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Hydrogen production by methanol steam reforming carried out in membrane reactor on Cu/Zn/Mg-based catalyst

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ABSTRACT

The methanol steam reforming (MSR) reaction was studied by using both a dense Pd-Ag membrane reactor (MR) and a fixed bed reactor (FBR). Both the FBR and the MR were packed with a new catalyst based on $CuOAl_2O_3ZnOMgO$, having an upper temperature limit of around 350 °C. A constant sweep gas flow rate in counter-current mode was used in MR and the experiments were carried out by varying the water/methanol feed molar ratio in the range 3/1–9/1 and the reaction temperature in the range 250–300 °C. The catalyst shows high activity and selectivity towards the CO_2 and the H_2 formation in the temperature range investigated. Under the same operative conditions, the MR shows higher conversions than FBR and, in particular, at 300 °C and H_2O/CH_3OH molar ratio higher than 5/1 the MR shows complete methanol conversion.

1. Introduction

In the last years, there was a significant world wide interest to find methods and processes to reduce the highly polluting emissions due to mobile sources, mainly internal combustion and diesel engines. One of the possible solutions to overcome this problem can be represented, for example, by using PEM fuel cell fed to hydrogen for both vehicular and small scale stationary applications [1,2].

The hydrogen is conventionally produced in large scale by the steam reforming of hydrocarbons such as methane or naphtha oil. For small and medium scale users, hydrogen is also produced from the methanol steam reforming (MSR). As a liquid fuel to produce hydrogen, the methanol shows some advantages with respect to other hydrocarbons because of its relatively low reforming temperatures (250–350 °C), lower sulphur content (<5 ppm) and ease of handling [3]. The disadvantages are represented by the lower energy density and lack of distribution infrastructure when compared to hydrocarbon fuels [4].

Hydrogen production from methanol takes place according to one or more of the following reactions: (a) methanol decomposition, (b) methanol steam reforming and (c) water gas shift (WGS) reaction as shown below [4]:

$$CH_3OH = CO + 2H_2 \quad \Delta H^\circ = 92.0\,\mathrm{kJ/mol} \tag{a}$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \quad \Delta H^\circ = 49.7\,\mathrm{kJ/mol} \tag{b}$$

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^\circ = -41.2\,\mathrm{kJ/mol} \tag{c}$$

Generally, the catalysts used for the MSR reaction are based on Cu, Pd, Ru, Ni, Zn or on a combination of these elements. It is also known that the preparation method as well as the operative conditions plays an important role in the catalytic performances inside the reactors [4]. In particular, the Cu-based catalysts have commonly a maximum operative temperature of 300 °C.

In fact, it is well known that the Cu-based catalysts suffer thermal deactivation at temperatures exceeding 300–350 °C mainly due to the Cu particles sintering [5]. Another important problem negatively affecting the Cu-based catalyst is the carbon deposition on the catalyst surface during the MSR, which is responsible for the catalyst deactivation [6].

In this work, a new Cu-based catalyst (composition: CuO 64%, Al_2O_3 10%, ZnO 24%, MgO 2% – $CuOAl_2O_3ZnOMgO$), having an upper temperature limit around 350 °C, was used in both the MR (membrane reactor) and the FBR (fixed bed reactor). In order to introduce basic sites, this highly selective catalyst contains an Mg promoter which avoids Cu sintering and carbon deposition [7]. Moreover, operating catalyst at low temperatures and using a high H_2O/CH_3OH feed ratio, coke formation is depressed. However, after

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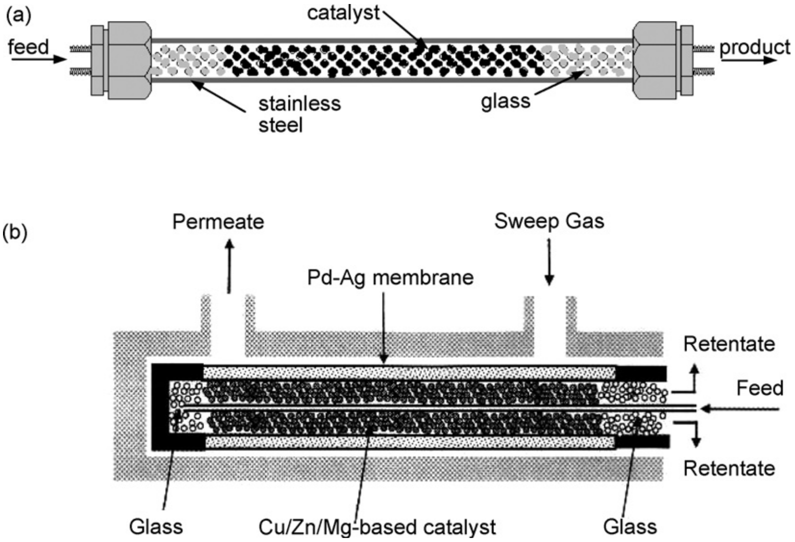

