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Innovative Catalytic Systems for Methane Steam Reforming Intensification

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Structured catalysts based on highly conductive carriers, can improve the heat transfer along the catalytic bed, allowing a flattened radial temperature gradient and a consequently higher performance. The effect of thermal conductivity of structured carriers on highly endothermic Methane Steam Reforming (MSR) reaction is investigated. The performance of the structured catalysts, obtained on Cordierite and Silicon Carbide (SiC) monoliths, demonstrates the direct correlation between the thermal conductivity of the carrier, the methane conversion and the hydrogen productivity. The evaluation of the monolith configuration shows that the SiC "wall flow" (WF) guarantees a better axial and radial thermal distribution, with respect to the SiC "flow through" (FT), resulting in better catalytic activity up to a temperature reaction of 750 °C. The comparison among the performance of the structured catalysts and the commercial 57-4MQ, provided by Katalco-JM, highlights the choice of structured catalysts, which require a lower temperature outside of the reactor, increasing the process efficiency.

1. Introduction

Hydrogen is the simplest and the most plentiful element in the universe; despite its simplicity and abundance, hydrogen is not naturally present in molecular form on the Earth, unless combined with other elements. Hydrogen is one of the main constituents of hydrocarbons from which can be extracted by reforming processes. Actually, the main technique to produce hydrogen is methane (or natural gas) steam reforming (SR), a catalytic endothermic process in which the hydrocarbon reacts with steam to produce hydrogen and carbon monoxide. The endothermic nature in such reaction requires that in one hand the process should be carried out at very high temperature (around 850 °C), in the other hand a considerable heat flux towards the reaction system is required to sustain the process to achieve high methane conversion (Yan et al., 2015). As a result, the requirement of transfer heat from an external source to a high temperature catalytic system determined the main part of operating and fixed costs, therefore resulting a key target in the process intensification direction. In this aim, the minimization of heat transfer resistance in the overall system (heating source – reactor – catalyst – gas phase) appeared the most viable solution. In particular, to achieve a uniform temperature in the whole catalytic volume may increase heat transfer rate. Previous studies demonstrated that highly conductive supports help to flat the radial and axial temperature profiles, so minimizing the heat transfer resistance from the heating medium to the catalytic volume, and obtaining a more uniform catalytic behaviour in the whole volume (Palma et al., 2012). In addition, the thermal advantages achieved by using highly thermal conductive honeycomb monolithic catalysts may be further enhanced by forcing the flux to cross the monolithic walls (Palma et al. 2015). In this aim the use of WF monoliths appears a viable solution towards the methane steam reforming intensification (Palma et al., 2016). Aim of this work was to evaluate the improvements in a MSR process due to the employing of high-conductive monoliths as catalytic supports; in particular, wall-flow configuration effect on system performances were evaluated. It is also demonstrated that rare hearts supports (CeO_2, ZrO_2) were characterized by an improved oxygen mobility (Polychronopoulou et al., 2011), resulting in an increased activity towards reforming reactions and in an enhanced resistance towards coke formation. In the present study, structured catalysts for MSR reaction were developed, by

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optimizing catalytic phase formulation (active phase percentage, support), and adhesion to the mechanical support.

2. Materials and methods

Nickel based catalysts supported on monolithic supports were prepared, in order to investigate the mechanical support role. Monolithic catalysts were prepared by the impregnation method, as reported in earlier works (Palma et al., 2016), by a dip impregnation in a slurry, up to reach a washcoat loading of 20 %wt, and then the Nickel was deposited on the coated monolith up to reach a loading of 5 %wt.

2.1 Carriers preparation

Silicon Carbide (SiC) and cordierite "flow-through" carriers were obtained by cutting a quasi-circular cross section from a commercial honeycomb monolith provided by Pirelli Ecotechnologies and Corning, respectively. The monoliths were properly shaped (diameter = 15 mm; length = 29 mm) to be located in the reactor, and were entrapped in a thermo-expandable ceramic mat (3M) in order to avoid bypass phenomena. The “wall-flow” carriers were obtained from the corresponding “flow-through”, alternately occluding the input and output sections of each channel with a high temperature resistant ceramic glue, with the aim to force the gas to pass through the porous walls of the inner channels. The as obtained carriers were calcined at 850 °C for 3 h to activate the surface.

