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Hydrocarbons valorisation to cleaner fuels: H_2-rich gas production via fuel processors

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ABSTRACT

This paper presents a panoramic overview of the experimental work carried out at *Politecnico di Torino* on the development of structured catalytic reactors for the production of H_2-rich streams from hydrocarbons, to be fed to PEM-FCs: short contact time catalytic partial oxidation (SCT-CPO) reactor for syngas production, micro-channelled reactors for syngas CO clean-up, water gas shift (WGS) and preferential oxidation (PROX). Concerning the reactor for methane SCT-CPO, 10% Ni deposited on irregular γ-Al_2O_3 particles presented the best performance (CH_4 conversion > 90%; H_2 selectivity > 95%) compared to 0.5% Rh deposited over γ-Al_2O_3 spheres. As regards the HT-WGS reaction, the best performance was obtained with the catalyst 1% Pt/(CeO_2 + TiO_2): it reached the thermodynamic equilibrium (inlet CO: 10% b.v.; WHSV = 40 Nl h^{-1} g_{cat}^{-1}) in the temperature range 450–525 °C, allowing the abatement of almost 60% of the CO present in the fed gas stream. Finally, the best performance towards CO-PROX reaction was obtained with the catalyst 1% Rh/(Al_2O_3 + 3A zeolite): it reached the complete CO conversion (inlet CO: 0.5% b.v.; WHSV = 40 Nl h^{-1} g_{cat}^{-1}; λ = 3) in the temperature range 130–160 °C, thus assuring an easy controllability of the system.

1. Introduction

The *World Energy Outlook 2009* from the International Energy Agency (IEA) sets out the present situation and the future scenario [1]: from 1980 to 2007 total world primary energy demand grew by 66%, and to 2030 it is projected to grow at a slightly less rate (40%, average 1.5% per year, from 503 EJ to 703 EJ). With United Nations predicted world population growth from 6.6 billion in 2007 to 8.2 billion by 2030, the energy demand should increase substantially with over 70% coming from developing countries, led by China and India [1].

On this point of view, H_2 as energy vector has received considerable attention as possible alternative to fossil fuels (FFs), when produced from renewable energy sources, like solar, wind or biomass. Actually 90% of H_2 production derives from FFs: of course, it will become a real large scale energy vector when many actual and crucial problems linked to its sustainable production, distribution and storage will be solved. Furthermore, its competition with other sustainable fuels as second and third generation biofuels is still an open question [2].

The supply of FFs will be limited in the future by the increasing reduction of the natural feedstocks. Moreover, the use of FFs creates big concerns in terms of harmful pollution and emissions of greenhouses gases from combustion processes [3]. Polymer electrolyte membrane fuel cells (PEM-FCs) have the potential to alleviate major problems associated with the production and consumption of energy. PEM-FCs, when supplied with H_2 derived from renewable energy sources (as solar, wind, biomass, etc.) produces only water as by-product: they have the potential to positively impact many areas, including environmental, economic, and energy security. PEM-FCs are also more efficient than present technologies in the conversion of chemical energy to power, even if their long-term stability must still be improved. Therefore, PEM-FCs can reduce either the problems associated with petroleum based energy production (air pollution, greenhouse-gas emissions) or the economic dependence on petroleum [4,5], if their production price will become competitive on the market. Anyway, there is still an open debate on the possible negative effects on the environment due to an exponential increase of PEM-FCs vehicles [6]: it is, in fact, actually unknown the environmental impact of unintended emissions of molecular H_2, including an increase in the abundance of water vapour in the stratosphere (plausibly by as much as about one part per million by volume). This would cause stratospheric cooling, enhancement of the heterogeneous chemistry that destroys ozone, an increase in noctilucent clouds, and changes in tropospheric chemistry and atmosphere-biosphere interactions [6].

Although H_2 is an attractive replacement for FFs, and the most abundant element in the universe, unfortunately it is not present in

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Table 1
Companies developing gasoline FP technologies (SR: steam reforming; POX: partial oxidation; WGS: water gas shift; PROX: preferential oxidation) [11–13].

