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An experimental study of multilayered composite palladium membrane reactors for partial oxidation of methane to syngas

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Abstract

Today only a small percentage of methane is used as a chemical feedstock to produce syngas that is a valuable feedstock for the production of higher hydrocarbons or methanol.

Currently, the process extensively used in industry for the production of syngas is the steam reforming of methane in large furnaces. The reaction is industrially operated under strong conditions resulting in several undesirable consequences: sintering of the catalyst, danger of explosion, very high carbon deposition and the use of high-temperature resisting materials.

A potential alternative technique to steam reforming processes for producing syngas is the partial oxidation of methane with oxygen, having over steam reforming the disadvantage that pure oxygen is required. Utilisation of air instead of pure oxygen is beneficial only if it can be performed by using a membrane reactor in which the membrane is permselective to oxygen.

Another route to produce syngas using the partial oxidation of methane is offered by membrane reactors, i.e. engineering systems that combine the separation properties of membrane with the typical characteristics of catalytic reactions.

It is well known that the use of dense palladium as membrane enables hydrogen product to permeate out through the membrane, shifting thereby conversions towards the values higher than thermodynamic equilibrium ones and providing pure hydrogen product. In fact, only hydrogen is allowed to permeate through dense palladium membranes.

In this work five reactors are investigated with respect to the partial oxidation of methane. In particular, the performance of a traditional reactor (TR), three composite ceramic palladium membrane reactors (MRa, MRb and MRc), and a dense palladium membrane Reactor (PMR), all having the same geometrical dimensions and using the same Ni-based catalyst, are evaluated in terms of experimental results of methane conversion to syngas and in terms of hydrogen selectivity.

A comparison between methane conversion at various temperatures and data in literature is also presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium membrane reactor; Partial oxidation; Syngas

1. Introduction

According to Parmaliana et al. [1], in January 1988, the ascertained and economically accessible reserves of natural gas, whose main component is methane, amounted world-wide to over 144 × 10^{12} Nm^3. Considering the same rate of consumption of the last decade, in the future, natural gas will still be used as energetic vector. On the other hand, annual global production and utilisation of hydrogen correspond to 5 × 10^{11} Nm^3 per year [2]. The current technology in the manufacture of synthesis gas (a mixture of carbon monoxide and hydrogen) is based mainly on the steam reforming of natural gas. In fact, the first

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step in natural gas conversion is the production of synthesis gas, used for example the ammonia/urea production and methanol synthesis production and in the steel industry as a reducing agent. After removal of carbon monoxide, hydrogen produced by steam reforming is extensively used by the oil industry in hydro-treating and in hydro-cracking processes.

The major part of hydrogen production from natural gas in the world, corresponding to 45 M t per year, is by steam reforming (highly endothermic) reaction [3]:

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H^\circ_{298} = +206\,\mathrm{kJ/mol}$$

Steam reforming has been practised for more than five decades. Nevertheless, other reactions have recently been considered, due to the following disadvantages:

- high temperatures (generally around 1100 K) and pressures (in the order of 3–4 MPa) are applied for methane conversions exceeding 95%;
- H_2/CO mole ratio of 3.0 is not the desired stoichiometry of some chemical reactions such as methanol and Fisher–Tropsch synthesis (that need H_2/CO mole ratio of 2.0).

In this reaction, an excess of H_2O is used to inhibit the carbon deposition:

$$CO + H_2O = CO_2 + H_2, \quad \Delta H^\circ_{298} = -41\,\mathrm{kJ/mol}$$

However, in this case, coupling steam reforming and water-gas shift reactions, only half of the hydrogen produced originates from methane, the other half is produced from water. The product gas has H_2/CO molar ratio higher than 3, suitable for hydrogen production, but not useful for liquid hydrocarbons production.

Another approach for syngas production originates from this demand: the reaction of dry reforming of methane that is more endothermic than steam reforming and gives a gas mixture having low H_2/CO molar ratio:

$$CH_4 + CO_2 = 2CO + 2H_2, \quad \Delta H^\circ_{298} = +247\,\mathrm{kJ/mol}$$

This reaction has received considerable attention in recent years. Numerous supported metal catalysts such as Ni, Ru, Rh, Pd, Ir and Pt have been tested [4–9]. However, the endothermicity of both the steam reforming and dry reforming reactions requires energy input. Vice versa, the partial oxidation of methane (POM) to synthesis gas is a mildly exothermic reaction that is free from limitations of the above reactions and would be more energy efficient. In fact POM, having a H_2/CO mole ratio of 2.0, would be a viable alternative reaction to the commonly methane steam reforming reaction for the syngas generation.

$$CH_4 + 0.5O_2 = CO + 2H_2, \quad \Delta H^\circ_{298} = -36\,\mathrm{kJ/mol}$$

Partial oxidation of methane to carbon monoxide and hydrogen have been studied, e.g., over: Ni-based catalysts [10–13], NiO/MgO catalysts [14], Ru monoliths [15], Ru/TiO_2 catalysts [16], Co/MgO catalysts [17], Pt monoliths [18,19], Ir catalysts [20].