2.2 Catalyst preparation

The washcoat slurry was prepared by suspending, under mechanical stirring, 19 wt% of ceria powder (Opaline®; Actalys HAS; Rhodia) in a colloidal solution of 1 wt% of psudobohemite (Pural SB; Sasol) and 1 wt% of methyl cellulose (Viscosity 4,000 cP; Sigma-Aldrich) at pH = 4 by nitric acid (Sigma-Aldrich). The washcoat mixture was finally vigorously stirred for about 24 h, to guarantee the perfect suspension of the solids content. The monoliths were dipped in the slurry and left for about 20 min to impregnate; the excess of slurry was removed by aspirating it with a vacuum pump and glass pipettes from the channels and the external walls. Subsequently the impregnated monoliths were dried at 120 °C for three hours and calcined at 850°C for three hours. This procedure was repeated up to the desired loading of washcoat inside the channels, which was 1.7 g for both SiC and cordierite monoliths, in order to conduct the catalytic tests on equal amount of catalyst to highlight the effect of the carrier. Subsequently the deposition of nickel was performed by wet impregnation in a proper aqueous solution of nickel acetate tetrahydrate (99.998 % trace metals basis, Sigma-Aldrich), and the final catalysts dried at 120 °C for three hours and calcined at 850 °C for three hours. For comparison the activity tests were performed also with a commercial Katalco$_{JM}$ 57-4MQ catalyst, provided by Johnson Matthey. In order to not affects the external heat transfer parameters, the same volume of commercial catalytic pellets (about 5 cm^3) was used in activity tests, so resulting in the same lateral surface of the catalytic volumes.

2.3 Catalysts characterization

The prepared catalysts were characterized by a series of physico-chemical analytical techniques. The chemical composition was evaluated by means of ARL QUANT’X ED-XRF spectrometer (Thermo Scientific). An aliquot of the washcoat was dried while an aliquot of the structured catalyst was grinded, the resulting powders were compressed to form a tablet and analyzed by the Fundamental parameters method. The ultrasound adherence test was performed to evaluate the resistance to mechanical stress (Piras et al., 2000) of the washcoat/SiC system; the samples were immersed in a beaker containing 150 mL of petroleum ether (Carlo Erba reagenti) and placed in a ultrasonic bath CP104 (EIA S.p.A.), the tests were performed by applying the 60 % of rated power for every cycle of 5 min at 25 °C. After each cycle the samples were dried in an oven at 120 °C for 30 min and weighed, to assess the loss in weight. BET surface area measurements were carried out with a Sorptometer 1,040 K (Costech International); the samples were chopped and placed in the apparatus tubes, degassed in vacuum at 150 °C for 1 h and the surface area measured by N_2 adsorption-desorption at 77 K. The porosimetric distribution was evaluated, by Hg penetration technique, with a “PASCAL 140” and “PASCAL 240” (Thermo Finnigan Instruments), in order to evaluate the variation of the porosimetric characteristics of the samples due to washcoat deposition. The crystal phases of the catalyst were identified by X-ray Powder Diffraction (XRD) with a D8 Advance (Brucker), in the 2θ range 20-80 °. The H_2-TPR experiments were carried out in the temperature range of 20-850°C with a heating rate of 10 °C/min by using a reducing stream of 500 Ncc/min composed of 5 % H_2 in N_2, and performed in the reactor described below for the catalytic tests.

2.4 Catalytic activity tests

The catalytic activity tests were performed in order to compare the performances of the prepared samples with a commercial Katalco$_{JM}$ Quadralobe catalyst: the catalysts were located in an AISI 310 stainless steel tubular reactor (internal diameter = 17 mm), at atmospheric pressure, fed with a steam to methane ratio of 3, at hourly space velocity GHSV of 100,000 h^{-1} (calculated as the ratio between the volumetric flow rate and the volume of the catalyst). All samples were reduced in-situ by 5 % of H_2 diluted in N_2 at a flow rate of 1,000 mL/min, from 20 to 850 °C with a ramp of 5 °C/min, prior the activity test. The temperature control of the reaction was ensured via an annular electrical furnace (nominal power 4 kW) supplied with three different heating zones, each operated by a TLK38 controller connected to a thermocouple in contact with the wall of the reactor, the temperature furnace ranged between 500-950 °C. The amount of gas and water sent to the reactor were controlled by a mass-flow (Bronkhorst) system, all the gases were supplied by SOL S.p.A. The water was vaporized in a coil placed in the entering part of the oven, before the mixing with the gaseous feed. The pressure upstream of the catalytic bed was monitored by a pressure transducer, the temperature control was achieved with two K-type thermocouples at the center input and output of the catalysts, both temperature and pressure were monitored by a Simex Multicon display and collected by means a Ni LabView custom application. The analysis of the gas from the reactor were performed on the dry current, removing the vapor via a Julabo F12 refrigerator, and carried out continuously by a Hiden Analytical mass spectrometer system, where the concentration of the masses corresponding to hydrogen, methane, CO and CO_2, was monitored.

