

Aluminum Foam based Catalysts for the CO-WGS Reaction

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In this paper, a comparative study between two structured catalysts, prepared by washcoating of highly conductive Aluminum foams, tested for the Water Gas Shift reaction, was presented. The procedure for the preparation of the catalysts was described, as well as the results of the characterizations and of the activity tests. The good resistance, to the mechanical stress, of the washcoated foams was highlighted from the low losses at the ultrasound adherence test. The effectiveness of the noble metal-based formulation was highlighted from the good performance of the catalysts, moreover the concrete possibility to realize a process intensification, was justified by showing the results of additional experiments, carried out at high gas hourly space velocity.

1. Introduction

The CO-Water Gas Shift (WGS), operating downstream of the reforming processes (Saeidi et al., 2017), allows to reduce the percentage of carbon monoxide in syngas stream to less than 0.3 vol%, to avoid the poisoning of the anode catalyst of the fuel cell (Lytkina et al., 2015) and to increase the yield in hydrogen. Substantially it can be considered the first purification step of hydrogen, upstream of important processes such hydrogen production and ammonia synthesis. WGS is an exothermic reversible reaction, thermodynamically favoured at low temperature; the industrial process provides two adiabatic stages, High Temperature Shift (HTS) and Low Temperature Shift (LTS), with an intermediate cooling (Amran et al., 2017). In these operative conditions, the heat of the reaction induces a thermal gradient on the catalytic bed, with a much higher temperature at the outlet of the bed, with respect the inlet, limiting the CO conversion in the HTS and disfavoring the kinetics in the LTS. The multi-stage reactors allow to obtain the kinetically optimum reaction pathway, with a large number of small steps, but of course the plant and operating costs must be weighed up against the productivity of the global configuration. Moreover, the growing need of small-scale plants, in the distributed production of hydrogen as energy vector, make this kind of configuration unsuitable and unprofitable. From the above consideration, it is clear that a strong intensification of the WGS process (Nemet et al., 2016), is highly advisable. The study of structured catalytic reactors has recently found large diffusion, in solving or overcome common problems of the catalytic processes, for example in soot abatement (Montenegro Camacho et al., 2017) and catalytic activity improving (Vita et al., 2018). Recently the group of Professor Palma focused the attention on the preparation and the study of structured catalysts, based on highly conductive aluminium foams (Palma et al., 2015), that allow to realize a redistribution of the thermal gradient, over the catalytic bed, in adiabatic conditions (Palma et al., 2016), for WGS applications. The idea was to increase the CO conversion, reducing the temperature at the end of the catalytic bed, by back diffusion of the heat to the inlet of the bed, obtaining a corresponding increase of the catalytic activity (Palma, Pisano et al., 2017). In this way, an intensification of the actually used processes is theoretically realizable (Figure 1a) moreover, with an appropriate catalytic formulation, a single stage process can be speculated (Figure 1b). The experimental results were also validated through a CFD modelling study (Palma et al., 2018), recently reported, in which a comparison between the performances of the two adiabatic reactor systems, powder and structured foam catalyst based, was shown. Cu-Zn are the most used catalysts in the LTS production processes (Oliveira et al., 2015), however they suffer of severe limitations, such as their pyrophoricity (Kam et al., 2010), resulting not able to sustain frequent start up and shut down stages, moreover they are not appropriate for mobile fuel cell applications and, primarily, are not suitable in view of a single stage WGS implementation. The most interesting alternative resides in the use of noble metal- based catalytic systems

(Lin et al., 2015) which, while being expensive, guarantee highly competitive performance, among the formulations reported in the literature.

