

Experimental and Numerical Investigations on Structured Catalysts for Methane Steam Reforming Intensification

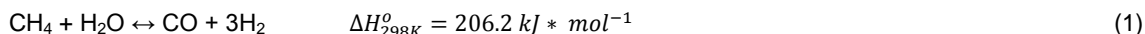
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Highly thermal conductive honeycomb structures were proposed as attractive catalyst supports in order to enhance heat and material transfer properties. This work is focused on experimental testing and preliminary numerical modeling of the methane steam reforming reaction performed on Ni-loaded SiC monolith, packaged into an externally heated tube: in particular, Flow Through and Wall Flow configurations were investigated. A preliminary steady-state heterogeneous 3D model was developed: the model equations include 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.

1. Introduction

The significant growth in world energy demand of the recent years resulted in a great increase of the importance of hydrogen; simultaneously, the hydrogen–fuel cells combination attracts the greatest interest in scientific research and technology innovation for hydrogen production. Actually, the main technology to produce hydrogen from hydrocarbon fuels is steam reforming (SR), a catalytic endothermic process in which a hydrocarbon (e.g., methane) reacts with steam to produce mainly hydrogen and carbon monoxide:



Due to its endothermicity, very high reaction temperature and heat flux towards the reaction system are required to achieve high methane conversion. In the process intensification direction, previous studies demonstrated that high thermal conductivity supports allow a flatter axial thermal profile along the catalytic bed (Palma et al., 2009), so resulting in a higher average temperature at the outlet section of the reactor, and consequently in larger hydrocarbon conversion (Halabi et al., 2011). Furthermore, the highly conductive supports ensure also a more uniform radial temperature profile, thus resulting in an improvement in heat transfer and reduction of hot-spot phenomena (Palma et al., 2012). Many studies focused the attention on the use of monolithic catalysts especially for endothermic reactions (Hui Liu et al., 2005), they ensure higher heat transfer rates compared to random catalyst packings (Zamaniyan et al., 2012). This positive effect is attributable to the shift in the dominant heat transfer process from convection to conduction (Boger and Heibel, 2005). Monolithic catalysts are also widely applied for clean-up of waste gases (Palma et al, 2013) because they allow to have low pressure drops and high gas-solid interfacial areas at the same time. These SiC monolithic catalyst supports were evaluated for a heterogeneously catalyzed methane steam reforming reaction, they showed a very flat radial temperature profile (Tronconi et al, 2004), demonstrating excellent heat transfer properties due to the high thermal conductivity of the structure overcoming the heat transfer limitations, which is one of the main problem of the conventional packed beds (Groppi and Tronconi, 2000). Structured monoliths exist in two different configurations: flow-through (FT) and wall-flow (WF) (Knoth et al., 2005). In the FT configuration the channels are open on both sides. In the WF solution alternate cell channel openings on the monolith face are blocked and at the

opposite end the alternate channel openings are blocked; the displacement by one cell defines inlet and outlet channels. In this way the gas stream cannot flow directly through a given channel but is forced to flow in the adjacent channels through the porous walls (Palma et al., 2013). Under steady state conditions the wall-flow reactor shows a higher conversion compared to a flow-through monolith with the same characteristics, under mass-transfer-limited conditions (high temperature and flow rate) (Dardiotis et al., 2006). The present study compares the reaction performances of the catalyzed wall-flow and flow-through monoliths under different operating conditions. Furthermore a three-dimensional first-principle model was developed and implemented in COMSOL Multiphysics (De Souza et al., 2013) in order to have a tool for simulation tests and validation of experiments in the WF and FT geometric configurations.

2. Experimental

2.1 Catalyst preparation

Silicon Carbide (SiC) monoliths (Pirelli Ecotechnology, 150 cpsi), were selected as support for the preparation of the structured catalysts. The monoliths were first stabilized in a furnace operating in air by calcination at 1,000 °C for 6 h, with a temperature programmed ramp of 20 °C min⁻¹: in this way the formation of a superficial layer of silica (SiO₂) was favored, and it has the function to create anchor points for the optimal deposition of the active species later added. The monoliths were suitably shaped to achieve the geometrical characteristics shown in Table 1:

Table 1: Monolith properties

Channel length [mm]	120
Channel width [mm]	1.500
Wall width [mm]	0.625
Number of channels	37

The preferred active species is nickel, due to the good activity in reforming reactions (Yuan et al., 2009) and low costs (Wanga et al., 2013), thus applied in many industrial steam reforming applications (Kolbitsch et al., 2008). The Ni-loaded SiC monolith was prepared by repeated impregnation phases in 1M nickel acetate solution (C₄H₆O₄Ni·4H₂O), drying (120 °C, 30 min) and calcination (20 °C min⁻¹ up to 600 °C, 2 h), in order to obtain a 30 %wt of active species. This procedure allows realizing a uniform and homogeneous distribution of the nickel oxide on the monolith walls and inside the porosity.

