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Hydrogen production from methanol by oxidative steam reforming carried out in a membrane reactor

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Abstract

The aim of this work is to study from an experimental point of view the oxidative steam reforming of methanol by investigating the behaviour of a dense Pd/Ag membrane reactor (MR) in terms of methanol conversion as well as hydrogen production. The main parameters considered are the operating temperature and the O_2/CH_3OH feed ratio. This is a pioneer work in the application of MR to this kind of reaction, whose goal should be to produce a CO-free hydrogen stream suitable for hydrogen fuel cell applications. The experimental results show that the MR gives methanol conversions higher than traditional reactors (TRs) at each temperature investigated, confirming the good potential of the membrane reactor device for this interesting reaction system.

Keywords: Pd/Ag dense membrane; Oxidative steam reforming; Methanol; Hydrogen production

1. Introduction

Today hydrogen is considered an energetic vector able to play a role of increasing importance in future energy systems, regarding in particular clean energy production. The availability of this gas in nature is poor, so the international scientific community is searching for alternative hydrogen sources by exploiting new chemical reaction systems. In particular, methanol steam reforming and oxidative methanol steam reforming can be considered promising ways for hydrogen production useful for the fuel cell applications. In addition, the use of air as a reactant with respect to conventional methanol steam reforming could improve both the methanol conversion and the hydrogen production, depending on the experimental conditions adopted. The interest in new routes for hydrogen production is due to the evidence that, nowadays, hydrogen as a vehicle fuel could require unacceptably high infrastructure costs. Vice versa, infrastructure costs for liquid fuels (for example methanol) should be sensitively lower. In this view methanol reforming can also be seen as a fuel source for producing hydrogen in situ at a local fuelling station [1].

When carried out in a traditional system, the methanol reforming leads to a hydrogen-containing mixture, so hydrogen needs purification (mainly due to the CO presence) before feeding a proton exchange membrane fuel cell becomes possible. Few recent studies in literature concern the investigation of the oxidative steam reforming of methanol for hydrogen production. Murcia-Mascarós et al. [2] proposed oxidative methanol steam reforming as a combination of methanol steam reforming with methanol partial oxidation:

$$CH_3OH + H_2O \Leftrightarrow 3H_2 + CO_2, \quad \Delta H^\circ_{298\,K} = +49.4\ \text{kJ/mol} \tag{1}$$

$$CH_3OH + \tfrac{1}{2}O_2 \Leftrightarrow 2H_2 + CO_2, \quad \Delta H^\circ_{298\,K} = -192.2\ \text{kJ/mol} \tag{2}$$

Velu et al. [3] carried out this reaction system on different catalysts based on CuZnAl(Zr), obtaining 90% methanol conversion at 230 °C in their experimental conditions. These

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authors studied the influence of the O_2/CH_3OH feed ratio on methanol conversion and on hydrogen production, demonstrating a significant influence of this parameter on the reaction system, that is further complicated by hydrogen combustion with oxygen:

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O_{(vap)}, \quad \Delta H^\circ_{298\,K} = -480.4\,kJ/mol \qquad (3)$$

Reitz et al. [4] studied the characterization of a commercial CuO/ZnO based catalyst for the oxidative steam reforming reaction of methanol, finding a key influence of Cu on methanol conversion, depending on the conversion rate of oxygen during the reaction.

More recently, Lenarda et al. [5] studied this reaction system over Pd based catalysts supported on $Zn/ZnAl_2O_4$; the high performance of this catalyst system for the selective hydrogen production has been assigned to the formation of PdZn alloys. Lenarda et al. [6] prepared a catalyst based on Pd and Pd/Cu in various proportions supported on ordered mesoporous ceria-doped alumina for the same reaction.

Globally, from this brief analysis, we can conclude that there is an increasing level of interest in hydrogen production by oxidative methanol steam reforming. To our knowledge, differing from other reaction systems producing hydrogen [7], there are no applications of membrane reactors to this reaction. It is well known that the main advantage of using an MR is its ability to perform both reaction and pure hydrogen removal in the same device: in this way, it could be possible to replace the traditional system (reformer + gas cleaning unit) with the membrane reactor device.

The objective of this work is to apply a dense tubular Pd/Ag MR to oxidative methanol steam reforming, focusing our attention on the influence of the main operating parameters, i.e. the temperature and the O_2/CH_3OH feed ratio, on methanol conversion. Particular attention is paid to hydrogen production as well as hydrogen, carbon monoxide and carbon dioxide selectivity.

2. Experimental

2.1. Description of the MR device

The membrane reactor (MR) consists of a tubular stainless steel module, length 28 cm, and i.d. 2 cm, containing a pinhole-free Pd/Ag (23 wt.% of Ag) tubular membrane permeable only to hydrogen with a thickness of 50 μm, o.d. 1.02 cm, length 15 cm. In particular, the dense membrane is welded to two stainless steel supports useful for the membrane housing. In the MR, catalyst pellets are packed in the membrane lumen (15 cm length) by means of glass spheres (2 mm diameter) placed into the stainless steel supports on both extremities of the membrane. One graphite o-ring (99.53% C and 0.47% S) furnished by Gee Graphite Ltd. (England), 2.8 g, ensures that permeate and lumen streams do not mix with each other in the membrane module. The Pd/Ag membrane was produced by a lamination technique in E.N.E.A. Laboratories (Frascati, Italy); details of this technique have been presented elsewhere by Tosti and Basile [8]. Experimental results regarding the characterization of this kind of membrane have been published in ref. [9].

