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Membrane reactor for the production of hydrogen and higher hydrocarbons from methane over Ru/Al_2O_3 catalyst

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Abstract

It is known that higher alkanes can be produced from methane over Ru, Pt or Co supported on silica by using a two-step reaction sequence. In this investigation, a dense Pd/Ag flat membrane reactor (FMR) and a traditional reactor (TR) are analysed referring to experimental data. The two-step reaction over Ru-based catalyst was chosen as a model reaction to be investigated. The experiments carried out in this study confirm that, using a membrane reactor, it is possible to obtain consumed methane values greater than the ones obtained in a TR for the first step operating at the same experimental conditions. A direct consequence should be an increase of the yield in higher hydrocarbons. In addition, this work shows that the membrane reactor performances can be improved by properly tuning the operating conditions. Experimental results of this work are compared with both experimental data obtained in a previous work using a dense Pd/Ag tubular membrane reactor (TMR) and experimental data reported in the literature.

Keywords: Membrane reactor; Hydrocarbons; Catalyst

1. Introduction

The most economical use of natural gas is to convert it into more valuable liquid chemical products. During the past few years, extensive efforts have been made to investigate both direct and indirect conversions of methane. Direct conversion of methane into higher hydrocarbons is a reaction with a thermodynamic limit: it can only take place at temperatures above 1200 K [1]; at this temperature graphite carbon is more stable than hydrocarbons such as ethane.

In order to increase catalyst lifetime and reaction selectivity, low temperatures would be needed. Some authors have demonstrated that methane conversion into higher hydrocarbons could occur at low temperature if methane is activated. The overall process can be viewed as a two-step sequence: methane adsorption and subsequent decomposition on the catalyst surface (at higher temperature) and subsequent hydrogenation (at constant or lower temperature).

The reaction can be carried out in two different ways: isothermal or non-isothermal one. In the last case, methane deposition at high temperature is followed by hydrogenation at low temperature. For what concerns the isothermal way, Belgued et al. [2] produced lighter hydrocarbons (from C_2 to C_7, saturated form) from methane at a constant temperature of 250 °C and atmospheric pressure over a Pt catalyst. With regard to the non-isothermal way, Koerst et al. [3] found that Ru- and Co-based catalyst are more selective for the formation of higher hydrocarbons with respect to Rh,- Ir,- Pt- and Ni-based catalyst; the same authors confirm that alumina support gives better results than silica support.

The objective of this investigation is to apply a palladium membrane reactor concept to this reaction system. 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 with respect to a traditional reactor (TR) since a membrane reactor combines the separation properties of membranes with the typical characteristics of catalytic reactions [4–11]. The two most common membrane geometries may be in the form of a tube or as a flat plate. This kind of reactor could improve the overall methane conversion at a given temperature; on the other hand, it is possible to obtain the same amount of decomposed methane at lower temperature with respect to a TR, so the total yield in lighter hydrocarbons increases, as reported by Garnier et al. [1]. Early investigations of the application of membrane reactors to this reaction have demonstrated higher conversions with respect to a conventional fixed-bed reactor [1]. Moreover, dense Pd or Pd/Ag membranes exhibit excellent selectivity

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towards hydrogen, so pure hydrogen recovering could also be obtained.

The aim of this work is to increase the production of lighter hydrocarbons with respect to a traditional system using a dense Pd/Ag (25% (w/w) Ag) flat membrane reactor (FMR). Experimental results are compared with the results obtained using a TR and with some literature data.

2. Experimental

A scheme of the laboratory plant was previously described elsewhere [12]. The reactor feed is regulated by mass-flow controllers, while outlet stream flow rates are measured by means of bubble flow-meters; gas compositions were determined by gas chromatograph (Perkin-Elmer Autosystem GC) using a TCD and a metal packed column, type Porapak-Q 50/80, with Ar as carrier gas at a flow rate of 8 ml/min. For what concerns the oven temperature, the following conditions were adopted: 45 °C for the first step, and then 100 °C in the second step. Moreover, in order to determine gas composition of both permeate and retentate streams simultaneously, another gas chromatograph was used (Carlo Erba 4200), adopting a TCD and a metal packed column, type Carboxen™1000, $T_{oven} = 45\,^{\circ}\mathrm{C}$, carrier flow rate (Ar) = 25 ml/min: in particular, this gas chromatograph was used to determine permeate composition.

The heating system was a thermolyne heating tape (Sigma-Aldrich) connected to an automatic PID controller (EC 4-133, Nuova-Thermics). The TR contained a multiple (4 points) thermocouple for temperature measurements. Flat membrane reactor (FMR) was equipped with a one-point thermocouple placed in contact to the external side of the flat stainless steel module.

TR consists of a stainless steel tube, length = 25 cm, i.d. = 0.67 cm, wall thickness = 1.25 cm. FMR consists of a flat stainless steel module containing a flat sample of a Pd/Ag (25% (w/w) Ag) membrane, membrane thickness = 50×10^{-6} m, geometrical size: $l = 20$ mm, $h = 35$ mm. Operating constrictions for the membrane: temperature up to 400 °C and transmembrane pressure difference up to 2 atm.

