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Development of a lab scale catalytic metal plate-channels reactor for CO preferential oxidation

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ABSTRACT

The last CO clean-up step based on the preferential oxidation (CO-PROX) can lead to a reduction of the CO concentration in the hydrogen-rich gas derived from hydrocarbons reforming down to at least 10 ppmv or below, so as to enable its direct feeding to standard PEM fuel cells. In this paper, a screening of powder Pt-based catalysts for CO preferential oxidation reaction was carried out; then the more active catalyst (1% Pt on 50% 3A zeolite and 50% γ-Al_2O_3, i.e. 1% Pt-MIX) was deposed by precursors solution spraying followed by *in situ* combustion synthesis (SCS) in a micro-channel metal plate reactor and the obtained structured system was tested with a synthetic feed stream simulating the WGS outlet composition. The 1% Pt-MIX catalyst was laid out on metal plates previously coated with thin γ-Al_2O_3 layer (15 μm thickness) by plasma spray technique to improve the catalytic material adhesion. A study was then carried out at $\lambda = 2O_2/CO = 4$ by varying the GHSV and the superficial catalyst load in a range values characterized by a satisfactory performance for a CO-PROX prototype reactor. The following results were, in fact, obtained with a catalyst load of 0.50 mg cm^{-2}: with GHSV equal to 2000 h^{-1} and 4800 h^{-1} the complete CO conversion (residual CO concentration less than 2 ppmv) with simultaneous O_2 conversion equal to 1 was obtained in the temperature range 194–214 °C and 215–225 °C, respectively.

1. Introduction

Automotive exhaust is currently one of the major pollution source. As a pollution-free and energy-saving power supply for electric vehicles, the proton exchange membrane fuel cell (PEM-FC) is one of the best candidates because of its high energy conversion efficiency (50–70%) and zero or nearly zero emissions. Hydrogen or a H_2-rich gaseous stream is the ideal fuel for PEM-FCs [1,2].

PEM-FCs fed with suitably cleaned-up reformate gas (the system for processing the primary hydrocarbon fuel into a H_2-rich gas is called fuel processor, FP) are regarded as the most promising candidates for small scale mobile and portable auxiliary power unit APU systems [1–4] in the power range exceeding several hundreds of Watts. In case high temperature PEM-FCs (HTPEM-FCs) are applied, the CO concentration in the reformate needs to be reduced to values around 1% vol. Low temperature PEM-FCs (LTPEM-FCs) are even more sensible to poisoning by CO and require a fed CO concentration between 10 and several hundreds ppmv depending on the membrane technology applied.

The CO clean-up for small scale applications is usually done by catalytic reaction systems, because alternative technologies, such as pressure or temperature swing adsorption, add too much space to the FP system. Membrane separation might offer an alternative process; however, the elevated pressure required represents a heavy hindrance, especially for the APU applications. Since, as mentioned above, tolerable levels of CO concentration for standard-grade LTPEM-FCs are 10 ppmv, with peaks of 50 ppmv for a few minutes, a further removal of CO from the gas stream has to be performed after the normally used WGS first clean-up step, which allows to reach residual CO concentration of 0.5–1% [5].

Preferential oxidation of CO to CO_2 (CO-PROX) is a widely studied [6–11] option to achieve the above residual CO levels in the reformate stream; it is an exothermic catalytic process which uses molecular O_2 fed on purpose. However, during the CO-PROX process, the H_2 present in the reformate stream should not be consumed at all to ensure reasonable FP efficiency. Therefore, both active and selective catalysts, taking into account the very low CO concentration compared to the H_2 one (from 1/30 to 1/60), are required to convert CO to CO_2 while minimizing the H_2 oxidation to H_2O.

