

# *Pure Hydrogen Production for Low Temperature Fuel Cells*

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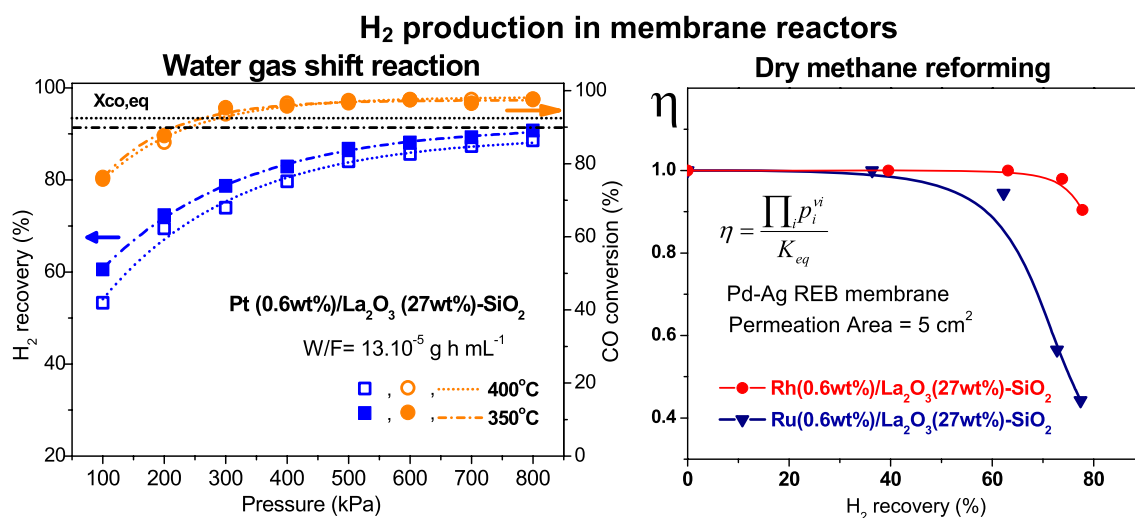
# Pure Hydrogen Production for Low Temperature Fuel Cells

Laura M. Cornaglia<sup>1</sup> · Eduardo A. Lombardo<sup>1</sup> Received: 26 October 2017 / Accepted: 17 January 2018 / Published online: 7 February 2018  
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## Abstract

The electric car industry is rapidly growing worldwide. There are two ways of providing the electricity needed in these vehicles, i.e. by means of either batteries or fuel cells. A reliable source of pure hydrogen is necessary for the latter alternative. Having in mind that the steam reforming of natural gas is at present the main source of this gas, different options for its production are discussed. This hydrogen needs further purification to get rid of the carbon monoxide (< 10 ppm) that irreversibly poisons the electrodes of the fuel cells. This work examines membrane reactors and hollow fiber membrane reactors. The latter are very attractive due to the severe mass (concentration polarization) and heat transport limitations that should be minimized at industrial scale. The work also presents examples of catalysts especially tailored for use in these applications. The main features of these formulations are high selectivity and stability. Their durability is directly connected with the sintering resistance and a very low activity to promote the formation of carbonaceous residues. The ultimate goal of this prospective contribution is to provide tools for the reader to evaluate present trends in research and the opportunities open in the field of H<sub>2</sub> fuel production suitable for fuel cell cars.

## Graphical Abstract

**Keywords** Methane reforming · WGSR · Combined reforming · Noble metal catalysts · Hollow fibers · Membrane reactor✉ Eduardo A. Lombardo  
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## Abbreviations

BET	Brunauer, Emmet, Teller surface area
BP	British Petroleum
CHFMMR	Catalytic hollow fiber membrane micro reactor
CRM	Combined reforming of methane

DEMCAMER	Design and manufacturing of catalytic membrane reactors
DRM	Dry reforming of methane
ELP	Electroless plating
FBMR	Fluidized bed membrane reactor
GHSV	Gas hourly space velocity
HFMR	Hollow fiber membrane reactor
MSR	Methane steam reforming
N-h	Non hydroelectric
OLC	Operability level coefficient
PBMR	Packed bed membrane reactor
POM	Partial oxidation of methane
REB	Robert E. Buxbaum (name of membrane manufacturer)
WGSR	Water gas shift reaction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Ytria stabilized zirconia

## 1 Introduction

The world is looking forward to using non-contaminating fuel alternatives as substitutes for fossil fuels. For stationary applications, there are different options that have been exponentially growing in several world regions. Between 2014 and 2015, the share of power generation by non-hydro (N-h) renewable sources grew by 15% worldwide. Wind energy had the largest growth increment but solar energy had the highest growth rate (33%). N-h accounted for 6.7% of power generation up from 2% a decade ago as reported in the BP annual review 2016 [1]. In 2016 the N-h share increased to 7.5% of power generation according to the BP annual review 2017 [1]. Wind energy provided more than half of the growth, while solar energy contributed almost a third despite accounting for only 18% of the total.