Company	Reformer type		CO clean-up		Max power
	SR	POX	WGS	PROX	[kW_e]
IMM Mainz GmbH	x		x	x	5
Johnson Matthey Fuel Cells Limited	x	x	x		6
General Motors Company	x		x	x	30
Hydrogen Burner Technology Inc.		x	x		42
Daimler Benz AG	x			x	50
International Fuel Cells Inc.	x	x	x	x	100

the free form, but in various compounds, mainly water and hydrocarbons. Therefore, H_2, like electricity, is an energy carrier and must be taken out from natural resources. Considering that around 75% of the increase in oil demand comes from transportation [1], the PEM-FCs use in this field could represent a valid option. Up today, the on-board H_2 storage is actually a difficult challenge: sufficient fuel must be stored to ensure driving distances comparable to gasoline- or diesel-powered vehicles [7]. Moreover, the large-scale H_2 utilization is delayed by lack of infrastructure (storage and distribution), which growth is very slow owing its actual moderate demand. Consequently, a feasible short-mid term solution, waiting for the realization of infrastructures for H_2 management, could be represented by the on-board H_2 production from gasoline, diesel or methane, supplied by the refilling stations [8]. In such a context, FFs utilization efficiency will be higher, compared to the direct use in internal combustion engines, generating lower unsafe emissions and reducing the CO_2 production by approximately 33% [7].

As a result, on-board H_2 production has become increasingly important for FCs applications, mainly as auxiliary power units (APU), and it represents a satisfactory transition way to the H_2 economy in mobile applications [5]. The fuel processor (FP) is the H_2 production system: the FFs reforming primary step is followed by a series of catalytic steps suitable for both increasing the reformate H_2 concentration and CO removing (for safe delivery of the H_2-rich stream to the FCs) [9]. Anyway, a FP must assure an efficient H_2 supply during start-up of the engine and during the transient steps of engine acceleration/deceleration. It is expected that the on-board power consumption in vehicles will play an increasingly important role; the on-board power demand has, in fact, increased significantly in the last decade and it is expected to grow even further. For passenger vehicles, Delphi Automotive Systems, an American vehicle electronic equipment supplier, predicted that the installed electric power on-board will increase to 10 kW_e before 2020 [10]. This power will only be ensured by APUs in the vehicle and will not be used for traction purposes. If traction is taken into account as well, it is expected that the installed power will double [10].

A commercially viable portable reformer requires high efficiency in terms of conversion of FFs, thermal management, compactness, and easy integration with the FC. In recent years, many companies have conducted extensive research on FPs to produce H_2 from FFs, mainly gasoline and diesel oil, as shown in Table 1 [11–13], to be connected with PEM-FCs mainly for automobile application. The main technical characteristics of a stationary FP for PEM-FCs, suggested by U.S. DOE guidelines [14], are reported in Table 2. The suggested specific power and power density for the entire APUs are 100 W kg^{-1} and 100 W l^{-1}, respectively [14], with an electrical efficiency >40% respect to the LHV of the employed fuel [14].

The present paper refers on experimental investigations currently under development at *Politecnico di Torino* on the three main steps of a FP: (i) short contact time (SCT) reactors for methane catalytic partial oxidation (CPO) to syngas; (ii) catalytic reactors for CO clean-up via water gas shift (WGS) reaction; (iii) catalytic reactors for further CO clean-up below 2 ppmv via CO preferential oxidation (PROX).

Table 2
Technical targets for stationary FPs (equivalent to 5–250 kW_e) to generate H_2-rich gas streams for PEM-FCs, according to DOE guidelines [14].

Characteristics	Target 2011
Cost	220 \$ kW_e^{-1}
Cold start-up time to rated power @ −20 °C ambient	<30 min
Transient response time (for 10–90% power)	1 min
Durability	40,000 h
Survivability (min and max ambient temperature)	−35–+40 °C
CO concentration in product stream	
Steady state	1 ppm
Transient	25 ppm
H_2S concentration in product stream	<4 ppbv (dry)
NH_3 concentration in product stream	<0.1 ppm

2. Experimental

2.1. Catalytic partial oxidation of methane in short contact time reactors

Partial oxidation is presently considered an alternative to steam reforming for H_2 generation from FFs in decentralized applications and for stationary or mobile FCs [15]. Methane CPO to CO/H_2 mixtures has been largely investigated; several catalysts were proposed based on noble [16,17] and non-noble metals [18,19]: Rh disclosed to be the most active and selective, noble metal, able to avoid or at least partially limit coke formation [17]. However, it is a very expensive noble metal and its price fluctuates significantly [20]. Cheaper and alternative metal-based catalysts (such as Fe-, Co-, and Ni-based ones) would be desirable. In particular, Ni catalysts have been widely investigated because of their low cost and relatively high activity in methane CPO [19].

