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An Ru-based catalytic membrane reactor for dry reforming of methane—its catalytic performance compared with tubular packed bed reactors

Luca Paturzo [a], Fausto Gallucci [a], Angelo Basile [a,*], Giovanni Vitulli [b,1], Paolo Pertici [b,1]

[a] Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, via P. Bucci, cubo 17/C, I-87030 Rende (CS), Italy
[b] Centro di Studio per le Macromolecole Stereordinate ed Otticamente Attive, CNR-CSMSOA, c/o Dipartimento di Chimica e Chimica Industriale, University of Pisa, via Risorgimento 35, I-50126 Pisa, Italy

Abstract

The methane reforming with CO_2 seems to be a promising reaction system useful to reduce the greenhouse contribution of both gases into the atmosphere. On this basis, and considering the potentiality of this reaction system, the dry reforming reaction has been carried out in an Ru-based ceramic tubular membrane reactor, in which two Ru depositions have been performed using the co-condensation technique. Experimental results in terms of CH_4 and CO_2 conversion versus temperature during time are presented, as well as product selectivity and carbon deposition. These experiments have also been carried out using a traditional reactor. A comparison with literature data regarding dry reforming reaction is also provided. Experimental evidence points out a good catalyst activity for the methane dry reforming reaction, confirming the potentiality of a catalytic membrane applied to the reaction system.

Keywords: Catalytic membrane; Syngas; Dry reforming; Methane; Carbon dioxide

1. Introduction

Natural gas conversion studies have been growing in the last few years, due to the great amount of this methane-enriched fuel underground. In fact, natural gas production increased from $2.524 \times 10^{12}\,\mathrm{N\,m^3}$ in 1990 to $2.969 \times 10^{12}\,\mathrm{N\,m^3}$ in 1999 [1]. As a consequence, in the next future natural gas will be used both as energetic vector and as valuable raw material for several industrial productions, including synthesis gas manufacturing. Furthermore, the increasing effect of greenhouse gases should be monitored, with the purpose of reducing their emissions in the atmosphere.

Syngas (H_2 + CO) is used for ammonia/urea production and methanol synthesis; hydrogen is extensively used by the oil industry in hydro-treating and in hydro-cracking processes, and also for fuel cell applications. The annual global production and utilisation of hydrogen is about $5 \times 10^{11}\,\mathrm{N\,m^3}$ per year [2], so the interest in making this valuable gas is increasing nowadays. The main process performed for syngas production today is the steam reforming of methane [3], a highly endothermic reaction ($\Delta H^\circ_{298\,\mathrm{K}} = +206\,\mathrm{kJ/mol}$) which requires high

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[*] Corresponding author. Tel.: +39-0984-492011; fax: +39-0984-402103.
E-mail addresses: a.basile@itm.cnr.it (A. Basile), pervit@dcci.unipi.it (P. Pertici).
[1] Tel.: +39-051-918224; fax: +39-051-918260.

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temperatures and pressures for achieving high methane conversion. So, expensive, high temperature and pressure resisting materials are required for carrying out this reaction.

Another approach for syngas production could be the dry reforming of methane, which is a little bit more endothermic with respect to the steam reforming of methane, but it produces a gaseous mixture with a lower H_2/CO molar ratio:

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

Although this reaction is more endothermic than the methane steam reforming, an industrial application of the methane dry reforming could allow to reduce the amount of greenhouse gases present in the atmosphere. In fact, the disadvantage due to the reaction cost (in terms of energy input as well as the cost of materials) could be balanced by the benefit deriving from the CO_2 consumption, with a consequent lowering of this greenhouse gas in the atmosphere.

This reaction is becoming more interesting during time: different kinds of catalyst were used, such as Ni, Ru, Rh, Pd, and Pt based [4–9]. However, as already stressed, the endothermic character of this reaction system needs an energy input.

One important limitation for making the dry reforming of methane a commercially viable reaction using traditional reactors (TRs) is due to thermodynamics, which limits reactants conversion. Nevertheless, methane (and carbon dioxide) conversion might be increased if both products of the reaction (or preferentially only one of them: hydrogen) could be selectively removed from the reaction system.