One important limitation in the production of POM reaction commercially viable is due to thermodynamics. In particular, the increase of pressure gives a decrease in equilibrium methane conversions [21].

A membrane reactor is an engineering device that offers the possibility to overcome the thermodynamic limitations, giving the possibility to attain a high methane conversion at lower temperature. In fact, a membrane reactor combines the separation properties of membranes with the characteristics typical of catalytic reactions [22–27]. In each of the above mentioned reactions, by selectively removing one of the products (generally hydrogen) from reaction mixture, the conversion of CH_4 was increased for steam reforming of CH_4 [28–30], dry reforming of CH_4 [31,32] and for POM reaction [33–40].

In some previous works, one of the authors [41,42] suggested the following procedure for obtaining a stable composite palladium membrane: (1) depositing a thin layer of palladium on a ceramic support; (2) utilising the composite membrane for carrying out a reaction; (3) depositing another layer of palladium. Their conclusion was that using the procedure of "deposition-use", it is possible to achieve a very selective and very stable composite palladium membrane.

In this work, in order to determine the differences in behaviour with respect to a particular chemical reaction, we used both the procedures: (a) "deposition-use"; (b) deposition without using the membrane from one deposition to another. In other words, we used this procedure for the deposition of seven different palladium layers on two ceramic supports. The obtained porous composite membranes are described below.

However, since porous membranes are characterised by high permeability but low selectivity, while, on the contrary, non-porous membranes have high selectivity but low permeability, a dense palladium membrane reactor was also used.

In this investigation, the membrane performance for POM is evaluated comparing the behaviour of a traditional reactor versus different membrane reactors.

2. Description of the process

2.1. Experimental apparatus

In this work, two different types of reactors, traditional reactor (TR) and membrane reactor (MR), have been used. TR is a stainless steel tube; geometrical dimensions: total length 25 cm; useful length 15 cm; i.d. 0.67 cm. For MR, three commercial TiO_2 tubular membranes (furnished by Shumacher, Germany) were used as a starting material for palladium deposition: length 25 cm; i.d. 0.67 cm; o.d. 1.02 cm; membrane thickness 0.175 cm; mean internal pore diameter 5 nm (referred to a support having 56 μm layer).

A dense tubular palladium membrane reactor (PMR) consists of a stainless steel module containing a pinhole free dense palladium membrane (furnished by Enea, Italy) having thickness 70×10^{-6} m, o.d. 1.02 cm, total length 25 cm, palladium length 14 cm, with an internal movable support.

Each membrane was placed inside a stainless steel module and sealed by means of graphite rings.

The lumen of each MR was packed with 3.149 g catalyst particles “Ni-5256 E 3/64” (furnished by Engelhard) containing highly dispersed nickel on silica support diluted with 1.19 g glass sphere particles 2 mm diameter. The catalytic bed was pre-treated using N_2 for 6 h using a flow rate of 1.02×10^{-3} mol/min at 480°C.

Gas flow rates of CH_4, O_2 and N_2 were stabilised by means of mass-flow controllers. Reaction tests were performed using this feed gas mixture: $CH_4/O_2/N_2 = 2/1/14$; $CH_4 = 2 \times 10^{-3}$ mol/min.

Permeate stream pressure (shell side) was held continually at 1 atm. The feed gas pressure ranged from 1.6 to 2.1 bar abs. During the reaction, the maximum temperature difference on the module was 1°C between the feed gas and retentate gas stream, the maximum pressure difference was 0.02 bar between the feed gas and retentate gas stream. The reaction temperature range was 250–550°C. No sweep gas was used (except for PMR). A Gas Chromatograph (Carlo Erba 4200) having a packed column Carboxen^{TM} 1000 for analysing gas mixtures was used with argon as carrier gas (25 ml/min), oven temperature 140°C, TCD detector at 250°C.