The options are not so clearly defined for mobile applications. This article focuses on the use of electric motors for all kinds of vehicles. These vehicles can be operated using either rechargeable batteries or fuel cells. At present, both options are in incipient stages: Nissan Leaf and Tesla cars lead the models using batteries. A listing of five battery car models with prices below US\$ 40,000 was published in June 2017 [2]. Besides, many other car companies that produce conventional vehicles, e.g. Honda, Toyota, Hyundai, Mercedes Benz, and G M [3] are offering fuel cell cars. A recent article [4] predicts that: “The automotive future belongs to Fuel Cells”. It points out: “Range, adaptability and refueling will ultimately put hydrogen fuel cells ahead of batteries”. However, later in the text, the author acknowledges the future coexistence of both battery and fuel cell operated vehicles according to the uses that best fit each one. In fact, the Economist shows significant data concerning the

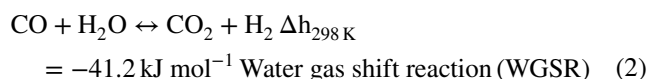
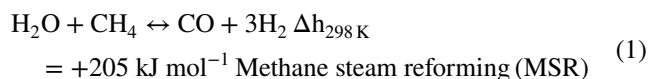
commercialization of battery operated electric cars [5]. The title of the article is very eloquent: “The death of the internal combustion engine”.

In fuel cells, hydrogen reacts with oxygen to produce electricity and water. In this way, not only a non-contaminating combustion product is generated but the Carnot cycle limitation of internal combustion engines is overcome as well. The practical efficiency of this device is ca. 50%, much higher than any internal combustion engine (ca. 20%). Therefore, the key issues right now are to produce hydrogen efficiently with minimum contamination and to secure the availability of pure hydrogen (< 10 ppm CO) in specially built gas stations at competitive prices. These stations are already operating in certain world regions such as the ones deployed in California where a fuel cell vehicle can operate all over the State thanks to the availability of conveniently located pure hydrogen fuel gas stations [6]. A similar situation occurs in some European regions (Norway, Denmark, Germany, etc.) where the geographic coverage varies among countries [7].

This contribution essentially deals with the production of pure hydrogen for use in fuel cells. Note that CO irreversibly adsorbs on the electrodes and decreases the fuel cell ability to operate. The limit of < 10 ppm of CO in fuel hydrogen is a consequence of the experimentally determined average life expectancy of the fuel cells.

## 2 Hydrogen Production

The most widely used method to produce this gas at industrial scale is the steam reforming of methane (Natural Gas). The hydrogen is treated to reach the required purity to be used in fuel cells (< 10 ppm of CO). Note that in this way important amounts of CO<sub>2</sub> are generated. An interesting option is the electrolysis of water but still with serious limitations derived from the low efficiency of this process [8].



In industrial practice, these two reactions are currently carried out in three different reactors. The second reaction, performed in the second (> T) and the third (< T) reactor, is used to purify the hydrogen stream. In fact, it was industrially introduced a century ago to produce pure hydrogen for ammonia synthesis.

If reaction (2) can be displaced to the right non-CO containing hydrogen could be obtained using appropriate catalysts in a single reactor. This could be done by reacting CO<sub>2</sub>

with an alkaline compound [9] or using a membrane reactor or both.

In the last couple of years, there are indications that reactions (1) and (2) could be performed in the same reaction vessel [10–12]. In any case, the retentate made up of carbon dioxide and water should be used downstream to produce useful chemicals such as urea, carbonates, bicarbonates (Fertilizers) and to supply minor applications such as gasified liquids, dry ice, inertization of packed food and other miscellaneous applications. Another beneficial effect of performing reactions (1) and (2) in a membrane reactor is the diminished CO and increased H<sub>2</sub> partial pressures that benefit hydrogen permeation rates. It is well known that CO strongly adsorbs on the membrane walls diminishing the H<sub>2</sub> permeability. A similar argument applies to CO<sub>2</sub> [13]; therefore, its absorption also increases the H<sub>2</sub> permeability.

Once the pure CO<sub>2</sub> and H<sub>2</sub> streams become available, they could be accurately metered to provide a feed stream for a Fischer–Tropsch unit able to process CO<sub>2</sub> instead of CO [14]. This represents a potential significant use of carbon dioxide to produce higher value chemicals and fuels.