A membrane reactor (MR) is an engineering device that offers the possibility to do this, achieving either higher methane conversion than a traditional process at a fixed temperature, or the same methane conversion but at lower temperature with the consequent energy saving. In fact, it combines the separation properties of membranes with the typical characteristics of catalytic reactions [10–15]: by selectively removing hydrogen from the reaction mixture, the conversion of CH_4 was increased for steam reforming of CH_4 [16–18] and for dry reforming of CH_4 [19–21].

In the present work, an experimental plant has been set to perform the reaction of dry reforming of methane to produce syngas. This reaction was carried out at first in a TR, and subsequently in a catalytic tubular MR. The tubular membrane used for this purpose is a composite catalytic Ru-based membrane, consisting of a mesoporous commercial ceramic tube in which an internal two-layers deposit of Ru nanoparticles has been realised. More in details, this work focuses on the effect of the catalytic tubular composite Ru-based membrane, not packed with conventional catalyst, and on the behaviour of the reaction system in terms of reactants conversion and products selectivity. The MR performance has been compared with experimental results obtained by using a traditional tubular reactor packed with two kinds of commercial Ru catalyst (5 and 0.5 wt.% of Ru, respectively). The experimental comparison regards methane and carbon dioxide conversion, as well as hydrogen and carbon monoxide selectivity at different temperatures for both reactors used. Carbon deposition effect on the reaction behaviour has also been focused. A comparison with literature data is also furnished.

2. Description of the experimental apparatus

2.1. Membrane preparation

The starting tubular support was an alumina ceramic tube (by SCT, France) vitrified at the ends. Two Ru layers have been consecutively deposited on the internal surface by decomposition at room temperature under hydrogen (atmospheric pressure) of the complex Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene), hereinafter signed as *Ru-complex*, following a synthetic procedure previously used to deposit ruthenium nanoparticles on solid supports [22]. More in details, the starting support has been filled with the yellow solution resulting from the dissolution of 0.1 g of *Ru-complex* in 10 ml of dry mesitylene, and the support was plugged at both ends. The system was placed in a Schlenk tube (a glass box) equipped with a side tape; in this box a pressure of 0.1 mm Hg was realised, and hydrogen was fed until the atmospheric pressure was reached. The box was left to rotate for one night. Then, the resulting uncoloured solution was removed and the ruthenium deposited on the internal side of the membrane was washed with a solution of pentane and dried under an Ar stream. Similarly the second layer of Ru was deposited starting from 0.072 g of *Ru-complex*. Using pentane as solvent, the diffusion of the solution from the internal (lumen) to the external side of the membrane was observed, with a resulting external deposition of the metal on the tubular support. The same procedure has been carried out for realising the second deposit of Ru.

2.2. Membrane reactor and traditional reactor

MR consists of a stainless steel module containing the two-layers Ru membrane. Geometrical dimensions of the ceramic support are length = 25 cm, i.d. = 0.67 cm, o.d. = 1.02 cm. Two consecutive depositions have been carried out: the first Ru layer consists of 32 mg of catalytic material, while the second one consists of 23 mg of the metal. TR is a stainless steel tube having the same geometrical dimensions of the ceramic membrane (i.e. length = 25 cm, i.d. = 0.67 cm). It was packed with 4 g of a commercial Ru/Al_2O_3 catalyst, in particular, a 0.5% Ru/Al_2O_3 catalyst (by Engelhard) and a 5% Ru/Al_2O_3 catalyst (by Johnson-Matthey) have been tested.

2.3. Experimental set up

The membrane was placed inside a stainless steel module and sealed by means of graphite o-rings. The catalytic membrane was pre-treated using H_2 for 3 h under a flow rate of 25 ml/min at 500 °C. The experimental plant used is depicted in Fig. 1. The experimental conditions were the following: $p = 1.2$ bar (abs), $CH_4/CO_2 = 1/1$, $CH_{4,FEED} = 70$ ml/min. The reaction temperature range was 350–500 °C. Two thermocouples were located at both ends of the module and used to keep the temperature constant at the set point value along the reactor. The reactor was heated using a heating tape connected to a temperature controller (set point). Permeate stream pressure (shell side) for MR was held continually at 1.01 bar. No sweep gas was used. 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.