For both kinds of reactor the same experimental conditions were used. In particular, they were packed with 5% Ru/Al_2O_3 (irregular cylindrical pellets, $d_{av} = 1.2$ mm), catalyst weight = 1.0 g, furnished by Johnson-Matthey.

In the first step of the reaction, the analysis was developed considering both reactors with a feed stream ratio $CH_4/N_2 = 1/5$, methane feed stream = 10^{-3} mol/min, operating in a co-current flow configuration, N_2 sweep = 1.15×10^{-2} mol/min (the last two conditions are valid only for FMR). Temperature was in the range between 150 and 400 °C. Pressure values were close to the atmospheric condition. Exposure time in the first step was ranged between 1.5 and 3 min.

Pure hydrogen (2.43×10^{-3} mol/min) was fed in the second step for both reactors. Moreover in order to avoid hydrogen loss, the shell side of the membrane reactor was closed after filling it with hydrogen. The procedure adopted was isothermal. After each run, the catalyst was treated with pure hydrogen flow (1.5×10^{-3} mol/min) at 400 °C for 2 h in order to have total desorption of each species from the catalyst surface; further, a nitrogen flow followed to eliminate hydrogen gas from the catalyst surface. Fig. 1 offers a schematic summary of the complete procedure followed to determine each experimental point. The procedure described in this figure was performed three times for each experimental condition. In the same figure, details about the membrane reactor configuration for steps 1 and 2 are also shown. This procedure led to a good results reproducibility. Each gas was used with purity percentage >99.995%.

The following analytical definitions were used:

$$\text{consumed } CH_4\% = \frac{CH_{4in} - CH_{4out}}{CH_{4in}} \times 100\ [\text{dimensionless}]$$

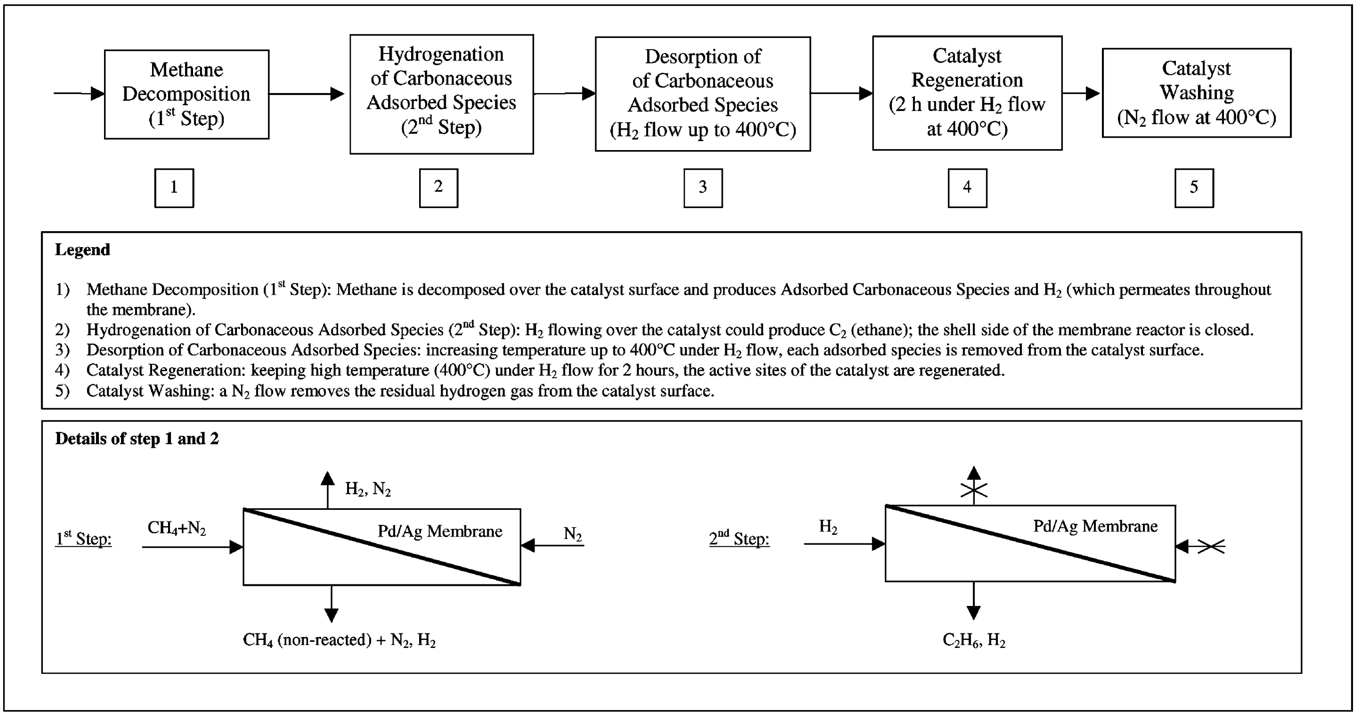
$$H_2 \text{ produced } \% = \frac{H_{2out}}{CH_{4in}} \times 100\ [\text{dimensionless}]$$

$$C_2 \text{ yield} = \frac{\chi_{C_2} V_{loop}}{22.4}\ [\text{mol}]$$

where χ_{C_2} is the molar fraction of C_2 in the gas chromatograph sampling loop of volume V_{loop}.