Fig. 1. Schemes of the FBR (a) and the Pd-Ag MR in counter-current mode (b).

each reaction test, the absence of coke on the catalyst was confirmed by: (a) the carbon balance closure, and (b) during the regeneration process where a pure hydrogen stream was fed into the catalyst bed (at 300 °C), no methane formation was detected. The MSR, when it is carried out in a FBR, leads to a hydrogen-containing mixture that needs purification before being fed to a polymeric electrolyte membrane fuel cell (PEMFC) mainly due to the CO produced which poisons the anodic catalyst [8,9]. Even if the current MSR catalysts are highly selective towards CO_2 and H_2, they still produce a relatively high CO concentration (usually 1.0–5.0%) due to the reaction (a) and to the reverse of the WGS reaction (c) [10].

In the chemical industry, commercially available purification processes such as the pressure swing adsorption (PSA) is already used to obtain high purity hydrogen from the product reactor stream. The main problem is the PSA efficiency which is generally lower than 85% [11], limiting the overall hydrogen recovery yield.

A MR is an alternative device to FBRs and is able to combine the reaction and the purification steps in only one system. In several previous works [11–17], the MSR, carried out in Pd-Ag and Pd-based MRs by using copper, zinc and ruthenium based commercial catalysts, was studied from both an experimental and a theoretical point of view. In some of these papers [13–17], the experimental influence of different parameters such as the membrane characteristics, the reaction temperature, the sweep gas flow rate as well as the different flux configurations and the oxygen addition was analyzed, concluding that the MSR carried out in MRs shows better performances in terms of methanol conversion and hydrogen production with respect to the FBR.

The aim of this work is to produce a new $CuOAl_2O_3ZnOMgO$ catalyst and to compare the performances of both the MR and the FBR by varying the feed molar ratio and the reaction temperature. Comparisons between experimental data from literature and this work are given in terms of methanol conversion, hydrogen production and hydrogen recovery. A discussion about the CO-free hydrogen recovery obtained by means of MRs is also presented.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst was prepared by adding drop wise a 1.25 M copper, zinc and aluminium nitrates (Aldrich, reagent grade) solution into a 0.25 M Na_2CO_3 (Aldrich, reagent grade) solution under vigorous stirring. During precipitation the pH was kept constant (~7). The precipitate was then aged for 2.5 h and washed thoroughly with distilled water in order to remove traces of sodium. The hydroxycarbonate precursor was then dried at 383 K for 12 h and calcined in air at 673 K for 12 h. The calcined Cu/Zn/Al catalyst was impregnated with a $Mg(NO_3)_2$ (Aldrich, reagent grade) solution of appropriate concentration to yield 2 wt.% of MgO. After impregnation the sample was dried and calcined as above.

2.2. FBR and MR description

The FBR is a stainless steel tube having a length of 250 mm and *i.d.* of 6.7 mm. The reaction zone is 150 mm long (Fig. 1a). The MR consists of a tubular stainless steel module, length 280 mm, *i.d.* 20 mm, containing a pine-hole free Pd-Ag membrane tube permeable only to hydrogen, having thickness 50 μm, *o.d.* 10 mm, length 150 mm. In particular, the dense membrane is joined to two stainless steel tube ends useful for the membrane housing. The Pd-Ag membrane was produced by a cold-rolling and diffusion welding technique [18,19] and its upper temperature limit is around 450 °C. To ensure that the permeate and the lumen streams do not mix with each other in the membrane module, one graphite *o*-ring (99.53% C and 0.47% S; 2.8 g) is used (Fig. 1b). In the MR, the catalyst is packed in the membrane zone (150 mm length) and glass spheres (<1 mm diameter) are used in order to pack the catalyst bed.