Pt–Al_2O_3 catalysts were extensively studied and found very active towards CO oxidation [12,13]; more recently Pt-supported zeolite catalysts were proposed thanks to their enhanced selectivity [14]. Previous our studies on different Pt–A zeolite catalysts [15–17] showed that the best performance, in terms of catalyst activity and selectivity, was obtained with a 1% Pt–3A zeolite catalyst, thanks to

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the specific structure of 3A zeolite support. As any CO-PROX unit should be normally integrated in a FP [4,18–20] after two WGS units to reduce the CO content, in this work 1% Pt-based catalyst, supported on a mixed system zeolite 3A and γ-Al_2O_3, suitably developed to obtain good adhesion on metallic surfaces (metal supports, compared to ceramic ones, offer higher mechanical strength and heat conductivity [21]; these characteristics are greatly appreciated in catalytic applications where heat fluxes are present), was deposed on a metal plate-channels structured reactor, typical of the micro-chemical technology (MCT) field; the so arranged reactor was then successfully tested for CO-PROX in H_2-rich streams. MCT is a new branch of chemical engineering originated in the early 1990s; it can greatly improve the efficiency of reacting systems and diminish their volumes and weights, necessities [22–28], that are mandatory in vehicles applications. The very low residence times associated with the improved heat and mass transfer in micro-structured reactors create, in fact, the conditions for higher productivities compared to traditional reacting systems.

2. Experimental

1% wt Pt–3A zeolite catalyst was prepared through Incipient Wetness Impregnation (IWI) method by using $Pt(NH_3)_4Cl_2$ as precursor [15–17]. The catalyst as powder was tested in a fixed bed micro-reactor (I.D.: 4 mm; fixed bed: 150 mg of catalyst particles held in place by flocks of quartz wool; micro-reactor heated up in a PID regulated oven; fed composition: 37% H_2, 5% H_2O, 18% CO_2, 0.5–1% CO, 1–2% O_2, He as balance; $\lambda = 2O_2/CO = 4$; $WSV = 0.33\ Nl\ min^{-1}\ g^{-1}$): a complete CO conversion to CO_2 (residual CO concentration less than 2 ppmv) with the simultaneous O_2 complete conversion in the temperature range 152–185 °C ($\Delta T = 33\ °C$) was obtained [15]. Therefore, the catalyst was chosen to be spread out on the metal surfaces of a structured plate-channels reactor. However, a serious problem arose due the poor adhesion of the 3A zeolite particles on metal surfaces.

Therefore, a Pt catalyst supported on γ-Al_2O_3, characterized by a more firm adhesion to metal surfaces, was suitably developed in our labs and exhibited reasonable CO-PROX activity when tested in powder in the fixed bed micro-reactor, as previously reported. This Pt-γ-Al_2O_3 catalyst was synthesized through the Solution Combustion Synthesis (SCS) method [29] in order to quickly obtain γ-Al_2O_3 with a high specific surface area: appropriate amounts of $Pt(NH_3)_4(NO_3)_2$, $Al(NO_3)_3\ 9H_2O$ and $CO(NH_2)_2$ (all from Aldrich) were dissolved in the minimum possible volume of water. After a few minutes stirring on a heating plate, to ensure proper homogeneity, the so-prepared solution was transferred in a capsule, which was placed into an oven kept at the constant temperature of 500 °C. Firstly, the aqueous solution underwent dehydration, then, the solid mixture frothed and swollen, until a fast and highly exothermic reaction took place and large amounts of gases evolved. A foamy and easily crumbled material was obtained to give a fine and volatile powder that was then finely ground in an agate mortar. The catalyst was not calcined as its synthesis occurred at sufficiently high temperatures compared to the CO-PROX working ones; it was reduced in H_2 flow rate ($50\ Nml\ min^{-1}$) at 350 °C for 2 h.

Consequently, to overcome the difficulty of 3A zeolite adhesion on the metal surfaces, a 1% Pt catalyst supported on a mixed carrier 50% 3A-zeolite + 50% γ-Al_2O_3 (1% Pt-MIX) was prepared by simultaneous SCS, with the zeolite powder dispersed as suspension in the precursors solution; the obtained 1% Pt-MIX (3A zeolite + γ-Al_2O_3) catalyst was finally reduced in H_2 flow at 350 °C for 2 h.

The 1% Pt-MIX powder catalyst was analyzed by high-resolution transmission electron microscopy (HRTEM, Jeol JEM 2010 apparatus) to investigate by picture the noble metal dispersion on the mixed support.

For tests on powder in the fixed bed micro-reactor, the outlet gas stream was analyzed through a gas-chromatograph (Varian CP-3800) equipped with a thermal conductivity detector (TCD), a Poraplot Q column (0.53 mm diameter, 30 m length) to separate CO_2 and H_2O, and a Molsieve 5A column (0.53 mm diameter, 25 m length) to separate CO, H_2 and O_2. The CO detection limit was verified to be equal to 2 ppmv.