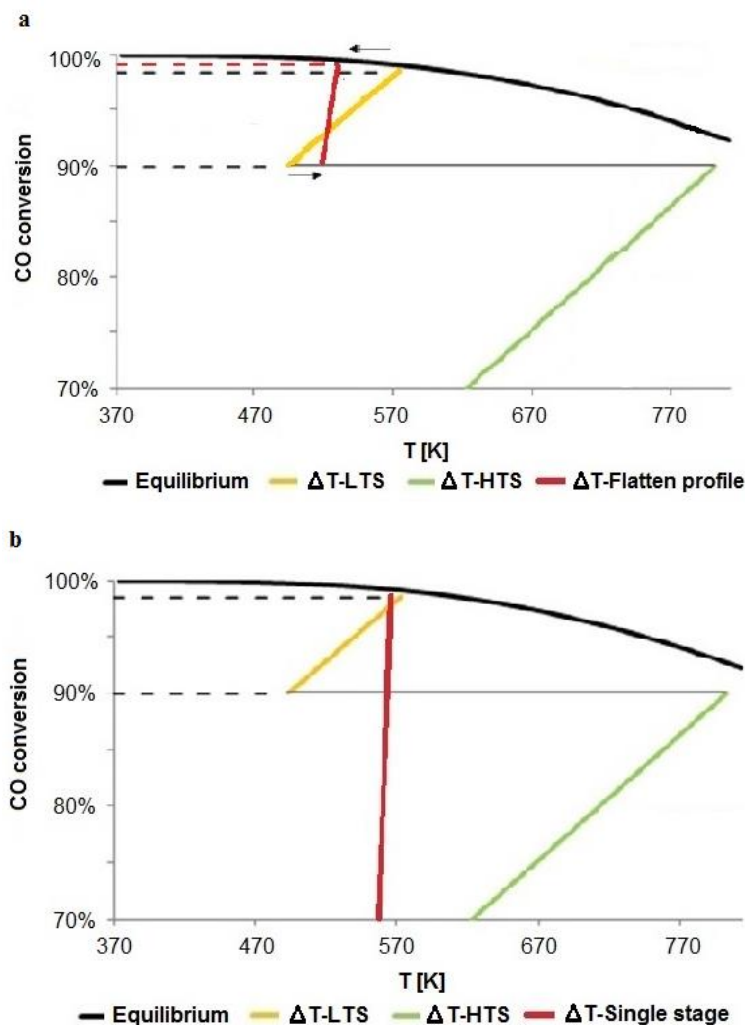


Figure 1: Schematic representation of the redistribution of the heat of reaction, in adiabatic conditions, with high thermoconductive catalysts

The bimetallic Platinum/Rhenium based catalysts seem to show the most interesting performance (Palma and Martino, 2017), in low/medium temperature range. This paper presents results on a comparative study between two structured catalysts, obtained by washcoating of aluminium foams, based on two different catalytic formulations, Pt/Re/CeO₂/Al₂O₃ and Pt/Re/ZrO₂/Al₂O₃, showing that the WGS single stage process is realizable through the coupling of a highly active formulation and a highly conductive carrier.

2. Experimental

2.1 Catalysts preparation

The washcoat slurry was prepared by suspending the γ -alumina (Puralox SCCa 150-200, provided by SASOL), previously ground, in a colloidal solution of pseudoboehmite (Pural SB, provided by SASOL) and methylcellulose (viscosity 4'000 cP, provided by Sigma-Aldrich) acidified with nitric acid (65 %, provided by Carlo Erba Reagenti) at pH \approx 4. The composition of the washcoat slurry was: 0.9 wt% of methylcellulose, 4.6 wt% of pseudoboehmite and 15.4 wt% of γ -alumina in distilled water. The aluminium foams (provided by ERG Materials and Aerospace), were shaped to obtain a cylinder of diameter 18 mm, length: 90 mm, porosity 10 PPI and relative density 10-12 %, subsequently were degreased with hexane and treated with a 0,1 N solution of hydrochloric acid for 20 minutes, washed with deionized water, dried in an oven at 393 K for 2 h and calcined at 773 K for three hours.

The as obtained carriers were washcoated by dip-coating procedure (Trottet et al., 2017), and the excess of washcoat removed by centrifuge at 800 rpm for three minutes, the resulting artefact was dried at 393 K for two hours and calcined at 723 K for three hours; this procedure was repeated until reaching the desired loading. The structured catalysts were obtained by impregnation of the washcoated carriers with the proper solution of cerium(III) nitrate (99.9 %-Ce) or zirconium(IV) dinitrate oxide hydrate (%Zr-26.4) provided by Strem Chemicals, by dipping the artefact in the solution for 20 minutes, then drying at 393 K for 2 h and calcining at 723 K for three hours; this procedure was repeated until reaching the desired loading of 28 wt% of ceria or zirconia support. The resulting artefacts were subsequently submitted to two consecutive impregnations with a solution of ammonium perrhenate ($\geq 99\%$) provided by Sigma-Aldrich, and with a solution of the tetrammineplatinum (II) nitrate (99%), provided by Strem Chemicals, after each impregnation they were dried at 393 K for two hours and calcined at 753 K for three hours (Figure 2).

