Stable hydrogen production by methane steam reforming in a two zone fluidized bed reactor: Experimental assessment

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HIGHLIGHTS

- Two zone fluidized bed reactor (TZFBR) is proposed for H$_2$ production by steam reforming of methane.
- A higher global yield to hydrogen has been observed in the TZFBR than conventional reactors.
- Working with the TZFBR there was no net coke formation.
- Better values of methane conversion were obtained, due to a better regeneration of the catalyst.

GRAPHICAL ABSTRACT
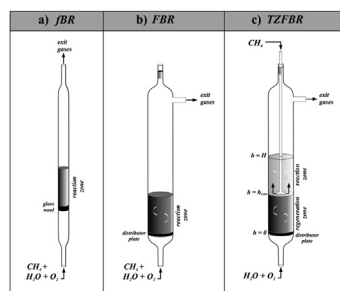
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ABSTRACT

The *Two Zone Fluidized Bed Reactor* concept is proposed for hydrogen production via the steam reforming of methane (SRM) including integrated catalyst regeneration. In order to study the effect of the contact mode, the oxidative SRM has been carried out over a Ni/Al$_2$O$_3$ catalyst using a fixed bed reactor (fBR), a conventional fluidized-bed reactor (FBR) and the proposed two-zone fluidized bed reactor (TZFBR). The technical feasibility of these reactors has been studied experimentally, investigating their performance (CH$_4$ conversion, CO and H$_2$ selectivity, and H$_2$ global yield) and stability under different operating conditions.

Coke generation in the process has been verified by several techniques. A stable performance was obtained in the TZFBR, where coke formation was counteracted with continuous catalyst regeneration. The viability of the TZFBR for carrying out this process with a valuable global yield to hydrogen is demonstrated.

1. Introduction

Natural gas reforming is the main source of hydrogen. The annual production of hydrogen is estimated at 400 billion m^3, North America being the most important producer (230 billion m^3) [1]. About 60% comes from natural gas reforming while the major part of the remaining 40% is produced from petroleum refining or naphtha reforming.
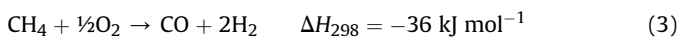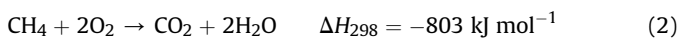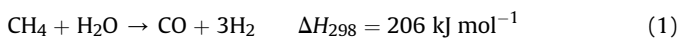
Steam methane reforming is an established technology for obtaining hydrogen for fuel cells and for the production of synthesis gas that can be used for the Fischer–Tropsch process to obtain methanol and dimethyl ether, using nickel supported catalysts [2]. However, there are two main problems in the steam reforming of methane: a) the reaction is endothermic and requires an external heating source; b) the nickel based catalysts require the use of high steam/methane ratios (3–3.5) in order to avoid coke formation that causes the deactivation of the catalyst [3].

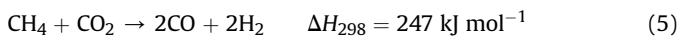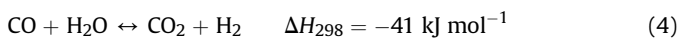* Corresponding author. Tel.: +34 976762393; fax: +34 976762142.
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Two alternatives have been studied in order to overcome these problems. The first is the reduction of the steam/methane ratio, which reduces the endothermic character of the reaction but which does not reduce the coke deposition. The second is the partial introduction of oxygen so that exothermic reactions take place (such as combustion or partial oxidation). The latter process, known as oxidative steam methane reforming (OSRM), is more efficient than conventional steam methane reforming. However, it also has some drawbacks such as 1) the formation of hot spots in the initial part of the bed [4], 2) the low activity of the nickel based catalysts due to the oxidation of the nickel metallic species, 3) selectivity loss and 4) coke formation in the final part of the bed due to the lack of oxygen [5].

In oxidative steam methane reforming, oxygen must be supplied to the reactor with the steam so that the steam methane reforming (endothermic, Eq. (1)) is combined with two exothermic reactions: methane combustion (Eq. (2)) and the partial oxidation of methane (Eq. (3)). In this way, the global process is autothermic.
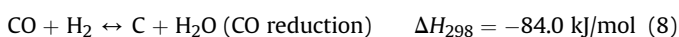
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_{298} = 206 \text{ kJ mol}^{-1} \qquad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -803 \text{ kJ mol}^{-1} \qquad (2)$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298} = -36 \text{ kJ mol}^{-1} \qquad (3)$$

Other reactions that can also occur in the process are the water gas shift reaction (WGS) (Eq. (4)) and dry reforming (Eq. (5)):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \qquad (4)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 247 \text{ kJ mol}^{-1} \qquad (5)$$

1.1. Coke formation

The high temperatures associated with steam reforming for hydrogen production also favour coke formation. The deactivation of nickel catalysts by carbon deposition is a significant problem in methane reforming caused by fouling of the Ni surface, blockage of the pores of the catalytic particles and disintegration of the support material [6]. Any measure resulting in the reduction of coke formation presents a significant economic advantage for the process. For this reason, the formation and elimination of coke remains an interesting topic.