The hydrogen permeation experiments showed that both Sievert and Arrhenius laws are followed. The apparent activation energy E_a is 33.31 kJ/mol, and the pre-exponential factor Pe_0 is 1.66×10^{-5} mol m/(m^2 s kPa$^{0.5}$). These values are compatible with experimental results reported in the recent specialised literatures [10–15]. The temperature dependence of hydrogen permeability can be expressed by the Arrhenius-like expression, that becomes in our case: $Pe = 1.66 \times 10^{-5} \times \exp(-4005/T)$. The Pd/Ag membrane shows infinite permselectivity to hydrogen with respect to other gases.

The upper temperature limit of the Pd/Ag membrane is 450 °C. The tubular membrane is plugged from one side, and reactants are fed by means of a stainless steel tube (o.d. 1/16 in., i.d. 1/40 in.) placed inside the membrane lumen; the end of this tube is at 1 cm from the plug of the membrane tube. In this way, reactants exit at the beginning of the catalyst bed, and both un-reacted and un-permeated species exit from the membrane lumen [9]. Fig. 1 shows a scheme of the membrane reactor (Fig. 1a) as well as some details concerning the tubular membrane (Fig. 1b).

2.2. Experimental apparatus and details

Fig. 2 shows a scheme of the experimental plant used for performing the reaction tests on oxidative methanol steam reforming. The MR is placed in a temperature-controlled PID oven. The reaction temperature is in the range between 200 and 260 °C, while the permeation tests are conducted in the temperature range 300–400 °C. The inert carrier and the sweep gas (N_2) as well as the O_2 reactant are fed by means of mass-flow controllers (Brooks Instruments 5850S) driven by a computer software furnished by Lira (Italy) used for all experiments. H_2O and CH_3OH are fed by volumetric pumps (type FMQG6) furnished by General Control (Italy). H_2O and CH_3OH liquid reactants are mixed and vaporised at 400 °C, and then carried by the inert carrier gas (N_2) into the reactor. The outlet stream is completely condensed to remove the un-reacted H_2O and CH_3OH, and then the dry gaseous stream flow rate is measured by means of bubble flow-meters; its composition is detected and analysed by using a temperature programmed HP 6890 Gas Chromatograph (GC) with two TCD detectors at 250 °C and He as carrier gas. The GC is equipped with three packed columns: Porapack R 50/80 (8 ft × 1/8 in.) and Carboxen^{TM} 1000 (15 ft × 1/8 in.) connected in series, Molecular Sieve 5 Å (6 ft × 1/8 in.). A 10-way valve was used to optimise the total time of the analysis, which was about 5.1 min; the apparatus is controlled by software furnished by Hewlett-Packard. The catalyst used is furnished by Synetix (UK),

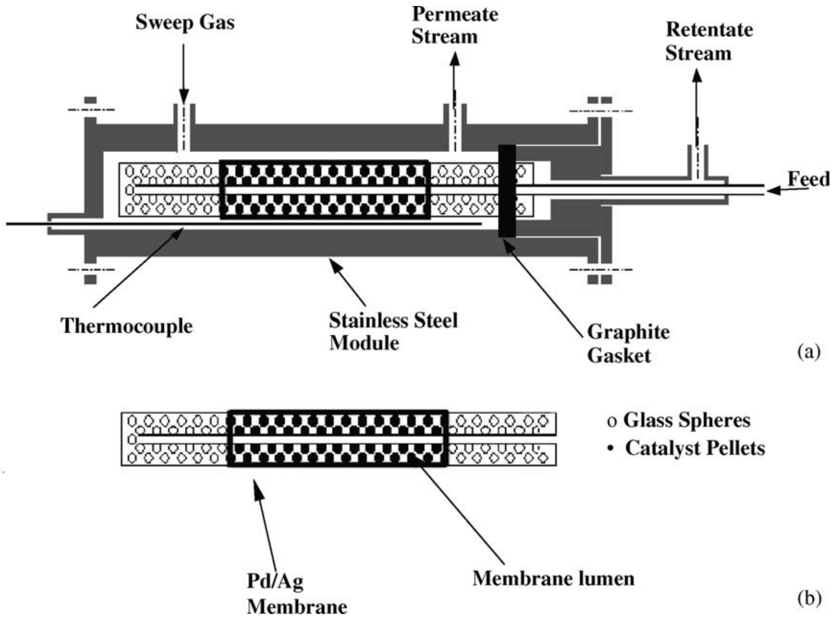

Fig. 1. Scheme of the membrane reactor (a) and the tubular membrane in detail (b).

