Hydrogen production from methane through catalytic partial oxidation reactions

S. Freni [a,*], G. Calogero [a], S. Cavallaro [b]

[a] *Istituto CNR-TAE, S.ta S. Lucia, 5-98125 Messina, Italy*
[b] *Dip. Chimica Ind. ed Ingegneria Mat. dell'Università, PO Box 29-98166 Sant'Agata di Messina, Italy*

Abstract

This paper reviews recent developments in syn-gas production processes used for partial methane oxidation with and/or without steam. In particular, we examined different process charts (fixed bed, fluidised bed, membrane, etc.), kinds of catalysts (powders, foams, monoliths, etc.) and catalytically active phases (Ni, Pt, Rh, etc.). The explanation of the various suggested technical solutions accounted for the reaction mechanism that may selectively lead to calibrated mixtures of CO and H_2 or to the unwanted formation of products of total oxidation (CO_2 and H_2O) and pyrolysis (coke). Moreover, the new classes of catalysts allow the use of small reactors to treat large amounts of methane (monoliths) or separate hydrogen in situ from the other reaction products (membrane). This leads to higher conversions and selectivity than could have been expected thermodynamically. Although catalysts based on Rh are extremely expensive, they can be used to minimise H_2O formation by maximising H_2 yield. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

During the last world war, Fischer and Tropsch developed an innovative process on the use of syn-gas for chemical production that could be of strategic importance and spur the synthesis of several chemicals with high industrial and commercial values [1]. Today, the growing demand of chemicals derived from syn-gas synthesis has led to the development of many processes. These processes can be formed by single step H_2/CO synthesis, like low-T or high-T Fischer–Tropsch processes, ammonia synthesis or oxygenate production, or by multistep H_2/CO synthesis. The most common source of syn-gas is now hydrocarbons and particularly natural gas [2]. It can be easily extracted from an estimated recoverable world reserve of 8×10^{15} ft^3 [3]. The commonest technology for the production of syn-gas is from natural gases based on catalytic methane reaction with steam (SRM) to produce a mixture of hydrogen, carbon monoxide and carbon dioxide, although ongoing research has proposed some alternative processes [4]. The most attractive appear to be catalytic partial oxidation (POM) and autothermal reforming (ATR). POM consists of the substoichiometric oxidation of methane, while the ATR integrates POM with SRM. Furthermore, the main features of ATR are:

(i) Low energy requirement, due to the opposite contribution of the exothermic methane oxidation and endothermic steam reforming;
(ii) Low specific consumption;
(iii) High gas space velocity (at least one order of magnitude relative to traditional SRM);
(iv) Preset H_2/CO ratio easily regulated by inlet CH_4/O_2/H_2O ratios and CO_2 recycling.

Besides the theoretical aspects involved in the development of the ATR process, a suitable and active catalyst needs to be available for commercialisation. We prioritised the development of different classes of catalysts, their preparation, evaluation and characterisation. We also endeavoured to improve reaction selectivity [5]. In this paper,

* Corresponding author. Tel.: +39-090-6241; fax: +39-090-624247; e-mail: freni@itae.me.cnr.it
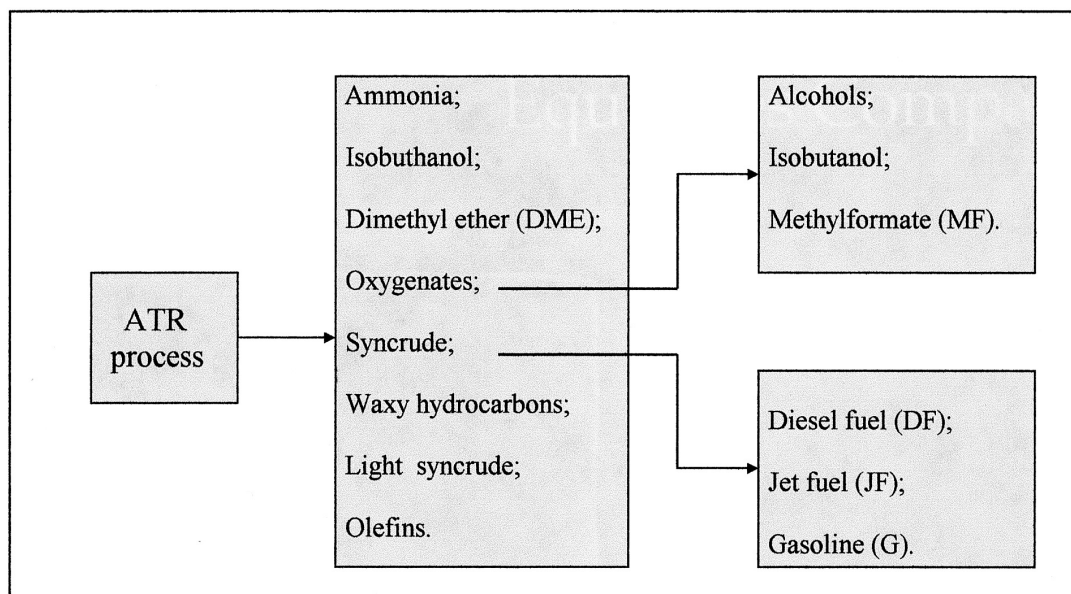
Fig. 1. One step H/C synthesis products.

we report a state-of-art analysis of catalyst improvements as well as of the critical aspects in the development of these technologies.

2. Processes and plants

The interest in the development of low cost technologies for the production of syn-gas are supported by several processes [6–8] based on its use as raw material (Figs. 1 and 2).

The ATR process, schematically shown in Fig. 3, foresees three main subsystems. The first is devoted to the treatment and balancing of process gases (desulfurisation and steam production), and to preheat the H_2/CH_4 and O_2/CH_4 mixtures. In a separated subsystem the condensation of steam and CO_2 recycling from exhaust are realised. The heart of the plant remains the subsystem comprising one or more reactors where the autothermal process is carried out.