Thermodynamically, the most feasible reactions for carbon formation are the following:

$$CH_4 \leftrightarrow C + 2H_2 \text{ (CH}_4 \text{ cracking)} \qquad \Delta H_{298} = 122.3 \text{ kJ mol}^{-1} \qquad (6)$$

$$2CO \leftrightarrow C + CO_2 \text{ (Boudouard)} \qquad \Delta H_{298} = -125.2 \text{ kJ mol}^{-1} \qquad (7)$$

$$CO + H_2 \leftrightarrow C + H_2O \text{ (CO reduction)} \qquad \Delta H_{298} = -84.0 \text{ kJ/mol} \qquad (8)$$

The yield for each reaction mainly depends on the temperature of the process. Coke formation from reactions (7) and (8) is less favoured when the temperature increases. However, coke formation through reaction (6) rises considerably at higher temperatures.

Minimisation of coking is one of the major factors governing the industrial application of steam reforming [7]. The thermodynamics of the process mean that reaction conditions that favour coke formation cannot be avoided, but operating conditions can be chosen to minimise coke. An example is increasing the steam/methane ratio in order to favour the gasification of carbon with steam (i.e. the reverse reaction of CO reduction).

Coke may be deposited on the nickel catalyst in various forms, all of which have unique characteristics and differences in reactivity [8]. This carbon formation, specifically under steam reforming conditions, may occur through three routes that result in different kinds of coke. At temperatures lower than 500 °C, adsorbed hydrocarbons may accumulate on the nickel surface and slowly polymerize into an encapsulating film, blocking and deactivating the nickel surface. At temperatures above 600 °C, pyrolytic coke formed by the thermal cracking of hydrocarbons may encapsulate and deactivate the catalyst particles. At temperatures higher than 450 °C, whisker carbon is the main product of carbon formation via a mechanism involving the diffusion of carbon through nickel crystals, nucleation, and whisker growth with a nickel crystal on the top. The whisker type carbon does not deactivate the nickel surface but can cause a breakdown of the catalyst by pore plugging.

1.2. Catalysts

For the oxidative steam methane reforming reaction, Ni-supported catalysts have mainly been used. In fact, the development of Ni catalysts for this process has been extensively studied [9–13]. Ni catalysts are cheaper and more readily available than noble metal based catalysts such as Pt and Rh. However, Ni-catalysts are easily deactivated in oxidative methane reforming due to the oxidation of the metallic species of Ni. Another problem with this process is the formation of hot spots. It has been reported that Rh and Pd based catalysts are effective for eliminating this hot spot formation [14–16], while Ni based catalysts tend to form these hot spots in the bed of the catalyst [13–15,17]. Nevertheless, noble metals such as Pt, Pd and Rh are not suitable components due to their limited availability and their high price. For this reason Ni-based catalysts have been more intensely studied in recent years by several authors [18–25]. In these works, Ni-based catalysts were doped with low quantities of noble metals. The intention was to achieve a high degree of resistance to the formation of hot spots by means of combining the high activity of nickel with the high reducibility of the noble metals.

1.3. Reactors

The use of the two-zone fluidized bed reactor (TZFBR) [26] could serve to prevent the aforementioned problems of oxidative steam methane reforming from occurring. With this reactor configuration, activity losses are not expected because regeneration takes place simultaneously with the reaction in the same vessel. The circulation of the solid particles in the fluidized bed would mean that its behaviour was that of an isothermal bed, avoiding the formation of hot spots. At the same time, the heat production in the regeneration step (i.e. coke combustion) would compensate for the endothermicity of the steam reforming. Moreover, it would be possible to reduce the steam/methane ratio (S/M) because the coke deposition problem associated with low S/M values is counteracted by its simultaneous regeneration.

This type of reactor consists of a fluidized bed where the oxygen–steam mixture is fed through the lower part of the reactor, while the methane is introduced at an intermediate point of the bed height. In this way, two zones are created in the reactor: in the lower part the greater part of the oxygen is consumed reacting with the reduced catalyst (regeneration zone), while in the upper part the desired chemical reaction takes place (reaction zone). The circulation of the solid between both zones enables a steady state to be achieved. This reactor allows the continuous regeneration of the catalyst, avoiding the transfer of large amounts of solid between reactors because a single vessel is used. There are two critical issues regarding the operation of a TZFBR. On the one hand, the gas phase oxygen must be consumed in the lower part of the reactor