The experimental tests on the powder catalysts were carried out in the temperature range of 100–300 °C, at O_2 to CO feed ratio ($\lambda = 2O_2/CO$) equal to 4 and with a weight space velocity $WSV = 0.33\ Nl\ min^{-1}\ g^{-1}$. Working with $\lambda = 4$ means to reach the maximum selectivity value of 25% when both CO and O_2 conversions are simultaneously equal to 1. The main role of the research in the field of Fuel Processors is to reach, in a sufficient wide temperature range (suitable for the CO-PROX reactor control), the complete conversion of CO (on the basis of the CO detection limit of the employed gas analyzer), with at the same time the complete conversion of O_2; the latter condition is required to be sure to employ the lowest O_2 excess rate thus maintaining as low as possible the H_2 oxidation losses. As a consequence, the residual CO concentration at the WGS clean-up step has to be reduced at the lowest as possible value (normally <1–0.5% b.v.). Anyway, the limitation of H_2 oxidation is not the mandatory issue in the CO-PROX step, if compared with the compulsory requirement of avoiding the CO poisoning effect on the low temperature PEM-FC electro-catalyst.

As concerns the preparation of catalyzed metal plates, to improve the catalyst layer adhesion, before the deposition of 1% Pt-MIX, the metal plate surface was covered with a shielding γ-Al_2O_3 layer by using a thermal spray technique [21,30]; the employed γ-Al_2O_3 was on purpose prepared by SCS from Al-nitrate and urea. The spray process allows to cover the metal sheets solid surfaces with coatings characterized by high mechanical and thermal stability together with a sufficient roughness. Two coatings with different thickness were prepared: a thin and a thick layer, of 15 μm and 45 μm, respectively.

The 1% Pt-MIX was then deposed on the metal plates through the two following different methods: (i) deposition of the catalyst on the plate surface by repeatedly spraying the precursors solution; (ii) immersion of the metal plates into the precursors solution. In both cases, the catalyst was developed by *in situ* SCS putting the wetted plates in oven at 500 °C. Excess of catalyst was removed by spraying compressed air.

SEM investigations (SEM-EDS, LEO Supra 35) on metal plates, deposited through the two different methods, were carried out in order to establish the most uniform and homogeneous catalyst layer deposition.

Four flat stainless steel metal plates (50 mm × 50 mm × 1 mm) were stacked in the structured reactor to form three square channels, each 0.6 mm in height; the reactor was heated up with electrical cartridges and fed with a gas stream having the same composition used for the fixed bed micro-reactor. The outlet gas was analyzed by means of the same system used for the powder catalysts screening tests. The tests on the lab structured reactor were carried out varying the catalyst superficial load and gas hourly space velocity (GHSV), but maintaining $\lambda = 4$.

The conversion of CO (ξ_{CO}) and O_2 (ξ_{O_2}), as well as the oxygen selectivity to CO oxidation (σ, assuming neither CO formation by reverse water gas shift – RWGS – nor CO consumption by methanation) were calculated for both the reactors as follows:

$$\xi_{CO} = 1 - \frac{[CO]_{out}}{[CO]_{in}},$$

$$\xi_{O_2} = 1 - \frac{[O_2]_{out}}{[O_2]_{in}},$$

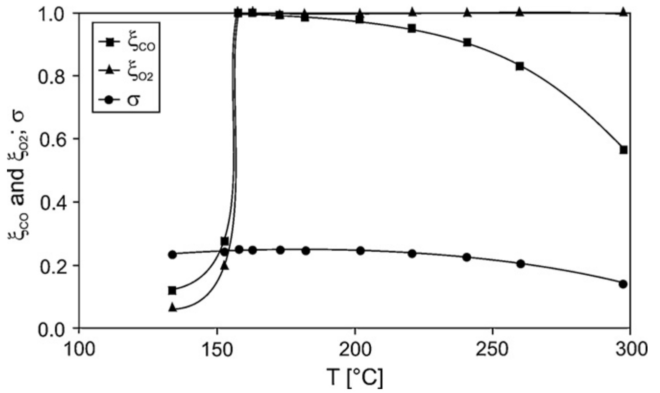

Fig. 1. CO and O_2 conversions and CO selectivity vs. temperature of the 1% Pt–Al_2O_3 powder catalyst prepared with SCS method.