2.3. Pure gases permeation experiments

Permeation experiments with pure gases show that the Pd-Ag membrane is permeable only to hydrogen and the linear trend of the hydrogen flux permeating through the membrane, Fig. 2a, confirms the following Sieverts' law:

$$J_{H_2} = \frac{Pe}{\delta} \cdot (p^{0.5}_{H_2\text{-lumen}} - p^{0.5}_{H_2\text{-shell}})$$

where J_{H_2} is the hydrogen flux permeating through the Pd-Ag membrane, Pe the hydrogen permeability, δ the Pd-Ag membrane thickness (50 μm), $p_{H_2\text{-lumen}}$ the hydrogen partial pressure in the retentate side, $p_{H_2\text{-shell}}$ the hydrogen partial pressure in the permeate side. Moreover, the linear trend of Fig. 2b suggests that

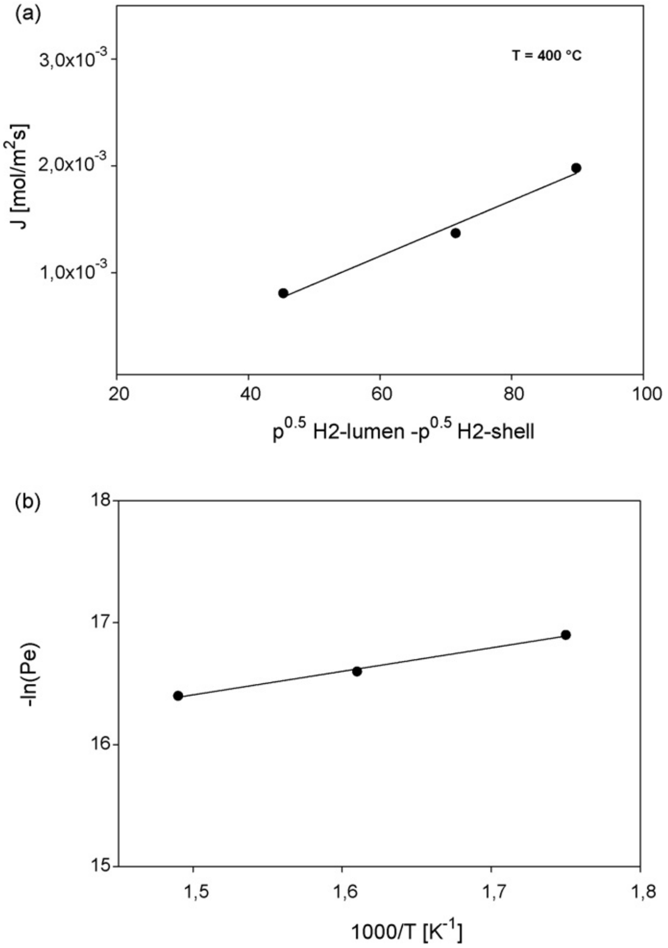

Fig. 2. Sieverts' plot (a) and Arrhenius plot (b).

the temperature dependence of the hydrogen permeability can be expressed by means of an Arrhenius-like equation:

$$\mathrm{Pe} = \mathrm{Pe}_0 \exp\left(\frac{-E_a}{RT}\right)$$

where Pe_0 is the pre-exponential factor, E_a the apparent activation energy, R the universal gas constant, T the absolute temperature.

The calculated E_a, 14.62 kJ/mol, and Pe_0, 1.0×10^{-5} mol m/(m^2 s kPa$^{0.5}$) are in good agreement with other experimental data found in literature for the same kind of Pd-based membranes [20]. Therefore, the overall hydrogen flux through the Pd-Ag membrane can be expressed by using the Richardson equation:

$$J_{H_2} = \frac{\mathrm{Pe}_0 \cdot \exp(-E_a/RT) \cdot (\sqrt{p_{H_2,\mathrm{lumen}}} - \sqrt{p_{H_2,\mathrm{shell}}})}{\delta}$$
$$= 2.0 \times 10^{-1} \exp\left(-\frac{1758.5}{T}\right) \cdot (\sqrt{p_{H_2,\mathrm{lumen}}} - \sqrt{p_{H_2,\mathrm{shell}}})$$

that combines the Sieverts' law and the Arrhenius equation.