Haldor-Topsoe [9] designed and set up a reactor for autothermal reforming formed by two different sections.
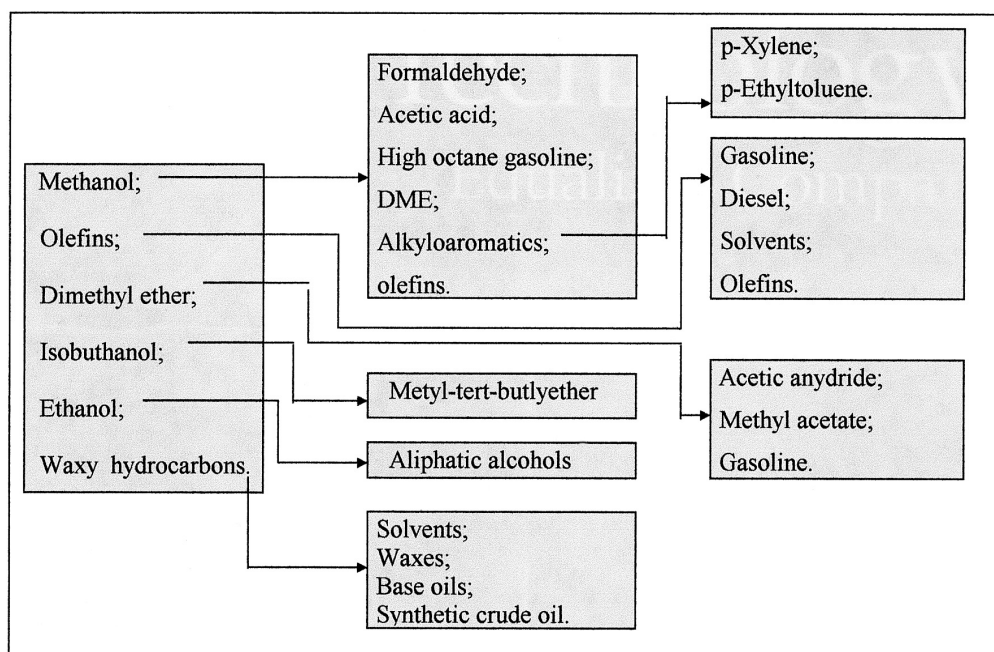
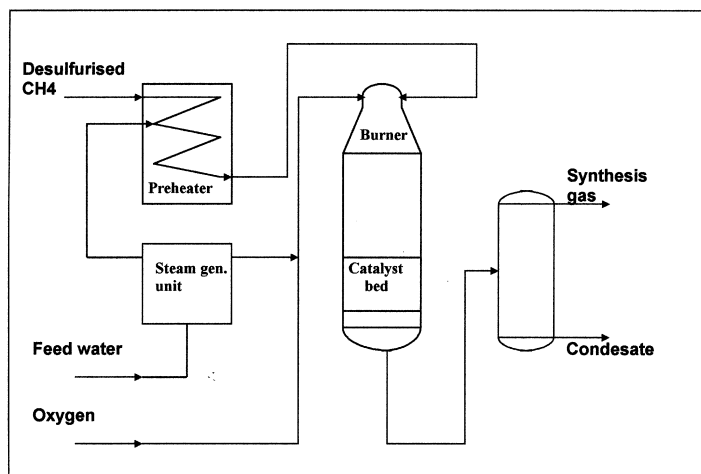Fig. 2. Two steps H/C synthesis products.

Fig. 3. Scheme of the ATR plant.

The upper side of the reactor consists of a burner for the substoichiometric oxidation of supplied methane, while the steam and dry reformings are carried out in the bottom. The appropriate design of this equipment is of fundamental importance to operate in condition of turbulence and to produce heat to supply the reformer section. The operating conditions in the burner foresees pressure up to 12 Atm at $T = 2200$ K. The main requirements for the burner are an elevate mixing degree of the process gases (steam, methane and oxygen), no coke formation, low temperature at refractory walls and outlet gas with constant flow and temperature. Full attention must be addressed to the problem of soot formation when precursors like acetylene and ethylene are produced by the combustion. The selection of high operation pressure and appropriate steam/carbon and hydrogen/carbon values are fundamental to avoid soot formation [10].

The bottom of the reactor is packed with a catalyst active towards the steam/dry reformings and shift reaction. The severe operative conditions require a catalyst with high mechanical properties and the geometry of the reactor will greatly influence the increase of pressure due to the flow of the process gases.

ICI developed [11] a process with two separated reactors. The first reactor is dedicated to prereforming of inlet fuel by steam, while the residual gases will react with oxygen on monolithic catalyst placed in the second reactor. Different geometry has been proposed by other authors [12,83]. Some interesting studies have been carried out on geometry of one step catalytic reactors. These researches pointed mainly to the POM process nevertheless some results can also be extended to the ATR. Tests carried out on fixed bed reactors [13–22] evidenced that most important features are the adiabatic working conditions and the
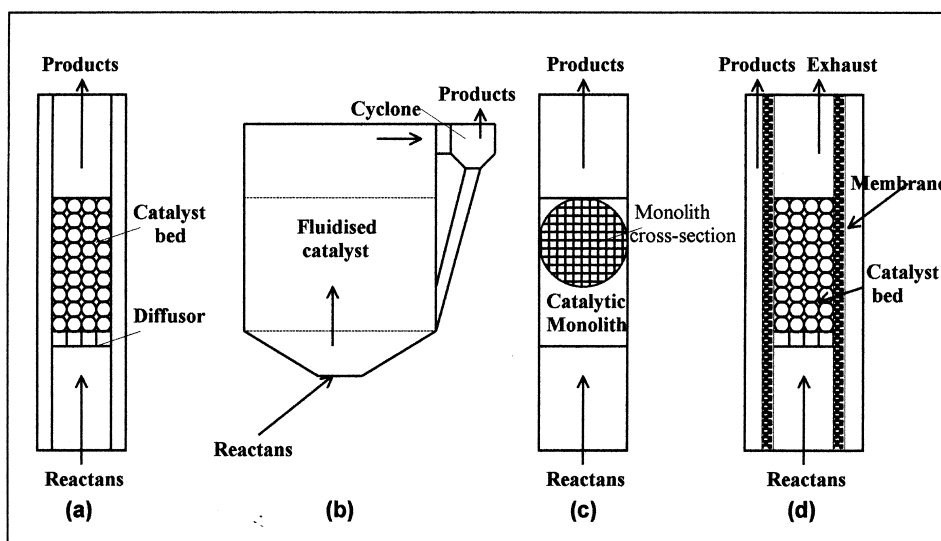
Fig. 4. ATR reactors with different geometry.