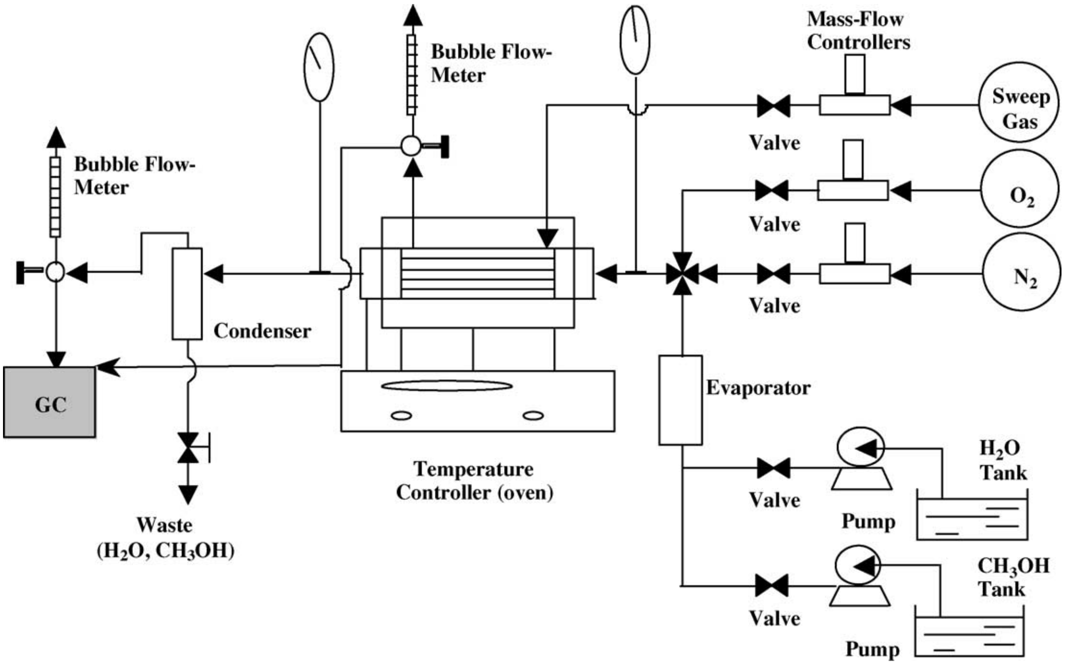

Fig. 2. Scheme of the experimental apparatus.

signed as ICI 83-3, having the following composition: 51% CuO, 31% ZnO, 18% Al_2O_3. The amount of catalyst used is 8 g, the particles being in the range of 250–400 μm in size. The catalyst activation procedure consisted of a first heating up of the reactor to 120 °C (rate 50 °C/min), then a second heating up to 180 °C (rate 25 °C/min) and afterwards the reduction at 180 °C for 24 h with a N_2/H_2 mixture (1.5% vol. H_2).

Table 1 shows the operating conditions adopted for the methanol oxidative steam reforming reaction. The reaction temperature is in the range between 200 and 260 °C, the lumen pressure is 2.6 bar (abs), except for the time tests carried out at a lumen pressure of 2.2 bar (abs) and the shell side pressure is kept to 1 bar (abs). The following definitions have been used to describe the MR performance on the basis of the experimental results achieved in this work:

$$\mathrm{CH_3OH\,conversion}\,(\%) = \frac{\mathrm{CO_{out}} + \mathrm{CO_{2,out}}}{\mathrm{CH_3OH_{in}}} \times 100$$

Table 1
Operating and feed conditions adopted for the oxidative methanol steam reforming

O_2/CH_3OH	Q_{CH_3OH} (mol/min)	O_2/H_2O	H_2O/CH_3OH	$N_{2,\ carrier}$ (mol/min)	$N_{2,\ sweep\ gas}$ (mol/min)	p_{lumen} (bar)	p_{CH_3OH} (bar)	p_{H_2O} (bar)	Space velocity ($mol_{CH_3OH}/(min\ g_{cat})$)
0 (TR)	3.6×10^{-3}	0	2.72	3.22×10^{-3}	–	2.6	0.563	1.53	4.5×10^{-4}
0 (MR)	3.6×10^{-3}	0	2.72	3.22×10^{-3}	8.28×10^{-4}	2.6	0.563	1.53	4.5×10^{-4}
0.09	3.6×10^{-3}	0.03	2.72	2.9×10^{-3}	8.28×10^{-4}	2.6	0.563	1.53	4.5×10^{-4}
0.17	3.6×10^{-3}	0.06	2.72	2.7×10^{-3}	8.28×10^{-4}	2.6	0.563	1.53	4.5×10^{-4}
0.25	3.6×10^{-3}	0.09	2.72	2.0×10^{-3}	8.28×10^{-4}	2.6	0.563	1.53	4.5×10^{-4}

Space velocity = methanol feed flow rate/catalyst weight.

$$H_2\ \text{selectivity} = \frac{H_{2,\text{out}}}{CH_3OH_{\text{in}} - CH_3OH_{\text{out}}} \times \frac{1}{3}$$

$$CO\ \text{selectivity} = \frac{CO_{\text{out}}}{CH_3OH_{\text{in}} - CH_3OH_{\text{out}}}$$

$$CO_2\ \text{selectivity} = \frac{CO_{2,\text{out}}}{CH_3OH_{\text{in}} - CH_3OH_{\text{out}}}$$

The subscript ''out'' indicates the total outlet flow rate of each species. Two outlet streams are present only for hydrogen, because the dense Pd/Ag membrane exhibits infinite permselectivity to H_2 (see Section 2.1). The hydrogen molar flow rate in the permeate stream has been defined as:

$$H_2\ \text{permeate} = \%H_{2,\ \text{perm}} \times \frac{Q_{\text{perm}}}{100}$$

where $\%H_{2,\ \text{perm}}$ is the molar fraction (expressed in %) of hydrogen in the permeate stream, and Q_{perm} the molar flow rate of the permeate stream.

