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Methane Steam Reforming Intensification: Experimental and Numerical Investigations on Monolithic Catalysts

Vincenzo Palma*, Antonio Ricca, Eugenio Meloni, Marino Miccio, Marco Martino, Paolo Ciambelli

University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
vpalma@unisa.it

Methane steam reforming is still the most economical route for hydrogen production. It generates hydrogen for refining processes, food industry, and recently for fuel cell applications. Recent studies focused on the application of structured catalysts in mass transfer limited-reactions indicated that there are potentially several advantages for monolithic reactor as compared to the packed reactors such as, especially in terms of lower pressure drop and better mass and heat transfer performances. So highly thermal conductive honeycomb structures were proposed as catalyst supports to enhance the heat and material transfer properties of the final catalysts. This work focuses on the experimental testing of the methane steam reforming reaction performed on a Ni-loaded SiC monolith packaged into an externally heated tube. In particular, the two flow configurations of Flow Through and Wall Flow were investigated and compared, the effect of a washcoat deposition was evaluated. The experimental tests indicate that the Wall Flow configuration may overcome the fixed-bed reactor problems, yielding a more uniform temperature distribution and more effective mass transport.

1. Introduction

The continuous growth of the world population, the technological advancement, the natural tendency of countries (especially emerging markets) to achieve higher standards of living are the main reasons of the increase in energy demand and the consequent development of greenhouse gases. The hydrogen, from the energy point of view, is an ultraclean fuel and generates energy without producing harmful waste for the environment. Despite the growing interest in renewable resources, due to the wide diffusion of fossil fuels and their low relatively costs, hydrocarbons fuel processing still remains the best solution for a period of transfer toward a hydrogen-based economy. The purpose of a fuel processor is to convert a hydrocarbon fuel (natural gas, gasoline, diesel) into a H_2-rich stream to fed a fuel cell system. A typical fuel processor consists of 3 main steps: a reforming unit, in which syngas is produced from hydrocarbons, a water gas shift unit and a preferential oxidation unit, aimed to removing CO from syngas. There are three primary techniques used to produce hydrogen from hydrocarbon fuels: steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR). Currently, the widely diffused technology to produce hydrogen from hydrocarbon fuels is steam reforming since it assures the highest hydrogen yield with respect to the other two approaches. Steam reforming is a catalytic endothermic process in which a hydrocarbon (e.g., methane) reacts with steam to produce mainly hydrogen and carbon monoxide:

$$CH4 + H2O \leftrightarrows CO + 3\ H2 \qquad \Delta H^\circ_{298K} = 206.2\ kJ\ mol\text{-}1 \qquad (1)$$

The process endothermicity implies that very high reaction temperatures and heat fluxes towards the reaction system are required to achieve high methane conversion. Great attention must be also devoted to the catalyst structure (e.g. powder, pellets, honeycomb, foams, etc.). In the process intensification direction, previous studies (Palma et al., 2009) have demonstrated that high thermal conductivity supports may allow for a flatter axial thermal profile along the catalytic bed, thus resulting in a higher average temperature at the outlet section of the reactor, and consequently in larger hydrocarbon conversion (Halabi et al., 2011). In addition, the

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highly conductive supports ensure a more uniform radial temperature profile, thus resulting in a better heat transfer and reduction of hot-spot phenomena (Palma et al, 2012). Structured monoliths exist in two different configurations: Flow Through (FT) and Wall Flow (WF) (Palma et al, 2015). In the FT configuration, the channels are open on both sides, while in the WF, the parallel channels are alternately plugged at each end (channels open in the inlet section are closed in the outlet section; channels open in the outlet section are closed in the outlet section) so forcing the exhaust gas flow through the porous walls. In our previous works (Palma et al., 2014) a preliminary steady-state heterogeneous 3D model was developed, that includes momentum, mass and energy balances. The experimental tests and the numerical simulations indicate that the Wall Flow configuration may overcome the fixed-bed reactor problems, yielding a more uniform temperature distribution and a more effective mass transport (Palma et al., 2014). Starting by these results, the present study compares the reaction performances of catalyzed SiC WF and FT monoliths in the methane SR process, in particular investigating the effect of ceria (CeO_2) based washcoat deposition.

