



Monolithic catalysts for methane steam reforming intensification: Experimental and numerical investigations



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HIGHLIGHTS

- Methane steam reforming reaction performed on Ni-loaded SiC monoliths.
- Highly thermal conductive honeycomb structures as attractive catalyst supports.
- Development of a preliminary steady-state heterogeneous 3D model.
- The wall flow configuration may overcome the fixed-bed reactor limitations.
- More uniform temperature distribution and more effective mass transport.

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ABSTRACT

Highly thermal conductive honeycomb structures were proposed as catalyst supports to enhance the heat and material transfer properties of catalysts. This work focuses on the experimental testing and preliminary numerical modeling 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. A preliminary steady-state heterogeneous 3D model was developed including momentum, mass and energy balances. The experimental tests as well as the numerical simulations indicate that the wall flow configuration may overcome the fixed-bed reactor problems, yielding a more uniform temperature distribution and more effective mass transport.

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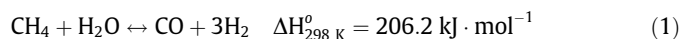
1. Introduction

The significant growth in world energy demand of the recent years has resulted in a great increase of the importance of hydrogen; simultaneously, hydrogen-fuel cells combination has created a great deal of interest in current scientific research and technology innovation for hydrogen production.

The two most diffused technologies for H₂ production are hydrocarbon fuels processing and H₂O electrolysis. 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 to a hydrogen based economy. The purpose of a fuel processor is to convert a hydrocarbon fuel (natural gas, gasoline, diesel) into a H₂-rich stream to feed 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, that have the aim of removing CO from syngas. There are three primary techniques used to produce hydrogen from hydrocarbon fuels: steam reforming (SR) in which hydrocarbon reacts with steam at high temperatures; partial oxidation (POX) in which hydrocarbon reacts with lean oxygen; and auto-thermal reforming (ATR) that results from a combination of the previous technologies in which hydrocarbon reacts with both steam and oxygen [1].

Currently, the main 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:



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,

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honeycomb, foams, etc.). In the process intensification direction, previous studies [2] 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 [3]. In addition, the highly conductive supports ensure a more uniform radial temperature profile, thus resulting in a better heat transfer and reduction of hot-spot phenomena [4].

In reforming processes, the choice and optimal setup of the catalytic system plays a significant role in plant design. Catalyst selection may greatly affect both the conversion degree as well as the selectivity of the reaction, with the presence of an active species rather than another one leading to different reaction products. Obviously, the catalyst selection should be made according to the defined operating conditions and based on the selected fuels. Several studies have demonstrated that nickel [5] as well as noble metals (Pt, Rh, Ru) [6] supported on Al_2O_3 or rare earth oxides show good activity toward reforming reactions [7]; improvements in stability and selectivity are achieved from bimetallic catalytic systems [8].

However, the wide diffusion of nickel in industrial steam reforming catalysts [9] as well as its lower price compared to noble metals [10], make Ni the preferred active metal for several aspects of the research field [11].

Many studies have focused on the use of high thermal conductive structured catalysts especially for endothermic reactions [9], since they ensure higher heat transfer rates compared to random catalyst packings: this positive effect is attributable to the shift in the dominant heat transfer process from convection to conduction [12]. Among the structured catalysts, monolithic shapes have a wide application in the clean-up of waste gases [13] because they allow for high filtration efficiencies and high gas–solid interfacial areas at the same time. Over recent years, the SiC monolithic catalyst supports evaluated for a heterogeneously catalyzed methane steam reforming reaction, showed a very flat radial temperature profile [14], 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 problems of the conventional packed beds [15]. Furthermore, such supports minimize pressure drops along catalytic bed [1].

Structured monoliths exist in two different configurations: flow-through (FT) and wall-flow (WF) [9]. In the FT configuration, the channels are open on both sides, while in the WF, the parallel channels are alternatively plugged at each end to force the exhaust gas flow through the porous walls [13].

Recent studies [16] have showed that under steady state conditions the wall-flow configuration may allow for a higher conversion when compared to a flow-through monolith with the same characteristics.

Starting from these premises, the present study compares the reaction performances of catalyzed SiC wall-flow and flow-through monoliths in the methane steam reforming process, under different operating conditions.

2. Material and methods

2.1. Catalyst preparation

Silicon Carbide (SiC) monoliths (Pirelli Ecotechnology, 150 cpsi), were selected as a support for the preparation of the structured catalysts. In order to be adapted to our cylindrical reactor, the monoliths were suitably shaped to achieve the geometrical characteristics shown in Table 1. The choice of a SiC based support was determined by the thermal conductivity values (about

Table 1
Monolith properties.

Channel length (mm)	120
Channel width (mm)	1.5
Wall width (mm)	0.625
Number of channels	37
Median pore diameter (μm)	17.40
Cell for square inch (cpsi)	150

$350 \text{ W m}^{-1} \text{ K}^{-1}$ at 25°C) that are significantly higher than those typically reported for widely applied supports materials like alumina (about $30 \text{ W m}^{-1} \text{ K}^{-1}$ at 25°C) or cordierite (about $3 \text{ W m}^{-1} \text{ K}^{-1}$ at 25°C).

The monoliths were first stabilized in a furnace operating in air by calcination at 1000°C for 6 h, with a temperature programmed ramp of $20^\circ\text{C min}^{-1}$. The formation of a silica (SiO_2) layer on the SiC granules was favored through this thermal pretreatment, with it having the function to create anchor points for the optimal deposition of the active species later added.

The SiC monoliths were activated by direct nickel deposition without washcoat deposition, achieved through a wet impregnation method. This technique consists of repeated impregnations phases in 1 M nickel acetate solution ($\text{C}_4\text{H}_6\text{O}_4\text{Ni}-4\text{H}_2\text{O}$), drying (120°C , 30 min) and calcination ($20^\circ\text{C min}^{-1}$ up to 600°C , 2 h), in order to obtain a 30 wt.% of the active species. This procedure allows to realize a uniform and homogeneous distribution of the nickel oxide on the monolith walls as well as inside the porosity.

2.2. Catalyst characterization

The prepared monolithic catalysts were characterized by BET analysis, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDAX), Temperature Programmed Reduction (TPR).

The surface area of the catalyst was measured by N_2 adsorption–desorption isotherms at 77 K (BET analysis) using a Sorptometer 1040 Kelvin apparatus by Costech International. Before taking the measurements, the samples were degassed in a vacuum at 150°C for 1 h.

The crystal phase of the nickel catalyst was identified by XRD with $\text{Cu K}\alpha$ radiation at 40 kV and 20 mA. The measurements were carried out using a D8 Bruker micro-diffractometer in the 2θ range of $20\text{--}80^\circ$ in steps of $0.02^\circ \text{ s}^{-1}$. A SEM analysis was performed using a Scanning Electron Microscope (SEM mod. LEO 420 V2.04, ASSING), and Energy Dispersive X-ray Spectroscopy (EDX), performed in an Energy Dispersive X-ray analyzer (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK).

The H_2 -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 Nc min^{-1} composed by 5% H_2/He . The TPR analysis was carried out in the reaction system described below.

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 Fig. 1, can be divided into 3 zones: feed, reaction and analysis.

The different parts of the lab-scale plant are connected using Teflon piping with an outside diameter of $1/8''$. The fastening of the pipes is achieved from stainless steel joints of the *Swagelok* type, to avoid the adsorption of the components on the walls.

The feed section consists of 6 mass flow controllers (MFC), which regulate the flow rates of gases used in the calibration and reaction phases of the system. They allow to feed methane,

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