Finally, the fraction of hydrogen recovered in the permeate with respect to the total hydrogen produced in the MR is defined as:

$$\%H_{2,\text{recovered}} = \frac{H_{2,\text{out permeate}}}{H_{2,\text{out permeate}} + H_{2,\text{out retentate}}} \times 100$$

The mass balance closure was within ±4%. The same table also shows the operating conditions adopted for the methanol steam reforming reaction ($O_2/CH_3OH = 0$) for both the MR and a TR tested for comparison.

3. Results and discussion

Fig. 3 shows methanol conversion versus temperature at various O_2/CH_3OH feed ratios. Methanol conversion generally increases with increasing temperature, at each value of the O_2/CH_3OH feed ratio. The O_2 stream in the feed gives an increase of methanol conversion, since at each O_2/CH_3OH feed ratio investigated the methanol conversion is higher than in the case of the steam reforming reaction ($O_2/CH_3OH = 0$). The highest methanol conversion is about 90% at 260 °C and $O_2/CH_3OH = 0.09$. The curves reported in Fig. 3 exhibit a different slope and shape, depending on the O_2/CH_3OH feed ratio value. The highest slope seems to be attributable to $O_2/CH_3OH = 0.09$. Vice versa, the trend related to O_2/CH_3OH feed ratio of 0.17 is quite increasing up to 240 °C; then, further upon increasing the temperature to 260 °C it remains almost constant. Concerning the O_2/CH_3OH feed ratio of 0.25, methanol conversion passes a maximum of 81% at 220 °C.

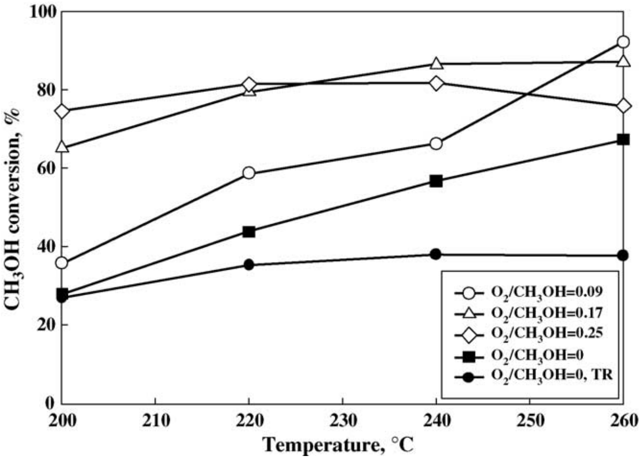

Fig. 3. Methanol conversion vs. temperature at various O_2/CH_3OH feed ratios. Catalyst ICI 83-3. $p_{\text{lumen}} = 2.6$ bar, $p_{\text{shell}} = 1.0$ bar, H_2O/CH_3OH feed ratio = 2.72, N_2 sweep gas flow rate = 8.3×10^{-4} mol/min.

The behaviour related to $O_2/CH_3OH = 0.17$ and 0.25 can be explained by taking into account the catalyst deactivation during time, a typical phenomenon in methanol oxidative steam reforming [16]. The deactivation velocity seems to increase with increasing O_2/CH_3OH feed ratio and temperature. In fact, the experimental tests reported in Fig. 3 have been carried out with increasing O_2/CH_3OH ratio. So, during time, and increasing both the O_2/CH_3OH feed ratio and the temperature, the expected methanol conversion increase has not been observed. A similar interpretation has been given by Reitz et al. [16] who used a CuO/ZnO based catalyst for the same reaction. These authors assume that the rapid catalyst deactivation is attributed to a change in the CuO structure, due to local hot-spots produced by the highly exothermic oxidation reaction involved in the overall reaction system (see reaction (2)). The increasing amount of O_2 in the reaction system produces a positive effect in terms of an increase of methanol conversion at 200 and 240 °C for $O_2/CH_3OH = 0.17$ and 0.25, but when increasing temperature,

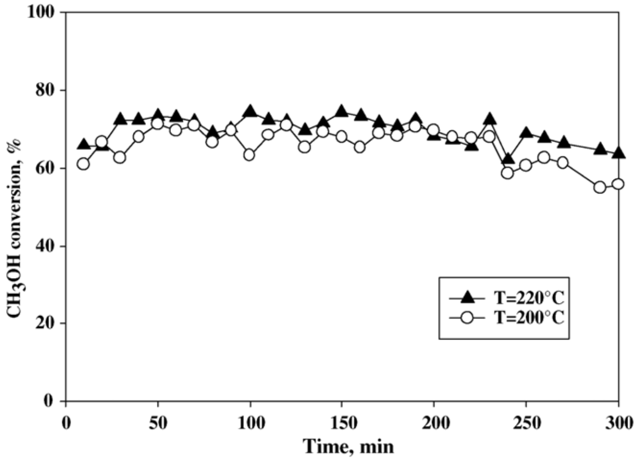

Fig. 4. Methanol conversion vs. time at two different temperatures in the MR. Catalyst ICI 83-3. $p_{\mathrm{lumen}} = 2.2$ bar, $p_{\mathrm{shell}} = 1.0$ bar, H_2O/CH_3OH feed ratio = 2.72, O_2/CH_3OH feed ratio = 0.25, N_2 sweep gas flow rate = 8.3×10^{-4} mol/min.