## 2.1 Critical Issues to Address in Membrane Reactors

1. Custom tailored catalysts are needed, e.g. development of non-noble metal catalysts with superior stability. Catalyst activity is strongly affected by the type of support used because it plays an active role in the reaction [10]. Recently, there have been several publications claiming the development of durable Ni containing catalysts for use in steam and dry reforming, a more demanding process. The addition of cerium oxide or even better ceria and lanthana stabilizes Ni formulations. A similar effect is achieved by adding either Mg or Ca; Refs. [15, 16] illustrate two representative cases. However, when trying to pack Ni catalysts in hollow fibers their high activity for the formation of carbonaceous residues invalidate this approach. This is why we suspect that Li and coworkers [17] tried Rh(2 and 4%)/CeO<sub>2</sub>, two very stable formulations that do not deactivate. In brief, despite the fact that noble metal containing formulations are expensive they are more durable and may compensate higher catalyst costs in the long run.
2. Membrane materials and related technologies are also key to the success of this approach. Pd and Pd-alloys are able to separate hydrogen selectively because of the high solubility and diffusivity of this gas in their lattice. In 2017, recognized specialists also published an updated and complete review on these topics [18]. The Pd based dense membranes can be classified into two groups: self-supported and composite membranes. Self-supported membranes are generally thick (higher than 25 μm) to have physical strength and present lower hydrogen per-

meability. Supported or composite membranes are made of thin Pd-based films deposited on porous supports and could be an economic option to overcome these limitations. Porous ceramic materials, glass and metals were successfully used as supports for the Pd films. It has been reported that porous ceramic substrates exhibit superior upper temperature limit. Instead, porous stainless steel supports are promising substrates mainly due to more resistance to cracking, thermal expansion coefficient similar to that of Pd, and also because of the simplicity of module construction. Nevertheless, the pore sizes and roughness of their surface weaken the deposition of a thin defect-free Pd membrane. Both could be modified with an intermediate component [19]. The penetration of this material into the pore structure of the substrate would lead to a more compact structure and it is also expected to be a diffusion barrier to inhibit the migration of the substrate components to the Pd layer.

Pure palladium films undergo hydrogen embrittlement particularly due to phase transition of the palladium hydride when exposed to H<sub>2</sub> at temperatures below the critical temperature of 566 K. This hydrogen embrittlement can be overcome by alloying palladium with Ag or Au decreasing the hydride transition temperature. Binary Pd alloys of Au and Ag show higher hydrogen permeabilities than pure Pd. The reasons for the permeability increase could be related to the increase of H atoms solubility and diffusivity that go together with the expansion of the Pd lattice by insertion of the moderately large alloying metal atoms. In the case of binary palladium-alloys, Yun and Oyama [20] proposed that H<sub>2</sub> permeance is generally proportional to the average atomic distances of the alloys. In the last few years, measurements of hydrogen transport through ternary alloy membranes have also been reported [19]. Employing self-supported membranes, Bredesen and co-workers [21] studied the addition of a number of minor ternary components to PdAg alloys, ~Pd75Ag20X5 (X = Au, Mo, Cu, Y) and they observed lower H<sub>2</sub> permeabilities than either pure Pd or the PdAg binary alloys. We have also studied several ternary alloys, PdAgCu, PdCuAu and PdAgAu, deposited by sequential electroless plating on porous stainless steel substrates modified with Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>. The PdAgAu ternary membranes displayed lower permeability than the Pd90Ag10 alloy membrane, but higher permeabilities than the other membranes in the 350–450 °C temperature range. In addition, they presented higher resistance to H<sub>2</sub>S, a common pollutant in fossil-derived syngas [19].

Li et al. [22] reviewed the latest progress of Pd based composite membranes covering both experimental and modeling studies. Their focus was placed on the critical issue of thermal and chemical stability, which remains

as one of the main obstacles for their commercial applications. They suggested that detailed investigations on microstructure and composition of Pd-based composite membranes, particularly in-situ characterizations undergoing thermal/gas treatment, are needed in order to get more relevant insights.

3. The transport phenomena play a detrimental effect on membrane reactor performance in industrial scale applications. The mass transport effect is better known in this field as concentration polarization. This effect is strongly dependent on the diameter of the reactor tubes. One way to reduce this effect significantly is using hollow fibers packed with adequate catalysts. Recently, several papers were published applying this concept [17, 23]. This strategy should be accompanied by the use of non-aggressive methods to deposit the membrane thin layer on top of the hollow fibers [23]. In this way, the catalyst is incorporated prior to the Pd membrane formation. The heat transfer is also greatly improved using this reactor type. Decreasing the reaction temperature but maintaining high conversion, selectivity and  $H_2$  permeability will reduce the cost of the membrane reactor and increase its durability. Several papers directly or indirectly address these issues [24, 25].

