



Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Innovative catalyst design for methane steam reforming intensification

Antonio Ricca*, Vincenzo Palma, Marco Martino, Eugenio Meloni

University of Salerno, Department of Industrial Engineering, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

ARTICLE INFO

Article history:

Received 15 May 2016

Received in revised form 27 October 2016

Accepted 1 November 2016

Available online xxxxx

Keywords:

Methane reforming
Process intensification
Structured catalyst
Hydrogen production

ABSTRACT

The employment of structured catalysts characterized by highly conductive carriers can result in improving the heat transfer along the catalytic bed, affording high performance with a flattened radial temperature gradient. This study focused on the Steam Reforming (SR) process intensification obtained by depositing the catalyst on a Silicon Carbide (SiC) monolith (porous walls, honeycomb shape), characterized by excellent thermal conductivity and mechanical resistance.

Experimental tests carried out on SiC catalytic honeycomb monolith demonstrated that the physical properties of the support resulted in a marked system performances enhancement. One of the most relevant limitation in SR processes is the difficulty in providing heat to the catalytic system in the operating high temperatures. The high thermal conductivity of the SiC allows to minimize heat transfer resistance from the heating medium to the catalytic volume and optimize the thermal management along the catalyst, so increasing the heat flux toward the reaction volume and in turn maximizing the reforming reactions rate. A further investigation evidenced that the SiC “wall flow” guarantees a better axial and radial thermal distribution, with respect to the SiC “flow through”, 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.

Therefore, the catalyst optimization in chemical and engineering points of view appeared able to enlarge the steam reforming operating window. In particular, the high conductive structured catalyst allowed to obtain appreciable performances for high reactants rate and relatively low temperature, without employing noble metals based formulations.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The growing attention on greenhouse gas pollutants emitted from combustion of fossil fuels and their environmental impacts have hugely increased the ambition towards clean fuels; moreover, political world is paying great attention against production of air pollutants, both in industrial and civil scenarios. Among other possibilities, hydrogen is the best candidate for the cleanest fuels which can replace fossil fuels. Despite hydrogen is the largest element available in the universe, it is not available in molecular form, but it is included in more complex molecules (mainly water and hydrocarbons), therefore processes for hydrogen recovery are needed.

In line to nowadays technologies, H₂ could be achieved by thermal, electrolytic and photolytic processes [1]. The latter two processes emerge for their “green skills”: in these processes, water is

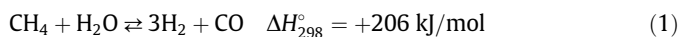
split into hydrogen and oxygen by electrical (in a very attractive route whereas electricity is generated by zero-carbon sources such as wind or solar) and light energies (e.g. solar light). Despite the growing interest of political and industrial worlds, hydrogen production through thermal (thermochemical) processes still remains the most diffused solution: hydrogen is obtained by chemical processes in which heat leads hydrocarbons to release hydrogen. Given the current state of technology, natural gas based H₂ production in large industrial plants is considered to be cheapest method available [2]. Three main technologies were available for hydrogen production by fossil fuels: steam reforming, partial oxidation and autothermal reforming: among them, steam methane reforming is the least expensive and thus the widest diffused, and natural gas steam reforming is currently used on a large scale to produce the main part of the commercial and industrial H₂ used today.

Catalytic steam reforming of natural gas, composed mostly of methane, is the conventional process used to produce hydrogen at industrial scale; the natural gas is mainly composed by methane

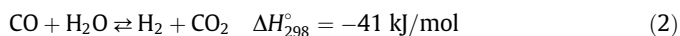
* Corresponding author.

E-mail address: aricca@unisa.it (A. Ricca).

(>80%), that reacts with steam to produce hydrogen and carbon monoxide (Eq. (1)).



The reaction is typically conducted at very high temperature, due to the endothermic nature, by feeding steam in excess with respect to stoichiometry, in order to promote hydrocarbon(s) conversion and to suppress cracking phenomena, that may lead to coke formation and thus catalyst deactivation [3,4]. Moreover, steam also acts as thermal vector in the reaction system, so reducing the requirement to a huge fuel pre-heating. Typically, aside steam reforming, water gas shift (WGS) occurs in the catalytic system (Eq. (2)) in which a part of carbon monoxide reacts with steam to produce further hydrogen.



WGS reaction is usually completed in a separated colder stage, finalized to CO elimination and the maximisation of hydrogen production.