2.2 Catalyst characterization

The prepared catalytic monoliths were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDAX), N₂ adsorption at -196 °C, applying BET method for the calculation of sample's surface area. The crystal phase of the nickel catalyst was identified by X-Ray Diffraction (XRD) with Cu k α radiation at 40 kV and 20 mA, by the mean of the D8 Brucker micro-diffractometer in the 2 θ range of 20-80° in steps of 0.02 ° s⁻¹.

2.3 Catalytic reaction system

The experimental tests were carried out in a tubular lab-scale catalytic reactor in isothermal conditions. The laboratory plant, schematized in Figure1, can be divided in 3 zones: feed, reaction and analysis.

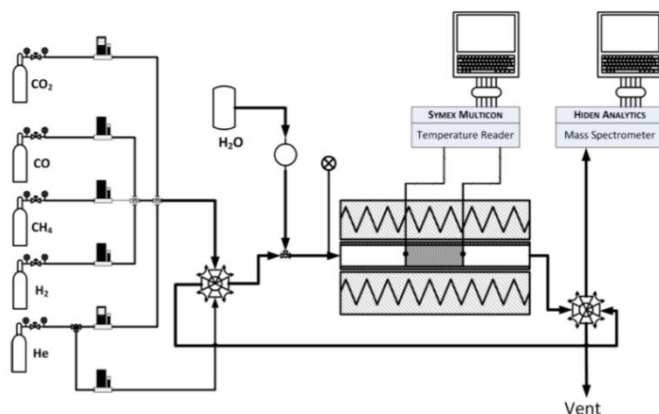


Figure 1: Experimental plant scheme

The feed consisted of 6 mass flow controller (MFC), which regulated the flow rates of gases used in the calibration and reaction phases of the system. For steam reforming tests the feeding also required distilled water pumped with a Watson Marlow 120U peristaltic pump. The water was vaporized in a coil in the entering part of the oven prior to mixing with the gaseous feed. A stainless steel AISI 310 tubular reactor was used, with a length of 38 cm, an internal diameter of 1.8 cm and a wall thickness of 0.4 cm. Systems for monitoring and controlling temperature and pressure were set up in order to evaluate the conditions in which the reaction takes place: in particular a pressure transducer, connected to the feed entrance, monitors the pressure upstream of the catalytic bed (since the pressure downstream of the catalytic bed was always maintained atmospheric, the measurement of the upstream pressure allows estimating the pressure drop on the catalyst), and two thermocouples were inserted in the center of the inlet and outlet section of the catalyst to measure the temperatures. The monolithic catalyst was placed in the reactor enveloped by a thermal-expanding mat (INTERAM by 3M), aimed to avoid the gas stream bypass. The temperature control of the reaction was carried out by placing the reactor in an annular oven, having a nominal power of 4 kW, provided by 3 different heating zones, managed by TLK38 regulators which allowed to control the temperatures and the heating rate of the oven, using 3 thermocouples placed in contact with the reactor. The analysis of the products in output from the reactor was carried out continuously by a Hiden Analytical mass spectrometer. All the steam in the stream leaving the reactor was removed by a Julabo F12 refrigerator: the concentrations produced from the analysis were therefore on a dry basis.

2.4 3D Reactor Model

A three-dimensional first-principle model was developed and implemented to simulate the flow inside the system and to obtain the concentration profiles along the length of the reactor, thus yielding the performance of the monolithic structured catalytic reactor. The 3D model was setup in order to identify an isothermal catalytic system able to sustain Methane Steam Reforming and Water-Gas Shift reactions on Nickel based structured catalysts. CH₄ and H₂O were considered as reactants, while H₂, CO, CO₂ and unconverted reactants were contemplated in the reaction domain. The model was made up by mass and momentum balances, which constitute a set of Partial Differential Equations (PDEs). They contemplated all the chemical kinetics and mass transport properties. The flow pattern was described by Computational Fluid Dynamics (CFD). Mass transfer limitations, reaction and the compressibility of the gas phase were considered. The PDEs were completed by the boundary conditions, which allowed also specifying the continuity of velocity and pressure between the porous solid and gas phase domains. The model is numerically solved using the Finite Element Methods (FEM) resort to the commercial software Comsol Multiphysics. The system geometry was realized using a CAD interface implemented in the COMSOL environment, then the physics properties were set for both the solid materials and the fluid.

