DELIVERABLE

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D3.5 – Palladium membranes

Revision: 1.2

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1. Executive Summary

The task 3.3 of the project BeingEnergy refers to the preparation and characterization of composite palladium membranes, namely ultra-thin palladium composite membranes supported on asymmetric alumina tubes, for methanol steam reforming (MSR) application. The goal was to produce a pure hydrogen stream and improving the methanol conversion, since the hydrogen is selectively removed and the backward reactions is prevented. At M24 it was intended to report the preparation and characterization of the palladium membranes, including stability tests.

The ultra-thin palladium composite membranes supported on asymmetric alumina tubes should have been developed by Dr. Alfredo Tanaka, who worked at UPORTO and was a member of the research team at the submission time of the project. Since Dr. Tanaka left UPORTO (May 2012), thin palladium membranes were not prepared nor characterized at UPORTO, as already mentioned in the Breakdown Structure (D1.2). As an alternative, it was considered the acquisition and characterization of alternative supported Pd membranes, in collaboration with ITM-CNR.

Extensive literature review was made on methanol steam reforming reaction performed in both conventional and membrane reformer reactors. Additionally, CuO/ZnO binary catalysts were tested in a conventional and membrane reactors configuration, using thin (7 μm thickness) composite Pd/Al_2O_3 membrane. Present commercially available palladium membranes show a benefit to the methanol steam reforming conversion only at temperatures above 220 °C. The BeingEnergy project targets an operating temperature of 180 °C, thus making unfeasible the use of palladium based membrane reformer.

Taking into account the comments and recommendations of the Mid-Term Review of the project (FCH-JU 2014 D2612) task 3.3 (Preparation and characterization of composite palladium membranes) was reassessed. Considering the lack of improvements regarding the development and characterization of palladium membranes, up to M24, and the increase complexity of the hybrid technology, no further efforts will be made regarding task 3.3.

2. Developed work

2.1 Literature review on conventional and membrane reformer reactors

To prepare the development of palladium membranes for MSR application, extensive review was done on methanol steam reforming reaction performed in both conventional and membrane reactors. Particular attention was attributed to the importance of the MSR catalysts preparation, application and feasibility of membrane reactors for MSR reaction.

The developed work produced the following publication:

A. Iulianelli, P. Ribeirinha, A. Mendes, A. Basile, Methanol steam reforming for hydrogen generation via membrane reactors: a review, Renewable & Sustainable Energy Reviews, 29 (2014) 355-368.

2.2 CuO/ZnO binary catalysts in a conventional and membrane reactors configuration

CuO/ZnO binary catalysts were characterized in a conventional MSR reactor and in a membrane reactor, using a thin composite Pd/Al_2O_3 membrane.

The effect of ZnO surface area and polarity on Cu/ZnO activity-selectivity was studied for MSR, using a conventional reactor. The ZnO surface area was varied by changing the calcination temperature of the prepared ZnO materials. Moreover, the polarity of the ZnO was modified using different Zn precursors, acetate or nitrate.

In order to increase the conversion at low temperatures (<200 ºC), while producing high purity H_2, the most performing catalyst was tested also in a Pd-alumina membrane reactor. The effect of varying the temperature and the operating pressure of the membrane reactor on methanol conversion, H_2-recovery and H_2-permeate purity was evaluated.

A paper will be submitted soon by partners UPORTO and ITM-CNR.

2.2.1 Experimental

Preparation of ZnO supports

ZnO samples were prepared by a modified hydrothermal method [1]. The following nomenclature for ZnO samples was used (Table 1), $Z_{nx\text{-}CT}$, where: x denotes the zinc precursor, zinc-acetate (Ac) or zinc-nitrate (N) and CT represents the calcination temperature in celcius degrees (Table 1). Accordingly, the $Zn_{Ac\text{-}375}$ sample was prepared from zinc-acetate as precursor and calcined at 375 ºC for 30 minutes.

Preparation of Cu/ZnO catalysts

Cu/ZnO catalysts were prepared by impregnation of the ZnO supports with an aqueous solution of copper nitrate (the amount of copper being calculated to achieve a nominal metal loading of 20 wt. %). The resulting cake was dried at 110 ºC overnight and calcined at 360 ºC during

8.5 h. As for ZnO carriers, Cu/ZnO catalysts will be denoted in terms of the ZnO supports calcination temperature (CT) and the type of zinc precursor used; thus when zinc nitrate was used the catalyst was denominated as $CuO/ZnO_{N\text{-}CT}$ and when prepared from zinc acetate it was denominated as $CuO/ZnO_{Ac\text{-}CT}$, where CT denotes the calcination temperature in ºC.