### 3 Water Gas Shift Reaction Conducted in Membrane Reactors

In 2015, we shared the authorship of a review that included WGS membrane reactors [26]. The pertinent conclusions for this section concern the following:

- i. The paucity of reaction rates and activation energies reported in the literature.
- ii. Significant data concerning catalyst deactivation is mostly missing.
- iii. In most cases, the methanation activity is not even mentioned.
- iv. Only a few studies deal with the poisoning effect of usual contaminants.

Searching the literature published between 2015 and August 2017, an important milestone is the publication of the DEMCAMER project report [27]. This E U project lasted for 4 years and well-known research teams of academia and industry from Holland, Italy and Spain participated in it. It provides pilot scale data for technologies using membrane reactors for five different processes including WGS.

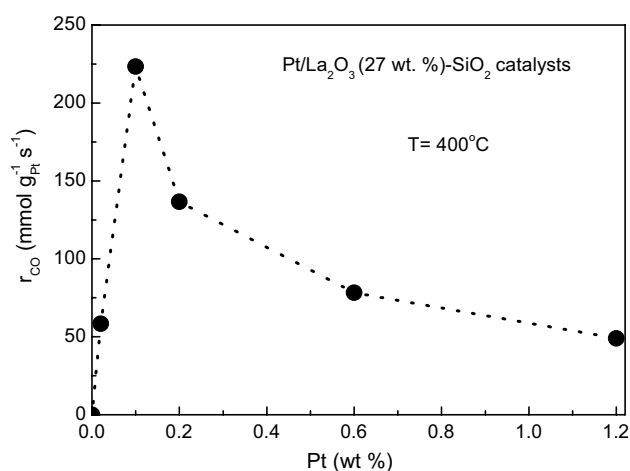
Another trend noticed in the period mentioned above is the revival of sorption enhanced membrane reactors with the publication of a well-documented review [9] and several articles, among them [28, 29]. Li and coworkers [30] also

proposed the sorption enhanced membrane reactor configuration (SEMR) that allows high purity  $H_2$  production coupled with in situ  $CO_2$  capture in the WGS. They studied a Pd/Ag membrane deposited of an alumina hollow fiber and hydrotalcite as  $CO_2$  sorbent, under reaction conditions. The variation of CO conversion with temperature was reported; however, no stability results were included.

The development of active and stable catalysts is another key point to achieve a competitive membrane reactor technology. In our Institute we have developed a catalyst that is active, selective, durable and contains a minimum amount of Pt (0.1 wt%) [31–33]. The noble metal is supported on  $La_2O_3(27 \text{ wt}\%)-SiO_2$ . Figure 1 shows the specific activities of formulations containing Pt loads between 0.02 and 1.2%. Note that the optimum Pt load is 0.1 wt%. All the formulations showed the same stability under reaction conditions [34].

In order to try to ascertain the origin of this behavior, bulk and surface techniques were used. BET measurements, XRD and laser Raman spectroscopy did not show any difference in texture or bulk structure of the fresh and used catalysts [34]. Surface parameters measured using XPS indicated that no modification in atomic surface concentrations occurred after use [34]. This is consistent with the absence of catalyst deactivation. However, an unexpected behavior was observed: The formulations containing Pt loads  $> 0.1\%$  exhibited two Pt signals at 70.8 eV ( $Pt^0$ ) and 71.7 eV ( $Pt^{\delta+}$ ) upon reduction in pure  $H_2$  at 400 °C while Pt(0.1%) only showed the metallic signal.

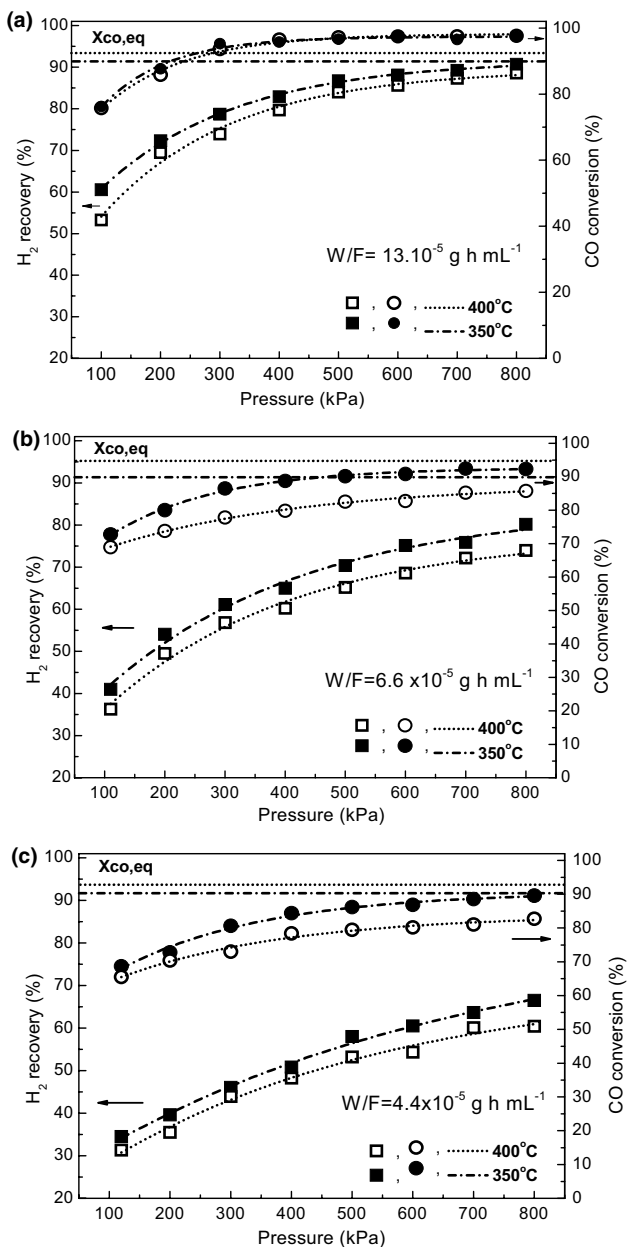
In order to verify that incomplete reduction was the cause of the catalytic behavior of the formulations with higher metal loads, the solids containing 0.1, 0.6 and 1.2% were reduced at higher temperature and the activity significantly