CH_4 and CO_2 conversions, as well as H_2 and CO selectivities, were calculated considering the following formulas:

$$CH_4\ \text{conversion}\ (\%) = \frac{CH_{4,FEED} - CH_{4,OUT}}{CH_{4,FEED}} \times 100$$

$$CO_2\ \text{conversion}\ (\%) = \frac{CO_{2,FEED} - CO_{2,OUT}}{CO_{2,FEED}} \times 100$$

$$H_2\ \text{selectivity}\ (\%) = \frac{H_{2,OUT}}{H_{2,OUT} + CO_{OUT} + CO_{2,OUT} + CH_{4,OUT}} \times 100$$

$$CO\ \text{selectivity}\ (\%) = \frac{CO_{OUT}}{CO_{OUT} + H_{2,OUT} + CO_{2,OUT} + CH_{4,OUT}} \times 100$$

Both permeate and retentate streams have been considered for MR, while only one outlet stream was considered for TR. In other words, TR has only one inlet stream (feed) and one outlet stream (products), while MR has one inlet stream (feed) and two outlet streams

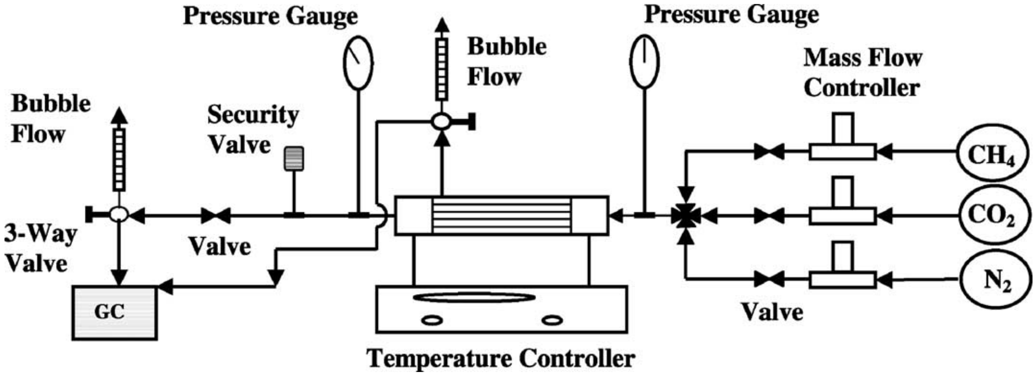


Fig. 1. Scheme of the laboratory plant.

(permeate and retentate). With regard to MR, the two outlet streams were separately analysed in terms of both flow rate and composition: this permitted to calculate the total outlet flow rate of each species, and so the terms in the formulas above.

Permeances of pure gases (hydrogen and nitrogen) have been performed with the same experimental apparatus. All gases used were >99.995% pure. Outlet gas streams were dried before sending to gas chromatograph. The atom mass balances generally closed to within ±8% in all experimental data reported in this work. Carbon deposition on the catalyst surface has been evaluated by feeding pure oxygen (110 ml/min) at 500 °C and thereby analysing the outlet gaseous mixture of the reactors during time with the gas chromatograph. For MR, the shell side was kept closed during the carbon deposition determination. Data on the gaseous C-containing species (mainly CO_2) were collected and processed with the trapezoid method of integration, in order to calculate the total amount of carbon in the outlet stream.

3. Results and discussion

3.1. Permeation tests

The Ru-based membrane was tested in terms of permeation using H_2 and N_2 gases. The main results are reported in Table 1, which shows permeances of the mentioned gases at 25 and 500 °C versus the average pressure $[=(p_{\text{lumen}} + p_{\text{shell}})/2]$. The maximum selectivity $\alpha(H_2/N_2)$ was 2.8 at 500 °C and $p_{\text{av}} = 0.02$ bar (rel), versus an ideal separation factor of 3.74 (Knudsen mechanism). The behaviour of pure gas permeances was found to be linearly increasing with increasing of average pressure, at a fixed temperature. Furthermore, permeation tests demonstrated that the permeation mechanism is due to combined effects of both Knudsen and Poiseuille mechanisms. In fact, the ideal separation factor (i.e. Knudsen mechanism) of H_2/N_2 is 3.74, higher than the experimental results of this work (2.3–2.8). Moreover, when Knudsen mechanism is present alone, gas permeance decreases if temperature increases; despite this, gas permeances increase if temperature increases when Poiseuille mechanism is present alone. The combination of the two cited effects is such that both H_2 and N_2 permeances increase with increasing temperature in our experimental conditions. Nevertheless, the second Ru deposition seems to poorly improve the membrane selectivity. It should be considered that the first Ru deposition was performed on the ceramic tube, while the second deposition was carried out on a heterogeneous surface consisting of uncovered ceramic pores plus partially or totally covered pores. In this condition, the total amount of deposited Ru increased, but probably this increasing was not proportional to the increase in the catalytic surface of the metal. Anyway, the second Ru deposition should reduce the pore size, increasing so the gas velocity throughout the membrane with respect to the starting ceramic material.