Two different alumina based catalysts (0.5% Rh/Al_2O_3 and 10% Ni/Al_2O_3) were prepared. The incipient wetness impregnation technique at room temperature was adopted to deposit the exact amounts of active metals over γ-Al_2O_3, starting from aqueous solution of $Rh(NO_3)_3$ [21,22] or nickel (II) nitrate hexahydrate dissolved in isopropyl alcohol [23]. The solutions were added drop by drop over the support meanwhile thoroughly mixing the whole mass. The as-prepared catalysts were left at rest overnight and then placed in oven with temperature ramp of 5 °C min^{-1} until 600 °C and then calcined in calm air for 2 h. Rh was deposited over 1 mm in diameter commercial Al_2O_3 spheres (Sasol Germany GmbH), whereas Ni over irregular particles obtained by crushing 3 mm in diameter Al_2O_3 spheres (Sasol Germany GmbH) and using the fraction sieved 600–1000 μm. Both the catalysts were characterized by FESEM (FESEM FEI Quanta Inspect 200 LV apparatus, coupled with EDAX GENESIS SUTW-sapphire detector) and by measuring the BET specific surface area via N_2 adsorption with an automated gas sorption analyzer (Micromeritics ASAP 2010 M apparatus), by degassing in vacuum for at least 12 h at 150 °C before analysis.

The catalytic activity of the prepared catalysts was determined in a fixed bed reactor, fully described in [21–23]. Briefly, CH_4 and O_2, mixed at room temperature, were fed to the reactor (Inconel 601 tube: 15 mm i.d.; 2 mm wall thickness; internal surface covered by an oxidized FeCrAlloy sheet to avoid contact between reactive gases and alloy wall, just to prevent any catalytic effect of alloy Ni) with O_2/CH_4 equal to 0.57. The catalyst fixed bed (1.5 g, ~2 cm of axial length) was arranged between two inert fixed beds: upstream, quartz bed (to complete the reagents static mixing) followed by high thermal conductivity SiC particles, to provide a shield for radiant energy emerging from the catalytic zone and promote reagents preheating. Downstream, low thermal conductivity quartz bed reduced heat losses and cooled slowly the outlet stream. Inlet and outlet gas temperatures were monitored by suitably located thermocouples. The outlet concentrations were measured using the following analysers: a hygrometer (GE) for humidity and a multiple gas analyzer (ABB) for H_2 (thermal conductivity module Caldos 17), $CO/CO_2/CH_4$ (infrared module Uras 14) and O_2 (paramagnetic O_2 module Magnos 106). The feed flow rate was adjusted accordingly to increase the weight hourly space velocity WHSV from 130 to 600 Nl h^{-1} $g_{cat}{}^{-1}$.

2.2. Water gas shift reaction in microchannelled reactors

Owing the demand of low both space and weight for on board vehicles APU systems, micro-structured reactors (MSRs) appear very promising in attaining maximum compactness. MSRs typically carry small channels with dimensions in the sub-millimeter range, with a high surface-area-to-volume ratio, which reduces diffusive transport limitations [24], and present the following advantages compared to conventional chemical reactors: (i) enhanced heat transfer; (ii) superior mass transfer; (iii) low pressure drop; (iv) short residence times. When the reactor plates are coated with catalyst, the heat generated by exothermic reactions (or required by endothermic ones) may be removed (or supplied) by design the reactor as a plate heat exchanger, thus improving the thermal management of the reactor itself [9]. This is the typical case for the WGS reaction. Considering that the reformate gas at the reformer outlet contains about 10% CO, the WGS reaction is the preferred process for the first CO removal: it reduces CO concentration to about 0.5–1% and simultaneously increases H_2 concentration [7]. Since at high temperatures CO conversion is equilibrium limited and at low temperatures kinetically controlled, normally two different WGS catalysts are commercially used. One for high temperature shift (HT-WGS), based on Fe and Cr oxides, reduces at 400–500 °C the CO concentration to about 2–5%. The second step (low temperature shift, LT-WGS) with Cu and ZnO on alumina catalyst, reduces CO concentration at 200–400 °C to about 0.5–1%.