**Fig. 1** Effect of Pt load over the catalytic activity ( $H_2O/CO=3$ ). Reproduced with permission from [34]. Copyright (2014), with permission from Elsevier

increased for the latter two samples but it was not modified for the 0.1% formulation [34].

The catalysts containing 0.1 and 0.6 wt% Pt were tested in the membrane reactor. The effect of temperature, pressure and space velocity upon CO conversion and H<sub>2</sub> recovery is reported in Fig. 2 for the Pt(0.6%) formulation [33]. Note that at a retentate pressure of 800 kPa, the CO conversion is ca. 95% and the H<sub>2</sub> recovery 85%. Both high values could be increased even more by modifying the operation variables



**Fig. 2** Effect of pressure, temperature and W/F upon the CO conversion and H<sub>2</sub> recovery (H<sub>2</sub> permeated/H<sub>2</sub> produced × 100) for Pt(0.6 wt%)/La<sub>2</sub>O<sub>3</sub>(27 wt%)-SiO<sub>2</sub>. (H<sub>2</sub>O/CO = 2) **a** GHSV = 3120 h<sup>-1</sup>; **b** GHSV = 6240 h<sup>-1</sup>; **c** GHSV = 9360 h<sup>-1</sup>. Reproduced with permission from [33]. Copyright (2013), with permission from Elsevier

and/or design parameters of the membrane reactor. The same information was reported for the Pt(0.1%) [34]. An important feature of these catalysts (Pt/La<sub>2</sub>O<sub>3</sub>(27 wt%)-SiO<sub>2</sub>) is the absence of methane formation under all the experimental conditions explored.

Note that the best catalyst used for WGS in a pilot size membrane reactor highlighted in the DEMCAMER report [27] operates at 400 °C, retentate pressure of 400 kPa and GHSV = 2500 h<sup>-1</sup> yielding CO conversion of 96% and H<sub>2</sub> recovery of 84%. Figure 2a shows that the performance of the INCAPE Pt formulation is very similar to their Re(0.09 wt%)-Pt(0.24 wt%)/CeO<sub>2</sub>-TiO<sub>2</sub> also at 400 °C. However, their deactivation run was only 18 h long and already showed ca. 10% decay in CO conversion [27, 35]. Note that the research reported in reference [35] was also part of the DEMCAMER project.

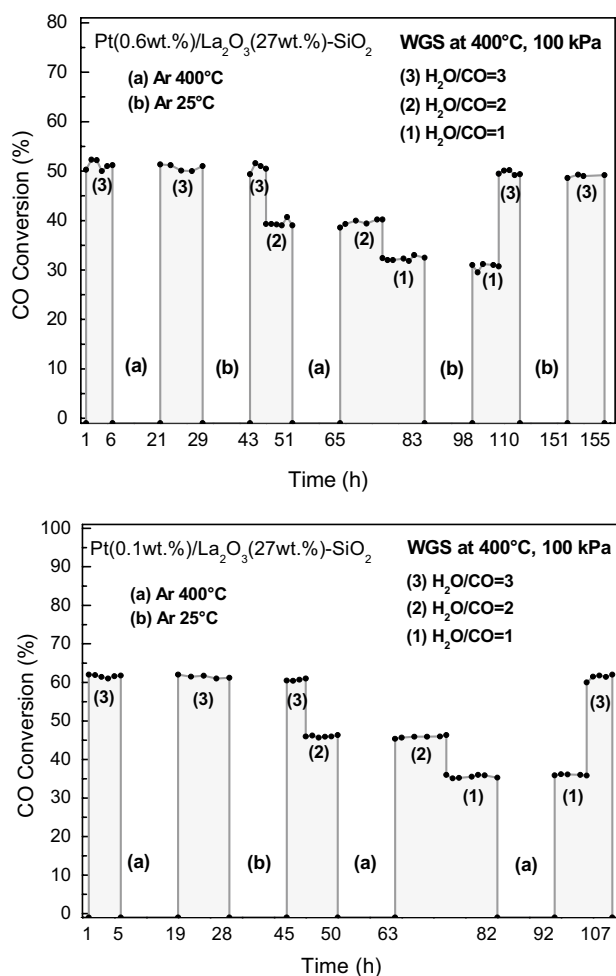
This behavior indicates that longer and more elaborated stability tests should be performed with this catalyst. For the time being, this catalyst is not yet ready for scale up. On the other hand, INCAPE catalysts did not deactivate after 50 h on stream at 400 °C [34].