2. Material and methods

Silicon Carbide (SiC) monoliths (Pirelli Ecotechnology, 150 cpsi), were selected as a support for the preparation of the structured catalysts. The choice of a SiC based support was determined by the thermal conductivity values (about 350 W m^{-1} K^{-1} at 25 °C) that are significantly higher than those typically reported for widely applied supports materials like alumina (about 30 W m^{-1} K^{-1} at 25 °C) or cordierite (about 3 W m^{-1} K^{-1} at 25 °C). The SiC monoliths were activated by nickel deposition, with and without a previous deposition of a washcoat.

The monolith washcoating was obtained by the dip impregnation in a lab-made slurry followed by drying and calcination steps. Slurry was realized by CeO_2 (Rhodia) dispersed in a solution of methyl cellulose (Sigma Aldrich) and pseudo-bohemite (2:1 weight-base) (CONDEA PURAL SB01). The dipping was repeated several time in order to reach a loading of 20 %wt of CeO_2 on the support. The nickel deposition on the washcoated and non-washcoated samples was by repeated wet impregnations steps in 1M nickel acetate solution ($C_4H_6O_4Ni{\cdot}4H_2O$) followed by drying (120 °C, 30 min) and calcination (20 °C min^{-1} up to 600 °C, 2 hr). 4 samples were so obtained, 3 on the non-washcoated support (10 % Ni/SiC, 20 % Ni/SiC, 31.8 % Ni/SiC) and 1 on washcoated support (20 % Ni / 20 % Wc/SiC).

The samples were characterized by several techniques in order to investigate the catalyst deposition effect. The specific surface area (SSA) was evaluated by B.E.T. method using a Costech International 1040 Kelvin Sorptometer. The nickel crystallite sizes were evaluated by starting from XRD analysis carried out by a D8 Brucker micro-diffractometer. The porosimetric characteristics of the samples have been measured by the Hg penetration technique using the “PASCAL 140” and “PASCAL 240” Thermo Finnigan instruments. The H_2-Temperature Programmed Reduction (TPR) measurement was carried out from room temperature to 900 °C with a heating rate of 3 °C min^{-1} by using a reducing stream of 1000 Ncc min^{-1} composed by 5 % H_2 in He. The H_2-TPR analysis was carried out in the reaction system.

The experimental tests were carried out in a lab-scale tubular reactor (D_{in} = 18 mm) in isothermal conditions. The monolithic catalysts were placed in the reactor enveloped by a thermal-expanding mat (INTERAM - 3M), in order to avoid the gas stream bypass. The temperature control of the reaction was assured by an annular electrical oven (nominal power 4 kW) provided with 3 different heating zones, each driven by a TLK38 regulator linked to a thermocouple in contact with the reactor wall. Reaction temperatures monitoring was assured by two thermocouples placed in the middle of the inner and outer section on catalytic system.

The activity tests were performed on the catalytic monoliths in the FT and WF configurations, decreasing temperature from 800 to 600 °C by using a cooling rate of 2 °C min^{-1}, with a H_2O/CH_4 feed ratio of 3:1 and with GHSV (Total flow rate / Total catalytic volume) variable in the range 750-25000 h^{-1}.

3. Results and discussion

3.1 Specific Surface Area

The Specific Surface Area (SSA) of the samples are reported in table 1; in the same table are also reported the crystallite size of deposited Ni, calculated by means of Scherrer formula.