Table 1 - Experimental parameters studied for the preparation of ZnO samples, calcination temperature series (ZnAc-CT: Ac Zn-acetate as precursor; CT: calcination temperature); Zn-precursor series ($Zn_{x\text{-}375}$: x stands for Zn-acetate (Ac) or Zn-nitrate (N); both samples were calcined at 375ºC).

Parameter studied	**Range**	**Sample name**	**SBET (m^2/g)**	**Polarity* $I_{(002)}/I_{(100)}$**
Calcination temperature (CT) (ºC)	300	$Zn_{Ac\text{-}300}$	64	0.76
	350	$Zn_{Ac\text{-}350}$	71	0.78
	375	$Zn_{Ac\text{-}375}$	80	1.10
	400	$Zn_{Ac\text{-}400}$	54	0.80
Zn-precursor	Zn-acetate	$Zn_{Ac\text{-}375}$	80	1.10
	Zn-nitrate	$Zn_{N\text{-}375}$	77	0.60

*: polarity of the ZnO carriers, measured as the ratio between XRD plane (002) and plane (100)

Characterisation of MSR catalysts using conventional rector

The activity and selectivity of the catalysts was determined for MSR reaction using an in house built set-up. Steam reforming of methanol was performed at atmospheric pressure in a tubular reactor (7.25 mm i.d.) placed inside an oven. The reaction temperature was recorded inside the packed bed reactor using a thermocouple. The reactor was loaded with 200 mg of catalyst (180-350 μm) diluted with 200 mg of glass spheres. Plug flow conditions were ensured keeping catalyst bed length to catalyst size ratio above 50 ($L_{reactor}/d_{particles}$ higher than or equal to 50) and the reactor diameter to size ratio above 30 ($d_{reactor}/d_{particles}$ higher than or equal to 30) [2]. Activity measurements were performed in the temperature range of 180 ºC to 300 ºC and space-time ratio of. $W_{cat.}\big/F^{0}_{CH_3OH} = 83\ \mathrm{kg_{cat.}} \times \mathrm{mol^{-1}} \times \mathrm{s}$. Prior to the catalytic activity measurements, the catalyst was reduced *in situ* using a diluted hydrogen flow (40 vol.% of H_2 balanced with N_2), at 240 ºC for 2 h. The gas feed flow rate was controlled by mass flow controllers from Bronkhorst (model F-201C, ± 0.1 FS). Required flow rate of methanol aqueous solution was controlled using a Controlled Evaporation and Mixing (CEM) system (Bronkhorst). The condensable reactants were separated from the gas mixture in a condenser at *ca*. 0 ºC, placed outside the oven.

Hydrogen and carbon dioxide were analysed in a quadruple mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320). Trace amounts of carbon monoxide were measured using a CO infra-red analyser (Signal Instruments, 7100 FM, accuracy: ±0.2 ppm). The methanol conversion (X_{CH3OH}) and CO selectivity (S_{CO}) were calculated by applying equations (1) and (2), respectively:

$$X_{CH_3OH}\left(\%\right) = \frac{F^{out}_{CO_2} + F^{out}_{CO}}{F^{in}_{CH_3OH}} \times 100 \qquad (1)$$

$$S_{CO}\left(\%\right)=\frac{F_{CO}^{out}}{F_{CO_2}^{out}+F_{CO}^{out}}\times 100 \qquad (2)$$

where $F_{CO_2}^{out}$ and F_{CO}^{out} are the carbon dioxide and carbon monoxide outlet molar flow rates while $F_{CH_3OH}^{in}$ is the inlet stream of methanol fed to the reactor.

Characterisation of MSR catalysts using a composite Pd-Al_2O_3 membrane reactor

The experimental membrane reactor is sketched in Figure 1 and its design is property of ITM-CNR. The composite Pd-based membrane is made of a thin Pd layer (~7 μm) deposited via electroless plating onto a porous Al_2O_3 support. The composite membrane has been produced by Nanjing University of Technology (the porous Al_2O_3 support was kindly offered by Gao Q Funct. Mat. Co.); it is 75 mm of length, 10 mm of O.D. and housed in a stainless steel module 120 mm length, 15 mm of O.D., equipped with two C-based gaskets at both membrane ends to prevent the mixing between permeate and retentate stream. The porous Al_2O_3 supported Pd-membrane was packed with a CuO/ZnO catalyst. Prior to the reaction tests, in order to evaluate the hydrogen/other gases ideal selectivity (equations (3)), the composite Pd-based membrane has been tested in pure gas permeation tests at T = 300 °C and transmembrane pressure (ΔP) equal to 1.0 bar.

$$\alpha_{H2}/_{other\ gas} = J_{H2}/J_{other\ gas} \qquad (3)$$

Where J_{H2} and $J_{other\ gas}$ represent the hydrogen permeating flux and the permeating flux of another gas taken in consideration. Afterwards, methanol steam reforming (MSR) reaction tests have been performed in the range of 220 °C - 300 °C, at 2 bar (abs.) of reaction pressure, ~1.0 h^{-1} as weight hourly space velocity (WHSV). The permeate pressure has been kept constant at 1.0 bar.