Typical steam reformers were constituted by a series of tubular reactors in which Ni-based catalysts were loaded. Due to the high endothermicity of reforming process, the reaction volume requires a huge amount of heat to be supplied by external heat sources: therefore, catalytic tubes were collected in top-fired reactors [5,6], appearing as tube-shell heat exchangers, in which shell side fuels combustion generates heat to be supplied to catalytic system. The heat transfer from heating medium to reaction system was pointed as one of the most critical step in the steam reformer, indeed it is commonly considered as the limiting step of the process [5]. In particular, heat transfer resistance could be identified both at reactor wall – catalytic bed and catalytic bed – gas phase interfaces. Moreover, the limited heat transfer characteristics of packed beds may result in a relevant temperature gradient, that in one hand causes a bad exploiting of the catalytic volume, in the other hand increases the heat transfer resistance from the heating medium to the reaction volume. As a result, in order to obtain the desired temperature in the catalytic volume, a very high heating medium temperature is required, thus resulting in the need of highly resistant reactor material, that negatively affects the fixed costs of the plant. On the other hand, a non-optimal heat flux towards reaction volume results in the need of higher superficial contact time (0.5–1.5 s [7]) of reactants in catalytic unit to reach the desired conversion target. To achieve the target of a more sustainable hydrogen production, a breakthrough in process intensification (both in terms of thermal management and reactions rate) is required [8]. Process optimization can be conducted though the optimization of catalytic formulation, but the core of process intensification is pointed on the catalytic reaction engineering: in this aim, great attention must be devoted to the catalyst structure (e.g. powder, pellets, honeycomb, foams, etc.).

In reforming processes, the choice and optimal setup of the catalytic system may greatly affect both the conversion degree as well as the selectivity of the reaction. 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 [9–11] as well as noble metals (Pt, Rh, Ru) [12] supported on Al_2O_3 or rare earth oxides (CeO_2 , ZrO_2 , La_2O_3 , Y_2O_3) show good activity toward reforming reactions [13–17]; improvements in stability and selectivity were achieved from bimetallic catalytic systems [18,19].

Great advantages are expected by exploiting structured carriers for catalyst deposition. Honeycomb monolithic catalysts are characterized by extremely low pressure drop (up to 2 orders of magnitude lower than packed beds), high geometric surface area and good mechanical strength and durability [20]. It is widely accepted that thermal management along the catalytic volume is a crucial

aspect of the catalysis of steam reforming process. Vakhshouri and Hashemi [21] demonstrated that in a typical configuration the process gas in a steam reformer records relevant radial and axial gradients along the whole catalytic bed, of course more pronounced in the inner part of the reformer. Such thermal profiles cause a bad exploiting of catalyst, that in turn leads to an increase of the overall catalytic volume. Several studies have demonstrated that high thermal conductivity carriers may facilitate a flatter thermal profile along the catalytic bed [22], both in axial and radial direction, thus resulting in a higher average temperature at the outlet of the reactor, and in turn in a larger reactants conversion [23]. Moreover, the achieved flatter thermal profile assures a better heat transfer towards catalytic volume and a reduction of hot-spot phenomena risks [24]. The heat transfer flux improvement ascribed to highly conductive supports was confirmed by Roh et al. [25], by comparing performances of traditional pellets and metallic monolithic catalysts characterized by the same catalytic formulation. It was demonstrated that monolithic carriers allowed an increase of the Nusselt number, resulting in a higher solid–gas heat transfer coefficient, that in turn allowed faster reactions rate, more relevant in severe operating condition, such as high temperature [26]. On the other hand, Chan and Lee [27] demonstrated that the more uniform thermal profile (both in axial and radial direction) helps catalytic system to address reaction pathways towards desired products. The improvements linked to structured catalyst was evidenced by Palma et al. [28] in steam reforming of ethanol: by transferring a catalytic formulation on SiC foams, total ethanol conversion and very high hydrogen yield can be achieved at very short contact times, without effects on catalyst stability. Moreover, it was also demonstrated that the employing of a high conductive foam carrier helps to reduce of 33% the heating medium temperature.

Aside the benefits linked to thermal conductivity of structured carrier, the active species distribution on catalytic surface is a key parameter for the overall system performances. It was demonstrated [29] that the coverage of carrier with promoters (Al_2O_3 , ZrO_2 , CeO_2 , etc.) assured enhanced performances in terms of activity, stability and resistance to coke formation. In this sense, the proper coating of carrier, as well as its resistance to thermal and mechanical stresses occurring during the process operation, becomes crucial to the catalytic system effectiveness. The inappropriate coating procedure, or the non-optimal compatibility between structured carrier and catalytic washcoat may cause a not negligible shrinkage of active coating, and subsequently a stripping off from substrate, that in turn may be subjected to a weak degradation.

In the direction of process intensification, a novel route could be addressed on miniaturizing the characteristic flow paths into well-defined structured geometries, exploiting the possibility of operating in narrow control limits and of increasing the throughput by numbering up the flow paths which eliminate complexities associated with traditional scaling-up efforts. In particular, it was demonstrated that wall flow (WF) monoliths (porous-walls monoliths with channels plugged alternately in the entry and exit section, that forces the gas to penetrate walls micro-channels [30]) may assure a higher reactants conversion when compared to a traditional flow-through (FT) monolith with the same characteristics [31].

This work focused on the effects of substrate in catalytic performances of a Nickel based formulation in the reaction of steam reforming of methane. The study evolved through the preparation of several structured catalysts, with the same formulation, on different carriers; the role of structured substrate was further evidenced by comparing performances of a commercial pellet catalyst.

Download English Version:

<https://daneshyari.com/en/article/4768694>

Download Persian Version:

<https://daneshyari.com/article/4768694>

[Daneshyari.com](https://daneshyari.com)