Table 1: Specific Surface Area of washcoated and non washcoated catalytic samples

Sample	SSA [$m^2 g^{-1}$]	Crystallite size [Å]
SiC	0.25	
10 % Ni/SiC	0.56	247.6
20 % Ni/SiC	0.81	199.0
31.8 % Ni/SiC	1.10	165.2
20 % Wc/SiC	29.79	
20 % Ni/20%Wc/SiC	21.91	145.0

As reported in Table 1, surface area increased by increasing nickel deposition values, probably due to the increasing surface roughness due to the calcination steps. The washcoat deposition resulted in a clear SSA increasing, up to 2 order of magnitude higher than the bare support. The lower specific surface area values seems to promote the nickel dispersion, and in turn, the low nickel crystallite size.

3.2 Hg porosimetry tests

The Hg porosimetric tests performed on washcoated and non washcoated catalytic samples evidenced that, as expected, the increase of the catalyst load on the non washcoated supports resulted in the decrease of the mean pore diameter. The washcoat previously deposition resulted in a further pore mean diameter decrease, from 17 μm (bare SiC support) to about 11 μm for the 20 % Wc/SiC sample and finally to 4.4 μm for the 20 % Ni / 20 % Wc/SiC sample, but in this case any occlusion of the pores was evidenced.

3.3 H_2 TPR Analysis

The H_2-TPR results are reported in table 2, as comparison of experimental and theoretical H_2 consumption during the reduction reaction of NiO (eq. 2), in the case of non washcoated and washcoated samples. The theoretical hydrogen uptake was evaluated by supposing that all the loaded nickel deposed on the samples (based on the nominal loading) was reduced from the oxidize state (NiO) to the metallic state (Ni).
The reaction for NiO reduction is:

$$NiO + H_2 \rightarrow Ni + H_2O \qquad (2)$$

Table 2: Comparison between experimental and theoretical H2 uptake in the TPR analysis performed on washcoated and non washcoated catalytic samples

Sample	Experimental H_2 Uptake [μmol g^{-1}]	Theoretical H_2 Consumption [μmol g^{-1}]
31.8 % Ni/SiC	0.033	0.029
20 % Ni / 20 % Wc/SiC	0.572	0.026

The TPR analysis assessed the good agreement of the experimental and theoretical H_2 uptake in the case of non washcoated sample, while the washcoat deposition improved sample reducibility (by anticipating the reduction temperature). On the other hand, for the washcoated sample, the higher H_2 experimental uptake than the theoretical one was devoted to the spillover phenomena due to the Ni/CeO_2 interactions (Sharma et al., 2012).

3.4 Catalytic activity tests

Activity tests were carried out in the WF and FT configuration catalysts by feeding 25 %vol CH_4 and 75 %vol H_2O; the activity test were performed with washcoated and non-washcoated monoliths. In all the reported experimental tests, atomic balances (C, H, O) were closed within 97%. Main results for the non-washcoated monoliths were summarized in Figure 1.