After preliminary studies on powdered catalysts for HT-WGS [25–27], the best performing ones, i.e., 1% Pt/CeO_2 and 1% Pt/(50% CeO_2 + 50% TiO_2), were tested in a microchannel laboratory reactor, equipped with a six platelets stack and heated by six electrical cartridges. The catalysts were deposited onto the microchannels of each platelet (50 × 50 × 1 mm; 49 channels per platelet; 0.26 mm width) by infusion pump method [25,26]: a precursors solution was filled inside the microchannels, then the catalytic layer was developed by solution combustion synthesis [26,28]. The procedure was repeated until the deposition of 1.15 g_{cat} per plate. The morphology of the coated catalytic layer was observed by SEM (SEM-EDS, LEO Supra 35). To carry on the catalytic activity tests, a flow rate of 100 Nml min^{-1} (WHSV of 40 Nl h^{-1} $g_{cat}{}^{-1}$, in the range normally operated for commercial scale microchannel reactors in WGS processes: 30–40 Nl h^{-1} $g_{cat}{}^{-1}$), composition 10% CO, 6% CO_2, 40% H_2, 30% H_2O, and He balance, was fed to the reactor. The temperature was varied in the range 300–550 °C. The outlet gas stream was analyzed through a Gas Chromatograph (Varian CP-3800) equipped with a thermal conductivity detector; the GC included a Poraplot Q column to separate CO_2 and H_2O, and a Molsieve 5A column to separate CO and H_2. Feed and product temperatures were determined by thermocouples.

2.3. CO preferential oxidation reaction in microchannelled reactors

Considering the sensitivity to CO poisoning of PEM-FCs electrocatalysts, even traces of CO must be removed from the H_2-rich stream before to feed it to APU. After the two WGS steps, the final CO clean-up can be carried out using CO-PROX reaction. The latter is an exothermic reaction involving reformate CO oxidation to CO_2 over a suitable catalyst consuming O_2 fed on purpose. However, for complete CO removal, an excess of O_2 must be fed and, therefore, part of reformate H_2 could be oxidized too, with consequent slight decrease in power generation. Therefore, both active and selective catalysts are required to convert CO to CO_2 while minimizing H_2 oxidation to water, taking into consideration that the suggested limits by DOE on CO tolerance for anodic electrocatalysts are 1 ppmv in steady-state and 25 ppmv in transient for a durability of 40,000 h (see Table 2 [14]).

The same micro-channelled reactor employed for the HT-WGS was used for testing catalysts for CO-PROX reaction. After a preliminary screening of catalysts at powder level [29–31], the best catalysts, i.e., 1% Pt/(50% Al_2O_3 + 50% 3A zeolite) and 1% Rh/(50% Al_2O_3 + 50% 3A zeolite) were selected for further tests in the microchannelled reactor. The adopted procedure for depositing the catalyst into the microchannels was the same infusion method as for the WGS catalysts, with same catalyst load: 1.15 g_{cat} per plate. The activity tests were carried out at the flow rate of 100 Nml min^{-1} (WHSV of 40 Nl h^{-1} $g_{cat}{}^{-1}$), with composition of 0.5% CO, 18% CO_2, 37% H_2, 5% H_2O, and He as balance. Oxygen was fed with λ (λ = O/CO) variable from 2 to 4. The temperature was varied in a range of 100–250 °C. The outlet gas stream was analyzed through the same Gas Chromatograph (Varian CP-3800) used for the WGS process. The CO detection limit was 2 ppmv.

