the biomass in the range 390–660 °C remained essentially unconverted for sand, alumina and 900/p. Since CO_2 formation in the final stage (390–660 °C) overlaps the conversion zone of methane (390–660 °C), the activity of the 800/p/Rh, 800/Rh and 900/p/Rh, 900/Rh probably consists in the methane oxidation in this temperature range.

On the basis of the oxygen balance between the oxygen contained in the biomass and that in the detected gaseous products, the catalysts, not pre-reduced before each run, should be partially reduced by the pyrolysis products.

At the end of each experiment the amount of coke deposited on the secondary bed material was determined by its oxidation at 800 °C after having cooled down the material under inert atmosphere. Fig. 6 shows the CO_2 profiles obtained for the different materials. The amount of deposited coke expressed in wt.% on dry basis is reported in Table 2.

The sand does not tend to form coke, whereas the calcined alumina appears to be very sensitive to coking as well as the perovskite catalysts, specially the one calcined at 900 °C. The Rh catalysts appear less susceptible to coking, however calcination at 900 °C tends to increase slightly the coke formation. Nevertheless, the least coked materials are those containing both active phases (900/p/Rh and 800/p/Rh).

In conclusion, the results of catalytic tests can be summarized as follows: all catalysts are able to convert tars, promoting reforming, total oxidation or, in a lesser extent, cracking of species released during biomass decomposition. In particular, the activity of perovskite catalysts, specially of the 900/p sample (as well as calcined alumina), is more addressed to cracking and total oxidation (confirmed by the presence of water in the liquid phase) rather than to reforming reactions with respect to other samples, favouring the coke formation. On the other hand, the presence of Rh is fundamental to favour the reforming of methane and light hydrocarbons, not totally converted by samples not containing the noble metal. The Rh containing samples can also oxidize methane emitted from biomass pyrolysis in the range 390–660 °C to CO_2. In particular, the samples containing both Rh and perovskite phases showed the highest reforming activity and the lowest cracking activity, lower amounts of coke having been observed on these samples.

A possible explanation of these evidences could be obtained by correlation with the reducibility of the different samples. The hardly reducible catalysts (800/p and 900/p) fundamentally provide a good cracking activity coupled with a slight oxidation activity. On the contrary, the samples reducible at lower temperature due to the presence of easily reducible rhodium oxide alone or even of cobalt oxide (800/Rh, 800/p/Rh, 900/Rh and 900/p/Rh) promote reforming of tars into syngas and depress coke formation. In particular, thanks to the barrier effect provided by the cobalt-lanthanum oxide, highlighted by TPR analysis, both in the perovskite-like (800/p/Rh) or spinel (900/p/Rh) form, the rhodium was more easily reducible than when deposited directly on the alumina support. Those two catalysts were, by far, the best candidates for tar gasification.

4. Conclusions

Al_2O_3 supported Rh-$LaCoO_3$ catalysts were tested in a fixed bed reactor under isothermal conditions feeding the gas mixture originated from the biomass decomposition carried out in a separate furnace. A preliminary screening of samples characterized by different chemical composition and calcination temperature was carried out to evaluate their catalytic performance in biomass tar conversion. All catalysts effectively convert tars into syngas with small amounts of methane and carbon dioxide, however, less reducible samples mainly show cracking and total oxidation ability whereas more reducible catalysts give the best performances in reforming tars. Combination of Rh and $LaCoO_3$ also reduces coke deposition likely through the prevention of less reducible $Rh(AlO_2)_y$ formation and preservation of reforming properties of rhodium oxide. These features, in addition to the high thermal stability of this catalytic system, represent the basis for a potential use of this material as a primary catalyst in a fluidized bed reactor.

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