The consumed CH_4 refers to the methane disappeared from the reaction system during the first step of the reaction. This amount of methane is adsorbed on the catalyst surface, and a portion of it reacts in the second step in order to produce higher hydrocarbons.

Pd/Ag flat membrane was produced by a lamination technique in E.N.E.A. laboratories (Frascati, Italy); the starting material was a Pd/Ag (25% (w/w) Ag) commercial foil (127 μm thickness) purchased from Metalli Preziosi (Milano, Italy); details have been presented by Tosti et al. [13]. The apparent activation energy from experimental tests concerning hydrogen permeation is $E_a = 10.3$ kJ/mol, while the pre-exponential factor is $Pe_0 = 7.63 \times 10^{-8}\ \mathrm{mol\,m/(s\,m^2\,Pa^{0.5})}$. These values are exactly the same as the membrane used in the tubular membrane reactor (TMR) [12]. Conceptually, from an engineering viewpoint, a tubular configuration for the membrane reactor could give better performance than the flat one due to the fluid-dynamic conditions. However, in laboratory-scale studies, the tubular membrane is more difficult to incorporate into a stainless steel module than a flat membrane. Moreover, the tubular membrane gives tight problems for assembling the membrane reactor module, due to the fact that it is welded to stainless steel supports at the ends: these are weak points for our membrane. On the other hand the flat membrane gives no problems for its assembling in a flat module, although it offers a lower permeating area for hydrogen with respect to a tubular membrane having the same reaction volume. In this paper, the flat Pd/Ag membrane was recovered from the tubular membrane after its cracking due to the thermal stress occurred during reaction tests.



Legend

1) Methane Decomposition (1st Step): Methane is decomposed over the catalyst surface and produces Adsorbed Carbonaceous Species and H_2 (which permeates throughout the membrane).
2) Hydrogenation of Carbonaceous Adsorbed Species (2nd Step): H_2 flowing over the catalyst could produce C_2 (ethane); the shell side of the membrane reactor is closed.
3) Desorption of Carbonaceous Adsorbed Species: increasing temperature up to 400°C under H_2 flow, each adsorbed species is removed from the catalyst surface.
4) Catalyst Regeneration: keeping high temperature (400°C) under H_2 flow for 2 hours, the active sites of the catalyst are regenerated.
5) Catalyst Washing: a N_2 flow removes the residual hydrogen gas from the catalyst surface.

Fig. 1. Scheme of the complete procedure followed to determine each experimental point.

Nevertheless, the FMR gives interesting performances when compared to the TMR in terms of unit of membrane area.

3. Results and discussion

The first step of the reaction, i.e. methane decomposition with subsequent hydrogen production, is an activated process [3]. Fig. 2 shows the logarithm of hydrogen production versus 1000/*T* (*T* is the reaction temperature in K) related to the catalyst used in this work (5% (w/w) Ru) and the experimental results obtained by both Koerst et al. [3] and Basile et al. [12]. It can be observed that for all the curves, the linear behaviour confirms the statement of activated process with regard to the first step. Moreover, the following activated energy values were found: 26 kJ/mol for Koerst et al. [3], 30 kJ/mol for this work and 46 kJ/mol for Basile et al. [12].

Fig. 3 shows a comparison among TRs, TMR [12] and FMR in terms of consumed CH_4 in the first reaction step at 300 °C versus time. It can be observed that all the curves show a maximum at 2 min. However, at 3 min CH_4 consumed is about 15% for TMR [12] and about 9% for TR. In the presence of the maximum methane consumed, the

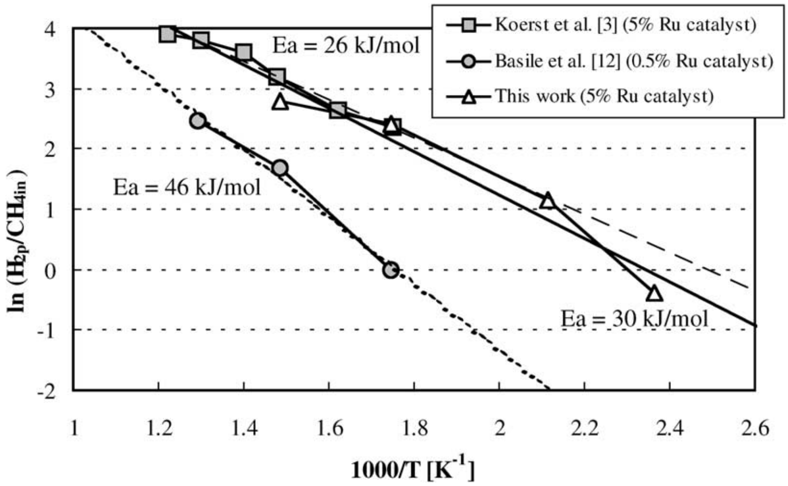


Fig. 2. Arrhenius plot for hydrogen production in the first step of the reaction for TRs.