3. Results and discussion

3.1. Catalytic partial oxidation of methane in short contact time reactors

FESEM analysis (not reported here, but visible on [21–23]) pointed out complete different structures for the two catalyst families. Micrographs showed on 0.5% Rh/Al_2O_3 an egg-shell distribution of Rh, forming a compact thin layer that coated totally external surface of the γ-Al_2O_3 particles but it was not present into the internal pores. The thickness of the catalytic layer was approx 50 μm. The 10% Ni/Al_2O_3 presented instead a porous structure, with long and narrow superficial leaf-shape structure, covered by Ni crystallite aggregates directly exposed on the surface particles. The EDS analysis (not shown here) confirmed the presence of Ni on the external surface equal to approx 20.5 wt%. whereas EDS analysis performed on the cross-section of a cut particle disclosed approx 10 wt%. Ni in the centre of the particle, proving, consequently, the existence of a Ni gradient from outside to the core of support particles. Practically, part of the deposited Ni resulted embedded in the Al_2O_3 matrix. The BET s.s.a. was equal to 140 and 108 m^2 g^{-1} for Rh/Al_2O_3 and Ni/Al_2O_3, respectively.

The activity test results are shown in Fig. 1 as CH_4 conversion and H_2 selectivity vs WHSV. CH_4 conversion was calculated as (inlet CH_4 molar rate − outlet CH_4 molar rate)/(inlet CH_4 molar rate), whereas H_2 selectivity as (outlet H_2 molar rate)/[2 × (inlet CH_4 molar rate – outlet CH_4 molar rate)]. Ni-based catalyst showed superior per-

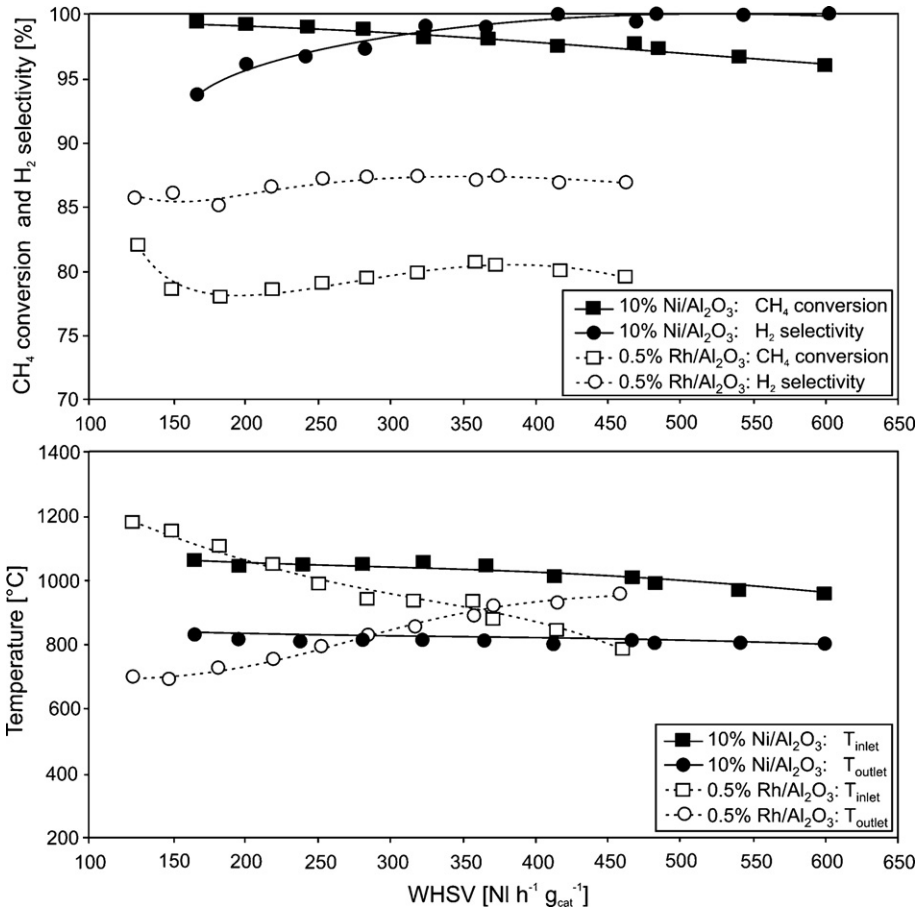

Fig. 1. SCT-CPO reactor performance: CH_4 conversion and H_2 selectivity, T_{inlet} and T_{outlet} vs. WHSV for the 0.5% Rh/Al_2O_3 and 10% Ni/Al_2O_3 catalysts.