reverse flow. Temperature of 1200 K, methane conversion up to 90% at residence time up to 0.1 s have been found. The use of fluidized bed reactors for the examined process have also been investigated [23–25]. This geometry offers the advantage of an optimal temperature distribution, with absence of radial and axial gradients and lower pressure drop with respect to a fixed bed operating at the same dimension and space velocity. Bharadwaj et Al. [25] obtained, with a fluidized bed reactor, operating at $T = 1123$ K, $P = 1$ atm, contact times between 0.1 and 0.3 s, CH_4/O_2 of 2.0 and 20% of steam in the feed gas, a methane conversion $> 99\%$ and CO selectivity of 0.65. Honeycomb reactors [26–28] allow working temperatures of 1313 K and space velocity up to 500.000 h^{-1} without formation of carbon. At last, authors [29] proposed ceramic membrane reactors. In this geometry, the reactor is configured as a conventional fixed bed followed by a ceramic membrane selective to hydrogen. The membrane operates in the Knudsen diffusion regime and influences the thermodynamic equilibrium of the process because the hydrogen is removed immediately when produced.
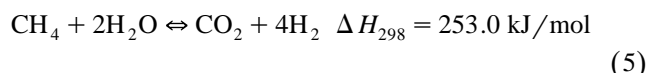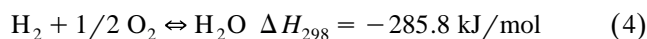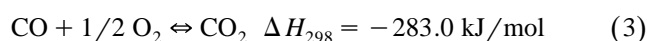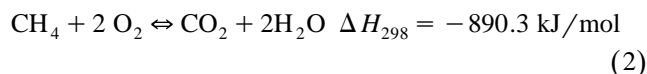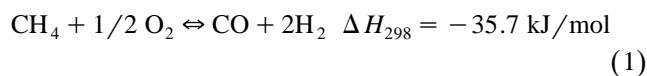
Fig. 4 reports a scheme of these reactors.

3. Reactions

The gases involved in the autothermal process reactions are oxygen, steam and hydrocarbons, such as natural gas or PLG or heavy hydrocarbons. The use of heavy hydrocarbons needs a preliminary prereforming to eliminate C_3-compounds that are precursors to soot formation.

The composition of equilibrated gas is a function of the equilibrium degree reached by each reaction, the catalyst nature, and in general, the operating parameters, such as temperature, pressure and contact time. From the thermodynamic point of view the main reactions are relatively few, nevertheless the kinetic scheme comprises more elementary phases [30]:

$$CH_4 + 1/2\, O_2 \Leftrightarrow CO + 2H_2 \quad \Delta H_{298} = -35.7 \text{ kJ/mol} \tag{1}$$

$$CH_4 + 2\, O_2 \Leftrightarrow CO_2 + 2H_2O \quad \Delta H_{298} = -890.3 \text{ kJ/mol} \tag{2}$$

$$CO + 1/2\, O_2 \Leftrightarrow CO_2 \quad \Delta H_{298} = -283.0 \text{ kJ/mol} \tag{3}$$

$$H_2 + 1/2\, O_2 \Leftrightarrow H_2O \quad \Delta H_{298} = -285.8 \text{ kJ/mol} \tag{4}$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \quad \Delta H_{298} = 253.0 \text{ kJ/mol} \tag{5}$$

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad \Delta H_{298} = 250.1 \text{ kJ/mol} \tag{6}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad \Delta H_{298} = 2.8 \text{ kJ/mol} \tag{7}$$

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2 \quad \Delta H_{298} = 247.3 \text{ kJ/mol} \tag{8}$$

Some parameters such as H_2O/CH_4, O_2/CH_4 and CO_2/CH_4 ratios can be considered the key for thermodynamic evaluation of ATR process. Substantially, variations of these parameters strongly influence thermodynamic equilibrium of the chemical reactions. As an example, in Fig. 5, we report the effect of H_2O/CH_4 and O_2/CH_4 ratios on the outlet gas composition. The relationship between $O_2/H_2O/CH_4$ and H_2/CO selectivity is evident.

Christensen at al. [31] explored how H_2O/CH_4, flow rate and temperature influence the equilibrated gas composition, as well as the limit of the soot-free condition.