Methane conversion and hydrogen selectivity were calculated considering for each MR both permeate and retentate flow rates: outlet gas streams were separated from H_2O produced using a glass column containing H_2O vapour adsorbent (drierite, furnished by the W.A. Hammond Drierite) before sending to Gas Chromatograph (Carlo Erba 4200). The atom mass balances generally closed to within ±8% in all experimental data were reported in this work.

Fig. 1 shows the schematic diagram of the experimental permeation and reaction system.

Methane conversion is defined as

$$CH_4\,(\%) = \frac{\Delta F(CH_4)}{F(CH_{4,in})} = \frac{F(CH_{4,in}) - F(CH_{4,out})}{F(CH_{4,in})} \times 100 \quad \text{(for traditional reactor)}$$

$$CH_4\,(\%) = \frac{\Delta F(CH_4)}{F(CH_{4,in})} = \frac{F(CH_{4,in}) - F(CH_{4,permeate}) - F(CH_{4,retentate})}{F(CH_{4,in})} \times 100 \quad \text{(for membrane reactors)}$$

Hydrogen selectivity is defined as

$$H_2\,(\%) = \frac{F(H_{2,out})}{F(H_{2,out}) + F(CO_{2,out})} \times 100 \quad \text{(for traditional reactor)}$$

$$H_2\,(\%) = \frac{F(H_{2,permeate}) + F(H_{2,retentate})}{F(H_{2,permeate}) + F(H_{2,retentate}) + F(CO_{2,permeate}) + F(CO_{2,retentate})} \times 100 \quad \text{(for membrane reactors)}$$

where $F(i)$ is the molar flow rate of the species i.

Permeabilities of pure gases (hydrogen and nitrogen) have been performed with the same experimental apparatus. All gases >99.995% pure were used.

For each reactor used, two thermocouples were located at both the ends of the modules. The first one

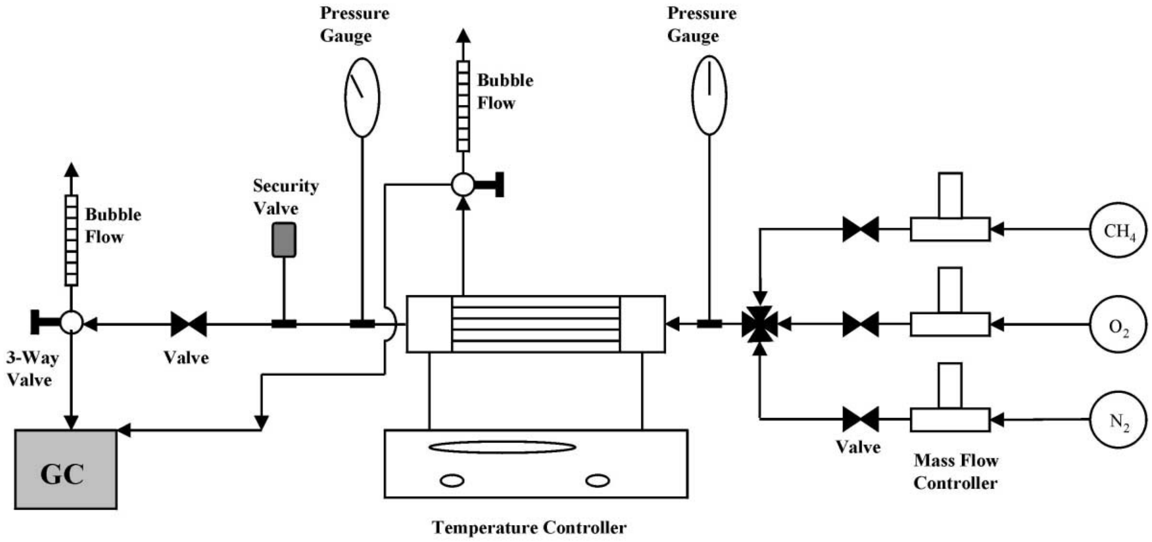

Fig. 1. Schematic diagram of the experimental permeation and reaction system.

was located in the feed side 1 cm inside the catalyst bed and used to keep the temperature at a constant value (set point). The second one was located in the retentate side 1 cm inside the catalyst bed to investigate the internal temperature while the reaction took place. A multiple (four points) thermocouple was used for measuring the temperature profiles. The reactors were heated using a thermolyne heating tape connected to a temperature controller (set point).