Table 1
Permeation results for the Ru-based membrane: comparison between the first and the second Ru layer membrane in terms of H_2 and N_2 permeance versus average pressure[a]

	First Ru layer	Second Ru layer
$T = 25\,^{\circ}C$		
P_{H_2}	2.53	0.079
P_{N_2}	1.05	0.034
$\alpha(H_2/N_2)$	2.4	2.3
p_{av}	0.02	0.76
$T = 500\,^{\circ}C$		
P_{H_2}	3.49	1.8
P_{N_2}	1.25	1
$\alpha(H_2/N_2)$	2.8	2.4
p_{av}	0.02	0.05

[a] P: pure gas permeance (10^{-5} mol/(s m^2 Pa)); α: H_2/N_2 pure gas selectivity $= P_{H_2}/P_{N_2}$ (dimensionless); p_{av}: average pressure $= (p_{\text{lumen}} + p_{\text{shell}})/2$ (bar, rel).

3.2. Reaction tests

The dry reforming of methane was successfully performed in both MR and TR. Fig. 2 shows the time-dependence of both CH_4 and CO_2 conversions at different temperatures for the MR: it should be observed that their behaviour seems to be quite constant from 20 min of reaction tests until the end (at 83 min). The absolute maximum CH_4 conversion (i.e. considering all of the 83 min of reaction) of 21% has been achieved at 500 °C and 42 min of reaction tests, while the absolute maximum CO_2 conversion of 23% has been achieved at 400 and 450 °C after 11 min of reaction tests. Vice versa, considering the average values

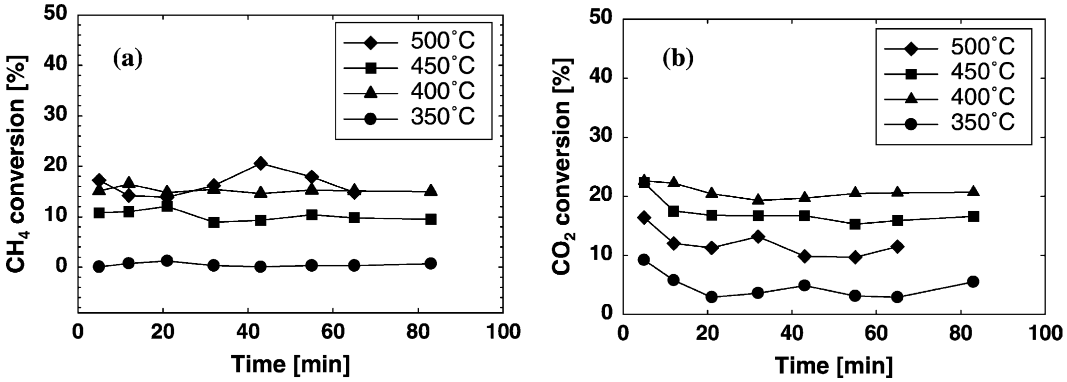


Fig. 2. CH_4 and CO_2 conversion versus time, at different temperature values, for the Ru-based MR, $CH_4/CO_2 = 1/1$, $CH_{4,FEED} = 70$ ml/min, $p = 1.2$ bar (abs), reaction time = 83 min: (a) CH_4 conversion; (b) CO_2 conversion.