3. Results and discussion

3.1 Samples characterization

The ultrasound adherence tests were performed in order to evaluate the resistance of the coating to a strong mechanical stress; the method consists in evaluating the weight loss caused by an ultrasonic cleaning (Palma et al., 2013) for the SiC and cordierite carriers. The weight loss percentage was calculated versus the lonely deposited washcoat. The losses recorded were around 18 %, while the highest loss was recorded with the cordierite carrier. These percentages are due to low alumina content and at the high calcination temperature, anyway, are in line with those reported in literature for similar catalysts (Pakdehi et al., 2015). The ED-XRF spectroscopic results substantially confirm the expected composition (Table 1). The SSA_{BET} trend shows that the washcoat loading induces a significant increase in the specific surface area of the monoliths (Table 1).

Table 1: Chemical composition (wt%) and textural properties

Sample	XRF					S_{BET} [m^2/g]	V Pore [mm^3/g]	Pore D_m [µm]
	SiC	Cordierite	Ni	Al_2O_3	CeO_2			
Washcoat pwd	-	-	-	3.89	96.11	31	-	-
5NiWcord	-	62.78	1,85	1.38	33.99	13	284.26	1.81
5NiWSiC/FT	74.35	-	1.28	0.98	23.39	12	248.19	6.13
5NiWSiC/WF	74.21	-	1.29	0.98	23.52	12	248.19	6.13
SiC	100	-	-	-	-	<1	329.78	17.0
Cordierite	-	100	-	-	-	<1	99.80	0.31

These results highlight the role of the washcoat, which allows to increase the surface area of the monoliths of two orders of magnitude, providing a better dispersion of the active metal. The porosimetric results show that the addition of the washcoat to the carriers, leads to a decrease of the average diameter and volume of the pores in the SiC and an increase in the case of cordierite. This effect is related to porosimetric characteristics of starting carriers, the SiC is characterized by porous inner walls, with an average pore diameter of about 17 µm, while cordierite is characterized by two orders of magnitude smaller pores, therefore, the adding of washcoat, adhering to the inner walls of the pores of SiC reduces the section and diameter, while in the second case, adhering to the inner surface of the channels creates roughness, which are similar to surface porosity. The XRD diffraction patterns of calcined 5NiWcord and 5NiWSiCFT structured catalysts, and the reference diffraction pattern of calcined ceria (not reported here) are characterized by the presence of the diffraction peaks of the relative carrier and of the ceria, arising from the washcoat, while no peak associated to nickel oxide and alumina is observed, probably due to the low metal loading, thus being below the detection limit of the method instrument. The diffraction pattern of ceria presents the characteristic cubic fluorite type phase in all structured catalysts, however the main peaks of ceria seem to be shifted in the cordierite structured catalyst; this phenomenon was related to the overlapping between the peaks of cordierite and ceria. The crystallite average size, calculated by Scherrer equation on the main peak of ceria (111), is reported in Table 2 both for the structured catalysts and for a sample of ceria powder, used for the washcoat preparation, calcined at 850 °C. The same value was obtained both for SiC-structured catalysts and the ceria powder, thus showing that the several calcination steps don’t affect the crystallite size anymore. It was not possible calculate this value for the cordierite-structured catalyst due the occurred overlapping.