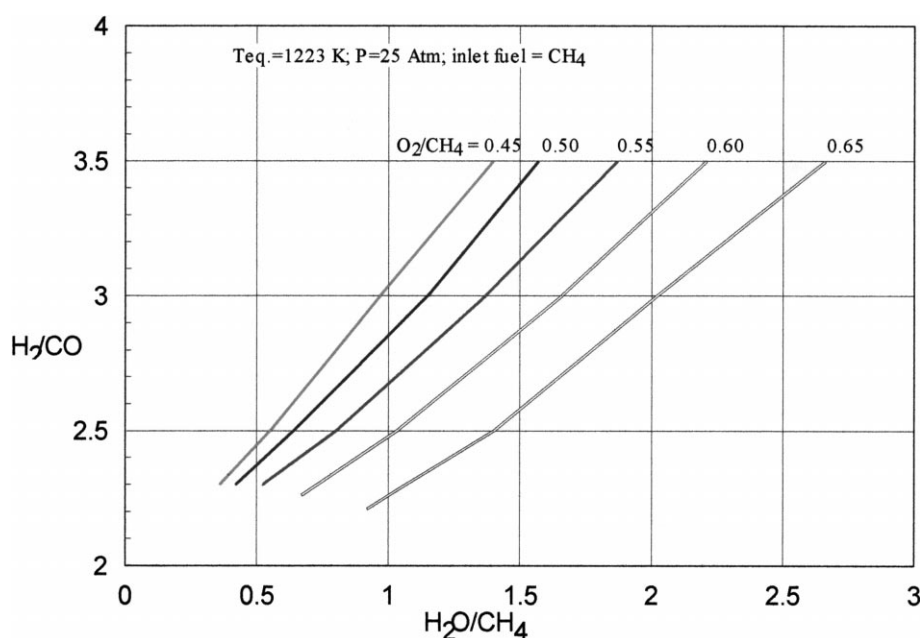Fig. 5. Effect of H_2O/CH_4 and O_2/CH_4 inlet ratios on outlet gas composition.

Theoretical analyses on the combined influence of the inlet H_2O/CH_4 and O_2/CH_4 values on the composition of produced syngas has been evaluated. These studies [32] have shown that an increase of the H_2O/CH_4 ratio enhances the production of hydrogen, when the steam reforming reaction is the prevailing reaction. On the contrary, a larger amount of oxygen makes methane oxidation the prevailing reaction and lowers the hydrogen production. The same authors chose as the quality index the CO/H_2 ratio because it gives a clear indication of which reaction represents the controlling step.

4. Economics

The development of an industrial process depends on several factors. For plant designed for the production of chemicals from CO/H_2, the costs of the syn-gas production plant is of fundamental importance because it represents the most consistent part of the overall investment costs. In plants for the methanol or ammonia syntheses, for instance, it is close to 50% of the total investment costs. A comparative economic evaluation among the different syngas processes has been developed by Peña et al. [33]. The comparison has been carried out by considering the following aspects: (i) consumption of raw fuels; (ii) consumption of energy; (iii) investments; (iv) operative costs. The study has been extended to the following processes: (1) conventional methane steam reforming, SRM; (2) partial oxidation, POX; (3) autothermal reforming, ATR; (4) methane combined reforming, CRM; (5) gas heated reforming, GHR; (6) combined autothermal reforming, CAR; (7) catalytic partial oxidation of methane, POM.

According to the above, their results indicate the ATR plant offers lower costs of about 18% with respect to the traditional SRM [9].

5. Ni-based catalysts

Before 1990 decade, few studies had addressed the development of specific catalysts for the methane oxy-steam reforming processes [34,35]. For this process, several authors proposed catalysts based on Ni supported on Mg-Al$_2$O$_3$ spinels [9], already used for the steam reforming reaction (SRM).

This family of catalysts have been investigated for several years [36], and now are of large use in the industry because they offer an appreciable catalyst activity, a good stability and low price. The catalyst available in commerce are composed of NiO supported on ceramic materials (α-Al$_2$O$_3$, MgO, MgMAlO$_x$ spinel, Zr$_2$O$_3$). The catalyst composition presents an averaged content of NiO equal to 15%, although, this value could reach extreme values of 7% to 79 wt.%. In general, the Ni dispersion and its surface area depend on the amount of metal deposited on the support. Thus, the surface area will increase with the Ni content but the crystallite utilisation will decrease due to a poor dispersion. Furthermore, some authors have prepared [37–39] catalysts with high content of finely dispersed Ni, but which show a tendency to sintering during the work.

The preparation of Ni catalysts requires the addition of small amounts of other compounds that improve the functional characteristics of the final product:

(i) Calcium aluminate (10 wt.% $\leq$ CaO $\leq$ 13 wt.%), that acts as binder improving the mechanical resistance of the catalyst pellets.
(ii) Potassium oxide (up to 7 wt.%), whose effect is to inhibit coke formation. This compound will be unstable without the presence of a stabilising agent.
(iii) Silica (up to 16 wt.%), that reacts with potassium oxide to form stable silicate. Both silica and potassium oxide will be unstable if used alone.

The presence of pressurised steam accelerates the decay of the catalyst structures (sintering and weakening). Thus, supports based on MgO although resistant to the high temperature are unstable if the reaction water is liquid (conditions of high pressure and low temperature) because they form hydroxides with desegregation and break down of pellets.

The supports based on Al$_2$O$_3$ and MgO form spinels with Ni. Moreover, it has been demonstrated [40] that Ni/MgO forms solid solution at high temperature and crystalline compounds at low temperature.

Prettre et al. [41] have been pioneers in the study the POM on Ni (10 wt.%) catalysts, supported on refractory materials at 923 K $< T <$ 1173 K.

A classic catalyst for steam reforming (Ni 25 wt.% on Al$_2$O$_3$) has been tested, in 1991, by Dissanayake et al. [17] on the POM at T $>$ 923 K. Choudhary et al. [18], moreover, have been successfully to obtain, with Ni/Al$_2$O$_3$ catalyst, CO and H$_2$ selectivities higher than expected by the thermodynamic equilibrium by working at extremely low contact times. This trend could be related to the formation of hot spots [19,20] due to an insufficient drain of the heat produced by the reaction in proximity of the catalytic sites. In this case, the yields must be correlated to the effective catalyst sites temperature rather than to the averaged bulk temperature.

The influence of the support on catalyst activity has been evaluated by a comparison of a series of Ni catalysts supported on Al$_2$O$_3$, SiO$_2$–Al$_2$O$_3$, SiO$_2$–ZrO$_2$ and H–Y zeolite. It has been seen that the more acid supports (SiO$_2$–Al$_2$O$_3$ and H–Y zeolite) reduce the catalyst's activity. To explain this behaviour, it is proposed that nickel reduction is very difficult on acidic sites and this results in insufficient formation of metallic active nickel [21]. Anyway the products distribution shows that on these catalysts the oxyreforming process can be represented by a combination of combustion, steam reforming and water gas shift reactions that, simultaneously, occur in the catalyst bed.