Another type of more demanding stability test was performed including start-up and shutdown cycles between 25 and 400 °C (Fig. 3) during more than a 100 h [33, 34].

Why are Pt(wt%)/La<sub>2</sub>O<sub>3</sub>(27 wt%)-SiO<sub>2</sub> so stable? A deeper look at the XRD profile of the calcined La<sub>2</sub>O<sub>3</sub>(27 wt%)-SiO<sub>2</sub> support [32] shows the formation of low crystallinity lanthanum disilicate. Let us recall that Pt/SiO<sub>2</sub> easily deactivates due to the weak metal-support interaction that leads to Pt sintering and that the very strong noble metal-La<sub>2</sub>O<sub>3</sub> interaction significantly lowers the catalytic activity of these formulations. Since our catalysts are very active and stable, it is concluded that the majority of the active Pt species should sit on the exposed disilicate surface reaching a balanced interaction strength. This is a speculation that deserves further research to not only prove or disprove our hypothesis but more important to eventually lead to the development of similar catalysts for other reactions. In fact, we have already extended the use of these supports to both dry and combined methane reforming catalysts (vide infra).

## 4 Methane Reforming Reactions Conducted in Membrane Reactors

The use of membrane reactors to shift the equilibrium of methane reforming reactions by a selective removal of hydrogen has been explored during the last decades. The recognized improvements are related to the design of appropriate reactors, newer membrane materials, decreasing the mass transfer limitations, improving heat supply to the reactor and



**Fig. 3** Stability test during the WGS reaction with start-up and shut-down cycles as indicated.  $W/F = 2.7\text{--}3.4 \cdot 10^{-7} \text{ g h mL}^{-1}$  [33, 34]. Reproduced with permission from [34]. Copyright (2014), with permission from Elsevier

process optimization combining other reactions with MSR [36, 37].

#### 4.1 Methane Steam Reforming

Two main reactor configurations were discussed by Basile et al. [37] and Iulianelli et al. [38] i.e. packed bed membrane reactors that have a very simple configuration, and fluidized bed membrane reactors (FBMR) that are typically characterized by enhanced mass and heat transfer rates, which favor more uniform temperature profiles.

The main conclusions from Basile et al.'s review are the following:

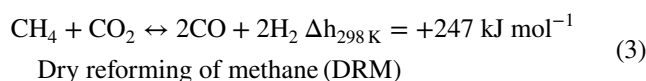
- i. Absence of information regarding the catalyst time on stream.
- ii. The effect of higher hydrocarbons or sulfur compounds contained in the methane stream.

- iii. Possible bubble-to-emulsion mass transfer limitations can reduce the FBMR performance and the fluidized catalyst can destroy the membrane.
- iv. From an industrial point of view, the costs of membranes and their stability with time on stream should be improved.

Besides, many contributions have shown significant improvements in hydrogen yield and purity plus process intensification for MSR performed in membrane reactors [39, 40]. In all the cases reported in the open literature, no information about durability of the membranes used (at least in terms of months) is provided for laboratory scale reactors. The only durability data was reported at demonstration scale for the long-term operated PBMR of Tokyo Gas. They ran the reactor at 8 bars and 550 °C to produce 40 Nm<sup>3</sup>/h of pure H<sub>2</sub>(99.99%) using as feedstock natural gas from the domestic Tokyo gas line. The H<sub>2</sub> was used to feed a low temperature fuel cell. The plant was operated for 13,000 h and according to the project report [41] maintained the specs of the H<sub>2</sub> fuel.

#### 4.2 Dry Reforming of Methane

This is an interesting alternative for hydrogen production when the supply of methane contains significant amounts of carbon dioxide (shale gas or biogas) or where the production of syngas with a H<sub>2</sub>/CO = 1 is required. Note that biogas mainly consists of 60–70% combustible methane and 40–30% carbon dioxide along with smaller amounts of other gases.