regarding the period from 20 min until the end of the reaction tests, the maximum CH_4 conversion of 16.4% was achieved at 500 °C, while the maximum CO_2 conversion of 20.8% was obtained at 400 °C. Moreover, in the same time range 20–83 min, the maximum selectivity was achieved at 450 °C: 1.52% for CO versus 0.46% for H_2. CO selectivity was always higher than H_2 selectivity, and this aspect can be explained considering that CO is also involved as a product in other chemical reactions with respect to H_2:

$CO_2 + C = 2CO$ (Boudouard reaction)

$CO_2 + H_2 = CO + H_2O$

(reverse water gas shift reaction)

$CH_4 + H_2O = CO + 3H_2$

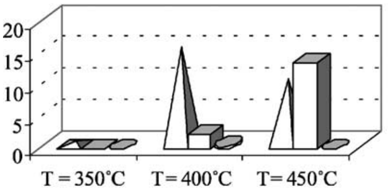
(steam reforming reaction)

A similar evidence has been found by Galuszka et al. [20], which studied the dry reforming reaction over a Pd-based catalyst packed in both a TR and an MR at 550–600 °C. In fact, at 550 °C they found a H_2/CO mole ratio of 0.85 in the outlet stream of MR. Comparing these results with our re-arranged experimental data mentioned above, at 450 °C we found a H_2/CO mole ratio of 0.30 in the outlet stream of MR, not directly comparable with results of Galuszka et al. [20] due to the different temperature. Anyway, this confirms the CO production higher than the H_2 one.

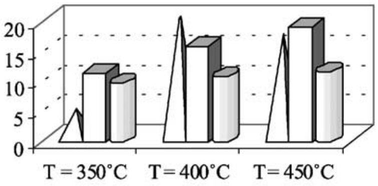
Let us still consider Fig. 2. CO_2 conversion was always higher than CH_4 conversion, except for $T =$ 500 °C, when CO_2 conversion was 12% against 16.4% for CH_4 conversion. Probably, CH_4 is involved in other chemical reactions which are favoured at high temperature, such as the steam reforming reaction, so the conversion of this species increased.

A comparison between MR and TR is given in Fig. 3, which shows CH_4 and CO_2 conversions (Fig. 3(a) and (b)), as well as H_2 and CO selectivities (Fig. 3(c) and (d)), at three different temperatures. For TR packed with both types of Ru catalyst, all of the mentioned parameters increase with increasing temperature from 350 to 450 °C. For example, CO_2 conversion increases from 11.23% at 350 °C to 19% at 450 °C in the TR packed with the 5% Ru catalyst. As we expected, the 0.5% Ru catalyst packed in TR gives lower CO_2 (and CH_4) conversion than the TR packed with the previous catalyst, due to the lower Ru content. For example, CO_2 conversion increases from 9.71% at 350 °C to 11.7% at 450 °C. The maximum CH_4 and CO_2 conversions have been obtained in MR at 400 °C: 15.2 and 20.8%, respectively. For MR, it is not immediate to observe an increasing trend of reactants conversion versus temperature, probably due to the fact that the temperature also affects gas permeation. This experimental evidence can be explained considering two opposite effects on methane conversion. From one hand, the preferential permeation of products as well as the endothermicity of the overall reaction system should give an increase in reactant conversions versus temperature with respect to a conventional reactor; on the other hand, a *quasi*-Knudsen permeation is negatively effected from the increas-

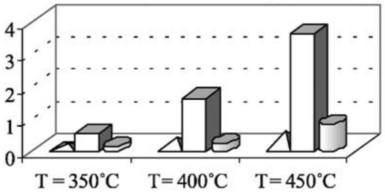
(a) CH_4 conversion [%]



(b) CO_2 conversion [%]



(c) H_2 selectivity [%]



(d) CO selectivity [%]

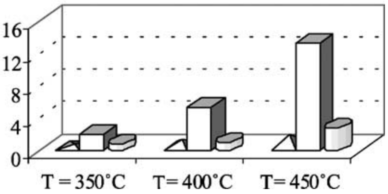


Fig. 3. Comparison between MR and TR in terms of reactant conversions, as well as products selectivity, versus temperature. $CH_4/CO_2 = 1/1$, $CH_{4,\mathrm{FEED}} = 70$ ml/min, $p = 1.2$ bar abs, reaction time = 83 min: (a) CH_4 conversion; (b) CO_2 conversion; (c) H_2 selectivity; (d) CO selectivity. Pyramid: MR (Ru); Prism: TR (5% Ru); Cylinder: TR (0.5% Ru).

ing temperature. So the benefit of the catalytic effect of the Ru membrane on the reaction system is not immediately predictable. It seems then that the use of MR systems requires very careful control of the characteristics of the membrane and catalyst as well as the reaction conditions in order to get benefit from the use of such a system.