However, this reaction mechanism, typically is favoured by high temperature ($T > 973$ K), while on a low temperature reduced catalyst (CoO/MgO) the reaction mechanism, first, involves formation of methoxide species (OCH$_3$) followed by its decomposition into carbon monoxide and/or oxidation to carbon dioxide an water [42].

For a series of unreduced Ni–rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb) oxide catalysts their activity in the temperature range 573–1073 K and their reaction start temperature T_s has been evaluated [43,44]. For these catalysts, T_s is between 808 and 833 K, which is much lower than that observed for the unreduced Ni–Al$_2$O$_3$ catalysts. It is interesting to note that the reaction at temperatures below T_s occurs only after carrying out the reaction on the catalysts at higher temperatures; moreover, the catalytic activity and selectivity at higher temperatures are not changed significantly when the temperature increases or decreases.

All the rare-earth based catalysts show small difference in their activity/selectivity and productivity, but a wide difference in carbon deposition rate has been found. Among rare-earth catalyst NiO–La$_2$O$_3$ is the best. It is, however, interesting to note that there is no significant effect of the heavy carbon deposition on the catalyst's activity, while the main problem is the drastic increase of the pressure drop along the catalyst bed. On these catalysts the carbon deposition is most probably due to the Boudouard reaction and the heterogeneous water–gas reaction [36]. However, at high temperature, methane decomposition is the main route to carbon formation in the catalysed process [45–47].

Almost all Ni-based catalysts suffer deactivation due to coke formation [16,45]. The resistance of the catalysts to coke formation can be enhanced by the addition of alkaline metal oxides to the catalyst formulation (CaO or MgO) [36]. Recently, Choudhary et al. [34], proposed the use of supports based on silico-aluminates pre-coated by alkaline oxides (MgO, CaO) that show lower coke deposition rate with respect to the catalysts without silico-aluminates (Ni/MgO and Ni/CaO) [35].

The class of perovskites comprises the oxides containing transition metals with a structure like that of natural perovskite (CaTiO$_3$). In general, the formula of a perovskite-type oxide is ABO$_3$ where the cation B is octahedral surrounded by oxygens and the site A is located in the cavities originated by the octahedrons. The substitution of A or B leads to the formation of some defects in the lattice. The catalytic activity of the perovskites, well known since 1970 [48], is correlated with the lattice's defects, even if the correlated kinetic mechanism has not been completely clarified [49].

Among various methods for the preparation of Ni based perovskites, it is possible to use aqueous solutions of acetate metals (Ni, Sr, La, etc.), in adequate proportions [50].

Hayakawa [51] investigated the influence of different preparation methods, as (a) citrate method; (b) impregnation method; (c) mixing method, on the catalytic properties of catalysts based on Ni (8.1 wt.%)-perovskite.

The first process starts from an aqueous solution of Ni nitrate + alkaline earth carbonates + Ti-tetrahydropropoxide that is treated and heated with citric acid and ethylene glycol until the formation of the sol. The sol will be decomposed in two steps (5 h at 473 K + 5 h at 773 K) and finally calcinated at 1073 K in air for 10 h.

In the impregnation method, the Ni nitrate, the citric acid and the ethylene glycol are added in an aqueous suspension of perovskite (Ca$_{0.8}$Sr$_{0.2}$TiO$_3$), earlier prepared by the citrate method. Then, the suspension is dried and calcinated in air for 5 h at 1073 K.

In the mixture method, the starting material is a mixture of metals oxides, ground and calcinated at 1073 K for 5 h.

The catalyst Ni(11.5 wt.%)/γ-Al$_2$O$_3$, used for comparison, is prepared by impregnation of commercial γ-Al$_2$O$_3$.

Some authors [52] proposed the use of Ce for improving the resistance of catalysts, based on Ni/Al$_2$O$_3$, to the sintering and to the coke formation. They suggest that Ce reduces the strong interaction between Ni and Al$_2$O$_3$, preventing Ni diffusion in the alumina lactice and the subsequent migration on the surface. Without Ce, the Ni will form crystallites on the catalyst surface that will be passivated by the simultaneous formation of coke.

The perovskites based on Ni and lanthanide [50], furthermore, have the advantages of being alkaline (Ln) and allowing a high dispersion of the Ni in the structure. In particular, Zhang and Verykios [53], carried out, simultaneously, steam and dry reforming reactions on Ni/La$_2$O$_3$ based catalysts, demonstrating that on these catalysts carbon deposition is very low. Chen et al. [54], also confirmed this for POM and dry-reforming (MCR) reactions on catalysts based on four component mixed oxides, containing La and Ni. The reduced tendency to produce carbon seems to be correlated, in this case, to the scarce presence of metallic Ni, at zero valence, on the surface. The Ni can be present on the surface as Ni^0, Ni$^+$ and Ni^{+2}, but, only the form Ni^0 is able to catalyse the homolitic splitting of C–H methane bonds with subsequent formation of coke, while the presence of trivalent metals (La^{+3} and Cr^{+3}) enhance the mobility of the O$^=$ into the lactice and the stabilisation of the Ni with valence + or 2 + [54].

6. Catalysts containing noble metals

The catalysts based on the use of noble metals seems to be more active for the POM and ATR reactions that based on Ni, as proposed by Ashcroft et al. [16] and Vernon et al. [22], but they are 100–150 times more expensive. Among different noble metals, Rh [55] has been widely investigated, and, also, Ru [56] and Ir [57] can be considered valid alternatives.

Kikuchi et al. [58] studied the methane steam reforming reaction and they have demonstrated that the reactivity of

different supported metals (5 wt.%) on SiO_2, follows this relative order: $Ru = Rh > Ni > Ir > Pd = Pt \gg Co = Fe$. Furthermore, the Ru and Rh appears to be the most stable between them.