formance compared to the Rh one: its CH_4 conversion was always higher than 95% (compared to an almost constant value of approx 80% for Rh/Al_2O_3), with H_2 selectivity increasing till values of 100% at the highest flow rates (compared to an almost constant value of approx 85% for Rh/Al_2O_3). As concerns the temperatures, Ni/Al_2O_3 presented always positive ΔT values ($\Delta T = T_{inlet} - T_{outlet}$), whereas Rh/Al_2O_3 showed an inversion temperature: until WHSV of about 370 Nl h^{-1} $g_{cat}{}^{-1}$, ΔT was positive, then it assumed negative values. A positive ΔT value allows supposing the presence and dominance of an indirect mechanism supporting the coexistence of two zones: the first one, at the catalyst entrance, with strongly exothermic CH_4 oxidation to H_2O and CO_2 (combustion zone), followed by a second zone where the strongly endothermic steam- and CO_2-reforming reactions are dominant (reforming zone) [16]. The temperature data for the Ni-based catalyst reflected this situation for all the tested WHSV range. The Rh-based catalyst, instead, was not able to maintain the combustion processes close to the inlet of the catalytic bed by increasing WHSV; as a consequence, the combustion zone moved upstream, reducing the reforming zone and the reactor performance. A further increase of WHSV could cause the reaction shutdown. The T_{inlet} reduction by increasing WHSV advocates difficulties in the feeds preheating by back radiation and conduction, enhanced by the increased inlet mass flow.

Usually, the use of base metals is preferable to that of rare or noble metals (expensive raw materials), even if the load of the more active noble metals to be placed on the support is lower. However, the low cost of Ni employed in the present case has the drawback of a significant degree of toxicity if released in the environment, depending on oxidation state and form. Anyway, the particularly adopted preparation method, which allowed to partially embedding Ni into the porous structure of Al_2O_3, is a challenging approach to produce sustainable catalysts with increased stability [32].

3.2. Water gas shift reaction in microchannelled reactors

SEM inspections (not reported here, but visible in [26]) showed a suitable and homogeneous catalyst distribution, practically deposited inside the microchannels, while the ridges were satisfactory clean. The performance of microchannelled reactor towards HT-WGS reactions is shown in Fig. 2. The performance of catalyst 1% $Pt/(CeO_2 + TiO_2)$ was better than that of the Pt deposited on CeO_2 only, as if TiO_2 in the carrier allowed better dispersing the metallic active phase. As demonstrated also by González et al. [33,34], Pt supported on Ce-modified TiO_2 support exhibited better activity performance compared to individual CeO_2 or TiO_2 Pt-supported catalysts. XPS characterization of the catalyst showed that Ce in the Ce–TiO_2 support was present in a highly dispersed state with a close interaction with Ti atoms. The contact between Pt and Ce in the Pt/Ce–TiO_2 catalyst made easy the reducibility of CeO_2 component in the support at low temperatures and also hindered the over-reduction of Ti at high temperature.

The 1% $Pt/(CeO_2 + TiO_2)$ catalyst, in fact, reached the thermodynamic equilibrium conditions (for the testes gas feedstock) in the temperature range 450–525 °C, allowing the abatement of almost 60% of fed CO at a temperature of approx 450 °C. Instead, catalyst Pt/CeO_2 reached the thermodynamic equilibrium at higher temperature, maintaining these conditions for a smaller temperature range (490–525 °C).