2.2. Membrane preparation

In this work three composite membranes were prepared starting from TiO_2 supports using an electroless plating technique. At first, the support material was cleaned using different solutions in order to remove various impurities. The activation was obtained using Sn^{2+} and Pd^{2+} solutions. The electroless solution consists of: source of Pd^{2+} ions; reducing and complexing agents; pH buffer (NH_3 aqueous solution, 28 wt.%). Operating conditions: 50°C, pH = 10.66. The palladium deposition takes place following the reaction:

$$2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd \downarrow + N_2 \uparrow + 4H_2O$$

During the deposition, the palladium density and the film thickness depend on the deposition time. The same technique and the same experimental procedure were used for preparing palladium films on TiO_2 supports. In particular:

- MR2a, two layers of palladium film, ‘a’ is the membrane vitrified at the ends; the support was vitrified at 800°C for 15 min after immersion of both ends in an Aremco-Seal^{TM} solution (type 617).
- MR*n*b, $n = 1, \ldots, 7$ is the number of Pd layers, ‘b’ is the membrane not vitrified at the ends and used for both permeation tests and reaction experiments after each deposition of palladium.
- MR7c, 7 is the number of Pd layers; ‘c’ is the membrane not vitrified at the ends and used for experimental tests only after seven consecutive depositions of palladium.

3. Results and discussion

3.1. Permeation tests

Using a scanning electron microscope, the thickness of both TiO_2 support and each layer of palladium was determined. In Table 1, the palladium layer thickness and the total thickness (support + palladium layers) are reported. In particular, it can be observed that

Table 1
Palladium thickness for MR*n*b ($n = 1, \dots, 7$) and for MR7c

Membrane	Pd total layer thickness (μm)	Total thickness (support+Pd) (μm)
TiO_2 support	0	56
MR1b	10	66
MR2b	12	68
MR3b	13	69
MR4b	17	73
MR5b	(18)	(74)
MR6b	19	75
MR7b	21	77
MR7c	16	72

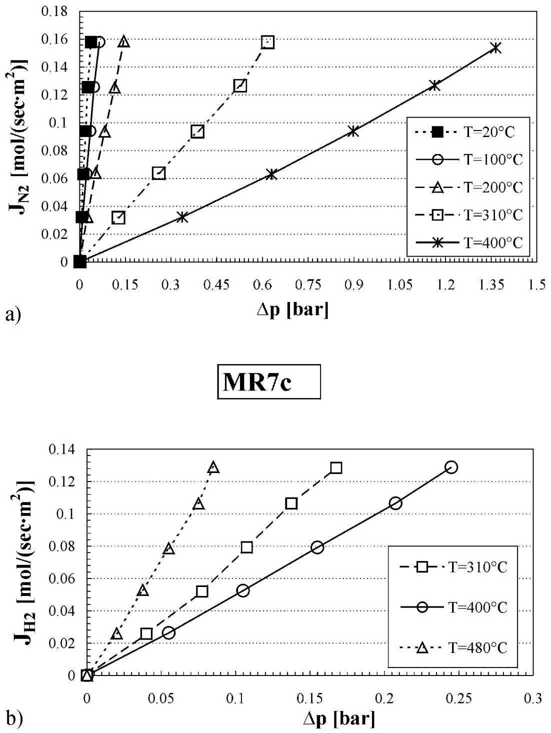

Fig. 2. Nitrogen flux (a) and hydrogen flux (b) versus differential transmembrane pressure for MR7c at different temperatures.

MR7b has a palladium thickness of 21 μm and MR7c has a palladium thickness of 16 μm: the two values are very close. For MR5b, the thickness was not determined directly by SEM, but from a linear interpolation between MR6b and MR4b thickness data.

All the composite palladium membranes prepared were tested for gas permeation at different temperatures and pressures. By referring to MR7c, in Fig. 2a, nitrogen flux versus differential transmembrane pressures is reported for the following temperatures: 20, 100, 200, 310 and 400°C. The nitrogen flux increases with increasing the differential transmembrane pressure and decreases with increasing temperature. In Fig. 2b, the hydrogen flux versus differential transmembrane pressures at 310, 400 and 480°C is shown. The hydrogen flux increases with increasing differential transmembrane pressure, and it decreases with increasing temperature from 310 to 400°C; however, the hydrogen flux increases with increasing temperature from 400 to 480°C. For this membrane, the separation factor H_2/N_2 increases with increasing temperature, in fact, it ranges from 3.07 at 310°C to 4.66 at 400°C.