Ru is the less expensive between the noble metal, and it is more stable than Ni because it does not form carbonyls with high vapour pressure at working conditions. Ru, more expensive than Ni, is extensively studied because of its catalytic properties. In fact, if supported on Al_2O_3 at very low concentration (0.015 wt.%) Ru is more active and selective than Ni [59]. If supported on SiO_2 [56], Ru is able to oxide the CH_4 at low temperature ($T = 673$ K).

Buyevskaya et al. [55] proposed the use of (Rh-black) or supported on γ-Al_2O_3 [60,61]. The experiments, carried out in a temporal-analysis-of-products reactor (TAP) by the use of in situ drift spectroscopy, evidenced that Rh^+ or Rh^{3+} formed the highly dispersed active sites for the oxidation of the methane. This reaction will proceed by two steps: the first one concerns the methane dehydrogenation followed by the oxidation of the formed C–Rh. Neither Rh^0 nor the Rh_2O_3 are directly responsible for the metal activation while the Al_2O_3 support will act as stabiliser of the Rh^{3+} and as a primary source of oxygen.

Basini et al. [57] and Sanfilippo et al. [62] carried out experiments at different pressures, contact times and temperatures, on Ir-based catalysts, for studying the mechanism of partial oxidation of methane on noble metals as proposed by Hickman and Schmidt.

Pt–Rh based catalysts, suitable for use in fluid bed applications, have been prepared by Bharadwaj and Schimdt [64] by impregnation of the respective salts on high-T sintered α-Al_2O_3. This support shows a very good resistance to the attrition, even if it presents a low surface area ($SA_{BET} = 0.3$ m^2/g). Some Pt/Al_2O_3 and Rh/Al_2O_3 catalysts, containing a metal percentage of 0.25–2.0%, have been prepared by starting from hexachloroplatinic acid and Rh nitrate, respectively. In the course of the catalyst production, the selection of an appropriate cycle of decomposition (time and temperature) will be the key factor to obtain 8–14 Å thin and continuous layers on the α-Al_2O_3 pellets (averaged diameter of 100 μm and superficial pores of 3-5 μm). These catalysts have been tested at different values of the contact time ($\tau = 0.1$–0.5 s). Rh and Ni showed higher activity and hydrogen selectivity with respect to the Pt. The best performance of Rh and its highest hydrogen selectivity can be explained through the mechanism proposed for the monoliths by Hickman et al. [65].

7. Catalysts at low pressure drop

A further line of research has been dedicated to the development of catalyst at low drop of pressure. This property allows operation at very low contact time and thus formation of secondary products is minimised. Hick-

man and Schmidt [66] explored the use of three different typologies of structure; extruded monoliths, ceramic foams and metallic gauzes.

The extruded monoliths have a rigid ceramic frame of different shape or geometry, on which the γ-Al_2O_3 is deposited by a washcoating technique. The so-prepared monoliths are then, treated with an organometallic deposition of noble metals by the incipient wetness method. The particles of the noble metal, dispersed on the alumina support, represent the active catalyst phase for the POM reaction. The ceramic frame of the monoliths are generally made by cordierite with square shaped cross section (400 square cells/in.^{2}). The washcoating procedure proceeds through the impregnation of the frame structure by an aqueous slurry of γ-Al_2O_3 (S.A. of powder $= 190$ m^2/g, porosity $= 80\% < 25$ μm) and HCl. After impregnation, monoliths are slowly dried, at $T < 100$°C, and calcined at $T = 550$°C, under a flow of air. This process can be repeated two or more times in order to enhance the amount of deposited alumina. The most delicate step in the process is the dispersion of the metal salts from which the catalyst will be obtained. Thus, if the solubility of these salts is very low (i.e., Pt(NO_3)$_2$ 6H_2O), the step of catalyst particles dispersion on the alumina can precede the washcoating, even if, in this case, the risk of formation of catalytic particle agglomerates must be taken into account. In practice, some experiments conducted on Ni and Pt monoliths, treated at $T = 550$°C, evidenced a remarkable effect of reduction of the catalyst particles dispersion when tested with the POM reaction at high temperature [67,82]. This effect can be minimised by increasing the calcination temperature to 1000°C. Ceramic foams [68] are sponge-like structures, that can be obtained from different materials (Al_2O_3, $SiAlO_X$, $MgO/SiAlO_X$, $ZrAlO_X$, SiC, etc.).

In the past, different authors [69–71] studied the influence of the ceramic supports on different kind of reactions, but only recently, Bodke et al. [68], investigated the influence of this typology of support on the POM reaction. They demonstrated that the washcoating process with γ-Al_2O_3 produces a layer at high microporosity on the walls of the monoliths that increases the specific surface area by a factor ten which explained the improvement of the catalytic activity. Although, Cybulski and Moulijn [72], reported that this effect cannot improve the catalytic activity because the process proceeds under laminar flow and the controlling step is represented by the mass transfer velocity.

Independently from the structures geometry (monolith or foams), it seems that the use of Zr_2O_3 instead of γ-Al_2O_3 improves the catalyst selectivity towards syn-gas and also its thermal stability [73]. The hydrogen selectivity of these catalysts seems to be correlated to the support porosity, in fact, it ranges from 83% to 93% for catalysts with 20 ppi (pores/in.) or 80 ppi, respectively. In this sense, the Zr_2O_3 based foams show higher micro porosity with respect to those based on other oxides. The compari-

son of results obtained by different metal oxides indicated that the feed gas seems to ignite more rapidly on the Pd catalyst than on the Ni catalyst [67,82].