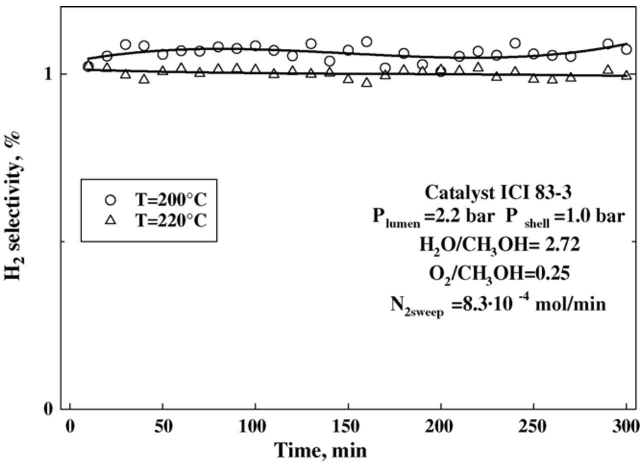

Fig. 5. Hydrogen selectivity vs. time at two different temperatures in the MR.

catalyst deactivation increasingly affects the reaction system. The temperature increase gives both an increase of methanol conversion and an increase of the rate of deposition of carbonaceous species on the catalyst surface, with a consequent loss of activity. In addition, it should be noted that reaction (2) is exothermic and its effect is relevant at higher O_2 concentration: the more O_2 is available, the higher the temperature increase due to this reaction. In turn carbon deposition is faster and catalyst deactivation occurs more quickly which results in a lower methanol conversion. This effect is slightly visible at $O_2/CH_3OH = 0.17$, while it is more pronounced at $O_2/CH_3OH = 0.25$, where the curve changes its shape.

In order to check the loss of catalyst activity during time, experimental tests at constant temperature have been carried out at the highest O_2/CH_3OH feed ratio of 0.25 and a lumen pressure of 2.2 bar (abs) for a total reaction time of 5 h. In particular, two temperatures have been investigated, 200 and 220 °C. Results of this analysis are given in Fig. 4. This investigation has been conducted by analysing the outlet streams of the MR every 10 min. An initially increasing transient status has been observed, followed by an oscillating trend, and concluded by a decreasing behaviour, at both temperatures investigated. This behaviour could confirm the assumed catalyst deactivation during time.

The hydrogen selectivity, vice versa, does not seem to be influenced by the reaction time, as observed in Fig. 5. In fact, from this figure, it is evident that at both temperatures investigated, the hydrogen selectivity keeps around 1 at 220 °C, and is slightly higher than 1 at 200 °C. Furthermore, the trend is quite constant, without an increasing or a decreasing region. These results indicate the presence of deposited carbon over the catalyst surface, especially at the lower operating temperature (200 °C): under this condition, the methanol reacted is overestimated and this produces a selectivity higher than 1. Similar trends have been observed for both CO and CO_2 selectivity, at the same operating conditions investigated in Figs. 3 and 4.

Considering the reactions (1) and (2) (mentioned in Section 1), it should be expected, from a thermodynamic viewpoint, a hydrogen production of 3 moles per mole of CO_2 (and CO). In our experiments this value is slightly higher than the classic thermodynamic prevision (Fig. 5), due to coke deposition. This coke contributes to catalyst deactivation during time and produces further hydrogen which explains the higher amount of H_2 produced per mole of CO_2. In order to preserve our membrane from damage, during our experiments it was not possible to quantify the total amount of carbon deposition due to the high temperature necessary to burn the carbon deposits. In fact both the catalyst and the Pd/Ag membrane have a maximum operating temperature lower than 450 °C. Using the same catalyst, in a traditional system, the temperature reached values around 600 °C during determination of carbon deposition by reaction with oxygen. In this last case (i.e. carbon deposition in the traditional system), we found a value of 0.117 g of C deposited after 5 h of reaction: this means a deposition rate of about 3.25×10^{-5} $\mathrm{mol_C}$/min, two order of magnitude lower than the methanol feed flow rate (3.6×10^{-3} mol/min).

Fig. 6 shows the total hydrogen production (retentate + - permeate stream) of the MR versus temperature at various O_2/CH_3OH feed ratios. Considering the steam reforming reaction ($O_2/CH_3OH = 0$), the trend is increasing with temperature. When oxygen is added to the reaction system, something changes, depending on the O_2/CH_3OH value. In fact, at $O_2/CH_3OH = 0.09$, the hydrogen production decreases with respect to the previous case, at each temperature investigated; furthermore, the difference between the two cases ($O_2/CH_3OH = 0$ and $O_2/CH_3OH = 0.09$) increase with temperature and reaches a maximum of about 3×10^{-3} mol/min at 260 °C. When $O_2/CH_3OH = 0.17$, hydrogen

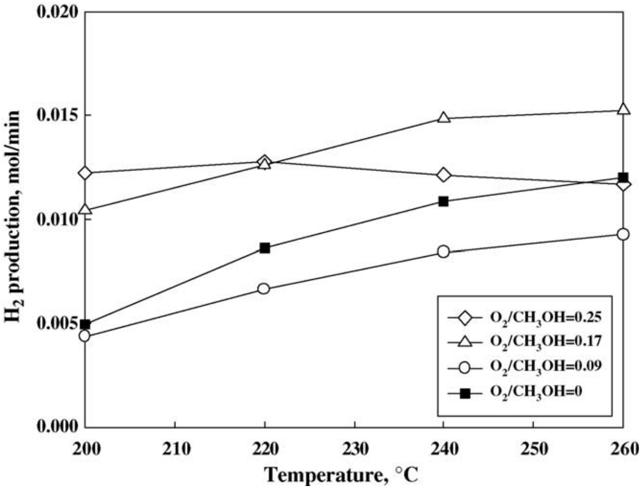

Fig. 6. Hydrogen production vs. temperature for the MR at various O_2/CH_3OH feed ratios. Catalyst ICI 83-3. $p_{\mathrm{lumen}} = 2.6$ bar, $p_{\mathrm{shell}} = 1.0$ bar, H_2O/CH_3OH feed ratio = 2.72, N_2 sweep gas flow rate = 8.3×10^{-4} mol/min.