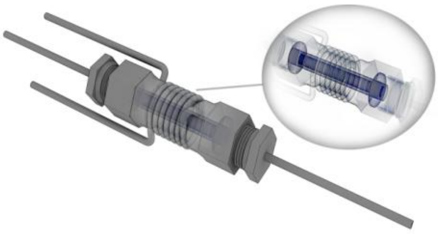

Figure 1 - Membrane reactor scheme for composite Pd-Al_2O_3 membrane

The scheme of the experimental lab plant is illustrated in Figure 2. The MR has been heated up under helium and a P680 HPLC pump (Dionex) has been used for supplying liquid methanol and water.

Afterwards, they have been vaporized, mixed with a constant flow rate of N_2 (8.0 mL min^{-1}) as internal standard gas and fed into the MR reaction side. The retentate stream was directed to a cold trap in order to condensate the unreacted water and methanol. Both permeate and retentate stream compositions were analysed using a temperature programmed HP 6890 GC with two thermal conductivity detectors at 250 °C and Argon as a carrier gas. The GC is equipped by three packed columns: Porapack R 50/80 (8 ft 1/8 inch) and CarboxenTM 1000 (15 ft 1/8 inch) connected in series, and a Molecular Sieve 5 Å (6 ft 1/8 inch).

During the pure gas experimental tests, the permeating flux of each gas among H_2, N_2 and He has been measured by a bubble-flow meter as an average value of, at least, 10 experimental points. Concerning the reaction tests, each experimental point obtained of this work represents an average value of, at least, 10 experimental points taken in 140 min at steady-state conditions with an error variation lower than 3 %. Before reaction, the catalytic bed was reduced by using hydrogen and helium at 280 °C for 2 h.

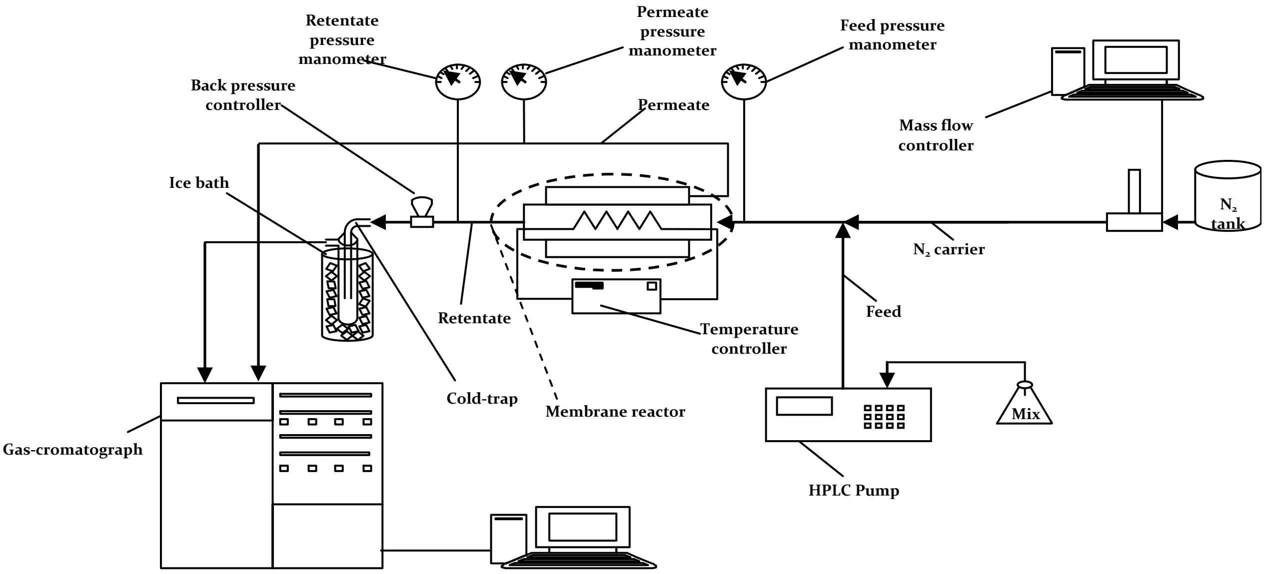

Figure 2 - Schematic flow-sheet of the experimental plant at lab-scale

2.2.2 Results

Catalytic activity of Cu/ZnO samples in the conventional reactor

The evolution of methanol conversion, H_2 and CO_2 yields with the reaction temperature for some representative Cu/ZnO catalysts is presented in Figure 3 and Figure 4. Over all the catalysts, the methanol conversion, H_2 and CO_2 yields increase with temperature, as expected. Regardless the catalyst and the temperature, H_2 and CO_2 are the main products, although some CO is also detected (Table 2). The CO yield depends on the reaction temperature and the support history (Table 2). The production of CO is being favoured at high temperatures. This is easily understood if we consider that CO is a by-product from side reactions such as methanol decomposition (MD) and reverse water gas shift (RWGS). Both reactions are favoured at higher temperatures due to their endothermic character, so explaining the evolution of CO with temperature.