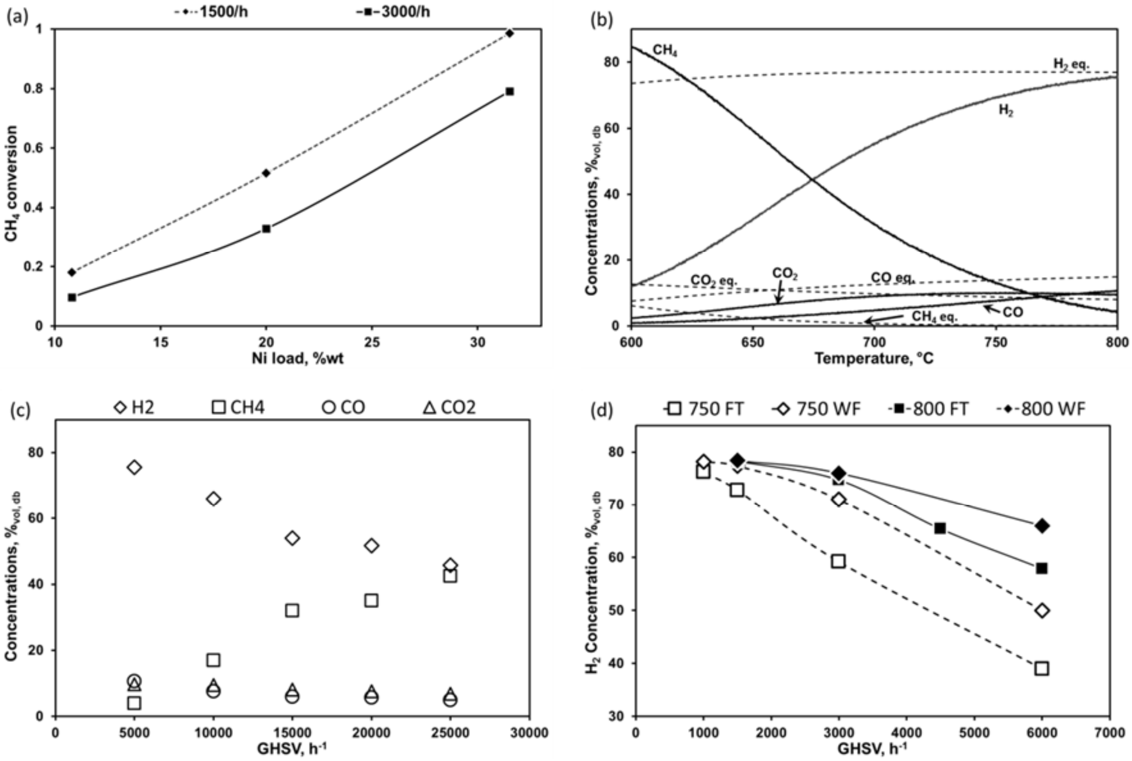

Figure 1: Catalytic performances of non-washcoated Ni/SiC samples vs (a) Nickel loading (800°C); (b) Operating temperature (31.8 % Ni/SiC-FT; GHSV = 1500 h^{-1}); (c) Gas Hourly Space Velocity (31.8 % Ni/SiC-FT; T = 800 °C); (d) Flux Geometry (31.8 % Ni/SiC).

The nickel load effect on the catalytic activity was firstly investigated (Figure 1a) on non-washcoated FT monoliths. The reported results remarked that the methane conversion strictly depends on the Ni loading; in particular in the investigated range a linear dependence between the methane conversion and Ni load seemed to occur. Moreover lower GHSV increased methane conversion.

The temperature effect on the reaction was investigated for the 31.8 % Ni/SiC FT sample by fixing the GHSV to 1500 h^{-1}. As reported in Figure 1b, a clear dependence between operating temperatures and catalyst performances was shown. The products concentrations approached the equilibrium values only at temperatures close to 800 °C. From this analysis, it emerges that a temperature of 800 °C is required by the Ni/SiC catalyst to achieve high CH_4 conversion and high H_2 yields.

Once the temperature was fixed, the GHSV effect on the product composition was studied (Figure 1c). A clear worsening in catalytic performances was observed as the GHSV increases, due to the reduction of the contact time between the gas stream and the catalytic surface.

Finally, the geometric effect of the catalytic system was investigated, by comparing catalyst performances in FT and WF configurations. The activity tests results, summarized in Figure 1d, highlighted the better performances of the WF configuration than the FT, in terms of hydrogen production at the same temperature and GHSV. The WF configuration enhancement was more evident in the more extreme conditions, i.e., at the lowest operating temperatures and at highest reactant flow rates where the heat and mass transfers may results limiting stages. Obtained results highlight the real benefit of the wall flow configuration that in one hand optimizes solid-gas contact in the wall porosity of the catalyst so maximizing mass transfer rate between the phases, on the other contributes to the flattening of the radial thermal profiles, optimizing so the thermal management in the catalytic volume.

As a final step, activity tests were performed on the wash-coated monoliths; the results for the monoliths in FT and WF configurations are reported in Figure 2.