Hickman and Schmidt [66] reported, also, that higher conversion and hydrogen selectivity can be obtained on Rh impregnated monoliths compared to those Pt impregnated. Furthermore, the use of Rh guarantees that the gas composition produced by the process will be closer to that predicted by the thermodynamic equilibrium and that the spacetime will be higher [67,82]. Very high values (up to 90%) of methane conversion and selectivity to hydrogen can be obtained, also, at pressure up to 5.0 Atm, on Rh-coated foam monolith [74]. The utilisation of metallic gauzes can be considered in the ATR process, as catalysts adopted for the industrial oxidation of NH_3 to NO and for the synthesis of HCN from NH_3, CH_4 and air. The gauzes have a structure that allows extremely low contact time, but they have a high mass/surface ratio and are, also, expensive. Some authors [75], working on Pt gauzes, obtained high CO selectivity, at low value of the contact time but without the total oxygen conversion and with a low selectivity to hydrogen.

On the contrary, Hickman and Schmidt [66], have tested the POM reaction on a Pt gauze with a 10% of Rh, and they have obtained oxygen conversion at high values of the selectivity to CO and H_2, and also, for low values of the contact time and CH_4/air ratio lower than 2:1. Hofstad et al. [76] studied Pt/10% Rh (1024 meshes/cm^2) gauzes, prepared from 60 μm wire. In this case, the catalyst has been in situ prereduced with hydrogen at 600°C for 1.5 h. The SEM analyses of the tested catalysts showed that the structure of the Pt gauze was damaged by formation of black-Pt, while this problem has not been encountered in the gauze formed by Pt with 10% of Rh.

8. Membrane-based processes

A membrane reactor combines the separation properties of a membrane with the performance of a catalytic system. Particularly, the palladium membranes can be used as a hydrogen separation medium, improving all equilibrium-limited reversible reactions [77]. A modified ceramic membrane, which was originally developed for application in the methane oxidative coupling process, has been already employed by Santos et al. [29] for POM, at pressures above atmospheric (2 Atm), with conversion and selectivity to H_2 close to 100%. Kikuki and Chen [78] propose a Pd-membrane for a POM reactor fed with air. A great economical advantage can be reached in this way, because the expensive air fractionation (needed for a conventional POM plant) is substituted by the less costly CO_2–N_2 separation. At last, the combined efforts of Amoco, BP Chemicals, Praxair, Sasol and Statoil developed an innovative technology, named OTM (Oxygen-Transport-Membrane) that can convert natural gas to syngas with excep-

tionally high selectivity [79]. In this process, a ceramic membrane, related to inorganic perovskites (Sr, Fe, Co_5O_x), permits integration of ATR with the separation of O_2. Air and natural gas are introduced in the opposite sides of the membrane. Oxygen from air is adsorbed, dissociated and ionised in one side, then it diffuses through the membrane and slowly reacts with methane in the other side, to give partial oxidation products.

9. Reaction mechanisms

The POM process with yield of 100% should give stoichiometric H_2 and CO, following the scheme of (React. (1)). In practice, whatever the catalytic system should be, there is an undesired formation of H_2O and CO_2 (products of the total oxidation), and in the absence of a reliable catalyst and excess of steam available for the ATR reaction, coke formation will rapidly occur with subsequent poisoning of the catalyst. The presence of CO_2 and H_2O is explained by the general accepted reaction mechanism [16,22] for the POM reaction that foresees the initial oxidation of part of the methane (React. (2)), followed by the *wet* and *dry* reforming of the methane that has not been oxidised, React. (6) and React. (8), respectively.

Catalysts supported on Si, Al, La or Mg oxides, always form coke due to the influence of the intrinsic characteristics of the supports. In fact, the acidity of the support promotes the catalytic decomposition of the methane [36], both by a direct mechanism (React. (9)) or through the Boudouard reaction (React.(10)):

Methane dissociation $CH_4 = C + 2H_2$ (9)

Boudouard reaction $2CO = C + CO_2$ (10)
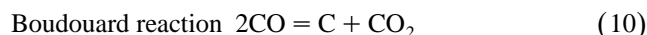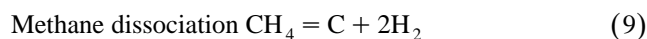
Thus, the supports with basic properties (MgO, Ln_2O_3, etc.) inhibit carbon formation, while those with acid properties (SiO_2) enhance it. The utilisation of low contact time improves the fast removal of the reaction products (i.e., CO) from the acid site toward colder areas that block the methane decomposition mechanism (quenching effect).

A further technological improvement is represented by the development of ceramic monoliths covered by metals that present low pressure drops and can operate at contact times of the order of 10^{-4} s. Hickman and Schmidt, studying the ATR reaction on metallic monolith (coated) [63–66] and proposed an alternative mechanism that foresees the direct formation of CO and H_2, already, in an initial step (heterogeneous mechanism presupposing the formation of superficial Me–C species). The Rh is the catalyst that especially favours this mechanism and gives the highest H_2 and CO selectivities. In the absence of acidic sites in the catalyst support and for high superficial thermal conductivity, coke formation can occur in the gas phase, only if the products are not be cooled.
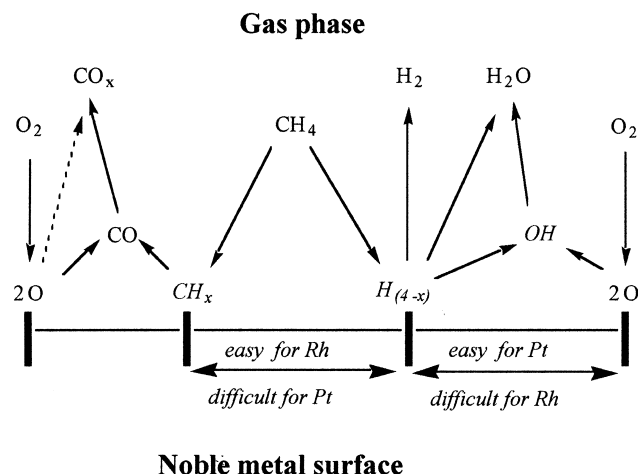
Gas phase

Fig. 6. Reactions mechanism for POM-ATR processes.