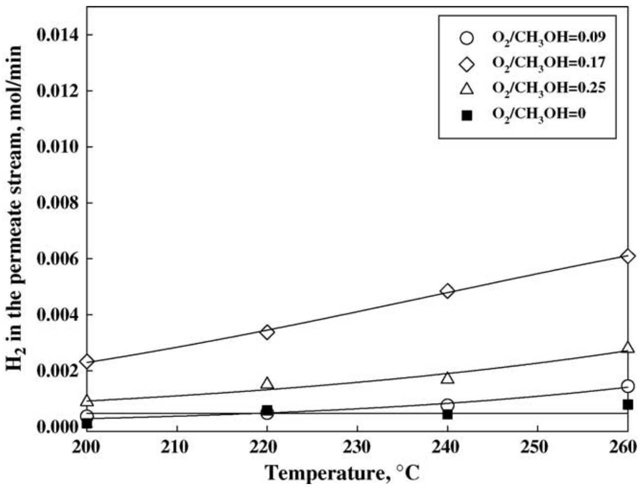

Fig. 7. Hydrogen permeated vs. temperature for the MR at various O_2/CH_3OH feed ratios. Catalyst ICI 83-3. $p_{\mathrm{lumen}} = 2.6$ bar, $p_{\mathrm{shell}} = 1.0$ bar, H_2O/CH_3OH feed ratio = 2.72, N_2 sweep gas flow rate = 8.3×10^{-4} mol/min.

production overcomes the one obtained at $O_2/CH_3OH = 0$ and 0.09. When the O_2/CH_3OH feed ratio is increased to 0.25, a different behaviour is observed: the hydrogen production is about 1.2×10^{-2} mol/min at 200 and 220 °C, and then decreases down to about 1.0×10^{-2} mol/min at 260 °C.

The behaviour shown in Fig. 6 can be explained by considering that part of the produced hydrogen reacts with the oxygen of the feed stream producing water. This could justify the comparison of the behaviour related to $O_2/CH_3OH = 0$ and 0.09. For the same consideration, at higher values of O_2/CH_3OH, the hydrogen produced should be lower, but the experimental evidence is in contrast to what is expected, so that the hydrogen produced overcomes what is obtained at $O_2/CH_3OH = 0$. Probably, the overall effect of oxygen addition is not immediate to detect. A positive effect can be found on hydrogen production, because oxygen addition promotes an increase of hydrogen production, since a reactant is added to reaction (2) of Section 1. However, the effect of oxygen addition apparently is more complicated and hence depending on the operating conditions an increase or a decrease of the hydrogen production rate might be observed.

The hydrogen selectivity is weakly influenced by the temperature and the O_2/CH_3OH feed ratio, as shown in Table 2: it is in the range between 1 and 0.93, while both methanol conversion (Fig. 3) and hydrogen production (Fig. 6) increase with increasing temperature. However, carbon deposition increases with temperature as well, and this could justify the slight decrease of hydrogen selectivity with increasing temperature: in fact, if carbon deposition increases, the un-reacted methanol in the outlet decreases, and the difference in the denominator of the definition of the H_2 selectivity (Section 2.2) increases, causing a decrease of the selectivity.

By focusing the attention on CO selectivity, which is responsible for the anodic catalyst poisoning of hydrogen fuel cells, the experimental values reported in Table 2 generally correspond to a CO-containing stream in the range of 500–5000 ppm CO, but it is important to stress that the CO-containing stream is the retentate, while the permeate stream does not contain any trace of CO, due to the perfect selectivity of the Pd/Ag membrane used towards hydrogen.

Considering this last stream, i.e. the permeate stream of the MR, Fig. 7 gives the permeated hydrogen flow rate versus temperature at each value of the O_2/CH_3OH feed ratio considered. The overall trend is slightly increasing when $O_2/CH_3OH = 0.09$ and 0.25, and it is quite increasing when $O_2/CH_3OH = 0.17$. The increasing trend is in agreement with the temperature dependence of the hydrogen permeability, which follows the Arrhenius-like expression

Table 2
H_2, CO and CO_2 selectivity (average value) vs. temperature at different O_2/CH_3OH feed ratios