$$\sigma = \frac{1}{2} \cdot \frac{[\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{out}}}{[\mathrm{O_2}]_{\mathrm{in}} - [\mathrm{O_2}]_{\mathrm{out}}}.$$

3. Results and discussion

3.1. Catalytic activity on powder: micro-reactor tests

The catalytic activity tests to determine the CO and O_2 conversions and the CO selectivity vs. temperature were carried out on the 1% Pt-γ-Al_2O_3 prepared by SCS method; the obtained catalytic performance is shown in Fig. 1. The complete CO conversion (residual CO concentration less than 2 ppmv) with $\xi_{O_2} = 1$ was reached in a limited temperature range 158–163 °C (ΔT = 5 °C).

In order to develop a suitable catalyst with good adhesion on the metallic surface of a CO-PROX plate-channels prototype reactor, a mixed Pt on zeolite and γ-Al_2O_3 catalyst was synthesized, as the possible solution to maintain also the total CO conversion in a wide temperature range, perhaps achievable owing to the presence of zeolite in the support.

Catalyst with 1% Pt on 50% γ-Al_2O_3 + 50% zeolite as mixed support was prepared and characterized by HRTEM analysis. The micrograph in Fig. 2 shows the satisfactory homogeneity of Pt distribution and Pt clusters of about few nanometres (average Pt particle size: 2 nm; range: 1–3 nm).

The catalytic performance, in terms of CO and O_2 conversion, and CO selectivity, is shown in Fig. 3. With the mixed-support, complete CO conversion (residual CO concentration less than 2 ppmv) was reached with, at the same time, $\xi_{O_2} = 1$ at a quite low temperature and retained in the temperature range 112–136 °C (ΔT = 24 °C). Therefore, as expected, the zeolite addition to the alumina carrier enabled to widen the temperature range of the complete CO conversion, as compared to that of the catalyst based on the γ-Al_2O_3 alone; however, it resulted lower than that obtained when only the 3A zeolite was employed as carrier.

3.2. Catalytic activity on the structured plate-channels rector

Once the best catalyst in powder, able to reduce the CO concentration below 10 ppmv in the synthetic reformate gas to be fed the FC, was established, the next step was allocated to its deposition on metal plates to be used in the prototype structured reactor.

Firstly the plates were covered with a γ-Al_2O_3 layer of two different thickness: a thin and a thick layer, of 15 μm and 45 μm, respectively. SEM images of the two different coating layers are shown in Fig. 4A and B; both coatings presented a quite variable thickness.

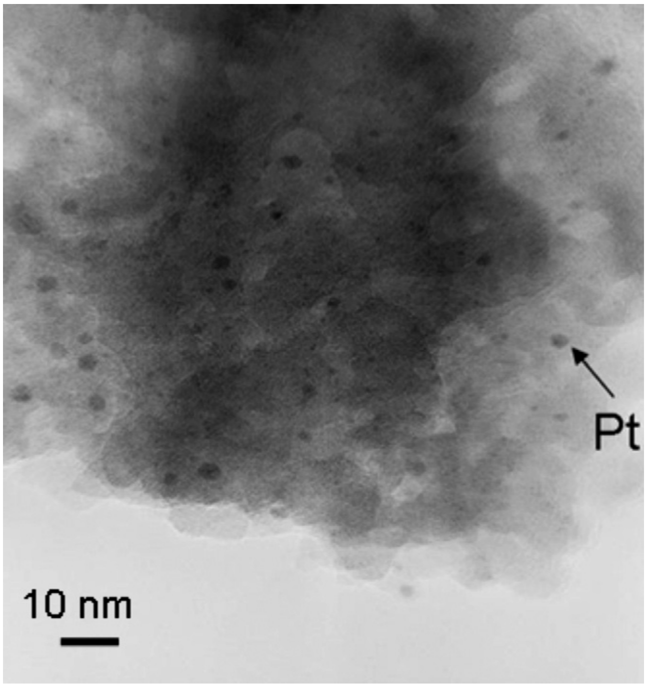

Fig. 2. HRTEM micrograph of 1% Pt–(50% γ-Al_2O_3 + 50% 3A-zeolite) powder catalyst.