Table 2: Average crystallite size of calcined catalysts and theoretical and experimental H_2 consumption in TPR experiments

	XRD			H_2-TPR	
Sample	CeO_2 (nm)	SiC (nm)	Cordierite (nm)	Experimental H_2-consumption (mmol/g)	Theoretical H_2-consumption (mmol/g)
5NiWcord	n.d.	-	17 (111)	2.13	0.84
5NiWSiC$_{FT}$	21 (111)	55 (102)	-	1.78	0.84
5NiWSiC$_{WF}$	21 (111)	55 (102)	-	2.78	0.84
Katalco 57-4MQ	-	-	-	5.69	-

The comparison between the experimental and theoretical hydrogen uptake obtained for the structured and commercial catalysts, in H_2-TPR experiments, evidenced a higher experimental value for the structured catalysts (Table 2), that is the result of the overlapping of broad peaks located in the temperature range 350-700 °C, due to the reduction of nickel oxides and of ceria itself. This complex superposition is mainly attributed to the ceria-alumina system, whose H_2-TPR profile strongly depends on the ceria/alumina ratio and on the type of established interaction. The hydrogen uptake of the two configuration of SiC-structured catalysts slightly differs, suggesting a possible effect of the carrier, moreover the hydrogen experimental consumption obtained with the commercial catalyst suggests a much higher loading of the active component, supposing an amount of Ni up to 6.7 times higher than monolithic samples.

3.2 Catalytic activity tests

Catalytic activity was investigated for the prepared samples by performing tests by assuring a reaction stream composed by 25 $_{vol}$% of methane and 75 $_{vol}$% of steam. The comparison between prepared monoliths and commercial catalysts was investigated; the results were summarized in Figure 1 and Figure 2: the results highlighted better performances of monolithic catalysts for temperatures higher than 600 °C with respect to the commercial formulation, allowing a methane conversion on commercial catalyst at 700 °C of about 61 %, while monolithic samples assured a conversion close to 73 %. For temperatures lower than 600 °C, an opposite trend was observed, since commercial catalyst highlighted a methane conversion up to double with respect to cordierite sample and a better activity also towards WGS reaction, as a higher carbon dioxide yield (not reported here) was recorded. Such behavior may be ascribable to Katalco catalyst features: since the loaded commercial sample contained a substantially higher amount of nickel (as reported in the previous paragraph), in the lower operating temperature range, characterized by reactions kinetics relatively low, the high content of active phase on commercial sample promoted higher conversion of methane as well as evident activity in WGS reaction.

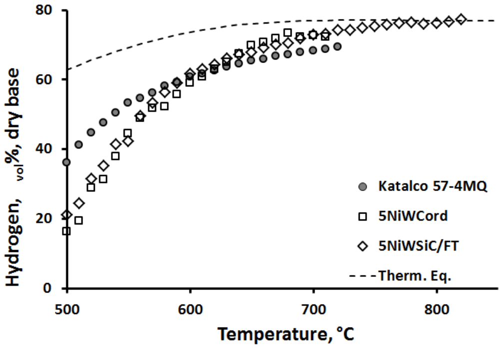

Figure 1: Hydrogen yield for commercial Katalco and honeycomb monolithic catalysts (operating conditions: GHSV=100,000 h-1, ratio H_2O / CH_4 = 3)

By increasing operating temperature, reactions kinetics were thermally enhanced, improving the performances of monolithic samples: for temperature higher than 650 °C, equilibrium approach of methane conversion for Katalco sample appeared almost unchanged, while monolithic samples achieved experimental results closer to thermodynamic predictions.

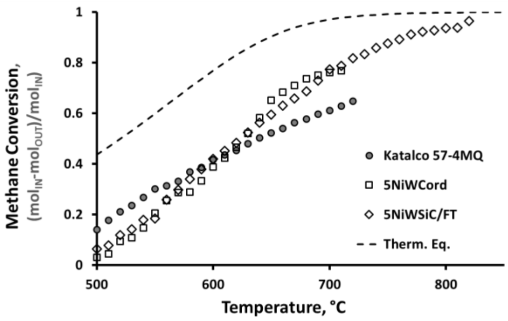

Figure 2: Methane conversion for commercial Katalco and honeycomb monolithic catalysts (operating conditions: GHSV=100,000 h^{-1}, ratio H_2O / CH_4 = 3)

As confirmation of proposed suppositions, both SiC and cordierite monolithic samples showed very similar performances at low operating temperature, both in terms of methane reforming and hydrogen yield, so confirming that nickel amount on samples was a dominant parameter in the considering temperature range. It is finally worth to underline that SiC catalytic monolith well approached thermodynamic equilibrium for temperature above 670 °C: the approach is more evident for hydrogen composition and CO_2 yield with respect to methane conversion, so underlining that water-gas shift reaction was better promoted by the system.