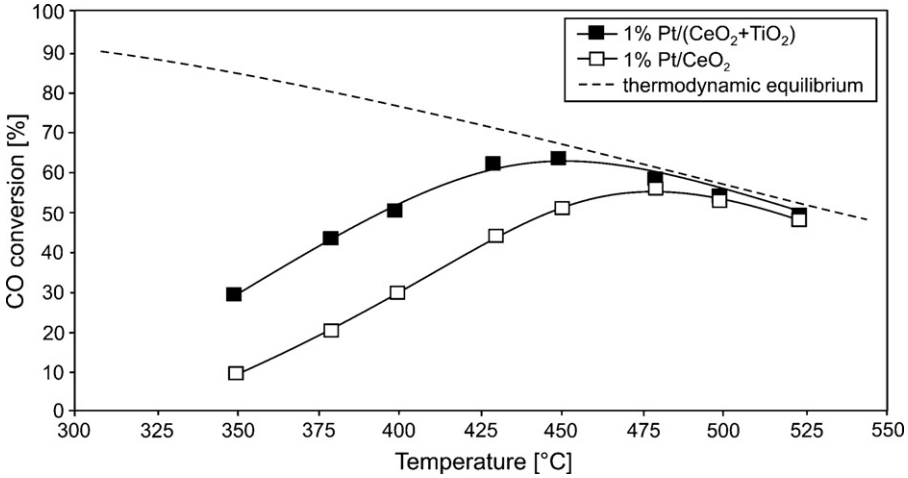

Fig. 2. Performance of the HT-WGS microchannel reactor: CO vs. *T* for the 1% Pt/(CeO_2 + TiO_2) and 1% Pt/CeO_2 catalysts (WHSV = 40 Nl h^{-1} g_{cat}^{-1}; inlet gas composition: 10% CO, 6% CO_2, 40% H_2, 30% H_2O, and He as balance).

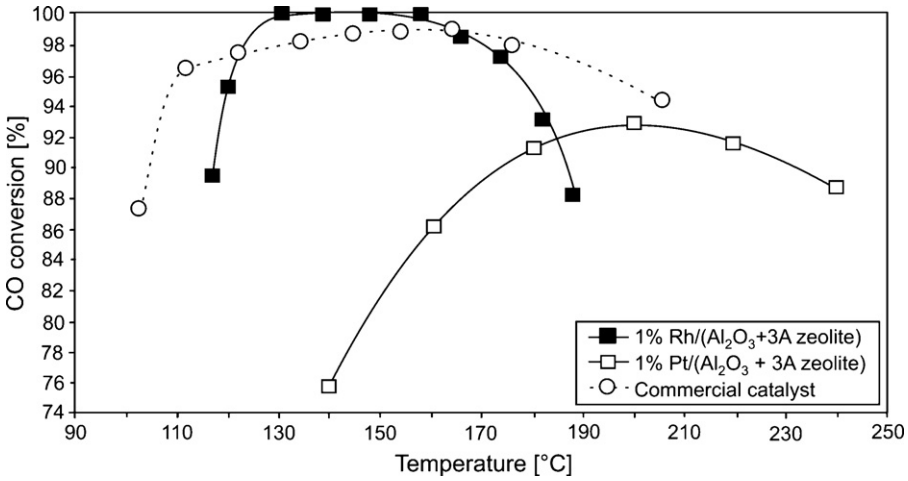

Fig. 3. Performance of the CO-PROX microchannel reactor: CO vs. *T* for the 1% Rh/(Al_2O_3 + 3A zeolite) and 1% Pt/(Al_2O_3 + 3A zeolite) catalysts, and a commercial one (WHSV = 40 Nl h^{-1} g_{cat}^{-1}; inlet gas composition: 0.5% CO, 18% CO_2, 37% H_2, 5% H_2O, and He as balance; λ = 3).

3.3. CO preferential oxidation reaction in microchannelled reactors

The catalytic activity of the micro-channelled reactor for the CO-PROX process is shown in Fig. 3. Catalyst 1% Rh/(Al_2O_3 + 3A zeolite) showed the best performance. It was the lone able to reach complete CO conversion, in a temperature range of 130–160 °C, whereas 1% Pt/(Al_2O_3 + 3A zeolite) reached its maximum conversion at 200 °C, with residual 700 ppmv of CO in the gas stream, therefore not confirming the favourable performance shown at the