This behaviour might be explained considering that the palladium film of MR7c is not a compact layer but contains some pinholes. This means that some holes of the TiO_2 support were completely plugged by the successive layers of palladium, but the large pores were not completely covered by the metal layers. The hydrogen gas permeates through both the dense part of the metal layers and the pinholes of the composite palladium membrane, whereas nitrogen gas can only pass through the pinholes. It is well known that the hydrogen permeation through palladium increases with increasing temperature, but Knudsen diffusion decreases slightly with increasing temperature. In this way, we can say that for the temperature ranging between 310 and 400°C, the composite palladium membrane behaviour is close to Knudsen diffusion (in fact, the separation factor H_2/N_2 is $3.07 < 3.74$ corresponding to the Knudsen value). For the temperature in the range between 400 and 480°C, the composite palladium membrane behaviour is close to the microporous diffusion (and the separation factor H_2/N_2 is $4.66 > 3.74$).

By referring to MR7b, in Fig. 3, the hydrogen and nitrogen permeances and the ideal separation factor H_2/N_2 versus temperature are shown. For each curve, by increasing temperature, there is a corresponding decrease. In the same figure, the Knudsen selectivity is also reported: the ideal separation factor H_2/N_2 is always less than Knudsen selectivity. The different behaviour of MR7b compared with MR7c might be explained considering that MR7b was stressed after each one of the seven palladium depositions by using the membrane for POM reaction tests, while MR7c

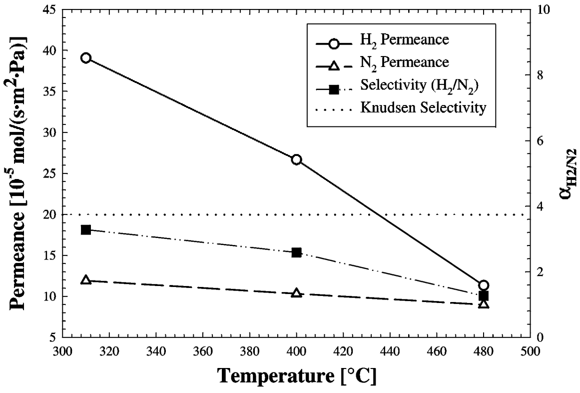

Fig. 3. Hydrogen and nitrogen permeances and ideal separation factor H_2/N_2 versus temperature for MR7b.

was used only at the end of the procedure of the seven palladium depositions. This means that for MR7b after each deposition of palladium, instead of MR7c, some pinholes were not progressively closed. The resulting membrane structure was more open for MR7b than for MR7c.

For what concerns PMR, the permeation tests using nitrogen and hydrogen at different transmembrane pressures and temperatures have shown that this membrane is permeable solely to hydrogen, i.e. the selectivity of hydrogen/nitrogen was infinite. Both the Arrhenius and Sievert laws are followed.

3.2. Palladium as catalyst

As it is well known palladium is a widely used as oxidation catalyst [43]. Palladium shows a high oxidation activity not only as a metal but also as palladium oxide. In fact, both palladium and palladium oxide are active oxidation catalysts. In other words, palladium might act as a combustion catalyst for complete oxidation of methane. In order to verify the effect of palladium as catalyst for POM reaction, some experiments have been carried out using the palladium dense membrane without Ni-based catalyst: no syngas was produced. Results are shown in Fig. 4 in which methane conversion is reported against reaction temperature. In the same figure, the thermodynamic equilibrium curve of methane conversion to carbon dioxide is also shown. The maximum methane conversion is 9.42% at 450°C; the minimum is 2.16% at 310°C. The conclusion is that palladium acts as a catalyst for the partial oxidation of methane but gives only complete conversion to CO_2. This means that among all the possible reactions [44], only the total combustion of methane takes place.

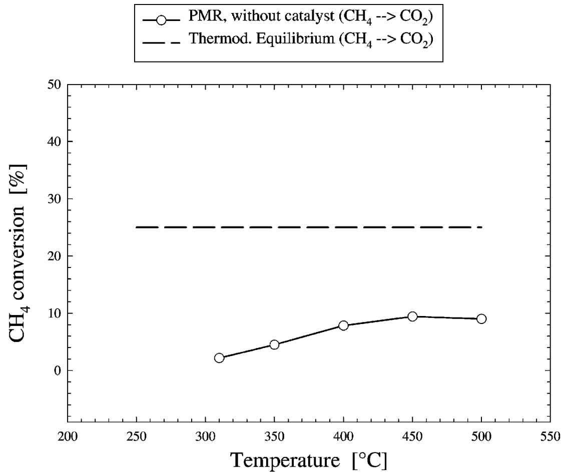

Fig. 4. Methane conversion versus temperature for palladium membrane reactor (PMR).