Temperature (°C)	$O_2/CH_3OH = 0.09$			$O_2/CH_3OH = 0.17$			$O_2/CH_3OH = 0.25$		
	S_{H_2}	S_{CO}	S_{CO_2}	S_{H_2}	S_{CO}	S_{CO_2}	S_{H_2}	S_{CO}	S_{CO_2}
200	1.003419	2.18×10^{-3}	0.99	1.002436	5.43×10^{-3}	0.99	0.99617	5.46×10^{-3}	0.99
220	1.006357	8.46×10^{-3}	0.99	0.996817	9.73×10^{-3}	0.99	0.995961	7.94×10^{-3}	0.99
240	0.949178	1.06×10^{-2}	0.99	0.956119	1.86×10^{-2}	0.98	0.935411	1.29×10^{-2}	0.99
260	0.949006	1.44×10^{-2}	0.99	0.953026	2.86×10^{-2}	0.97	0.932348	1.63×10^{-2}	0.98

$Pe = Pe_0 \times \exp(-E_a/RT)$, where Pe_0 and Ea are the pre-exponential factor and the apparent activation energy, respectively (their values are reported in Section 2.1). The highest trend is given by $O_2/CH_3OH = 0.17$. Something similar has been obtained in terms of hydrogen production for $T > 220$ °C (Fig. 6), where this value of O_2/CH_3OH gives a high methanol conversion at $T > 220$ °C (Fig. 3). According to the Sievert and Arrhenius laws, the factors most affecting the hydrogen permeation through the membrane are the temperature and the square root difference of the hydrogen partial pressures in the lumen side and in the permeation side, respectively. This means that, for example, by increasing the O_2/CH_3OH feed ratio from 0 to 0.09, reaction (2) takes place producing hydrogen (i.e. its partial pressure increases) and giving a local temperature increase: both factors promote an increase of the hydrogen permeation flux through the membrane. A further increase of O_2/CH_3OH from 0.09 to 0.17 gives a similar but more pronounced effect and finally the last increase of O_2/CH_3OH from 0.17 to 0.25 produces a decrease of the permeated hydrogen, because part of the hydrogen is consumed by means of the excess oxygen.

Probably, a O_2/CH_3OH feed ratio of 0.17 is a good compromise to get high methanol conversion, high hydrogen permeation and production, and limited catalyst activity loss.

Fig. 8 shows the fraction of hydrogen recovered in the permeate stream (i.e. $H_{2,\text{ out permeate}}$/total H_2 produced, %) versus temperature for each value of the O_2/CH_3OH feed ratio considered. In each case the amount of the produced hydrogen, which permeates through the membrane, increases by increasing the temperature. This is due to the better performance in terms of hydrogen permeation of the membrane at high temperature and also because, at high temperature, the partial pressure of hydrogen in the reaction zone is higher and so the permeation is accelerated. Also in this investigation, the best performance in terms of the fraction of hydrogen removed is achieved when $O_2/CH_3OH = 0.17$, because the hydrogen partial pressure square root difference between the reaction zone and the permeation zone is higher than in the other cases. This also confirms that in case of $O_2/CH_3OH = 0.25$ part of the hydrogen produced reacts with the oxygen giving a lower hydrogen partial pressure in the reaction zone. Comparing the experimental results in terms of CH_3OH conversion versus temperature (Fig. 3) with the $\%H_{2,\text{ recovered}}$ (Fig. 8), it is possible to observe, for example, that at 200 °C the CH_3OH conversion increases with increasing the O_2/CH_3OH feed ratio from 0.09 to 0.25 (Fig. 3), while the ratio $\%H_{2,\text{ recovered}}$ increases when O_2/CH_3OH increases from 0.09 to 0.17, and afterwards decreases when O_2/CH_3OH increases from 0.17 to 0.25, at the same temperature. This can be explained by considering the definition of CH_3OH conversion: in fact, the amount of CO_2 produced increases with increasing the O_2/CH_3OH feed ratio, due to the relevance of reaction (2); this last reaction causes a local temperature increase, so that hydrogen permeation increases when O_2/CH_3OH increases from 0.09 to 0.17 (Fig. 8). When O_2/CH_3OH further increases up to 0.25, a major part of the H_2 produced is consumed by reaction (3), so the $\%H_{2,\text{ recovered}}$ dramatically decreases. A similar consideration can be carried out at $T = 260$ °C, but now reaction (2), which is exothermic, proceeds slower and CH_3OH conversion decreases with increasing the O_2/CH_3OH feed ratio (Fig. 3). Anyway, the trend of $\%H_{2,\text{ recovered}}$ is analogous to the previous one (Fig. 8).

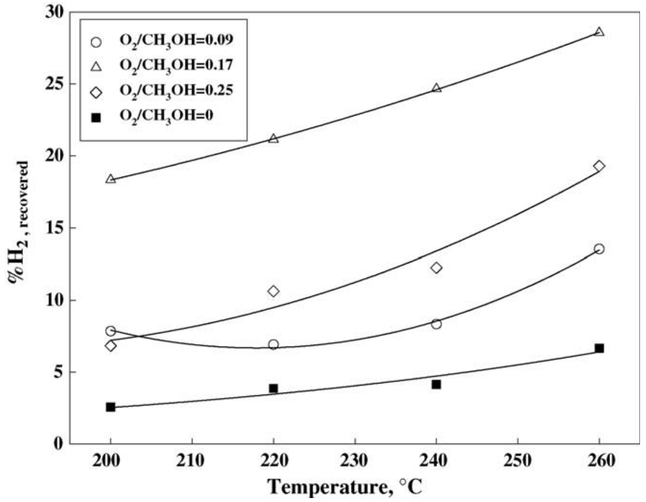

Fig. 8. $\%H_{2,\text{ recovered}}$ vs. temperature for the MR at various O_2/CH_3OH feed ratio. Catalyst ICI 83-3. $p_{\text{lumen}} = 2.6$ bar, $p_{\text{shell}} = 1.0$ bar, H_2O/CH_3OH feed ratio = 2.72, N_2 sweep gas flow rate = 8.3×10^{-4} mol/min.