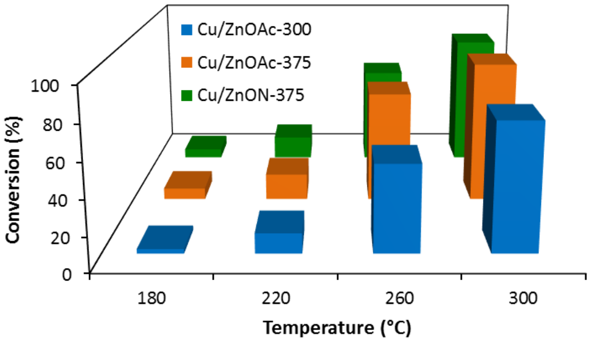

Figure 3 - Evolution of methanol conversion with reaction temperature for Cu/ZnO$_{Ac-300}$, Cu/ZnO$_{Ac-375}$ and Cu/ZnO$_{N-375}$ catalysts

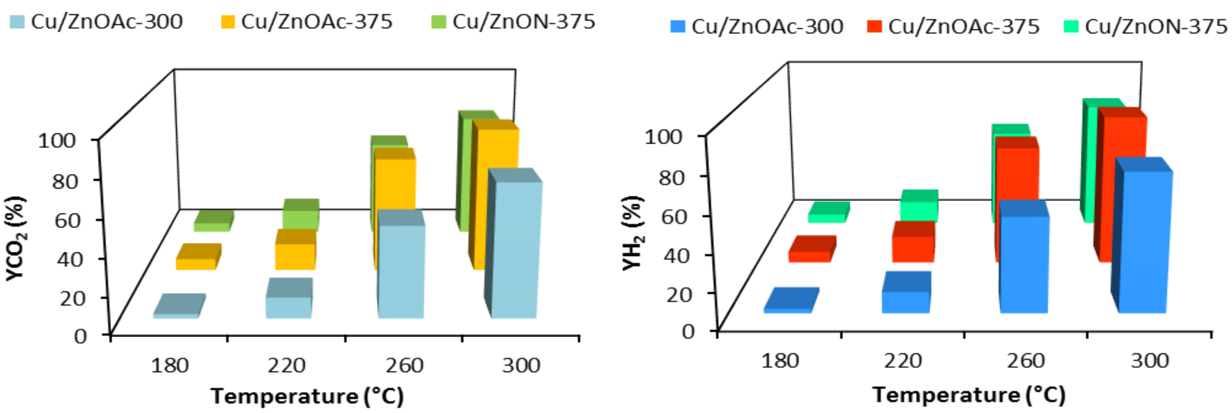

Figure 4 - Evolution of hydrogen (YCO_2) and carbon dioxide yields (YH_2) with reaction temperature for CuO/ZnO_{Ac-300}, CuO/ZnO_{Ac-375} and CuO/ZnO_{N-375} catalysts

The variation of the methanol conversion as a function of the specific surface area of ZnO support is illustrated in Figure 5. It is evident from this figure that the conversion of the Cu/ZnO samples is directly related to the surface area of ZnO support: the higher the SBET, the higher the conversion. This could be due to the fact that ZnO supports with higher surface areas are able to better disperse Cu particles, leading to a higher number of exposed active sites (Cu sites) and consequently to higher activity. It is also interesting to note that catalysts prepared from ZnO supports with similar surface areas (Cu/ZnO_{Ac-375} and Cu/ZnO_{N-375}) also display similar conversion values (Table 2, which is in good agreement with the previous assumption.

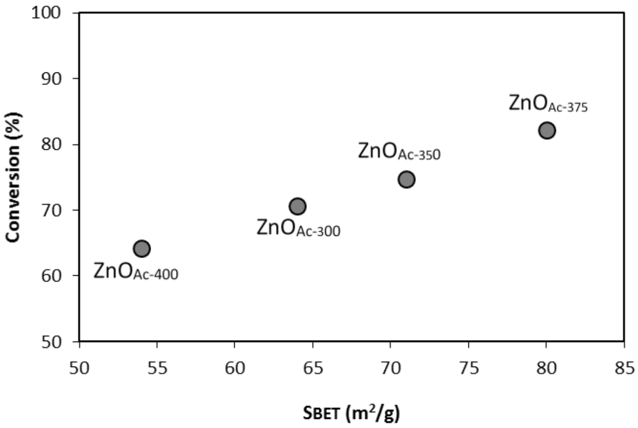

Figure 5 - Dependence of methanol conversion (measured at 300 ºC) on the specific surface area of ZnO carriers

On the contrary, there is no clear correlation between the CO production and the surface area of ZnO carriers, as inferred from Figure 6. In fact, all the catalysts obtained from ZnO with different SBET produce similar amounts of CO (Table 2). However, the two catalysts with similar surface areas but very different polarity (CuO/ZnOAc-375 and CuO/ZnON-375) show the largest difference in selectivity.