2.4. Operating conditions and parameters

The reactor (FBR or MR) is placed in a temperature-controlled P.I.D. (Proportional + Integral + Derivative Control) oven and the reaction temperatures ranged between 250 and 300 °C. The sweep gas (N_2) used for the MR in counter-current mode is fed by means of a mass-flow controller (Brooks Instruments 5850S), driven by a computer software furnished by Lira (Italy). Both the reactants, water and methanol, are fed by means of volumetric pumps (type FMQG6) furnished by General Control (Italy).

The reaction pressure is kept constant at 1.3 bar by means of a regulating-valve system placed at the outlet side of the reactors (retentate side for the MR). Concerning the MR, the permeate pressure is always 1 bar and the constant sweep gas flow rate is 1.38×10^{-2} mol/min in counter-current mode. The water/methanol feed ratio ranges between 3/1 and 9/1. The liquid reactants are mixed, vaporised and, then, fed in the reactor. The retentate stream is passed over a cold-trap in order to condensate unreacted methanol and water, which are analyzed in order to evaluate the methanol concentration in the condensed volume. Both the dry retentate and permeate streams were measured by means of a bubble flow-meter and the outlet molar flow rate of each species was calculated by multiplying the retentate or permeate stream flow rates by the composition of the species, detected by using a temperature programmed HP 6890 Gas Chromatograph (GC) with a TCD (Thermal Conductivity Detector) detector 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$^{\mathrm{TM}}$ 1000 (15 ft. × 1/8 in.), connected in series, and a Molecular Sieve 5 Å (6 ft. × 1/8 in.); a 10-ways valve was used to optimise the analysis total time, which was about 7 min. This apparatus is controlled by a software furnished by Hewlett–Packard. Considering the MR, since it has two outlet streams (permeate and retentate), two TCD detectors were simultaneously used for measuring their composition at the same time. Both the FBR and the MR are packed with 3 g of $CuOAl_2O_3ZnOMgO$. Before reaction, the catalyst was pre-heated using N_2 up to 300 °C under atmospheric pressure and, afterwards, reduced by using H_2 (flow rate 15 ml/min) for 2 h at the same temperature.

Preliminary experiments for the MSR were performed at different conditions to analyse the products of the reactions. The analysis of the gas stream (by GC) detected as products: carbon monoxide, carbon dioxide and hydrogen. A flat temperature profile along the reactor during the reaction has been observed by using a three points thermocouple inserted into the lumen of both the FBR and the MR.

The following definitions are used for describing the FBR and the MR performances:

$$CH_3OH\ \mathrm{conversion}(X_{CH_3OH}, \%) = \frac{CH_3OH_{\mathrm{in}} - CH_3OH_{\mathrm{out}}}{CH_3OH_{\mathrm{in}}} \cdot 100$$

$$H_2\ \mathrm{selectivity}(S_{H_2}, \%) = \frac{H_{2,\mathrm{out}}}{H_{2,\mathrm{out}} + CO_{\mathrm{out}} + CO_{2,\mathrm{out}}} \cdot 100$$

$$CO\ \mathrm{selectivity}(S_{CO}, \%) = \frac{CO_{\mathrm{out}}}{H_{2,\ \mathrm{out}} + CO_{\mathrm{out}} + CO_{2,\ \mathrm{out}}} \cdot 100$$

$$CO_2\ \mathrm{selectivity}(S_{CO_2}, \%) = \frac{CO_{2,\ \mathrm{out}}}{H_{2,\ \mathrm{out}} + CO_{\mathrm{out}} + CO_{2,\ \mathrm{out}}} \cdot 100$$

$$H_2\ \mathrm{production\ (mol/s)} = H_{2,\mathrm{out}}$$

$$H_2\ \mathrm{production\ rate(mmol/kg_{catalyst}\ s)} = \frac{H_{2,\mathrm{out}}}{m_{\mathrm{catalyst}}}$$

$$m_{\mathrm{catalyst}}\ \mathrm{(kg)} = \mathrm{catalyst\ mass}$$

$$H_2\ \mathrm{recovery,\ (H.R.,\%)} = \frac{H_{2,\mathrm{permeate}}}{H_{2,\mathrm{permeate}} + H_{2}\text{-}\mathrm{retentate}} \cdot 100$$