The 1% Pt-MIX catalyst was synthesized on the thermal spray γ-Al_2O_3 layer by *in situ* SCS at 500 °C in oven through two different deposition methods of the precursors solution-suspension on the plates surface: (i) by repeatedly spraying; (ii) immersion of metal plates into precursors solution, both followed by SCS. Excess of catalyst was removed by spraying compressed air and the plates resulted to be covered with a quite homogeneous layer.

The SEM comparison in Fig. 5 of the catalyst morphology on metal plates covered through the two different methods shows that by using the spraying technique (Fig. 5A) the catalyst surface layer appeared more uniform and without the localized big scales typically produced with the immersion method (Fig 5B). The repeated spray procedure was then chosen for the next tests.

Preliminary catalytic activity test on structured reactor was carried out on plates with thin alumina layer, where 1% Pt-MIX catalyst was laid out with a superficial load equal to 0.42 mg cm^{-2}. Test was performed feeding reformate gases with GHSV = 2000 h^{-1} and λ = 4. The determined CO and O_2 conversion and selectivity are shown in Fig. 6. The maximum CO conversion, with ξ_{O_2} equal to 1, was lower than 1 showing a minimum CO concentration at the reactor

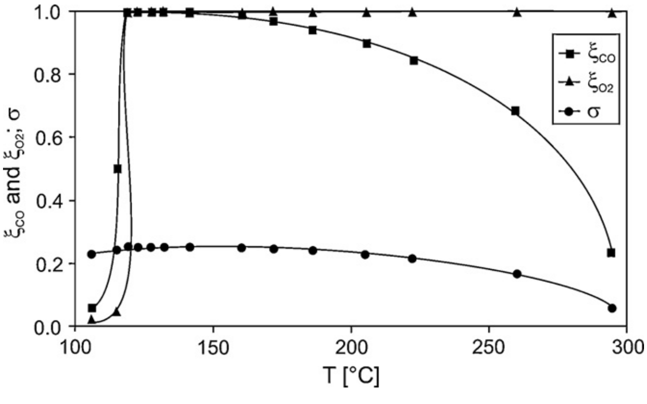

Fig. 3. CO and O_2 conversions and CO selectivity vs. temperature of the 1% Pt–(50% γ-Al_2O_3 + 50% 3A-zeolite) powder catalyst.

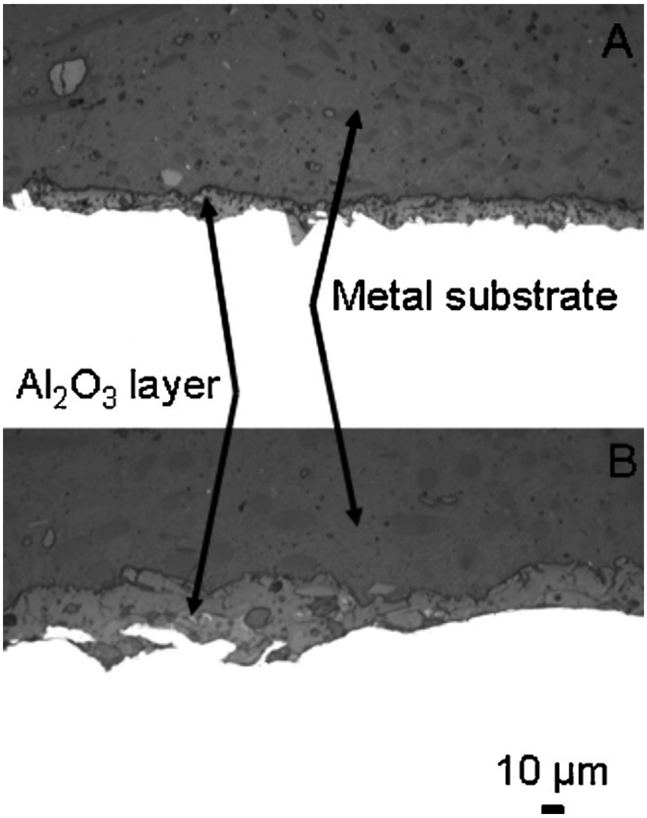

Fig. 4. SEM images of metal plates coated with thin (A) and thick (B) γ-Al_2O_3 layer.