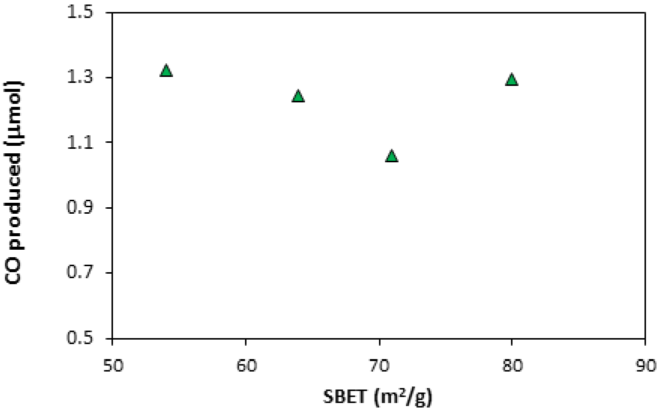

Figure 6 - Evolution of CO produced during MSR at 300 ºC with the specific surface area of ZnO carriers

The variation of CO amount with ZnO polarity is illustrated in Figure 7. Data presented in this figure suggest that the selectivity (regarded as CO produced) of Cu/ZnO catalysts is related to the polarity of the ZnO supports. A low polarity (lower defects number) of the ZnO support gives less selective samples, namely, producing higher CO amounts and vice versa. This becomes clear comparing the selectivity of the two samples prepared from different ZnO-precursors, which are also the samples with the highest difference in polarity (0.60 and 1.1 for CuO/ZnON vs. CuO/ZnO375, respectively; Figure 7). Clearly, the lower the polarity, the higher is the CO production.

The polarity of ZnO is related to the presence of defects. Typical ZnO materials exhibit a würtzite structure with the polar planes corresponding to the basal planes of the hexagonal würtzite unit cell [3]. The würtzite configuration has preferential exposure of non-polar facets (lower polarity). It is well-accepted that higher proportion of polar facets means also a higher number of defects, such as oxygen vacancies, that may play a crucial role in methanol and water activation. As already mentioned, the polar planes of ZnO have null activation energy for the dissociation of methanol and water molecules, being preferential sites for MSR reaction.

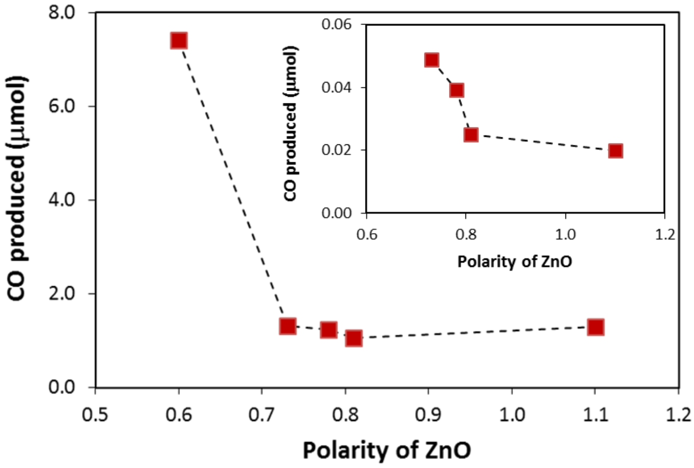

Figure 7 - Dependence of CO production (recorded at 300 ºC) on the polarity of ZnO carriers

The CO is indicated as a product of the unimolecular decomposition of methyl formate or from the decomposition of formaldehyde. Since ZnO is an amphiphilic molecule the presence of a higher proportion of non-polar planes could favor the later reactions and therefore promote the production of the undesirable CO, so explaining the lower selectivity of Cu/ZnO samples prepared from less polar ZnOs.