The subscript "out" indicates the total outlet molar flow rate of each species. In particular, for the FBR only one outlet stream is present for each species, while for the MR there are two outlet streams (permeate and retentate). In particular, in the permeate stream only hydrogen and sweep gas are present because the

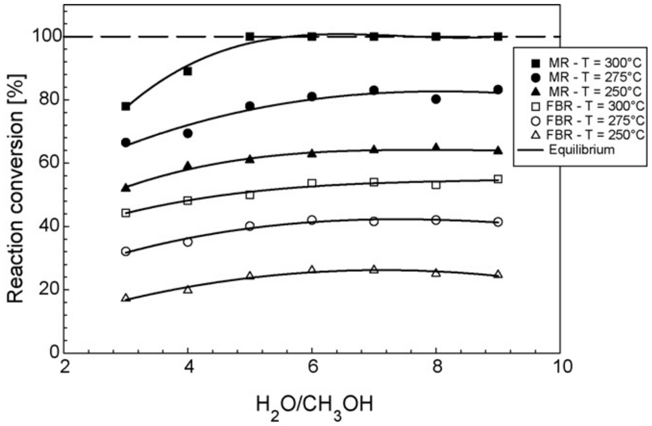

Fig. 3. Reaction conversion versus H_2O/CH_3OH molar feed ratio at different temperatures for the FBR and the MR. Reaction pressure = 1.3 bar and permeate pressure = 1 bar.

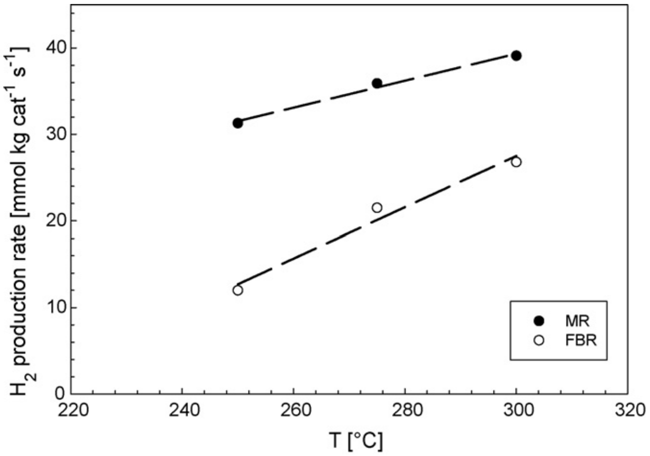

Fig. 4. Reaction temperature influence on the hydrogen production rate for the FBR and the MR using the $CuOAl_2O_3ZnOMgO$ catalyst. H_2O/CH_3OH = 6:1, reaction pressure = 1.3 bar, permeate pressure = 1 bar, sweep gas flow rate = 1.38 × 10^{-2} mol/min in counter-current mode.

dense Pd-Ag membrane exhibits an infinite selectivity towards H_2/other gases.

3. Results and discussion

The experimental results are illustrated as a comparison between the MSR reaction performances obtained in the MR and the FBR. All the experimental results reported in the present work are average values of different experimental points (at least five) taken in a fixed operating time (1 h). Moreover, the standard deviation was lower than 4% for each experimental point. The balance on the C is closed with a ±5% error.

Fig. 3 reports the methanol conversions in both the FBR and the MR versus the feed molar ratio at different temperatures. At 300 °C and at 6/1 H_2O/CH_3OH ratio, complete conversion is reached in the MR, while in the FBR it achieves a maximum value of 55%. Moreover, for each temperature and H_2O/CH_3OH ratio, the methanol conversion in the MR is higher than the FBR one. In fact, the Pd-Ag MR allows the selective hydrogen removal from the reaction side, promoting the equilibrium of the reactions (a), (b) and (c) shift towards the products, enhancing the methanol conversion. In particular, according to the Richardson equation by increasing the temperature a higher hydrogen flux through the Pd-Ag membrane takes place and a higher hydrogen removal from the retentate is realized. Consequently, according to the Le Chatelier principle, the reaction equilibria shift towards the products allowing to reach higher methanol conversions than the FBR.

Fig. 3 also shows that, at each temperature, the methanol conversion increases in both the reactors between 3/1 and 6/1 H_2O/CH_3OH ratio and then, the conversion reaches a plateau, probably because a higher water excess in the feed is not necessary to improve the methanol conversion by the reactions (b) and (c).