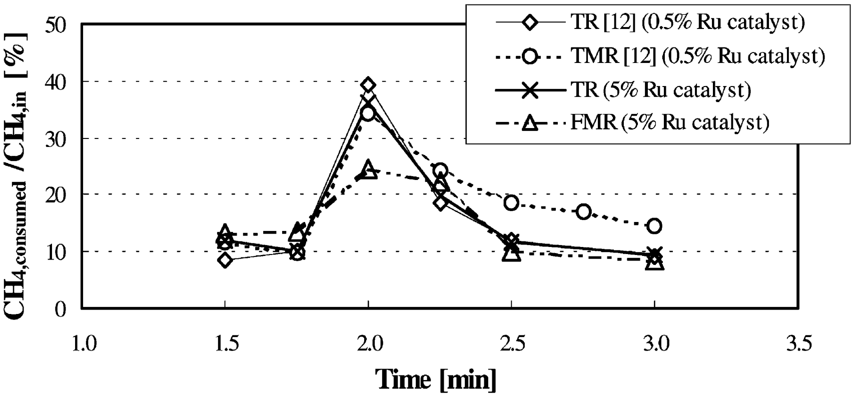


Fig. 3. Amount of consumed CH_4 in the first step versus time for TRs, TMR [12] and FMR, $T = 300\,^{\circ}C$, $P = 1\,bar$.

maximum experimental error occurred, that was about 15%, due probably to the non-steady character of the reaction system.

Fig. 4 shows a comparison among TRs, TMR [12] and FMR in terms of hydrogen production in the first step versus time. It is evident that experimental values for TR packed with 5% Ru catalyst are higher than the others, although the total amount of CH_4 consumed in this reactor seems to be almost the same as the one detected in the TR packed with 0.5% Ru catalyst. Probably, the major Ru percentage in the catalyst gives a lower hydrogenated carbonaceous species amount on the catalyst surface. On the other hand, if the total amount of consumed methane is almost constant, probably using a higher Ru percentage as the catalyst, the amount of the decomposed methane is higher than the one obtained at lower Ru percentage. For both TMR [12] and FMR, the amount of hydrogen production is the sum of permeated hydrogen with non-permeated hydrogen. Consider that the calculation of H_2 in the permeate stream for membrane reactors was carried out by using the experimental permeability of the Pd/Ag membrane, so the total H_2 production in the first step could be underestimated. This aspect is related to the fact that it was very difficult to detect H_2 in the permeate streams, as the hydrogen partial pressure was close to zero in the shell side.

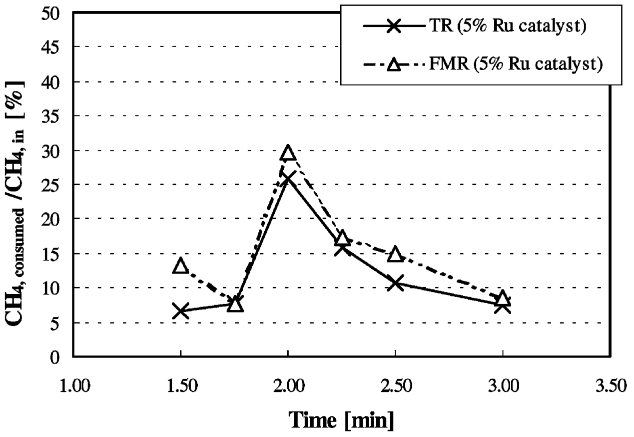


Fig. 5. Consumed methane in the first step versus time for TR and FMR packed with 5% Ru catalyst, $P = 1\,bar$, $T = 150\,^{\circ}C$.

Fig. 5 offers a comparison between TR and FMR in terms of consumed methane versus time at 150 °C; both reactors are packed with 5% Ru catalyst. It is evident that the two kinds of reactor exhibit a similar behaviour, showing a maximum at time = 2 min: at this time, consumed methane is about 30% for FMR, while it is 26% for TR.

Table 1 shows a comparison between TR and FMR at the two operating temperatures of reaction tests, 150 and 300 °C.

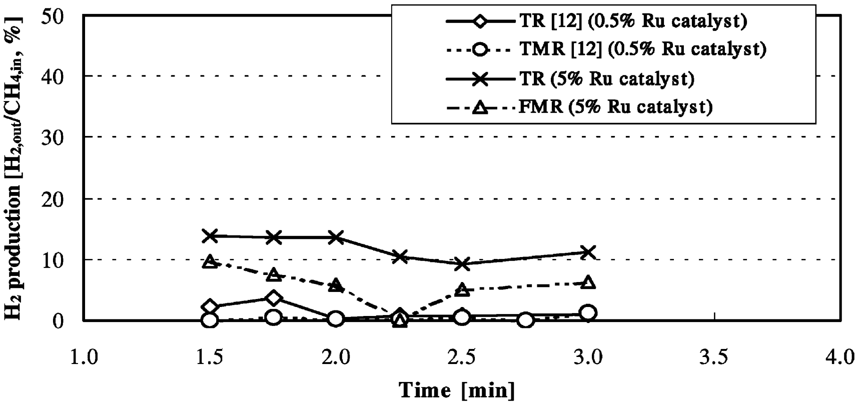


Fig. 4. Amount of H_2 produced in the first step versus time for TRs, TMR [12] and FMR, $T = 300\,^{\circ}C$, $P = 1\,bar$.