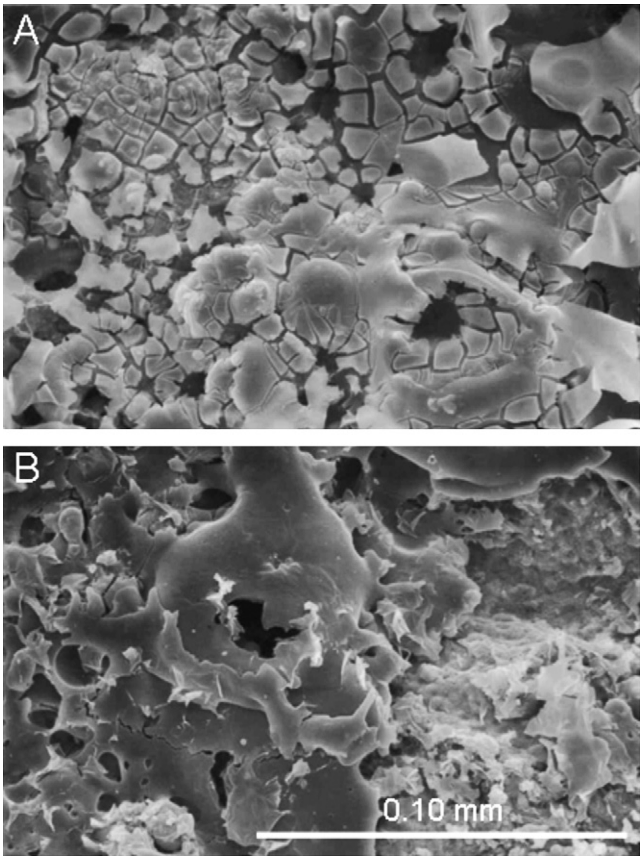

Fig. 5. SEM images of metal plates after catalyst deposition with spray (A) or immersion (B) method.

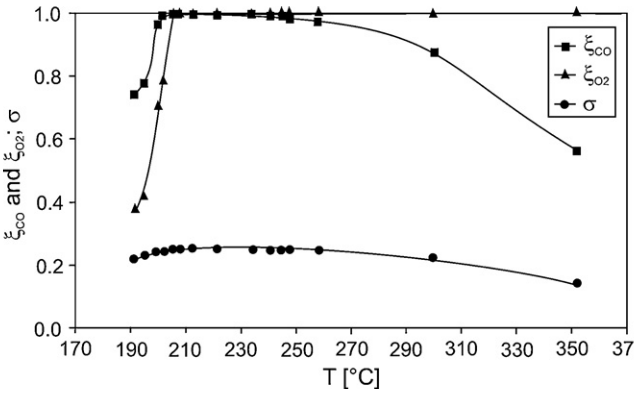

Fig. 6. CO and O_2 conversions and CO selectivity vs. temperature of the structured reactor with metal plates covered with thin γ-Al_2O_3 layer: GHSV = 2000 h^{-1}; catalyst load = 0.42 mg cm^{-2}.

outlet of about 100 ppmv, probably because of the low catalyst load; then, for the next tests the catalyst superficial load was increased of about 20% till to 0.50 mg cm^{-2}.

For comparison, a test at GHSV = 2000 h^{-1} and at $\lambda = 4$ was carried out on plates with both thin and thick γ-Al_2O_3 layer (Fig. 7). Complete CO conversion (residual CO concentration less than 2 ppmv) was reached with the two different type of plates, but in different temperature range: 194–214 °C ($\Delta T = 20$ °C) for the thin γ-Al_2O_3 layer and 188–211 °C ($\Delta T = 23$ °C) for the thick one. Moreover, for the thin γ-Al_2O_3 layer plates, CO conversion was kept higher by increasing temperature; on the contrary, in the field of lower temperatures, the thick plates showed a slightly higher CO conversion compared to thin plates.

As no substantial differences were determined in the performance of thin and thick γ-Al_2O_3 layer plates, the next tests were carried out on plates covered with thin γ-Al_2O_3 layer, in order to save in coating material.