It should be noted that the MR at 250 °C shows higher conversions than the FBR at 300 °C, pointing out that by using the MR, working at milder conditions than the FBR, it is possible to obtain better performances with a resulting energy saving and a longer catalyst life.

Concerning the product selectivity, reported in Table 1, in both the FBR and the MR the $CuOAl_2O_3ZnOMgO$ catalyst shows high selectivity towards the hydrogen and carbon dioxide formation (selectivities ranging within 74% and 76% and 23% and 25%, respectively). This fact is probably due to the catalyst effect on the reaction system similarly to other catalysts used for the MSR

Table 1
Gas reaction selectivity for the Pd-Ag MR (a) and TR (b) at different temperatures and H_2O/CH_3OH molar ratios

MR	T = 300 °C			T = 275 °C			T = 250 °C		
H_2O/CH_3OH	S_{H2}	S_{CO}	S_{CO2}	S_{H2}	S_{CO}	S_{CO2}	S_{H2}	S_{CO}	S_{CO2}
9	73.4	0.7	25.9	76.1	0.4	23.5	76.6	0.3	23.1
8	74.7	0.4	24.9	76.2	0.4	23.4	76.0	0.3	23.7
7	74.4	0.6	25.0	76.0	0.4	23.6	76.0	0.2	23.8
6	74.0	0.6	25.4	75.8	0.5	23.7	75.9	0.2	23.9
5	73.9	0.7	25.3	75.9	0.4	23.6	75.7	0.2	24.1
4	74.5	0.6	24.9	76.6	0.3	23.1	76.4	0.2	23.4
3	73.4	0.7	25.9	76.4	0.3	23.3	76.1	0.2	23.7
TR	T = 300 °C			T = 275 °C			T = 250 °C		
H_2O/CH_3OH	S_{H2}	S_{CO}	S_{CO2}	S_{H2}	S_{CO}	S_{CO2}	S_{H2}	S_{CO}	S_{CO2}
9	76.8	0.5	22.7	75.9	0.8	23.3	76.9	0.5	22.7
8	76.6	0.5	22.9	75.8	0.7	23.5	76.6	0.5	22.9
7	76.6	0.5	22.9	75.9	0.9	23.2	76.7	0.5	22.8
6	76.1	0.6	23.3	75.8	0.9	23.3	76.8	0.5	22.7
5	76.1	0.6	23.3	75.8	1.0	23.2	76.8	0.5	22.7
4	76.1	0.7	23.2	75.8	1.2	23.0	76.8	0.6	22.6
3	76.3	0.5	23.2	75.7	1.8	22.6	76.6	0.6	22.9

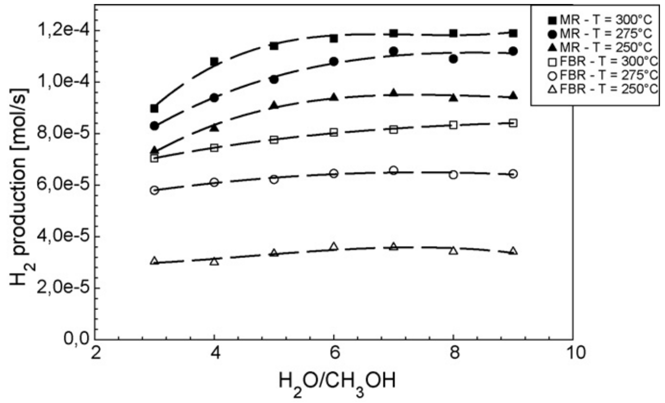

Fig. 5. Hydrogen production versus H_2O/CH_3OH molar rate at different temperatures for the MR and the FBR. Reaction pressure = 1.3 bar, permeate pressure = 1 bar.

reaction, being able to suppress the reaction (a) favouring a low CO formation [9,21,22].

Fig. 4 shows, for both the MR and the FBR, the hydrogen production rate versus the temperature at H_2O/CH_3OH feed ratio 6/1. In both the reactors, the hydrogen production rate shows a linear trend, demonstrating that no catalyst deactivation due to carbon deposition or sintering phenomena takes place in the range 250–300 °C, while the catalyst deactivation was found in literature for some Cu-based catalyst during the MSR [1,3,4].