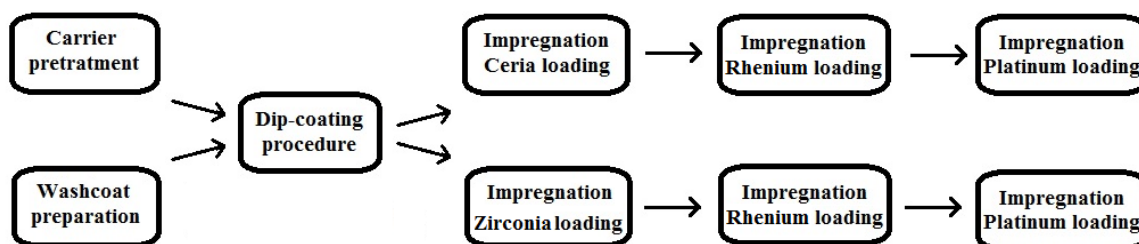


Figure 2: Catalysts preparation procedure

2.2 Catalysts characterization

The chemical compositions of the catalysts were evaluated by an ARL™ QUANT'X Thermo Scientific™ EDXRF spectrometer, with a Fundamental Parameters method. The B.E.T. specific surface areas were evaluated by means a dynamic N₂ adsorption measurement at -196 °C, on samples previously degassed at 150 °C for 30 min in a flow of helium, with a Costech Sorptometer 1040. The resistance of the alumina coating over the carriers to the mechanical stress was evaluated by ultrasound adherence test (Yasaki et al., 1993), by dipping the washcoated foam in a beaker containing 100 mL of petroleum ether, provided by Carlo Erba reagenti, and applying the 60 % of rated power of a ultrasonic bath CP104 (EIA S.p.A.) at 25 °C, filled with distilled water, for six cycles of five minutes. The reducibility of the catalysts was evaluated by means of H₂-TPR; the experiments were carried out in the same reactor used for the activity tests, described below, with a reducing stream of 500 Ncc/min of 5 vol% of hydrogen in nitrogen, applying a heating rate of 10 °C/min.

2.3 Experimental tests

The catalytic activity tests were carried out, on the pre-reduced catalysts, in a stainless-steel tubular reactor with an internal diameter of 30 mm and a length of 40 cm, at atmospheric pressure, in the temperature range 470-680 K and at a gas hourly space velocity (GHSV) of 10,000 h⁻¹ and 20,000 h⁻¹, by feeding a reactive mixture composed by 8 vol% of CO, 30 vol% of H₂O and 62 vol% of N₂ balance. The catalysts were surrounded by a thermo-expanding pad of 0,5 cm of thickness and the temperature of the bed was monitored by two thermocouples located at inlet and at the outlet of the catalysts. The catalytic performances were evaluated in terms of CO conversion X_{CO} (1) and selectivity to hydrogen Y_{H_2} (2).

$$X_{CO} = \frac{\dot{N}(CO_{in}) - \dot{N}(CO_{out})}{\dot{N}(CO_{in})} \quad (1)$$

$$Y_{H_2} = \frac{\dot{N}(H_{2out})}{\dot{N}(CO_{in}) - \dot{N}(CO_{out})} \quad (1)$$

Where \dot{N} represents the molar rate supplied (in) and the molar rate at the outlet of the reactor (out).

The composition of the gas stream at the outlet of the reactor was analysed on dry basis, by an ABB system equipped with a non-dispersive infrared analyser Uras 14 for CO, CO₂ and CH₄ and a thermal conductivity detector Caldos 17 modules for H₂.

3. Results

3.1 Catalysts characterization

The chemical compositions of the catalytic washcoat were checked through ED-XRF, the results showed that the two catalysts were loaded with similar active components percentage (Table 1).