3. Results and discussion

3.1 Catalyst characterization

The results of the BET analysis performed on the bare and on the catalytic monoliths are summarized in Table 2.

The values in Table 2 show that the growing catalyst load over the bare monolith induced an increase of the BET specific surface areas, as expected, since the deposition of active species on a support increased surface roughness to the composite, without plugging pores.

XRD analysis showed that the increase in the Ni load resulted in the intensification of the NiO signals, as can be seen in Figure 2.

Table 2: Specific Surface Area of the SiC filters

%wt of Ni	SSA _{BET} (m ² /g)
0	0.25
3.8	0.42
15%	0.81
31.5%	1.10

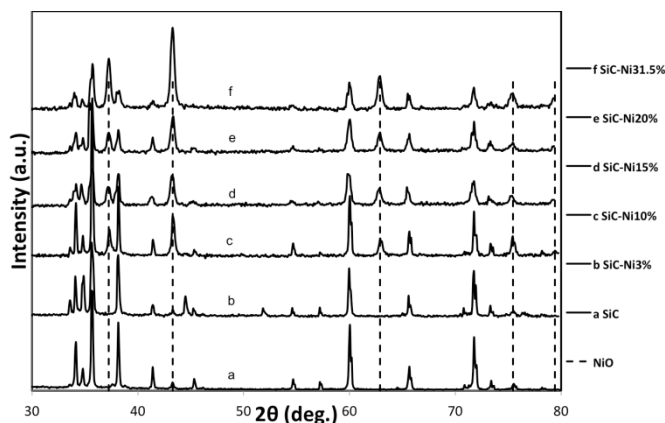


Figure 2: XRD patterns for different Ni loads. (a) SiC, (b) 3 %Ni/SiC, (c) 10 %Ni/SiC, (d) 15 %Ni/SiC, (e) 20 %Ni/SiC, 31.5 %Ni/SiC

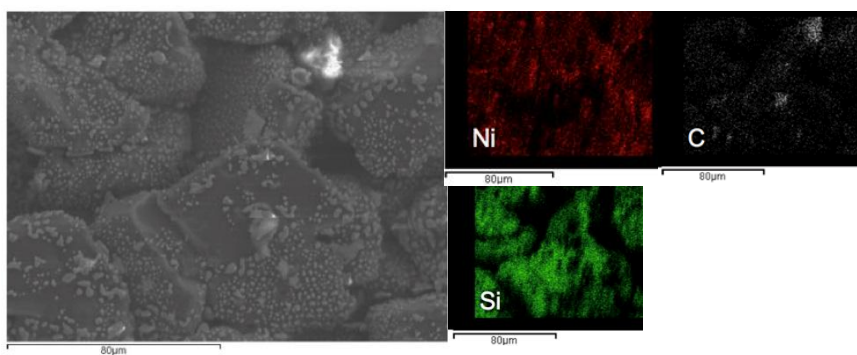


Figure 3: SEM images of the catalytic surface of the monolith at different magnitudes

SEM and EDAX images (Figure 3) proved a uniform distribution of the active species over the SiC surface, thus confirming the effectiveness of the preparation procedure.

In particular the Figure 3 reveals that on the catalytic filter the encountered elements are C and Si, the structural elements, and Ni, the active species: these results confirmed that with our catalytic filter preparation procedure, we can obtain the deposition of the active species on the support without any washcoat.

3.2 Catalytic activity tests

The activity tests were performed on the catalytic monoliths in the FT and WF configurations, in the temperature range of 750 - 800 °C and at different Gas Hourly Space Velocity (GHSV) values. The catalyst performances were investigated at atmospheric pressure and with a feed characterized by 25 %_{vol} CH₄ and 75 %_{vol} H₂O. The GHSV is calculated as the ratio between the volumetric flow rate and the volume of the catalyst as obstacle. The nickel load effect on the catalytic activity was firstly investigated. The methane conversion at 800 °C as function of the Ni load, reported in Figure 4, highlighted that high conversion was reached only with a 31.5 %wt Ni load, which was used in the next reaction tests.

The geometric effect was investigated comparing the reaction tests in the flow-through and wall-flow configurations. The activity tests results, summarized in Figure 5, highlighted the better performances of the WF configuration than the FT, in terms of hydrogen production at the same temperature and GHSV.