Table 1
Percentage of consumed methane for TR and FMR at 150 and 300 °C

	TR (300 °C)	TR (150 °C)	FMR (300 °C)	FMR (150 °C)
$CH_{4,cons}/CH_{4,in}$ (%)	16.50	12.72	16.52	15.39

This comparison is based on the integral average values of the percentage of consumed methane in the first step. These values were obtained using the trapezoid method applied to the areas below the experimental curves of Figs. 2 and 4, in the range 1.5–3 min. It is possible to observe that:

1. Consumed methane increases with increasing temperature, for TR: from 12.72 to 16.50%.
2. Consumed methane slightly increases with increasing temperature, for FMR: from 15.39 to 16.52%.
3. At 150 °C, consumed methane is higher for FMR and lower for TR: 12.72% (TR) and 15.39% (FMR).
4. At 300 °C, consumed methane keeps almost constant for both reactors: 16.50% (TR) and 16.52% (FMR).

According to the thermodynamics, the amount of consumed methane increases with increasing temperature for the same device. According to the Arrhenius law, the hydrogen permeability increases with increasing temperature, so in FMR there are two contributions to the consumed methane. A major increase in the consumed methane would be expected for FMR than TR operating at the same conditions. However, although these results confirm the potentiality of FMR with respect to TR at 150 °C (15.39% versus 12.72%), the expected improvement due to FMR was not observed at 300 °C (16.52% versus 16.50%). It seems that the fluid-dynamic character of the device used affects the behaviour of the reaction system much more than the effect of hydrogen removal due to the membrane, since TR is a tubular reactor while FMR is a flat one.

A suitable comparison would be performed using a tubular membrane reactor (TMR) operating at the same conditions as the TR. A comparison among the experimental results obtained in this work, Garnier et al. [1] and Basile et al. [12] in terms of consumed methane versus temperature is reported in Fig. 6. Operating conditions of Basile et al. [12] are as the same of the ones reported in this work, except to the percentage of the Ru catalyst. Operating conditions of Garnier et al. are: 1 g 5% Ru/Al_2O_3 catalyst, surface area $= 250\,m^2/g$, time = 3 min, diluted methane as feed ($Q_{tot} = 8.2$ ml/min, $CH_4/Ar = 0.2/8$), Ar sweep gas flow rate = 180 ml/min.

It is to be noted that these last conditions are quite different from the ones used in this work, so it is difficult to make a direct comparison between the membrane reactor performances. Nevertheless, at 300 °C the consumed methane was 15% for TMR [12], 9% for FMR, versus 63% for Garnier et al. [1]. In order to explain the difference between TMR [12] and FMR, although FMR is packed with 5% Ru catalyst while TMR [12] is packed with 0.5% Ru catalyst, it can be stressed that the membrane surface of FMR is seven times lower than the one of TMR [12]. In order to compare the same reactors in a uniform viewpoint, different representations can be done referring to:

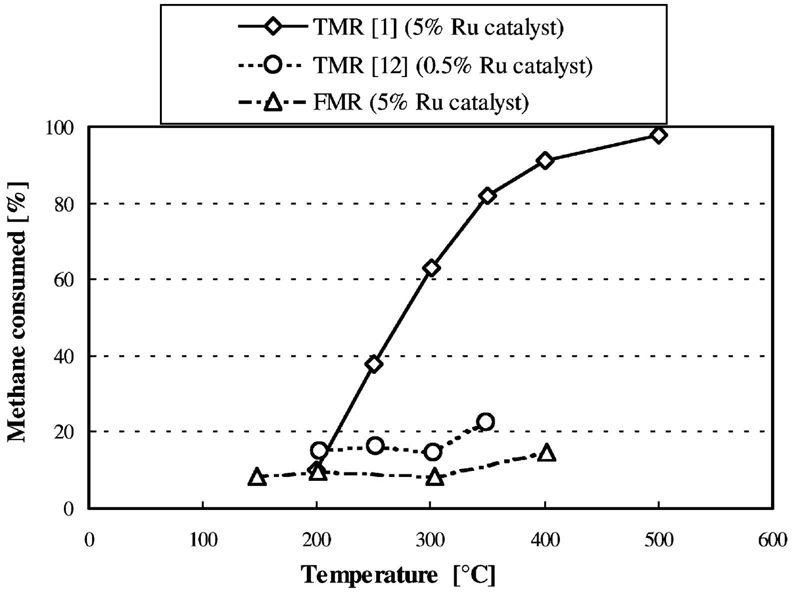


Fig. 6. Comparison among this work (FMR), Garnier et al. [1] (TMR) and Basile et al. [12] (TMR) in terms of consumed methane versus temperature.