Finally, it has been observed that CO selectivity is always higher than H_2 selectivity also in the TR packed with both types of catalyst.

The total Ru amount deposited inside MR is 55 mg, while the Ru content in TR is 200 mg if the 5% Ru catalyst is considered, and 20 mg if the 0.5% Ru catalyst is packed. In this situation, defining the time factor as the catalyst (Ru) amount per unit of CO_2 feed rate (70 ml/min), time factor is $7.86\times10^{-4}\ g_{\mathrm{Ru}}\ \mathrm{min/ml}_{CO_2}$ for MR, $2.86\times10^{-3}\ g_{\mathrm{Ru}}\ \mathrm{min/ml}_{CO_2}$ for TR containing the 5% Ru catalyst, and $2.86 \times 10^{-4}\ g_{\mathrm{Ru}}\ \mathrm{min/ml}_{CO_2}$ for TR packed with the 0.5% Ru catalyst. A comparison of CH_4 and CO_2 conversion per unit of time factor, at 400 °C, is reported in Table 2. It is observable that both CH_4 and CO_2 conversion decrease when changing from MR to TR (5% Ru) and then to TR (0.5% Ru). Considering the CH_4 conversion per unit of time factor, it is shown that MR gives the best performance, while, with regard to the CO_2 conversion per unit of time factor, MR performance is lower than TR (0.5% Ru). These results confirm the good catalytic activity of the Ru deposited inside the ceramic membrane, since a fine dispersion of the metal acts in the sense of increasing the activity of the catalytic surface. Results related to the CO_2 conversion per unit of time factor demonstrate that a major research effort is needed in the Ru deposition technique and/or in the treatment of the Ru deposit for improving the catalytic performance; in fact, the main goal should be the highest reactivity of the catalytic metal towards both reactants of the reaction system. Considering again Table 2, it should be observed that the gap between CH_4 and CO_2 conversion in MR is 5.6%, while this difference is about 13.7% for TR (5% Ru) and about 10.5% for TR (0.5% Ru). This experimental evidence might be due to the different catalyst distribution present in MR and TRs. Even if detection of the Ru dispersion was not done to evaluate active surface of catalyst, such a difference could lead to make unfavourable the chemical side-reactions involving CO_2. This justifies the lower gap between CH_4 and CO_2 conversion in MR. These aspects can be viewed as an improvement of the catalyst activity in terms of reactants conversion, due to the mentioned Ru dispersion technique over the ceramic support.

3.3. Carbon deposition

Among the noble metals, Ru catalyst is demonstrated to exhibit the highest catalytic activity towards the CO_2 reforming reaction [9]. Although thermodynamics predicts the formation of carbon when operating with carbon dioxide and methane alone,

Table 2
Comparison between MR and TR in terms of CH_4 and CO_2 conversion per unit of time factor, $T = 400\,°C$, $CH_4/CO_{2,FEED} = 1/1$, $CO_{2,FEED} = 70$ ml/min, $p = 1.2$ bar (abs) (the term in the brackets refers to the Ru percentage in the catalyst pellets packed in the TR)