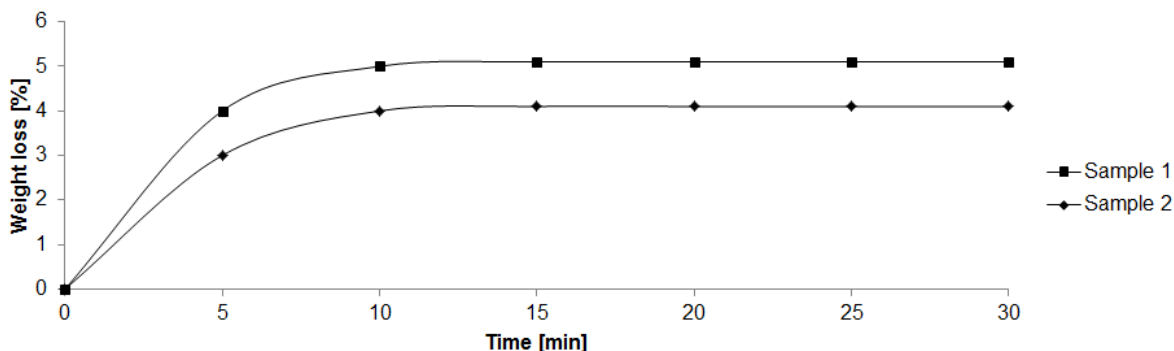


Figure 3: Washcoat weight loss vs. time during the ultrasonic treatment of the washcoated foams

The ultrasound test was performed on both the washcoated foams to try out the resistance to the mechanical stress of the alumina layer; the percentage of loss was less than 5 wt%, with respect the weight of the lonely alumina loaded (Figure 3), in both cases, highlighting the strong adherence of the realized layer to the aluminum carrier. The B.E.T. surface area highlighted the ability of the alumina washcoat to dramatically increase the surface area of the aluminum carriers, which is less than 1 m²/g, while the difference between the two catalyst is attributable to the support loading. The hydrogen uptake, during the H₂-TPR experiments, was higher than the theoretical one in the case of ceria-based catalyst, while close to the theoretical in the case of the zirconia-based catalyst, highlighting the occurrence of the spill over effect in a reducible oxide such as ceria, characterized by a high oxygen mobility of the lattice (Prins, 2012).

Table 1: Chemical composition

Sample	Chemical composition of the catalytic washcoat (wt%)					S _{B.E.T.} (m ² /g)	H ₂ chemisorbed (mmol/gcat)
	Pt	Re	CeO ₂	ZrO ₂	Al ₂ O ₃		
PtReCeAlF10	0.69	0.39	28.60	-	70.32	44	0.2
PtReZrAlF10	0.73	0.41	-	28.14	70.72	38	0.1

3.2 WGS activity tests

The activity tests were carried out to two different GHSV; the tests at 10,000 h⁻¹ were performed in order to evaluate the efficiency of the catalysts, in Figure 4 were reported the steady state CO conversions as function of temperature, for both the catalysts.

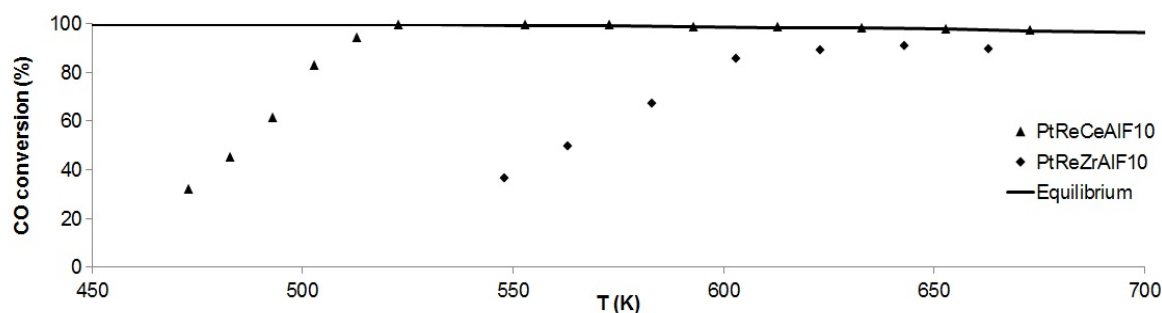


Figure 4: Comparison between the CO conversion of PtReCeAlF10 and PtReZrAlF10 catalysts.