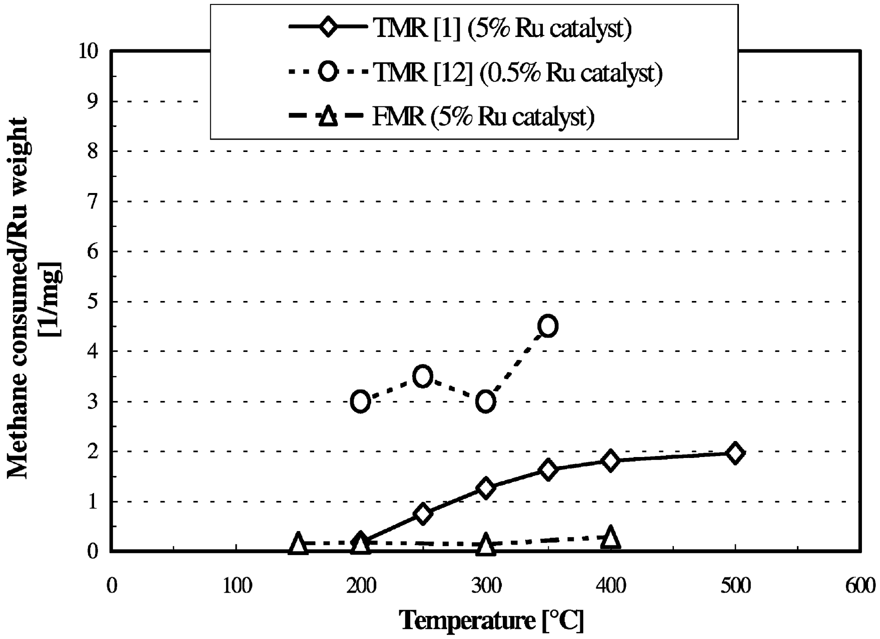


Fig. 7. Comparison among this work (FMR), Garnier et al. [1] (TMR) and Basile et al. [12] (TMR) in terms of consumed methane per weight of Ru catalyst versus temperature, first step, $P = 1$ bar, exposure time = 3 min.

a) the unit of amount of Ru catalyst used for the reaction;
b) the membrane area for hydrogen permeation;
c) the unit of time factor (expressed as catalyst weight per CH_4 fed in the first step).

For this purpose, Figs. 7–10 are proposed, considering consumed CH_4 expressed in %, membrane surface expressed in cm^2, Ru weight expressed in mg. In particular, Fig. 7 shows a comparison among this work, Garnier et al. [1] and Basile et al. [12] in terms of consumed methane per weight of Ru catalyst versus temperature for different membrane reactors: it is possible to observe that TMR [12] gives the best performances when compared to the other two membrane reactors. For example, at 300 °C, the value of consumed CH_4/Ru weight is $3\,mg^{-1}$ for TMR [12], $1.27\,mg^{-1}$ for TMR [1] and $0.15\,mg^{-1}$ for FMR. However, referring also to the unit of membrane area, Fig. 8 shows that TMR [12] gives the highest values for temperature lower than

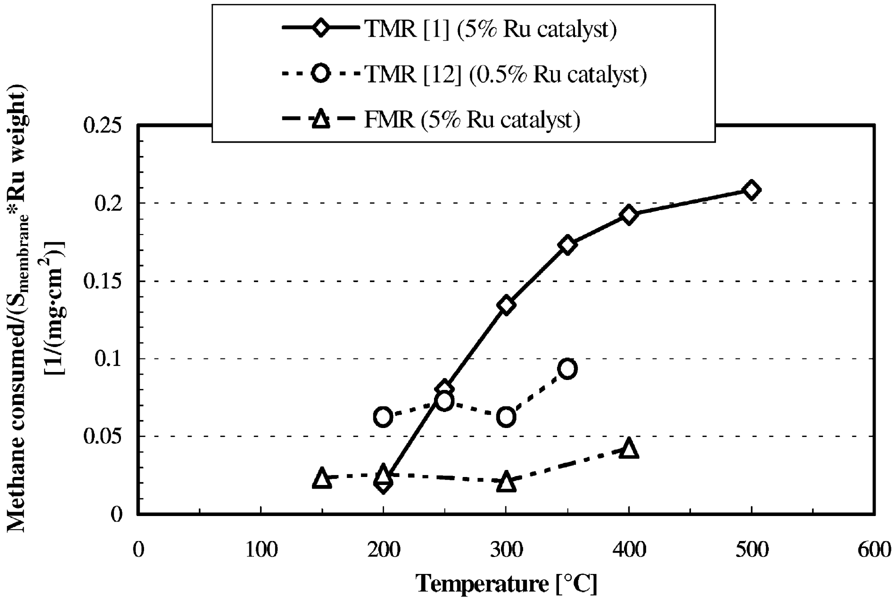


Fig. 8. Comparison among this work (FMR), Garnier et al. [1] (TMR) and Basile et al. [12] (TMR) in terms of consumed methane per weight of Ru catalyst and membrane surface versus temperature, first step, $P = 1$ bar, exposure time = 3 min.