The carbon dioxide reforming shows certain limitations due to the simultaneous occurrence of the reverse water gas shift reaction.

For the dry reforming of methane reaction, different combinations of materials, catalysts and membranes have been employed. In many cases, an increase in the methane conversion when extracting H<sub>2</sub> from the reaction side occurred. The results depended on the conditions under which the reactions were carried out such as W/F, reactant concentration, membrane selectivity and permeability, carbon deposition of the catalyst (which would contribute to its deactivation) and membrane deterioration.

In our group, we employed a dense Pd/Ag membrane, with 100% selectivity towards hydrogen, to produce ultrapure hydrogen. To optimize the membrane reactor operation, a balance between the hydrogen produced and the hydrogen removed is a necessary condition. The choice of the catalysts is critical for reactions carried out in membrane



reactors. However, this topic has been underestimated in the last few years. In most cases, a suitable catalyst with long-term stability and no carbon deposition has to be developed.

For La-containing noble metal catalysts, we reported [42] a high stability attributed to an intermediate strength metal–support interaction. For Rh and Ru solids supported on La<sub>2</sub>O<sub>3</sub> and high surface area La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [43, 44] this interaction was very strong. However, when a binary La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> material was the support, an appropriate interaction aroused [45] yielding formulations with high activity and stability. As said above, an optimum medium strength interaction was observed in the case of Pt/La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> WGSR catalyst.

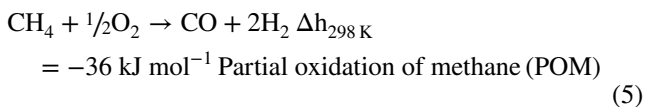
To take into account the catalyst activity and its ability to restore the chemical equilibrium upon H<sub>2</sub> permeating out, an equilibrium fraction of the dry reforming reaction of methane was defined [42] as follows:

$$\eta = \frac{\prod_i p_i^{\nu_i}}{K_{eq}} \quad (4)$$

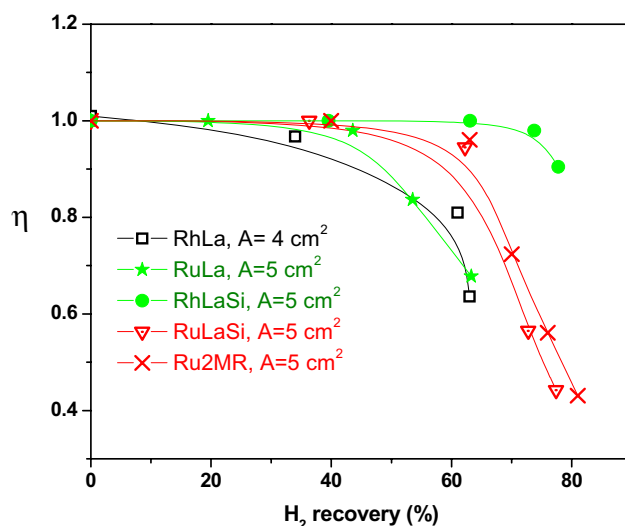
where  $p_i$  is the outlet partial pressure of each reactant and product in the reaction side of the membrane reactor,  $\nu_i$  are the DRM stoichiometric numbers, and  $K_{eq}$  is the equilibrium constant. This fraction shows the approach to equilibrium of this reaction. If the composition corresponds to thermodynamic equilibrium, this ratio is equal to 1.

The best catalysts developed in our group were selected for this comparison, Rh and Ru supported on La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> and Ru/La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (Ru2MR) [42–46]. The membrane reactor was built with a commercial PdAg membrane (REB). Figure 4 shows the  $\eta$  values determined for DRM reaction at 550 °C. When a high hydrogen recovery was reached (close to 80%), the Rh solid could keep a  $\eta$  value equal to 0.9. This would indicate that for the most active catalyst, it would be possible to obtain a high hydrogen recovery maintaining the capacity to restore the thermodynamic equilibrium. This behavior is related to the high activity of this La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> formulation [45].

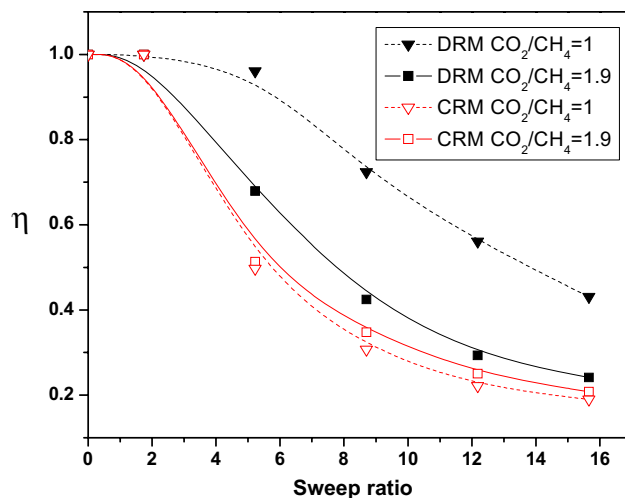
The practical interest of the DRM reaction could be increased by coupling this process with an exothermic reaction, such as the partial oxidation of methane.