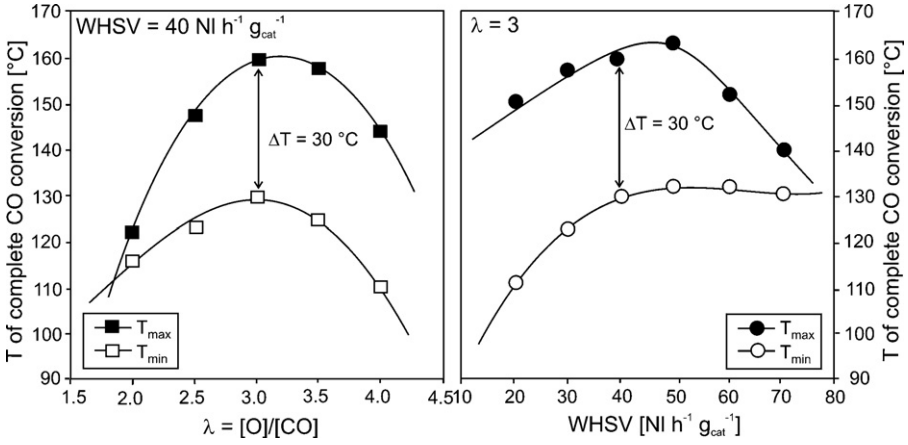

Fig. 4. Performance of the CO-PROX microchannel reactor coated with 1 Rh/(Al_2O_3 + 3A zeolite) catalyst: effect of the λ and WHSV on the *T* window of complete CO conversion (inlet gas composition: 0.5% CO, 18% CO_2, 37% H_2, 5% H_2O, and He as balance).

powder level tests. The commercial catalyst, tested as a reference catalytic material, reached its maximum conversion at 165 °C with still 150 ppmv of CO in the outlet stream.

On the best selected structured catalyst, a sensitivity analysis was performed by varying first the λ value (maintaining the same WHSV), then the WHSV value (maintaining the same λ = 3). The results are shown in Fig. 4. At constant WHSV, a low O_2 concentration (low λ value) allowed obtaining a complete CO conversion at low temperature, with a small ΔT of CO complete conversion. By increasing λ up to value of 3, the CO complete conversion was reached at slightly higher temperature and with a wider ΔT of CO complete conversion. For λ > 3, the CO complete conversion started at lower temperature, maintaining a ΔT of CO complete conversion of approx 30 °C. Of course, by increasing λ, the CO complete conversion resulted slightly improved, with the minimum temperature shifted to lower values, but with higher H_2 losses due to its oxidation to H_2O. The optimal value can be considered λ = 2.5, ensuring a ΔT of CO complete conversion reasonably wide for reactor temperature control, with an acceptable H_2 loss by oxidation.

Concerning the WHSV variation effect, up to 50 Nl h^{-1} $g_{cat}{}^{-1}$ the system was able to assure CO complete conversion with ΔT value of at least 30 °C. For higher WHSV values, ΔT decreased, giving a more difficult reactor control: the contact time reduction did not allow carrying on properly the CO preferential oxidation, leading thus to a decrease of both the minimum temperature at which the complete CO conversion was reached and the ΔT range of CO complete conversion.

4. Conclusions

The employment of H_2 in PEM-FCs technologies could ensure significant advantages in terms of efficiency and environmental impact, representing thus an important alternative to the conventional energy production systems. As far as the actual lack of infrastructure for sustainable H_2 production, storage, and distribution is concerned, waiting for further infrastructures development, PEM-FCs fed with H_2, produced from fossil fuels reforming to generate at least auxiliary power on-board vehicles, represent a valid and interesting way to overcome the actual unfavourable situation. The present work presents the main experimental work carried out at *Politecnico di Torino* on the development of structured catalytic reactors for the production of H_2-rich streams to be fed to PEM-FCs. Syngas production was carried out in a methane SCT-CPO. 10% Ni deposited on irregular γAl_2O_3 particles presented the best performance (CH_4 conversion > 90% and H_2 selectivity > 95%), compared to 0.5% Rh deposited over γ-Al_2O_3 spheres. The syngas CO-clean-up steps were carried out on micro-channelled reactors. In particular, the best performance towards HT-WGS reaction was obtained with catalyst 1% Pt/(CeO_2 + TiO_2): it reached the thermodynamic equilibrium (inlet CO: 10% b.v., WHSV = 40 Nl h^{-1} $g_{cat}{}^{-1}$) in the temperature range 450–525 °C, allowing the abatement of almost 60% of the fed CO. The best performance towards CO-PROX reaction was obtained with catalyst 1% Rh/(Al_2O_3 + 3A zeolite): it reached complete CO conversion (inlet CO: 0.5% b.v.; WHSV = 40 Nl h^{-1} $g_{cat}{}^{-1}$; λ = 3) in the temperature range 130–160 °C, assuring a quite good controllability of the system.

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