	Type of reactor		
	MR	TR (5% Ru)	TR (0.5% Ru)
Ru weight (mg)	55	200	20
Time factor (g_{Ru} min/ml_{CO_2})	7.86×10^{-4}	2.86×10^{-3}	2.86×10^{-4}
CH_4 conversion (%)	15.23	2.17	0.35
CH_4 conversion/time factor ((g_{Ru} min/ml_{CO_2})$^{-1}$)	1.9×10^4	7.6×10^2	1.2×10^3
CO_2 conversion (%)	20.8	15.9	10.8
CO_2 conversion/time factor ((g_{Ru} min/ml_{CO_2})$^{-1}$)	2.6×10^4	5.6×10^3	3.8×10^4

it is possible to depress this phenomenon using Ru. Table 3 shows the amount of carbon deposition in both MR and TR after 83 min of reaction tests. Furthermore, long-term experiments (1560 min, not reported in Table 3) using TR packed with the 5% Ru catalyst have demonstrated a constant trend of reactants conversion and products selectivity versus time: in fact, at 500 °C, CH_4 and CO_2 conversions, and H_2 and CO selectivities, maintained their value around 18, 29, 16 and 40%, respectively, with a total carbon deposition of 4.2×10^{-3} g, near the 2.2×10^{-3} g of deposited carbon after 83 min experiments. These results confirm the potentiality of Ru as the catalyst which gives depression effect for the carbon deposition in this kind of reaction. Considering that MR contains 55 mg of Ru, while TR contains 200 or 20 mg of the metal (depending on the Ru percentage in the catalyst pellets, see Table 3), it is observed that MR gives the highest carbon deposition per unit of Ru weight. In fact, considering the ratio between the deposited carbon (expressed in grams, from Table 2) and the Ru weight (expressed in grams) at 450 °C, it is obtained a ratio of 0.5 g_C/g_{Ru} for MR, 0.02 g_C/g_{Ru} for TR (5% Ru), and 0.06 g_C/g_{Ru} for TR (0.5% Ru). Moreover, Fig. 4 shows the carbon deposit versus methane conversion for both TR and MR, at 400 and 450 °C. Both reactors show that carbon deposit increases with increasing the methane conversion. For example, when methane conversion increases from 2.17% (400 °C) to 13.57% (450 °C) in the TR (5% Ru), the carbon deposit increases from 1.2×10^{-3} to 3.8×10^{-3} g. Nevertheless, when methane conversion increases from 10.23% (450 °C) to 15.23% (400 °C) in the MR, the carbon deposit increases from 2.59×10^{-2} to 2.68×10^{-2} g. In order to realise a good catalytic membrane for the dry reforming reaction, these aspects suggest that it is not enough to finely deposit in a simple way the catalytic metal, but it should be also monitored the structure of the deposited layer. In fact, it is well known that a commercial catalyst results from a very complex know-how, which concerns the catalyst composition, structure, active surface, etc. So, a generic deposition is not enough for producing a good catalyst. As a consequence, a catalytic membrane

Table 3
Deposited carbon versus temperature for TR and MR, reaction time = 83 min

T (°C)	MR carbon (g)	TR (5% Ru) carbon (g)	TR (0.5% Ru) carbon (g)
350	–	8.5×10^{-4}	2.5×10^{-3}
400	2.68×10^{-2}	1.2×10^{-3}	–
450	2.59×10^{-2}	3.8×10^{-3}	1.2×10^{-3}
500	2.57×10^{-2}	2.2×10^{-3}	1.0×10^{-3}

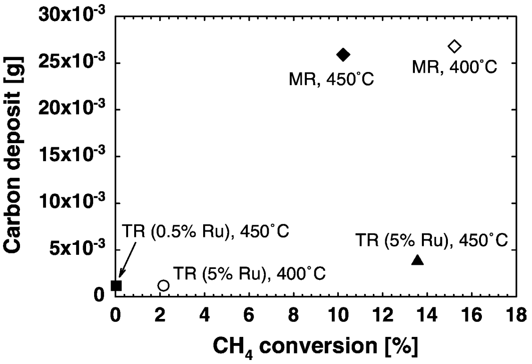


Fig. 4. Carbon deposit versus CH_4 conversion for both TR and MR. $CH_4/CO_2 = 1/1$, $CH_{4,FEED} = 70$ ml/min, $p = 1.2$ bar abs, $T = 400$ and 450 °C.