The results reported in this work show that a significant amount of pure hydrogen can be produced applying the MR to the reaction system considered. If the reader is interested in an economic evaluation aimed to establish the practical benefit of a membrane device inside a reaction plant, it should be said that, generally, the hydrogen permeation is affected by the membrane thickness. In our case the membrane thickness is 50 mμ, but better performance can be achieved decreasing this parameter. Also the membrane cost can be decreased by decreasing the membrane thickness, but a complicated analysis is necessary for evaluating the economical impact of the membrane on the overall process, and this is not the aim of this paper.

Fig. 9 shows a comparison with some literature data in terms of methanol conversion versus temperature. Our MR experimental results have been compared with experimental results of TRs achieved by other authors. To our knowledge, there are no experimental works in literature concerning MR applied to oxidative steam reforming of methanol, so the MR of this work ($O_2/CH_3OH = 0.17$) is compared with the TR of Murcia-Mascarós et al. [2] and Velu et al. [3]. Form Table 1, the space velocity (SV) in this paper is 4.5×10^{-4} $mol_{CH_3OH}/(\min g_{cat})$, calculated from the methanol feed flow rate divided by the catalyst weight; while the SV of Velu

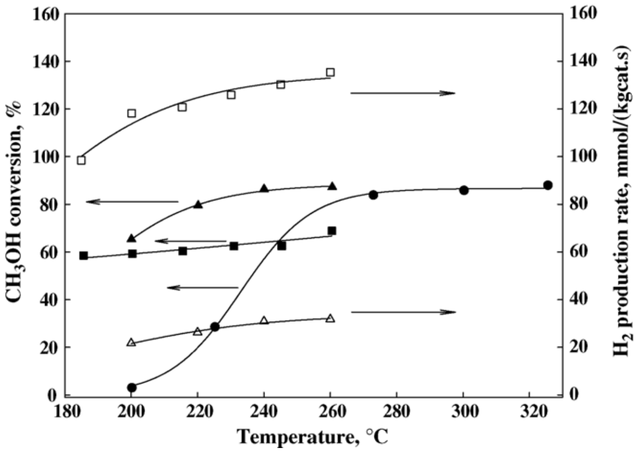

Fig. 9. Methanol conversion vs. temperature: comparison with some literature data. (●) Murcia-Mascarós et al., TR [2]; (■) Velu et al., TR [3]; (□) Velu et al., TR [3]; (▲) this work, MR ($O_2/CH_3OH = 0.17$); (Δ) this work, MR ($O_2/CH_3OH = 0.17$).

et al. is 3.918×10^{-1} mol/(min g_{cat}) (the corresponding data of Murcia-Mascarós et al. is not available). Comparing the two SVs, it is evident that the SV in our work is three orders of magnitude lower, permitting a significantly higher conversion than observed by Velu et al. Moreover, with regard to the hydrogen production rate, Velu et al. reported high values, in the range 98–135 mmol/(kg_{cat} s). However, if we consider the produced hydrogen stream, in our work the produced hydrogen increases from 1.0×10^{-2} mol/min at 200 °C up to 1.5×10^{-2} mol/min at 260 °C, at $O_2/CH_3OH = 0.17$, versus 7×10^{-4} up to 8×10^{-4} achieved by Velu et al. The main reason for such a difference is attributed to the pure hydrogen removal through the membrane that pushes the equilibrium limit towards higher values producing both high methanol conversion and high hydrogen production. In the temperature range investigated (200–260 °C), methanol conversion of the MR overcomes that of the TRs, demonstrating a high performance towards methanol conversion. In principle, it should be possible to use an MR for achieving the same methanol conversion as in a TR, but operating at a lower temperature, thus resulting in energy savings.

4. Conclusions

The oxidative methanol steam reforming carried out in a dense tubular Pd/Ag membrane reactor has been investigated using a commercial catalyst. Two main operating parameters have been analysed, the reaction temperature in the range 200–260 °C and the O_2/CH_3OH feed ratio in the range 0–0.25. Experimental results in terms of methanol conversion are encouraging for future works in this direction: in particular, among the various interesting results, the highest methanol conversion of about 90% has been achieved at 260 °C and $O_2/CH_3OH = 0.09$, versus a maximum value of 83% achieved at 325 °C in a TR found in literature. A significant influence of the O_2/CH_3OH feed ratio has been observed, indicating a key role in the choice of this parameter in order to optimise the overall reaction system.

All the oxygen fed into the MR was consumed, and the maximum hydrogen removed from the reaction zone was 28.6% at 260 °C and $O_2/CH_3OH = 0.17$ in the permeate stream. Only this hydrogen removed is useful for fuel cell applications because it is a CO (and CO_2) free hydrogen stream. This result can be affected by the membrane thickness and the membrane length. Increasing the membrane length and/or reducing the membrane thickness, the removed fraction of hydrogen increases. Also this aspect could be studied in a future work in order to maximize the hydrogen removal from the reaction zone. An economic study is needed to choose the best operating conditions but, in principle, a decrease of the membrane thickness will be beneficial due to a decrease of the membrane cost.

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