The scheme of the proposed reaction is shown in Fig. 6. For this mechanism, the highest production of steam on Pt than Rh [63–66] is correlated to the activation energy to the OH formation that results higher on Rh (20.0 kcal/mol) than on Pt (2.5 kcal/mol).

Alternatively to Hickman and Schmidt [63,66], Bharadwaj and Schmidt [64] and Hickman et al. [65], Basini et al. [57] proposed that the CO_2 is also produced on the metal surface together with CO (see dotted arrow in Fig. 6). This is justified by the fact that reducing the contact time ($\tau < 10^{-3}$ s), the selectivity towards CO_2 increases.

10. Coke formation

The problem of the carbon deposition is present when C-containing fuels are utilised. The mechanisms through which carbon deposition occurs, include:

1. Formation of amorphous flakes and filamentous carbon due to CO decomposition.
2. Formation of encapsulating carbon due to the decomposition of hydrocarbons.
3. Pyrolytic carbon generated by thermal cracking of hydrocarbons.
4. Soot formation in the substoichiometric methane oxidation.

The possibility of formation of filamentous carbon is consistent when hydrocarbons are in contact with particles of transition metals that act as catalyst and it is predicted by the methane direct dissociation (React. (9)) or by the Boudouard reaction (React. (10)).

Sacco and al. [5] noted that transition metals show catalytic activity towards carbon formation in the following order Fe > Co > Ni and the ordering of carbon deposition activity depends directly on the decomposition temperature of the carbides. In the region of O–C–H phase diagram where the reducing conditions are prevailing, the carbon rate deposition is proportional to $P_{CO} \cdot P_{H2}$. In the zone of carbides formation, this process follows an exponentially law for Fe and Co while for Ni is valid a linear dependence on gas-phase carbon activity. The Ni particles are most active on methane decomposition and form filamentous carbon that content Ni traces, while Fe and Co are most active in the CO decomposition forming amorphous flakes and filamentous carbon. In general, filamentous carbon produces mechanical strengths that can cause the breakdown of the catalyst pellets and blockage of gas channels.

The higher hydrocarbons, in contact with Ni particles, tend to form aromatic structures. The polymerisation is promoted into a layer of non-reactive deposits that encapsulate and deactivate the Ni surface [36]. The thermal cracking of hydrocarbons in a catalytic reactor, is also promoted by the transition metals contained in the stainless steel forming the coil and reactor walls [80]. The coke deposition forms thick layer that produced losses of efficiency or catalyst deactivation if it occur on the heat exchanger or reactors walls.

The substoichiometric combustion of the methane proceeds to the production of CO through formation of C_2^+ compounds that can be precursors of the poly-aromatic hydrocarbon formation (soot) [8]. The favourable conditions for soot formation are low temperature and low pressure, as it can be encountered during the start-up of plant.

The means by which carbon deposition can be avoided include the following:

· Controlled gas composition. The carbon formation mechanism is based on the methane or CO decomposition. The earlier reaction proceeds endothermically and the second one exothermally, thus there is a critical temperature below that affinity for carbon formation by the methane decomposition will be present, otherwise, there is another critical temperature above that affinity is shown by CO decomposition reaction. This equilibrium depends by the gas composition and it is influenced also by steam reforming and shift reactions. Complex, thermodynamic evaluations can lead to the definition of the safe limits for carbon formation as function of S/C and H/C ratios. As general rule, an increasing amount of steam or hydrogen inhibits the carbon formation. In syn-gas technologies, the adopted values for the S/C ratio is 2.0, even if variation can be acceptable as a function of the specific conditions of the processes.

· Smaller catalyst particle size.

· Basicity of the catalyst support. It has been found that basic support like MgO show lower tendency to coke formation than acidic supports. For this reason, basic oxides are added as promoters to catalyst acidic supports.

· Deposition of inert layer on hardware stainless steel walls. This solution avoid the fuel thermal cracking because the contact between hydrocarbons and metal is not allowed.

· Optimisation of the burner design and controlled parameter during plant operations.

11. Concluding remarks

The syn-gas production from natural gas, by both POM and ATR processes, has been reviewed. Typically, hydrogen is produced from CH_4 by steam reforming reaction (SRM), that gives a high H_2/CO ratio (close to 3), but needs a consistent heat supply due to its strong endothermicity. POM and ATR reactions represent an alternate way for producing syn-gas without heavy energy penalties, also if a lower H_2/CO ratio (from 2 to 3) is achieved. For some applications (i.e., fuel cells with heat cogeneration [81] the thermal balance is a crucial factor, and H_2 production can be increased (if needed) by the water-gas shift reaction (WGS). Moreover, for particular chemical processes, the H_2/CO ratio close to 2 is exactly the desired value (i.e., methanol and Fischer–Tropsch synthesis) and POM application results in an improvement of the process [65]. In addition, smaller reactors (or higher throughput) are possible, because the POM reaction is significantly faster than SRM. Steam reforming reactors typically work at contact time ≈ 1 s, while for POM it can be less than 10^{-2} s [66].

On the kinetic point of view, the same catalytic system can be used for SRM, POM and ATR, due to the analogous mechanism, but some specificity is needed to avoid a too large amount of CO_2 and to minimise the soot formation. Catalysts at high activity and low pressure drop (noble metals supported monoliths) can give good conversion also at low contact time ($\tau \le 10^{-2}$ s). The homogeneous reactions, provided by equilibrium, are stopped because of their slowness and the total oxidation is minimised. Rh catalysts [68], further, improve the selectivity by minimising the water formation, but are still too expensive. New membrane technologies can represent a future improvement of POM and ATR thanks to their capability to move all equilibria by in situ subtracting the produced hydrogen. Particularly, it appears very interesting the use of ceramic porous membrane reactors as feeder for a molten carbonate fuel cell plant devoted to the combined production of heat and electricity [4].

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