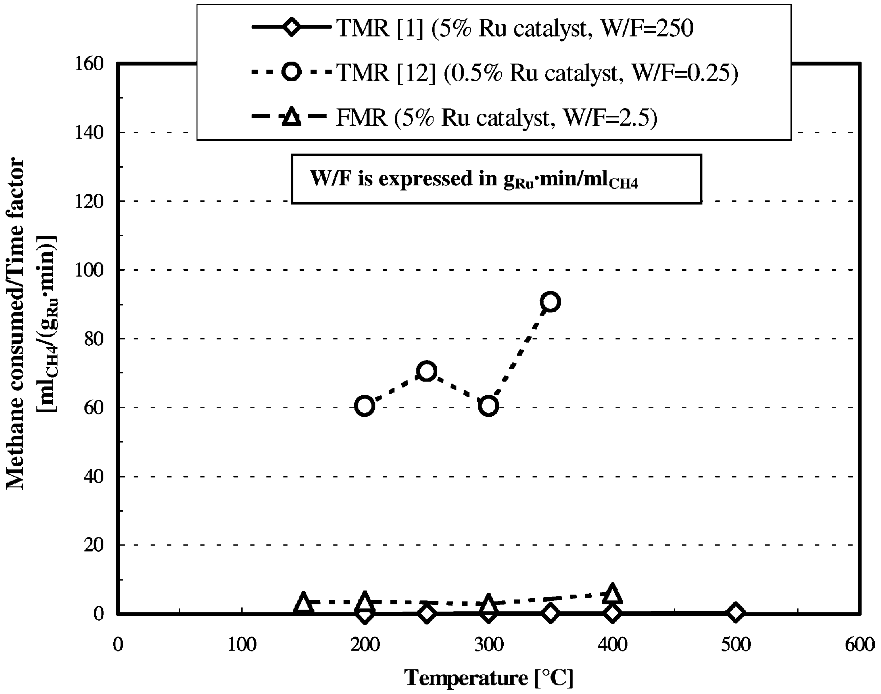


Fig. 9. Comparison among this work (FMR), Garnier et al. [1] (TMR) and Basile et al. [12] (TMR) in terms of consumed methane per time factor versus temperature, first step, $P = 1$ bar, exposure time = 3 min.

250 °C. In particular, at 250 °C TMR [1] and TMR [12] give 0.08 and 0.07 $\mathrm{mg^{-1}\,cm^{-2}}$ of consumed CH_4/($S_{membrane}$·Ru weight), respectively; while at 200 °C TMR [1] and FMR give the same value (0.02 and 0.026 $\mathrm{mg^{-1}\,cm^{-2}}$, respectively), against 0.062 $\mathrm{mg^{-1}\,cm^{-2}}$ for TMR [12]. In this comparison, at low temperature the TMR equipped with 0.5% of Ru catalyst gives better performances than the TMR equipped with 5% of Ru catalyst. In Fig. 9 a comparison among TMR [1], TMR [12] and FMR referred to the consumed CH_4 per unit of time factor clearly shows that TMR [12] gives the highest values. This seems to confirm the requirement of optimising the reaction system with respect to all the parameters involved in the process. In this direction, another comparison among TMR [1], TMR [12] and FMR

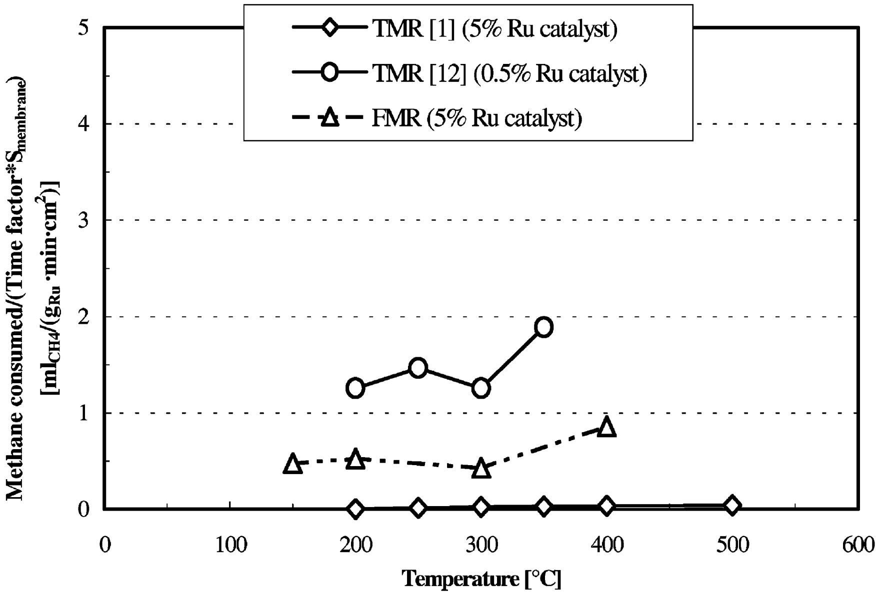


Fig. 10. Comparison among this work (FMR), Garnier et al. [1] (TMR) and Basile et al. [12] (TMR) in terms of consumed methane per time factor and membrane surface area versus temperature, first step, $P = 1$ bar, exposure time = 3 min.