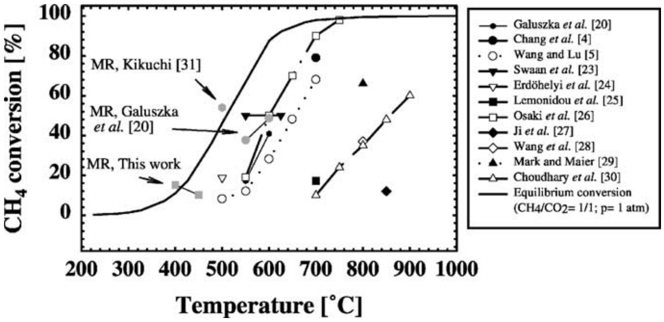


Fig. 5. Dry reforming of methane: comparison with literature data in terms of CH_4 conversion versus temperature.

should be realised by making special efforts towards the active surface of the metal deposited on the ceramic support.

3.4. Comparison with literature data for the dry reforming of methane

A comparison among results reported in this work and literature data in terms of CH_4 and CO_2 conversion versus temperature is offered in Figs. 5 and 6. In particular, experimental results of several authors have been reported, as well as the thermodynamic equilibrium curve. All experimental data reported below the equilibrium curve, in the legend, are referred to TRs, while the experimental data reported above the equilibrium curve, in the legend, are referred to MRs. Although it should be considered that both CH_4 and CO_2 conversions depend on the operating conditions (feed flow rate, feed ratio, temperature, pressure, catalyst weight), it is expected that, generally, conversion in MRs overcomes the one related to TRs. However, the performance of an MR depends on a suitable matching between the membrane properties and the operating conditions adopted. In fact, with regard to the dry reforming reaction, at 500 °C the highest methane conversion has been reached by Kikuchi [24] using an MR (Fig. 5), while at 550 °C the highest methane conversion has been reached by Swaan et al. [23] using a TR. Kikuchi [24] found a CH_4 conversion of 52% at 500 °C, CH_4/CO_2 feed ratio of 1/1, time factor of $4.48 \times 10^3\,g_{cat}\,min\,mol^{-1}$ using his MR, versus 47% predicted from thermodynamic equilibrium. This confirms that in some experimental conditions conversion in MRs can overcome the one related to TRs. Fig. 6 shows that CO_2 conversion is generally below the thermodynamic equilibrium curve, except for 400 °C where CO_2 conversion is about 20% (this work) versus about 15% predicted from equilibrium. Also this evidence demonstrates that the reaction behaviour depends on a suitable matching between the membrane properties and the operating conditions adopted.

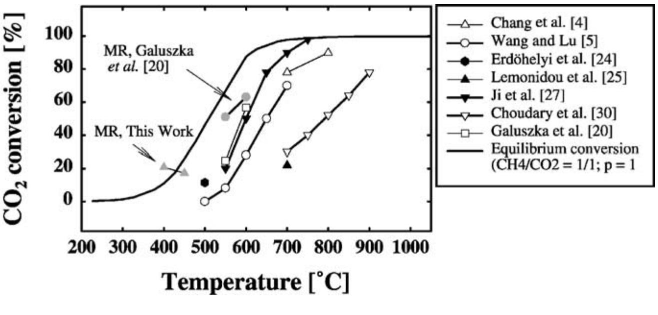


Fig. 6. Dry reforming of methane: comparison with literature data in terms of CO_2 conversion versus temperature.

4. Conclusions

Methane and carbon dioxide conversion into syngas via dry reforming reaction has been studied in a catalytic MR containing a two-layers Ru membrane, in which Ru was deposited in a very simple way by decomposition under hydrogen of the particularly reactive complex Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene), *Ru-complex*. Gas permeation tests showed that the H_2/N_2 selectivity of the composite membrane is lower than the Knudsen one. The consecutive Ru deposition inside the commercial ceramic support seems to affect reactants conversion and products selectivity, at each temperature investigated. The conclusions of this work can be summarised considering that a special and deeper investigation is needed, in order to tune the structure of the Ru deposited inside the tubular ceramic membrane, and realising a very active metal layer for the reaction of interest in the direction of both increasing reactants conversion and decreasing carbon deposition during the reaction. The catalytic metal should depress the carbon formation in spite of the thermodynamic potential. Ru could act in this way, but a special effort has to be done for make an active surface of the metal which reduces this deposition when it covers a porous commercial membrane. The dry reforming of methane seems to be a feasible technology, and membrane systems could penetrate this target in the future, not only from a separation viewpoint, but also from an integrated reaction–separation device application.

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