The PtReCeAlF10 catalyst approached to the equilibrium from 530 K above, and showed a conversion of 30 % at 470 K, on the contrary the PtReZrAlF10 catalyst didn't approach to the equilibrium in all the temperature range studied, showing a conversion of 90 % at 640 K. The hydrogen selectivity was excellent for both catalysts, from 600 K downwards, while a very low percentage of methane occurred for higher temperatures. These results were attributed to the reducibility properties of the two catalysts, which are intimately related to the presence of the support, ceria in the case of PtReCeAlF10 and zirconia in the case of PtReZrAlF10. Ceria support can be considered both a structural and a chemical promoter, due to enhanced oxygen store capacity (OSC), deeply related to the rapid reduction/oxidation cycles of the ceria with the reagents (Saw et al., 2016), taking itself part to the WGS reaction (Shido et al., 1992), on the contrary zirconia is not a reducible oxide, therefore it is not able to supply reactive oxygen.

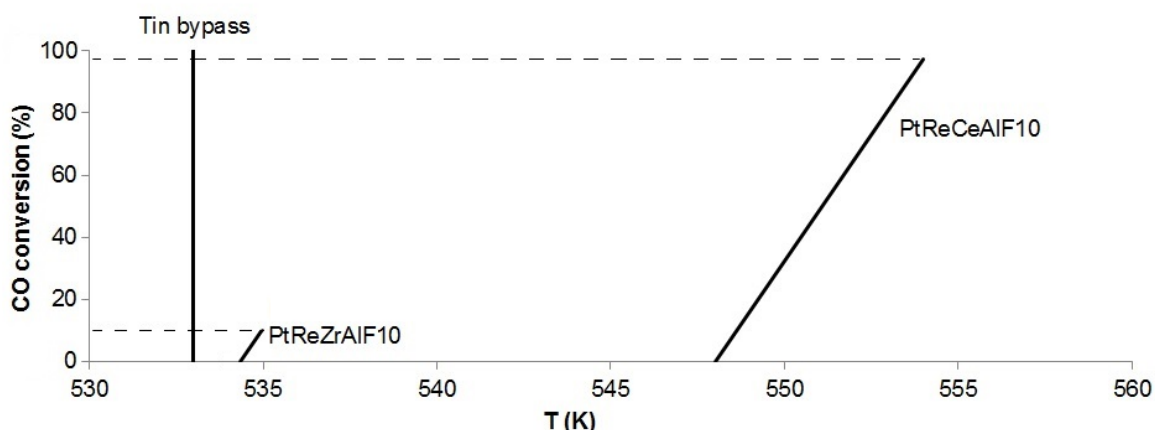


Figure 5: Comparison ΔT and the CO conversion, starting from a bypass inlet temperature of 533 K, between PtReCeAlF10 and PtReZrAlF10 catalysts

In Figure 5 the differences of the temperature between the inlet and the outlet of the catalytic bed vs. the CO conversion in an adiabatic experiment, for the two catalysts, were reported. To realize this condition the GHSV was set to 20,000 h⁻¹; the catalysts were heated with an overheated flow of nitrogen and water until reaching a thermal equilibrium at 533 K, temperature at which the nitrogen was substituted with a mixture of CO diluted in N₂, maintaining the volumetric flow unchanged. The difference of the temperature and the conversion was monitored until reached a new thermal equilibrium, the heat of the reaction of course increased the temperature over the bed, and after 60 minutes was considered stable and the CO conversion was evaluated. The low activity of the PtReZrAlF10 catalyst makes it unable to generate a sufficient heat of reaction, to approach the equilibrium. On the contrary the heat of the reaction of the PtReCeAlF10 catalyst allowed to reach a temperature near 554 K corresponding to a CO conversion higher than 99 %, moreover the difference of temperature is more or less 6 K, that is much lower than the theoretical for a powder catalyst, in the same conditions (Palma et al., 2016). The reduction of the difference of the temperature was attributed to the presence of the conductive carrier, that was able to realize a redistribution of the heat of the reaction along the bed. Referring to the scheme reported in Figure 1, it may be said that, PtReCeAlF10 catalyst can be considered a serious candidate to the realization of a WGS single stage process.

4. Conclusions

In conclusion, a comparative study between two Pt/Re-based structured catalysts, characterized by two different supports, ceria and zirconia, was presented. The ceria loaded catalysts showed a much higher activity, for the WGS reaction, with respect the zirconia one, in all the temperature range studied; moreover, further experiments, carried out in adiabatic conditions, highlighted the huge difference in the activity of the two catalysts. This performance was explained as the result of the high reducibility of ceria support, due to the extreme mobility of the oxygen the lattice, moreover, the test performed in adiabatic conditions, made the PtReCaAlF10 catalyst a serious candidate in view of the realization of single stage process.

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