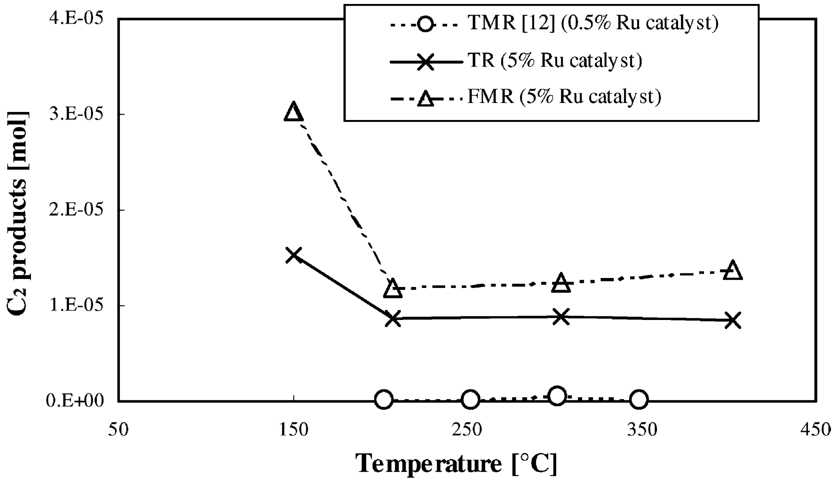


Fig. 11. Comparison among TR (this work), TMR [12] and FMR (this work) in terms of C_2 production versus temperature, $P = 1$ bar, exposure time = 2 min (first step) for TR and FMR, exposure time = 3 min for TMR.

is given in Fig. 10, in which the consumed CH_4 is normalised with respect to both the time factor and the membrane surface area. From this figure, it is evident that FMR might work better than TMR [1], although this comparison is made using a non-physical variable on the *y*-axis. Generally speaking, it seems that the use of the kind of configuration (flat or tubular) requires a very careful control of both the characteristics of the membrane (membrane area, thickness, and so on) and the reaction conditions (feed rate and composition, catalyst weight, and so on) for getting the best performances.

Fig. 11 offers a comparison among TMR [12], FMR and TR in terms of C_2 production versus temperature. It is to be noted that only ethane was detected as a product in our experimental conditions. Considering the amount of ethane produced, the figure shows the best performance in the second step of the reaction of FMR with respect to both TR and TMR [12]. The maximum production of ethane was obtained at 150 °C: about 3×10^{-5} mol C_2 produced for FMR, and about 1.5×10^{-5} mol C_2 produced for TR. These two results seem to be in agreement with Belgued et al. [14]: these authors found a maximum value of C_2 production at a similar temperature value, about 8.5×10^{-7} mol C_2 produced at 160 °C. It is to be noted that the major amount of Ru in the catalyst leads to a great production of C_2. It is evident that the amount of C_2 produced using 5% Ru catalyst in this work was higher than the one produced by Basile et al. [12] using 0.5% Ru catalyst. In particular, the difference between the two cases was about two orders of magnitude: an increase of one order of magnitude in Ru percentage in the catalyst (from 0.5 to 5% Ru) gives an increase of two orders of magnitude in C_2 production (from 10^{-7} to 10^{-5} mol) in our experimental conditions.

Nevertheless, generally speaking, a tubular membrane could give the best performances due to some advantages over both FMR and TR. For example, considering the same operating conditions, TR needs a larger catalyst volume to achieve the same conversion of TMR, while FMR needs a larger membrane area. However, only an optimisation study would determine the best configurations to be used. Ultimately, an economic evaluation could help to better establish the real advantages of one kind of reactor over the other, but this is not the intention of this paper.

4. Conclusions

The experiments carried out in this study show that using Pd/Ag membrane reactor, it is possible to obtain consumed methane values greater than the ones obtained in a TR for the first step. An indirect consequence should be an increase of the yield in lighter hydrocarbons. This concept was well stressed by experimental tests with 5% Ru catalyst for both TR and FMR.

In this way, it is possible to produce in the FMR a higher amount of ethane from the same amount of methane fed in the TR. Particular attention should be paid to the fact that an increase of one order of magnitude in Ru percentage in the catalyst (from 0.5 to 5% Ru) gives an increase of two orders of magnitude in C_2 production (from 10^{-7} to 10^{-5} mol) in our experimental conditions. The potentiality of the tubular configuration is confirmed in the first step of the reaction system, although the flat module gives no problems regarding both sealing and weakness of the metallic membrane.

Finally, no activity loss for the catalyst was observed after each cycle of reaction. Furthermore, no carbon deposition was detected over the catalyst and/or the membrane surface after each whole cycle of reaction: in fact, feeding oxygen at 450 °C, neither CO nor CO_2 were detected in the outlet streams of both kinds of reactor.

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