Table 2 Methanol conversion, CO_2 and H_2 yields, and CO amount measured at 220 ºC and 300 ºC in the conventional fixed bed reactor

Sample	**X_{CH3OH} (%)**		**Y_{CO2} (%)**		**Y_{H2} (%)**		**CO produced (μmol)**
Temperature (ºC)	220	300	220	300	220	300	300
CuO/ZnO_{Ac-300}	11.7	70.6	11.6	70.3	11.7	73.1	1.32
CuO/ZnO_{Ac-350}	13.8	74.8	13.7	73.6	13.8	76.5	1.25
CuO/ZnO_{Ac-375}	15.9	82.2	15.7	80.9	16.1	84.1	1.29
CuO/ZnO_{Ac-400}	7.9	64.2	7.8	60.1	7.9	62.5	1.06
CuO/ZnO_{N-375}	14.7	80.1	14.1	72.7	14.3	75.6	7.42

MSR with a composite Pd-Al_2O_3 membrane reactor(MR)

Before reaction tests, the permeation characteristics of the fresh Pd/Al_2O_3 membrane have been investigated at T = 300 °C and Δp = 1.0 bar. Table 3 shows the ideal selectivities obtained during the pure gas permeation tests, meanwhile confirming that the composite Pd-based membrane is not full selective to hydrogen permeation with respect to all other gases.

Table 3 Permeation characteristics of the fresh composite Pd/Al_2O_3 membrane

Pure gas (*i*)	**J_i [$mol\cdot m^{-2}\cdot s^{-1}$]**	**Permeance$_i$ [$mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$]**	**$\alpha_{H2/i}$**
H_2	$1.42\cdot 10^{-1}$	$1.42\cdot 10^{-6}$	1
N_2	$2.36\cdot 10^{-5}$	$2.36\cdot 10^{-10}$	> 6000
He	$4.29\cdot 10^{-5}$	$4.29\cdot 10^{-10}$	~ 3300

Successively, the reaction tests on MSR in the composite Pd/Al_2O_3 MR were carried out by varying the temperature in the range 220 °C – 300 °C, at 2.0 bar (abs), H_2O/CH_3OH feed molar ratio equals to 2.5/1 and WHSV = 0.95 h^{-1}. The aim of this first experimental campaign has been to evaluate the Zn-Ac catalyst performance in terms of activity and stability with time on stream. Table 4 illustrates the variation of both methanol conversion and gas selectivities at different temperature. As shown, the higher the temperature the higher the conversion, confirming that Zn-Ac catalyst is particularly active at higher temperature. In particular, it is worthy of notice that a temperature increase allowed two positive effects on the MR system: the first effect is due to the thermodynamic owing to endothermic characteristic of the MSR reaction; the second one is due to the H_2 permeation through the membrane (shift effect). In the latter case, at higher temperature the hydrogen permeation through the membrane is enhanced and, consequently, this induces a higher H_2 removal from the reaction to the permeate side, favouring the shift of the MSR reaction towards further products formation as well as higher methanol consume.

Table 4 Methanol conversion (into gas) and gas selectivity (H_2, CO and CO_2) at different temperature, WHSV = 0.95 h^{-1} and transmembrane pressure = 1.0 bar

Product gas selectivity	**220 °C**	**260 °C**	**300 °C**
H_2	74.56	74.46	74.18
CO	0.75	0.88	1.25
CO_2	24.69	24.66	24.57
CH_3OH conversion [%]	12.4	47.1	97.4

Concerning the catalyst performance, by taking into account the hydrogen selectivity reported in Table 4, it has been possible to affirm that this catalyst is particularly active towards hydrogen generation and able to depress CO formation. Furthermore, Figure 8 highlights the stability of the catalyst as confirmed by the constant trend of H_2, CO, CO_2 selectivities with respect to time on stream up to 3 h of operation at steady state conditions. A similar trend was confirmed in all the MR experimental tests of this work, suggesting that the catalyst is stable under long time operation.

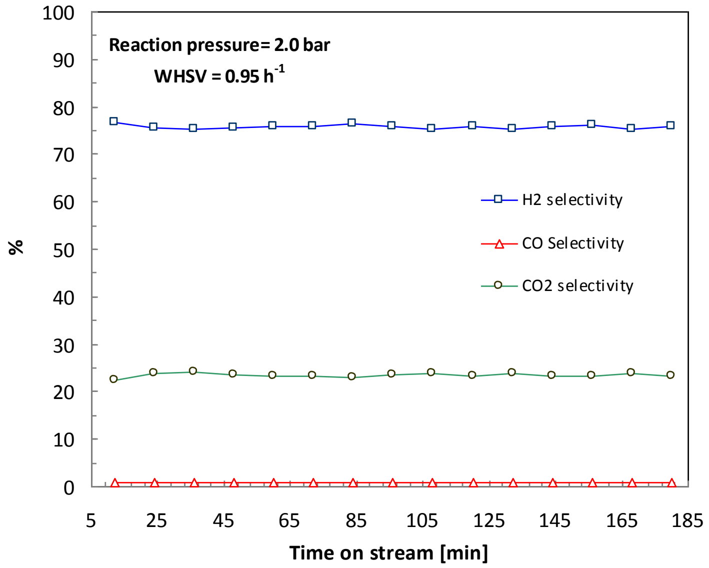

Figure 8 - Gas selectivity vs time on stream for MSR reaction in the Pd/Al_2O_3 MR at T = 220 °C, transmembrane pressure = 2.0 bar, WHSV = 0.95 h^{-1}, H_2O/CH_3OH = 2.5/1