A further investigation is reported in Fig. 5, which shows the level of methane conversion as a function of the inlet pressure for the different reactors employed:

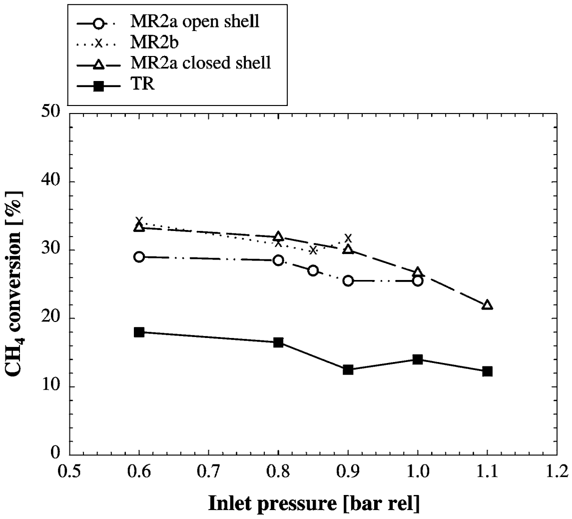

Fig. 5. Methane conversion versus inlet pressure for TR, MR2a open shell, MR2a closed shell and MR2b at 450°C; $CH_4/O_2/N_2 = 2/1/14$.

TR, MR2a open shell, MR2a closed shell and Mr2b at 450°C and $CH_4/O_2/N_2 = 2/1/14$.

As expected for TR [21], the use of higher pressure lowers methane conversion because of the unfavourable equilibrium conditions. The same considerations are valid for membrane reactors. In fact, our MRs show the same trend observed by Santos et al. [33] using a modified ceramic membrane for the same reaction.

In the same Fig. 5, it is evident, e.g., at 0.6 bar rel, the methane conversion for membrane reactors is higher than for the traditional reactor. This is well known in literature and is attributed to the capacity of a membrane reactor to subtract product species from the reaction system. However, for this reaction, the presence of palladium acting also partially as an additional catalyst increases methane conversion for MRs with respect to TR.

MR2a was operated in two modes: closed shell and open shell. In the first case, both the shell-side inlet and exit ports were closed and the reactor operated as a traditional reactor. When the shell was closed, the membrane reactor worked as a traditional reactor. The conversion of methane in MR2a is higher in closed shell mode than in membrane operation mode. This fact might be explained in this way: the membrane MR2a does not have an infinite selectivity H_2/other gases, meaning that all the species can permeate through the membrane. In other words, when the shell side is open, part of the reactants permeates through the pinholes reducing the methane conversion. It seems that there are two conflicting effects: the hydrogen (and other products of the reaction) removal tends to increase the methane conversion, while the reactant loss through the membrane decreases methane conversion. In our experimental conditions, considering that the mass of palladium is exactly the same in MR2a open shell and MR2a closed shell, the last effect should prevail.

For what concerns the comparison between MR2a (open shell) and MR2b (open shell), in the same figure we can observe that the methane conversion is higher in MR2b than MR2a. Considering that MR2a and MR2b start from the same support and that the same palladium deposition procedure was adopted, the behaviour difference in methane conversion must only be due to the vitrification procedure of the ends carried out at high temperature (800°C) for the support of MR2a. In fact, it is well known that at $T > 500°C$, the morphological structure of the TiO_2 support changes and the average pore sizes tend to increase. In this way, although the quantity of the palladium deposited was the same, the morphology of the resulting composite membrane was different for MR2a and MR2b.

After these experimental results, the deposition of other layers of palladium on the inner surface of membrane MR2a was interrupted.

3.3. Carbon deposition

After experiments carried out in traditional reactor, MR2a and MR*n*b ($n = 1, \ldots, 7$), pure oxygen at 500°C for half-an-hour was burned off: the gas streams at the exit were analysed by a Gas Chromatograph.

No quantifiable carbon deposition in the combustion (i.e. CO and CO_2) was detected. In order to obtain further investigation concerning the carbon deposition, MR4b was fed with 150 ml/min of oxygen at 500°C for 36 h. Both the shell-side inlet and outlet ports were closed (i.e. the reactor operated as a traditional reactor). CO_2 was the only product of the combustion reaction and the carbon deposited corresponds to 0.00072 g. Results of the determination of carbon deposition are shown in Table 2.

