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Innovative structured catalytic systems for methane steam reforming intensification

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ABSTRACT

The use of structured catalysts based on highly conductive carriers may allow a flattened radial temperature gradient along the catalytic bed due to a better heat transfer, so obtaining 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, prepared starting by Silicon Carbide (SiC) monoliths, in the "wall flow" (WF) and "flow through" (FT) geometric configurations, demonstrates the direct correlation between the thermal conductivity of the carrier, the methane conversion and the hydrogen productivity. In particular the tests showed that the SiC "wall flow" (WF) monoliths guaranteed a better axial and radial thermal distribution, with respect to the SiC "flow through" (FT) ones, resulting in better catalytic activity up to a temperature reaction of 750 °C. Furthermore, 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, so increasing the overall process efficiency.

1. Introduction

Hydrogen is nowadays considered the most promising energy vector, thanks to its high capacity of storing energy from primary sources [1]. Despite considerable efforts to identify new green technologies and sources for hydrogen production, the use of fossil sources and the traditional production methods, are still widely affordable [2]. Among the production processes of hydrogen, the Steam Reforming of natural gas is still the less expensive and the most widespread industrial process, suitable for economies of scale and widely involved in the ammonia and methanol production processes. The Steam Reforming (SR) is a highly endothermic equilibrium reaction [3], the standard enthalpy reaction for methane is about 206 kJ/mol however, for more complex hydrocarbons, it can reach much high values, for example for n-C_7H_{16}, the ΔH°_{298} is about 1108 kJ/mol [4]. The Methane Steam Reforming (MSR) is normally described as the result of two main reactions, the reforming (Eq. (1)) and the water gas shift (WGS) reactions (Eq. (2)),

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \ \Delta H^\circ_{298} = 206\ \text{kJ/mol} \qquad (1)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \ \Delta H^\circ_{298} = -\ 41\ \text{kJ/mol} \qquad (2)$$

The thermodynamic of the system, coupled with the actually used catalysts, allow to reach acceptable conversions only for reaction temperature exceeding the 700–750 °C [5]; to realize this hard conditions, over the catalytic bed, it required a large amount of heat, so the process temperatures must be forced above 1000 °C. The most widespread process configuration provides two stage, in the first stage methane and steam react at 700–800 °C, thus obtaining a conversion of the hydrocarbons up to 90%, in the second stage an amount of air is added to react with a part of the hydrogen, generating the necessary heat to reach a temperature of the reaction mixture of 1000–1200 °C, allowing an almost complete conversion [6]. So high process temperatures however present several problems, especially related to the resistance and durability of the materials, but also to the overall process efficiency in terms of produced hydrogen per supplied energy. On the basis of the above consideration it seems clear that the main problem of this kind of process, is related to the transfer of heat to the catalytic bed. The typical radial thermal profile of a catalytic bed, packed with pellets provides a considerable thermal gradient between the side wall and the center of the bed, part of the heat supplied, necessarily dissipates, with a decreasing from 1200 °C, at the outside, to 700 °C at the center of the catalytic bed (Fig. 1), making it necessary a huge expenditure of energy [7–10].

Much efforts were made in the direction of the preparation of new and more active catalytic formulations at low temperatures [11], or in the use of new technologies, such as non-thermal plasma [12]. However a process intensification [14] [13] seems to be a much more promising

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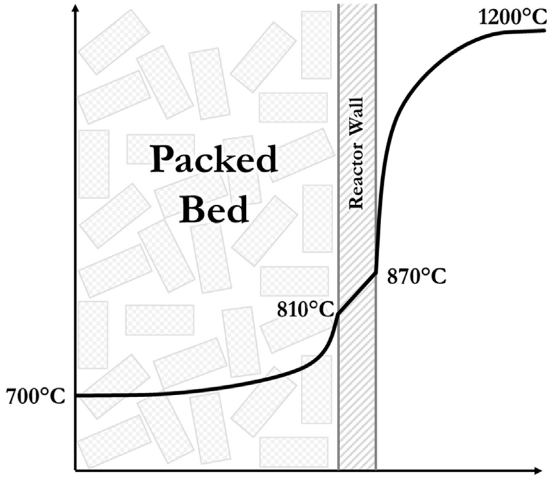

Fig. 1. Schematic representation of the temperature profile in a reactor for steam reforming.