More in details, at each temperature, in the MR a higher hydrogen production rate than in the FBR is achieved. This can be related to the positive effect of the hydrogen permeation through the membrane on the methanol conversion, which results in a higher hydrogen production in the MR than the FBR. In particular, at 250 °C the MR is able to give a hydrogen production rate 160% higher than the FBR. The difference between the MR and the FBR decreases at higher temperatures (300 °C) because the MR reaches 100% methanol conversion while FBR is still far from the total conversion. The same trend reported in Fig. 4 for H_2O/CH_3OH = 6/1 was found for higher H_2O/CH_3OH feed ratios.

Concerning the hydrogen production, Fig. 5 shows that the MR gives better results than the FBR in the whole range of feed ratios and temperatures investigated. The hydrogen production behaviour follows the methanol conversion (Fig. 3). In fact, according to the Richardson equation, when the temperature increases a higher hydrogen flux through the membrane occurs and, therefore, a higher hydrogen removal from the reaction side is obtained, resulting in a shift of the reaction equilibrium towards the products (accordingly to the Le Chatelier principle).

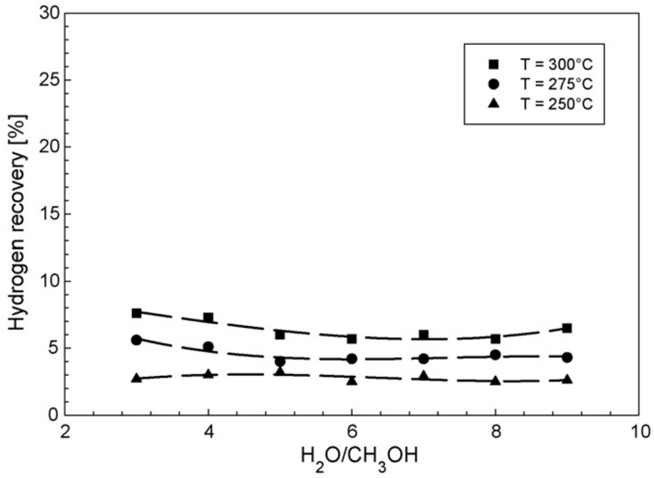

Fig. 6. Hydrogen recovery in the Pd-Ag MR versus H_2O/CH_3OH molar ratio at different temperatures. Reaction pressure = 1.3 bar, permeate pressure = 1 bar.

In other words, the MR allows to give at least two advantages with respect to the FBR working at the same operative conditions: higher performances, in terms of methanol conversion and hydrogen production, and the possibility to obtain a CO-free hydrogen stream in the permeate side available, e.g., to be directly fed to a PEMFC system.

With the aim of producing a CO-free hydrogen stream, an important parameter to be considered in the MR is the hydrogen recovery which represents the percentage of the hydrogen produced recovered in the shell side of the MR. This is possible because of the infinite hydrogen permeation selectivity of the Pd-Ag membrane with respect to the other gases.

Fig. 6 shows the hydrogen recovery versus H_2O/CH_3OH feed ratio at different temperatures. It can be seen that, by increasing the temperature, the hydrogen recovery increases because, according to the Richardson equation, the hydrogen flux through the membrane increases with the temperature too. Concerning the effect of the H_2O/CH_3OH feed ratio on the hydrogen recovery, no relevant differences can be observed in the whole range of feed ratios investigated. In fact, from thermodynamic considerations, an increase of the H_2O/CH_3OH feed ratio results in a higher methanol conversion and a higher hydrogen production. Otherwise, according to the permeation laws, the higher water content results in a

Table 2
Comparison in terms of methanol conversion between literature data and this work

	T (°C)	Sweep gas flow rate (mol/min)	H_2O/CH_3OH	Hydrogen production (mol/s)	H.R. (%)	Conversion (%)
Pd-Ag MR [13]	350	1.60×10^{-2}	4.5	1.76×10^{-4}	10	86
Pd-Ag MR [13]	450	1.60×10^{-2}	4.5	2.04×10^{-4}	15	100
Pd-Ag MR [13]	450	3.20×10^{-2}	4.5	3.68×10^{-4}	40	100
Pd-Ag MR this work	300	1.38×10^{-2}	5.0	1.15×10^{-4}	8	100