These results seem to confirm for the same reaction the experimental results obtained by Hochmuth [45] over a monolith supported catalyst. On the other hand, Torniainem et al. [46] predicted thermodynamically the formation of graphite for CH_4/O_2 ratios greater than 1.9 on Ni catalyst but only for high reaction

Table 2
Amount of carbon deposited on different reactors. Experimental conditions: $O_{2,in} = 150$ ml/min; $T = 500°C$; both shell-side inlet and exit ports were closed

Reactor type	Time (h)	Amount of C deposited (g)
TR	0.5	0
MR2a	0.5	0
MR1b	0.5	0
MR2b	0.5	Trace
MR3b	0.5	0
MR4b	0.5	0
MR4b	36.0	0.00072
MR5b	0.5	0
MR6b	0.5	Trace
MR7b	0.5	0

Table 3
Methane conversion for different kinds of reactor, $P_{\mathrm{in}} = 0.6$ bar rel, $CH_4/O_2/N_2 = 2/1/14$, $CH_{4,\mathrm{in}} = 2 \times 10^{-3}$ mol/min, $W_{\mathrm{CAT}} = 3.15$ g, $N_{2,\mathrm{sweep}} = 1.56 \times 10^{-2}$ mol/min (for PMR)

	TR	MR7b	MR7c	PMR
$T = 400°C$	18.3	37.8	36.8	45.3
$T = 450°C$	25.4	47	48	56.2

Table 4
Hydrogen selectivity for different kinds of reactor, $P_{\mathrm{in}} = 0.6$ bar rel, $CH_4/O_2/N_2 = 2/1/14$, $CH_{4,\mathrm{in}} = 2 \times 10^{-3}$ mol/min, $W_{\mathrm{CAT}} = 3.15$ g, $N_{2,\mathrm{sweep}} = 1.56 \times 10^{-2}$ mol/min (for PMR)

	TR	MR7b	MR7c	PMR
$T = 400°C$	40.6	49	50.4	34
$T = 450°C$	50.8	61	58.8	46

temperature ($T > 800°C$). Kikuchi and Chen [31] confirmed that under some experimental conditions, the carbon deposition is low, being more pronounced only with methane conversion higher than 50–60%.

3.4. Methane conversion and hydrogen selectivity

The experimental results are summarised in Tables 3 and 4. In particular, Table 3 shows a direct comparison among TR, MR7b, MR7c and PMR in terms of methane conversion at 400 and 450°C. According to thermodynamics, methane conversion increases when temperature changes from 400 to 450°C. In fact, at 400°C methane conversion was found to be 18.3% for TR, 37.8% for MR7b and 36.8% for MR7c, while at 450°C methane conversion was 25.4% for TR, 47% for MR7b and 48% for MR7c. Both MR7b and MR7c give similar methane conversion values at the two investigated temperatures, demonstrating that the same methane conversion can be reached either using the membrane after each deposition or not. H_2/N_2 selectivities for MR7c were in the range between 3.07 at 310°C and 4.66 at 400°C, while for MR7b H_2/N_2 selectivities were in the range between 3.28 at 310°C and 2.58 at 400°C, less than Knudsen value (3.74). The order of magnitude of the selectivities is the same for