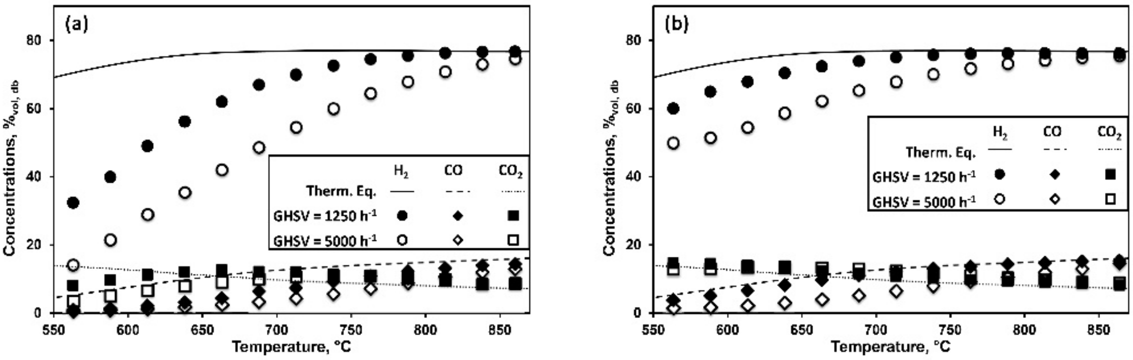

Figure 2: Catalytic activity of 20 % Ni / 20 % Wc/SiC samples in FT (a) and WF (b) configurations.

The reported results evidenced the better performances obtained in the WF configuration respect to the FT. The WF catalysts played a crucial role especially for the more severe operating conditions (high GHSV, low temperature) in which heat and mass transfer rates become a key parameter. At the lower GHSV value, the WF catalyst resulted in a product composition very close to the thermodynamic equilibrium in the main part of the investigated temperature range.

The role of the washcoat on catalytic performances was highlighted in Figure 3. Reported results assessed that washcoated samples were able to dramatically reduce the gap with the thermodynamic equilibrium, resulting in a more than twice methane conversion up to 700 °C (in conditions far to the thermodynamic equilibrium). The oxygen-storage capacity, proper to the cerium oxide, accelerates the migration of oxygen from steam to the carbon (Polychronopoulou et al., 2011), so resulting in a clear increasing in catalytic system performances.

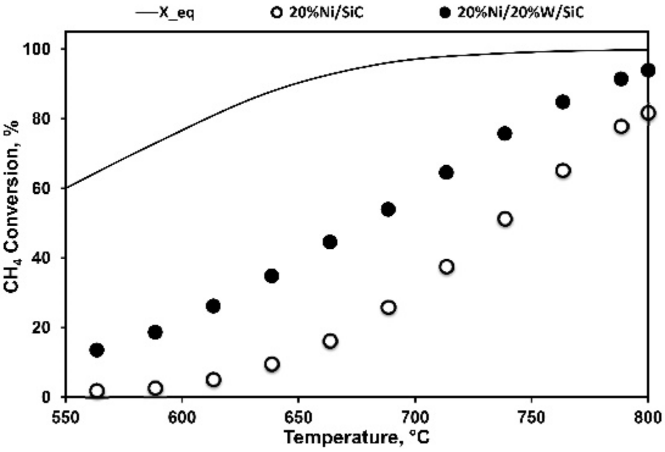

Figure 3: Comparison of CH_4 conversion in non-washcoated and washcoated activated wall flow monoliths (GHSV = 5000 h^{-1}).

4. Conclusions

An advanced experimental reaction system was set-up in order to verify the influence of flow configuration in monolithic catalysts on methane SR. The activity tests showed the better performances of the monolithic reactor in the WF configuration with respect to the FT, in terms of hydrogen yields at the same temperature and GHSV: in particular the results highlighted that the preliminary deposition of a washcoat on the support increases the specific surface area, so allowing a better dispersion of the active species and a consequent better catalytic activity, particularly at lower temperatures. Finally, the experimental results demonstrated that high thermal conductivity monolithic catalyst in WF configuration allowed to overcome the energy and mass limitations, which are the main bottlenecks of the commercial steam reforming catalysts.

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