way, which involves also the design of new catalytic configurations. Structured catalysts, based on highly conductive carriers, due to the capability of flatten the thermal profile over the catalyst, are able to reduce the difference of temperature between the side wall of the reactor and the center of the bed and, therefore, a lower temperature of the furnace is required, for a given heat flux [15]. Among the most promising materials in the field of structured carriers, the silicon carbide (SiC) or carborundum, plays a major role; SiC is mainly a synthetic material, it exists in nature as extremely rare mineral called moissanite, it is a polymorph material but the most common crystalline structures are the α and the β forms. Silicon carbide, due to its characteristics, is used for various applications, as semiconductor for electrical applications, as abrasive for its hardness, as filter in clean-up of waste gases [16,17], as fuel in the steel production, and many other special applications [18]. Recently SiC has found wide applications also in the field of the heterogeneous catalysis [19], as highly conductive support, in the methane steam reforming process intensification [20]. The novelty in the use of these structures is that they allow to realize an excellent heat transfer, in a manner not achievable with the conventional beds; the high thermal conductivity of SiC allows, in fact, to overcome the heat transfer limitations, with a consequent improvement of the performance of the catalysts in the endothermic processes, such as steam reforming [21]. The SiC honeycomb monoliths can be realized in two configurations, flow-through and wall-flow, the former have the channels open on both sides, the latter are characterized by alternatively closed channels and porous side walls, as showed in Fig. 2.

The wall-flow configuration is of particular interest in the field of catalysis, because it forces the reagents to flow through the walls, making available also the part of the catalyst embedded in the walls themselves. The common SiC monoliths are characterized by low surface area (S.S.A) therefore, the most widespread strategy to increase it, provides the impregnation by dip-coating procedure of the monolith with a high surface area washcoat slurry [22]. The washcoat composition depends on the requirements of the final catalysts, however the most common formulations are based on high surface area aluminas, a coating polymer and the desired support. The preparation procedure provides the dispersion of the support in a colloidal solution, obtained by dissolving pseudoboehmite in acidic solution, a vigorous stirring generates the homogeneous suspension, the sample is then dried and calcined. The washcoated monoliths are subsequently impregnated with the active metal, dried and calcined to obtain the desired catalyst. Among the supports of most interest, for sure, the ceria is one of the most interesting, especially for what regards the excellent oxygen store capacity [23], accepting oxygen in oxidizing and transferring under reducing conditions, and the promoter capacity against of several metals. Concerning the active components, many works were recently reported on the use of noble metals [23] and Cobalt [24,25], for the steam reforming process, however the less expensive Nickel-based catalysts are still widely spread [26]. Unfortunately the Ni-based catalysts suffer of deactivation due to coke formation [27] and metal sintering [28], however, recently interesting results were reported on the use of ceria as promoter of the oxidative removal of carbonaceous species [29]. On the basis of these reported results, the Ni/CeO_2-Al_2O_3/SiC catalytic system seems to be highly promising for methane steam reforming applications. In this work we report the preparation of structured catalysts, obtained by washcoating SiC monolith with a ceria/pseudobohemite slurry (95% wtCeO_2/5% wtpseudobohemite) and subsequent impregnation with nickel salts, in order to reach a 5% wt load of nickel with respect to washcoat; these catalysts, identified as 5NiWSiC/FT and 5NiWSiC/WF depending on the flow configuration, were fully characterized and tested, and the results compared to the performance of commercial catalysts (Katalco$_{JM}$ Quadralobe) for methane steam reforming.

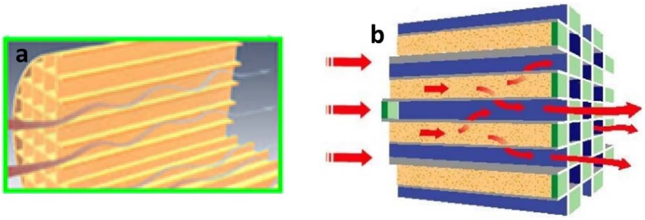

Fig. 2. schematic representation of Flow Through (a) and Wall Flow configuration (b).

2. Materials and methods

2.1. Carriers preparation

SiC "flow-through" carriers were obtained by cutting a quasi-circular cross section from a commercial honeycomb monolith provided by Pirelli Ecotechnologies. The monoliths were properly shaped (diameter = 16 mm; length = 31 mm; total volume = 6.4 cm^3) to be located in the reactor, and were entrapped in a thermo-expandable ceramic mat (3 M) in order to avoid bypass phenomena. In Table 1 the geometric characteristics of the monoliths are summarized.

The "wall-flow" carriers were obtained from the corresponding "flow-through", alternately plugging the inlet and outlet sections of each channel with a high temperature resistant ceramic glue, so forcing the gas to pass through the porous walls of the inner channels. The prepared carriers were calcined at 850 °C for 3 h, so allowing the coating of the SiC particles with SiO_2 streaks, which can greatly help the washcoat adherence to the filter [30].

2.2. Catalysts preparation

The washcoat slurry was prepared by dispersing, under vigorous stirring, 19 wt% of ceria powder (Opaline®; Actalys HAS; Rhodia) in a colloidal solution obtained by dissolving 1 wt% of psudobohemite (Pural SB; Sasol) and 1 wt% of methyl cellulose (Viscosity 4000 cP;

Table 1
Geometric characteristics of the employed monoliths.

	SiC
Wall thickness [mm]	0.55
Side channel [mm]	1.65
Length [mm]	31.00
Weight [g]	5.7
Diameter [mm]	16.00
Channels [number]	37