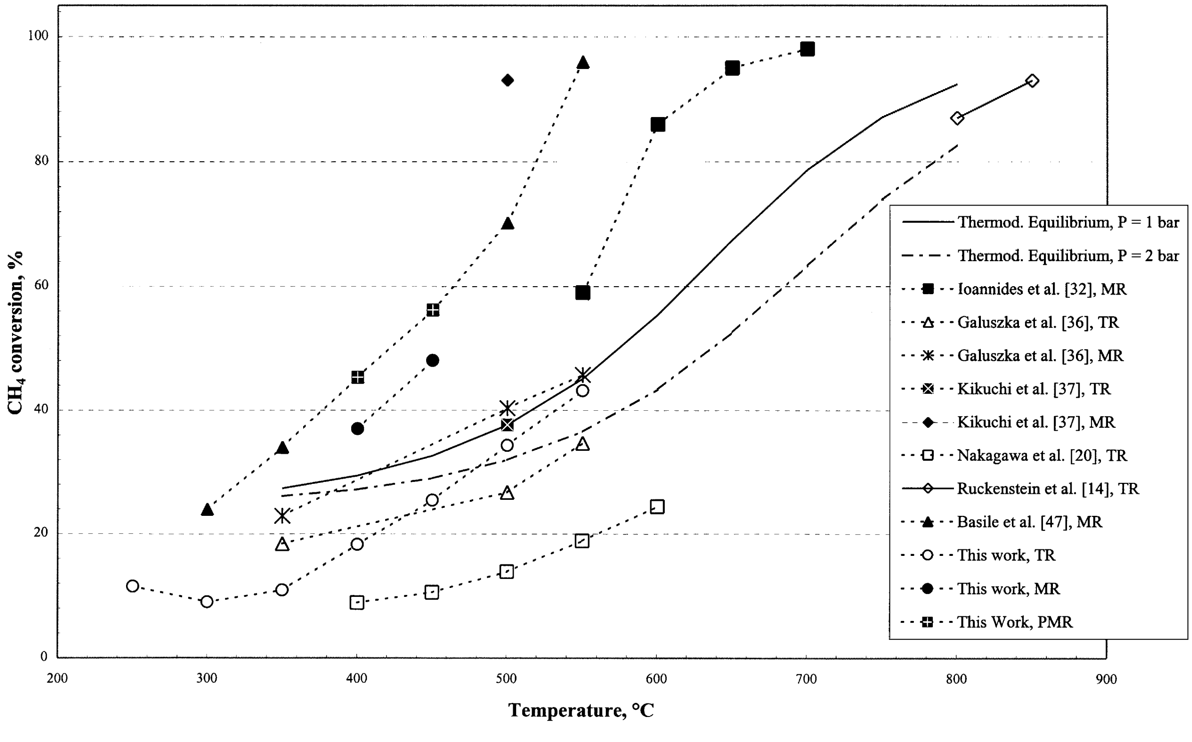

Fig. 6. Methane conversion versus temperature: comparison of experimental data with literature data.

both membranes in the range of temperature considered. This strengthens the idea that the behaviour of both membranes should be the same in terms of both methane conversion and hydrogen selectivity.

In Table 3, PMR shows the highest methane conversion: 45.3% at 400°C and 56.2% at 450°C. This is due to the infinite selectivity H_2/other gases of PMR. In fact, different from MR7b and MR7c in which the reactants also permeate through the membrane, in PMR only hydrogen permeates, so methane conversion increases due to Le Chatelier–Brown principle.

However, Table 4 shows the hydrogen selectivity for TR, MR7b, MR7c and PMR at 400 and 450°C using a feed ratio $CH_4/O_2/N_2 = 2/1/14$. According to thermodynamics, hydrogen selectivity increases when the temperature changes from 400 to 450°C. In fact, at 400°C hydrogen selectivity was found to be 40.6% for TR, 49% for MR7b, 50.4% for MR7c, and 34% for PMR, while at 450°C hydrogen selectivity was 50.8% for TR, 61% for MR7b, 58.8% for MR7c and 46% for PMR.

In particular, PMR reached the lowest value of hydrogen selectivity at 400°C. The reason for this kind of behaviour can be explained in this way: although methane conversion increases, this reactant is involved in more than one reaction [44], so that the total amount of products (undesired ones too) increases and hydrogen selectivity is negatively affected.

From these results, it is clear that it is quite indifferent using directly a membrane having seven palladium layers or a membrane having seven palladium layers that have been used (i.e. stressed) after each palladium layer deposition: no effect is observed on both methane conversion and hydrogen selectivity. In fact, both methane conversion and hydrogen selectivity for MR7b are close to the ones that are related to MR7c.

In order to compare our experimental results with literature data, in Fig. 6, various experimental results are summarised. Since all experimental data have been obtained at 1 and 2 bar, the corresponding thermodynamic equilibrium curves are also considered. It is evident that experimental data of traditional reactors are always below the corresponding thermodynamic equilibrium curve. Vice versa, all experimental data regarding membrane reactors are always above the corresponding thermodynamic equilibrium curve. This means that palladium membranes enhance the catalytic conversion of methane.

4. Conclusions

Conversion of methane to syngas via partial oxidation reaction has been studied in four different membrane reactors (named MRa, MRb, MRc, PMR) as well as in a traditional reactor. The main conclusions of the present experimental work are the following:

- Conversion of methane was remarkably higher in membrane reactors than in the traditional reactor. Applying membrane reactors, conversions exceeding equilibrium are achieved.
- It is quite indifferent using directly a membrane having seven palladium layers or a membrane having seven palladium layers that have been used after each palladium deposition.
- According to literature data, no carbon was found on catalyst under the conditions investigated.

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