Since the space velocity (GHSV = 2000 h^{-1}) used in the previous catalytic activity tests was low compared to real conditions in FPs, the flow rate fed to the structured reactor was increased till a GHSV equal to 4800 h^{-1}. GHSV values between 3000 and 5000 h^{-1} are typical for CO-PROX applications in micro-structured reactors [19].

The comparison between the two tested GHSV values (catalyst superficial load = 0.5 mg cm^{-2}; $\lambda = 4$) is shown in Fig. 8. Increasing GHSV the temperature range of complete CO conversion (residual CO concentration less than 2 ppmv) shifted to higher values (215–225 °C) and its width was reduced from 20 °C to 10 °C, maintaining, anyway, a sufficient value for the reactor control.

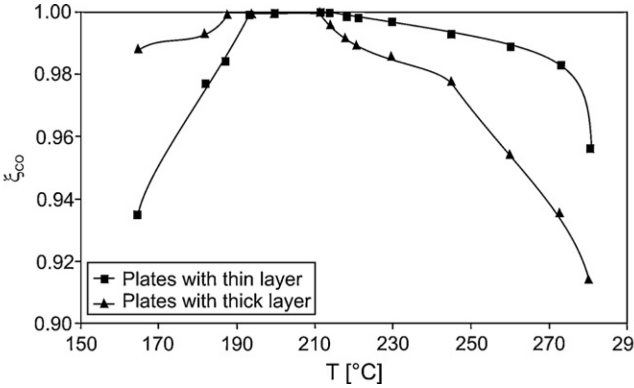

Fig. 7. CO conversion vs. temperature in the structured reactor: comparison between metal plates covered with thin and thick γ-Al_2O_3 layer. GHSV = 2000 h^{-1}; catalyst load = 0.5 mg cm^{-2}.

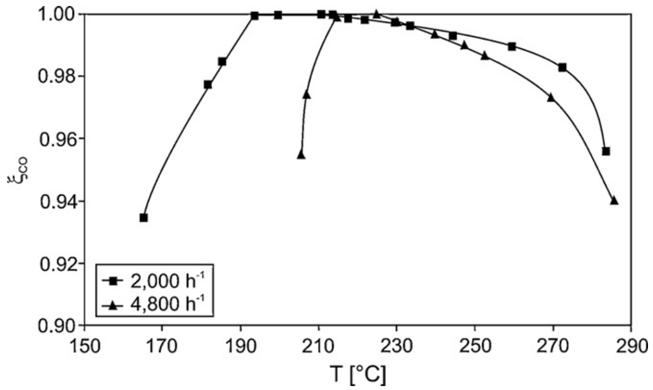

Fig. 8. CO conversion vs. temperature in the structured reactor: metal plates covered with thin γ-Al_2O_3 layer at two different GHSV values. Catalyst load = 0.5 mg cm^{-2}.

4. Conclusion

This work focused on the development of a CO-PROX catalyst to be deposed on a metal plates structured reactor in order to reduce the CO concentration in the H_2-stream produced by reforming in a FP, thus rendering it suitable to be fed to PEM-FCs.

A preliminary screening on Pt-based catalysts in powder supported on different carriers, allowed to determine a good catalytic material, active for the complete CO conversion ($\xi_{CO} = 1$, residual CO concentration less than 2 ppmv): 1% Pt on a mixed support system of 50% 3A-zeolite with 50% γ-Al_2O_3.

The 1% Pt-MIX catalyst was deposed (by precursors solution spraying followed by *in situ* SCS) on metal plates previously coated with γ-Al_2O_3 by plasma spray with two different layer thickness. As an equivalent performance was reached with both thin and thick plates, a deeper study varying the gas hourly space velocity and the superficial catalyst load was carried out with thin γ-Al_2O_3 layer (15 μm) in a range of operating conditions satisfactory for the performance of a CO-PROX prototype reactor, obtaining the following results: with a catalyst load of 0.50 mg cm^{-2}, GHSV equal to 2000 h^{-1} and 4800 h^{-1} allowed complete CO conversion (residual CO concentration less than 2 ppmv) with simultaneous O_2 conversion equal to 1 in the temperature range 194–214 °C and 215–225 °C, respectively.

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