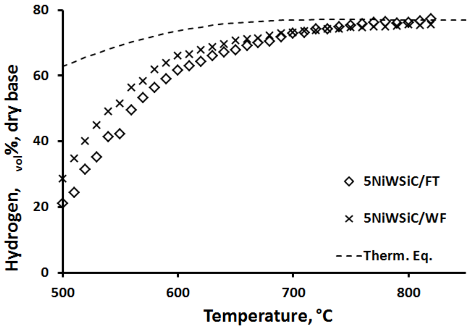

Figure 3: Hydrogen yield for SiC supported catalysts in WF and FT configuration (operating conditions: GHSV = 100,000 h^{-1}, ratio H_2O / CH_4 = 3)

The excellent performances of such catalysts towards WGS may be ascribable to the high affinity of ceria supported catalysts towards CO-shift reaction (Jeong et al., 2013), it is however relevant to remark that high activity of Ni/CeO_2 based catalysts in such reaction should require an optimal Ni morphology (particularly primary particle size and shape), thus enhancing redox properties of catalytic system (metal and support) (Kubacka et al., 2016).

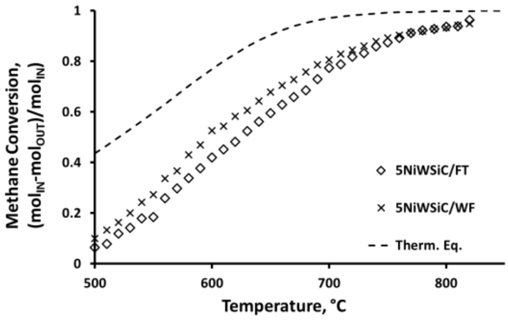

Figure 4: Methane conversion for SiC supported catalysts in WF and FT configuration (operating conditions: GHSV = 100,000 h^{-1}, ratio H_2O / CH_4 = 3)

The comparisons of the activity of SiC based catalysts in FT and WF configuration are reported in Figures 3 and 4. The reported results evidenced an excellent approach to thermodynamic equilibrium for both catalysts at temperatures higher than 700 °C and no appreciable differences among them were observed, while at lower operating temperatures, slightly better performances were recorded for the wall-flow catalysts. This is probably due to the flux geometry of process stream in the WF sample: the gases are forced to flow through the porous channel walls, on which catalyst (both washcoat and nickel) is deposited, so allowing the complete exploitation to the reaction stream; on the contrary this is not the case of flow through configuration. The observed phenomenon is in agreement to hydrogen uptake evaluated in samples reduction (Table 2), in which similar SiC samples, activated by the same amount of catalyst, reported a higher H_2 consumption for the WF catalyst than FT, since WF configuration minimized diffusional limitations, allowing a more evident reduction of superficial ceria structure.

4. Conclusions

In this work the feasibility to use high thermal conductivity carriers for the preparation of highly efficient catalysts for the Steam Reforming Process is investigated, in particular reporting the comparison between the performance of Cordierite and SiC carriers, in WF and FT configuration, and with a commercial Katalco 57-4MQ catalyst. The structured catalysts were prepared by washcoating the carriers with a ceria-based colloidal suspension and subsequent wet impregnation with nickel acetate solution, in order to obtain a washcoat loading of 1.7 g and of 5 wt% of nickel respect to the washcoat. The ultrasound adherence test confirmed a good resistance of the washcoat to the mechanical stress. The estimated surface area showed that the addition of washcoat was essential for increasing the surface area available for interaction between the reacting gases and active species. The porosimetric analysis evidenced the decrease of the carrier pores diameter due to deposition of washcoat in the porosity of SiC. The evaluation of the crystallite size from XRD diffractograms suggested that no sintering phenomenon took part during the repeated calcinations, which took place in catalyst preparation. The H_2 uptake in the H_2-TPR experiments suggested a much higher loading of nickel on the Katalco 57-4MQ catalyst. The catalytic activity tests showed that structured catalysts allow a flattening of the radial thermal profile, and in particular SiC carriers in WF configuration showed a higher catalytic activity than the other monoliths, especially at temperatures below 750 °C, so leading to higher performance of the process that, under equal operating conditions, leads to a higher methane conversion and hydrogen yield. It can therefore be concluded that the use of supports in SiC has the conjugated advantages of increasing the hydrogen yield and a lower temperature demand outside the reactor, allowing an overall increase in the efficiency of the process.

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