Pressure effect

The second section of the experimental campaign of this work has been devoted to study the MR performance for obtaining high-grade hydrogen stream from permeate side. Therefore, the reaction tests have been carried out at 330 °C, feed molar ratio equal to 1.5/1, WHSV = 2.73 h^{-1} and by varying the reaction pressure between 1.5 bar - 2.5 bar (abs). In detail, Figure 9 shows the hydrogen permeate purity and hydrogen recovery at 330 °C at various reaction pressures.

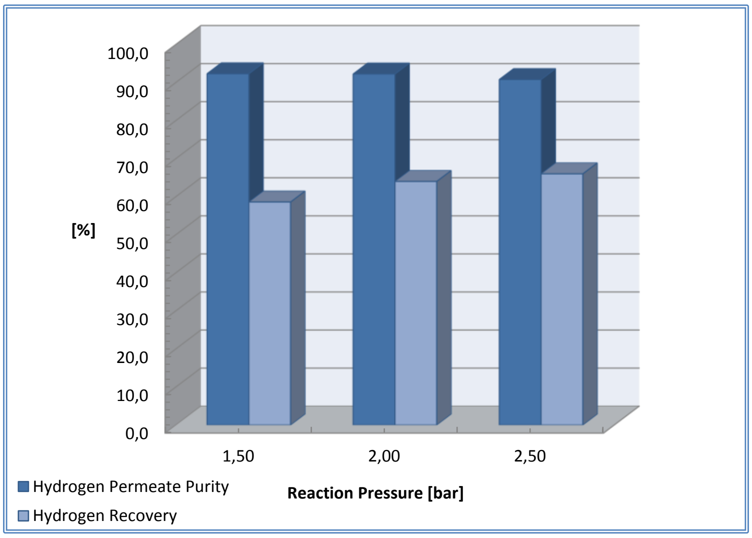

Figure 9 - Hydrogen permeate purity and hydrogen recovery vs reaction pressure at 330 °C, $H_2O/CH_3OH=1.5/1$ and WHSV=2.73 h^{-1} during MSR reaction in the Pd/Al_2O_3 MR

The hydrogen recovery increases as much as the reaction pressure is higher, overcoming 65 % at 2.5 bar. Indeed, a higher reaction pressure maximizes the hydrogen permeation driving force inducing a higher hydrogen permeating flux through the membrane. As a consequence, more H_2 is removed from reaction side and collected in permeate side, enhancing the hydrogen recovery. Nevertheless, the hydrogen permeate purity decreases by increasing the reaction pressure. In fact, at higher transmembrane pressure, besides hydrogen the other gases are forced to pass through the defects of the composite membrane, globally provoking a lower hydrogen composition in the permeate side, with a consequent reduction of the hydrogen permeate purity. However, as reported in Table 5, no CO was noticed in the permeate side.

Table 5 - Flow rates of the gases present in the permeate stream at different reaction pressure during MSR reaction at 330 °C, WHSV = 2.73 h^{-1}

	Reaction Pressure [bar]		
Flow rate gas - permeate	**1.5**	**2.0**	**2.5**
H_2 [mL·min^{-1}]	1.27	1.90	1.97
CO_2 [mL·min^{-1}]	0.11	0.16	0.2

WHSV effect

The effect of WHSV during MSR reaction on the MR performance has been also studied by choosing the operating conditions to recover as much as possible hydrogen from permeate side. Therefore, hydrogen recovery and hydrogen permeate purity have been evaluated at reaction pressure of 2.5 bar, T = 330 °C, H_2O/CH_3OH feed molar ratio equal to 1.5/1 and various WHSV. Thus, Figure 10 illustrates that hydrogen recovery increases by decreasing WHSV because the lower the WHSV the higher the residence time of the reactants in the catalytic bed. This effect is advantageous for generating more hydrogen, which corresponds in a higher hydrogen retentate partial pressure, and, then, in an enhancement of the hydrogen permeation driving force with a consequent improvement of hydrogen recovery, equal to around 75 % at 1.37 h^{-1}.