Table 3
MSR in MRs: operating conditions and methanol conversions comparison between literature data and this work

Reactor type	Membrane	Catalyst	Catalyst weight (g)	*T* (°C)	Sweep gas flow rate (mol/min)	H_2O/CH_3OH	Reaction pressure (bar)	Conversion (%)
MR [13]	Pd-Ag	$Ru\text{-}Al_2O_3$ 5%	3.0	400	1.60×10^{-2}	4.50	1.30	100
MR [11]	Pd-Ag	$Cu/ZnO/Al_2O_3$	7.5	250	1.30×10^{-2}	2.43	1.25	70
This work	Pd-Ag	$CuOAl_2O_3ZnOMgO$	3.0	300	1.38×10^{-2}	5.00	1.30	100
This work	Pd-Ag	$CuOAl_2O_3ZnOMgO$	3.0	250	1.38×10^{-2}	3.00	1.30	52

dilution of the hydrogen produced, thus decreasing the hydrogen partial pressure in the retentate side (i.e. a reduction of the permeation driving force). In practice, the two effects of the H_2O/CH_3OH feed ratio compensate each other, thus resulting in an almost constant hydrogen recovery with the feed ratio. It should be considered that the low values of the hydrogen recovery are mainly due to the low reaction pressure considered in this work. A way to increase the hydrogen recovery value, for each temperature, is the increase of the reaction pressure which results in a higher driving force for the hydrogen permeation through the membrane. Moreover, the hydrogen flux through the membrane is promoted by high temperatures due to the Arrhenius like dependence of the hydrogen permeation with the temperature.

In other words, both higher temperatures and the difference between the square roots of hydrogen partial pressure on retentate and permeate sides could provide the increase of the hydrogen permeation, allowing a higher hydrogen recovery. In fact, as illustrated in Table 2, with the same Pd-Ag MR, the hydrogen recovery increases with the temperature, being 8% at 300 °C and 15% at 450 °C at the same reaction pressure. Moreover, it can be seen that by decreasing the hydrogen partial pressure in the permeate side of the reactor (i.e. by increasing the sweep gas flow rate) the hydrogen recovery increases too. In fact, it is 15% at sweep gas flow rate 1.6×10^{-2} mol/min, while it increases up to 40% at 3.2×10^{-2} mol/min. It should be highlighted that, in both these two last cases, the methanol conversion is 100%, thus the operative conditions reported in Table 2 were chosen in order to increase the CO-free hydrogen recovery.

Table 3 reports a comparison between the MR performances of the present work with literature data. It is possible to observe that, the methanol conversion achieved at 300 °C with the $CuOAl_2O_3ZnOMgO$ is the same (100%) as the one obtained by using a commercial 5% Ru-based catalyst working at 400 °C. Considering a commercial Cu-based catalyst, it can be seen that at 250 °C its performances are comparable with the ones obtained with our catalyst. In fact, 67% methanol conversion is obtained by using 7.5 g of the commercial Cu-based catalyst, while 52% methanol conversion is obtained, in the same experimental conditions, by using 3 g of our new $CuOAl_2O_3ZnOMgO$ catalyst.

Moreover, no deactivation of the new catalyst has been observed up to 300 °C.

4. Conclusions

The methanol steam reforming reaction has been studied from an experimental point of view in both a FBR and a Pd-Ag MR using a new $CuOAl_2O_3ZnOMgO$ catalyst. The MR showed better performances in terms of methanol conversions and hydrogen productions than the FBR one working at the same operative conditions. The $CuOAl_2O_3ZnOMgO$ catalyst exhibited high reaction activity in the temperature range 250–300 °C. Complete methanol conversion was achieved in the MR at 300 °C and H_2O/CH_3OH ratio higher than 5/1, while in both the FBR and the MR the carbon monoxide selectivity was lower than 1%. No carbon deposition and catalyst sintering phenomena were noticeable in both the reactors between 250 and 300 °C.

A comparison in terms of hydrogen recovery and methanol conversion was reported between the MR packed with $CuOAl_2O_3ZnOMgO$ catalyst and other commercial catalysts from literature. In order to optimise the hydrogen recovery in the MR, the effect of operative parameters such as the sweep gas flow rate and the reaction pressure will be evaluated with a deeper scouting in a future work.

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