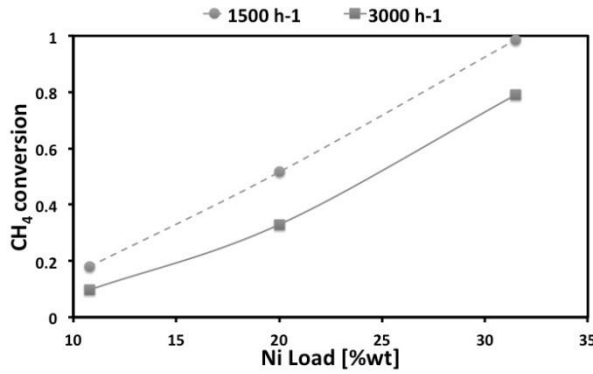


Figure 4: Methane conversion as a function of the nickel load for 2 different GHSV at 800°C (S/C=3).

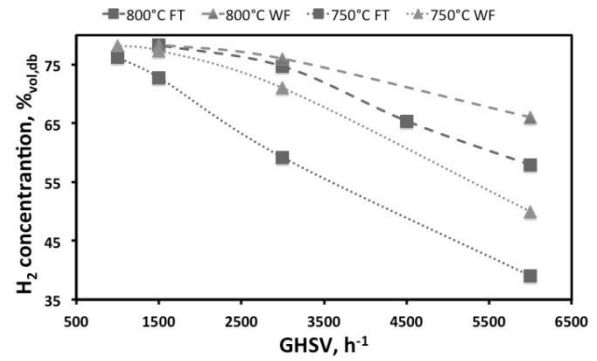


Figure 5: Comparison of H₂ content in FT and WF configurations at different temperatures and GHSV values.

The WF configuration enhancement was more evident at the lowest operating temperatures and at highest reactant flow rates where the heat and mass transfers were limited.

3.3 3D Reactor Model

Methane steam reforming can be completely described by the independent reaction of steam reforming and water-gas shift:



The kinetic scheme chosen in this work was proposed by Haberman e Young (Le Bars and Worster, 2006), and it is widely used to simulate the reaction rate (mol m⁻³ s⁻¹) of MSR and WGS on nickel catalyst.

$$r_{MSR} = k_{MSR} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - \frac{p_{\text{CO}} p_{\text{H}_2}^3}{K_{eq_{MSR}}} \right) \quad (3)$$

$$r_{WGS} = k_{WGS} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{eq_{WGS}}} \right) \quad (4)$$

Rate constants are defined by Arrhenius equations:

$$k_{MSR} = 2395 \exp \left(\frac{-231266}{RT} \right) \quad (5)$$

$$k_{WGS} = 0.0171 \exp \left(\frac{-103191}{RT} \right) \quad (6)$$

where T (K) is the temperature, R the universal gas constant (8.3145 J mol⁻¹ K⁻¹) and p_i the partial pressure of the i-th component in the gas phase.

The equilibrium constants were evaluated using the following expressions that highlight the temperature dependency:

$$K_{eq_{MSR}} = 1.0267 \times 10^{10} \times \exp(-0.2513Z^4 + 0.36665Z^3 + 0.5810Z^2 - 27.134Z + 3.277) \quad (7)$$

$$K_{eq_{WGS}} = \exp(-0.2935Z^3 + 0.6351Z^2 + 4.1788Z + 0.3169) \quad (8)$$

$$Z = \frac{1000}{T(K)} - 1 \quad (9)$$

To describe the flow in the gas phase domain, the Navier-Stokes (NS) and the continuity equations were adopted; to take in account the reactions is necessary to add N-1 mass balances, where N represents the number of components present in the system. Mass balances considered that the sum of the diffusion and convective contributes matches the generation terms. The mass fraction of the last component was determined by subtracting the sum of the mass fractions of all the other components from unity.

The simulation results for the FT and WF configurations well approached the experimental results, and evidenced the better behavior of the WF option, mainly due to the better heat and mass transfer management along the catalyst, since the methane conversion and thus the hydrogen production were higher for the WF configuration. The WF configuration enhancements resulted more evident for the more severe operating conditions (for the higher reactants rate and the lower operating temperature).

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. A numerical model was developed and implemented in COMSOL Multiphysics in order to have a tool for simulation tests and validation of experiments. The activity tests highlighted 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. The computer aided simulations allowed to deeply investigate the whole reactive system, analyzing in particular the gas flow motion in the free channels and in the monolith porosity. COMSOL results were in a quite good agreement with the kinetic analysis and experimental results, confirming the better performances of the WF configuration with respect to the FT geometry. Finally, the experimental and numerical modeling coupled results demonstrated that high thermal conductivity monolithic catalyst wall flow configuration allowed to overcome the energy and mass limitations, which are the main bottlenecks of the commercial pelletized steam reforming catalysts.

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