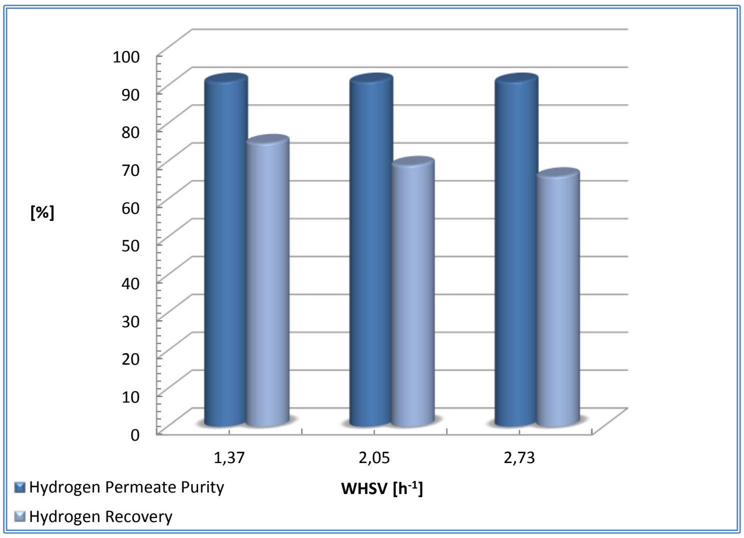

Figure 10 - Hydrogen permeate purity and hydrogen recovery vs WHSV at 330 °C, $H_2O/CH_3OH=1.5/1$ and reaction pressure = 2.5 bar during MSR in a Pd/Al_2O_3 MR

Furthermore, the hydrogen permeate purity did not vary significantly with WHSV according to constant value of around 91%. Also in this case, no CO presence was noticed in the permeate side.

At the end of the whole experimental reaction campaigns, the permeation characteristics of the Pd/Al2O3 membrane have been checked once again at *T* = 300 °C and ΔP = 1.0 bar. Table 6 reports the new ideal selectivities values, which are different with respect to the measurements realized with fresh membrane. This probably occurred because of the effect of thermal cycles, greatly affecting the gas permeation characteristics of the composite Pd-membrane.

Table 6 - Permeation characteristics of the composite Pd/Al_2O_3 membrane at the end of the whole experimental campaign

Pure gas (*i*)	**J_i [mol/m^2·s]**	**Permeance$_i$ [mol·m^{-2}·s^{-1}·Pa^{-1}]**	**$\alpha_{H2/i}$**
H_2	$9.87 \cdot 10^{-2}$	$1.95 \cdot 10^{-6}$	1
N_2	$2.60 \cdot 10^{-5}$	$5.14 \cdot 10^{-10}$	~ 3800
He	$6.70 \cdot 10^{-5}$	$1.32 \cdot 10^{-9}$	~ 1500

3. Conclusions

Ultra-thin palladium composite membranes supported on asymmetric alumina tubes, for methanol steam reforming (MSR) application, were not prepared at UPORTO as originally planned, due to Dr. Tanaka leaving the university just before the start of the project.

Alternatively, extensive literature review was made on MSR performed in both conventional and membrane reactors, and CuO/ZnO binary catalysts were prepared and tested in both reactors configuration, using thin composite Pd/Al_2O_3 membrane, in collaboration with partner ITM-CNR.

The effect of ZnO surface area and polarity was studied on Cu/ZnO activity-selectivity for MSR. The activity of Cu/ZnO catalysts shows a marked dependence on the surface area of the ZnO supports; the catalysts having the higher surface area also exhibits the higher activity. On the other hand, the results seem to point out that the selectivity of the prepared Cu/ZnO catalysts is related to the polarity of ZnO carriers: the increase on the polarity leads to higher selectivity (lowers the CO yield).

The most performing catalyst (CuO/ZnO_{Ac-375}) was tested in a Pd/Al_2O_3 membrane reactor. Unfortunately, the use of the Pd membrane reactor did not bring significant increase in the conversion at low temperatures (<220 °C). In fact, the best result was reached at 300 °C, with 97% of methanol conversion. Furthermore, a good stability of both conversion and gas selectivity has been noticed during the process operation.

With the aim of emphasizing the high grade hydrogen production, in the second section of experimental tests the best result was achieved at 330 °C, 2.5 bar and at WHSV = 1.37 h^{-1}, with a hydrogen recovery of around 75 % and a hydrogen permeate purity of more than 90%.

The Pd-based MR can represent a valid choice as an alternative device to the CRs at high temperature (> 300 ºC), due to its capability to reach high methanol conversion in combination to the recovery of a CO-free hydrogen stream in the MR permeate side, useful for PEMFC supplying.

Task 3.3 was reassessed to respond to the comments and recommendations of the Mid-Term Review of the project (FCH-JU 2014 D2612). Considering that the development and characterization of ultra-thin palladium composite membranes have demonstrated that this technology is useful for temperature higher than 300 °C (below this temperature, the palladium falls down owing to the poisoning of CO and for the embrittlement phenomenon due to hydrogen permeation), no further efforts will be made regarding the task 3.3. This innovative task will be considered in future projects.

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