By combining these reactions (CRM) and varying the concentrations of O<sub>2</sub> and CO<sub>2</sub>, the H<sub>2</sub>/CO ratios can be modified to increase the viability of the process. We studied the CRM reaction in membrane reactors employing the Ru and Rh catalysts combined with Pd composite membranes supported on zeolite modified substrates and self-supported commercial (REB) Pd/Ag membranes [44, 47].



**Fig. 4** Variation of the equilibration reaction ratio as a function of H<sub>2</sub> recovery for the dry reforming reaction. Pd–Ag commercial membrane reactor, Reaction temperature = 550 °C. A = permeation area, W/F = 1.5 × 10<sup>-3</sup> g h mL<sup>-1</sup>. RhLa: Rh/La<sub>2</sub>O<sub>3</sub> (square), RuLa: Ru/La<sub>2</sub>O<sub>3</sub> (star), RhLaSi: Rh/La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (filled circle), RuLaSi: Ru/La<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (down triangle) and Ru2MR: Ru/La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (times). Reproduced with permission from [44]. Copyright (2013), with permission from Elsevier

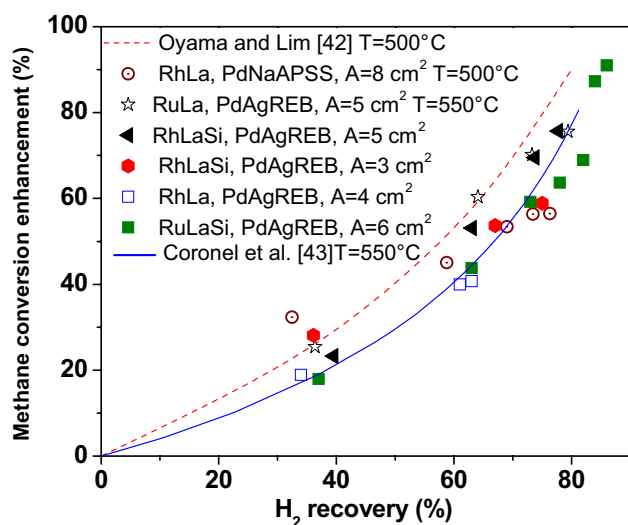


**Fig. 5** Ability of the catalyst to keep the retentate equilibrated as a function of sweep ratio (sweep gas flow rate/methane feed flow rate ratio) for Ru2MR. T = 550 °C, ΔP = 0, catalyst mass = 1.5 g, W/F = 1.5 × 10<sup>-3</sup> g h mL<sup>-1</sup>. The membrane reactor was built with a Pd–Ag commercial membrane (permeation area = 6 cm<sup>2</sup>). Reproduced with permission from [44]. Copyright (2013), with permission from Elsevier

The  $\eta$  values calculated for different feed conditions for Ru supported on lanthanum oxycarbonates are shown in Fig. 5. For all conditions,  $\eta$  starts from unit and, when

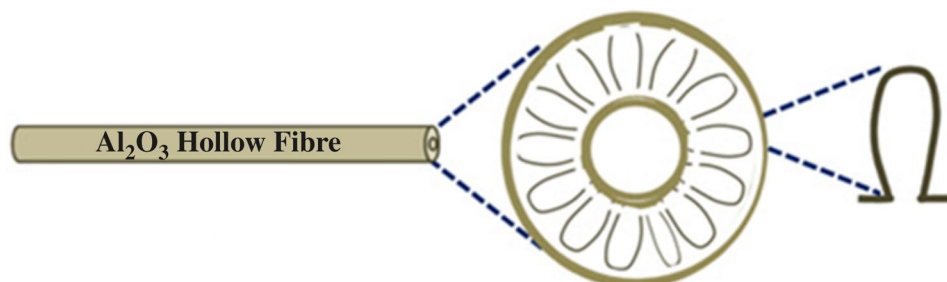
the sweep ratio is higher than 5.3, the  $\eta$  value decreases indicating that when a high amount of  $H_2$  is removed from the system, the catalyst cannot restore the equilibrium. This behavior was less pronounced for DRM conditions with a  $CO_2/CH_4$  ratio equal to 1. In the case of the CRM reaction, the same behavior was observed but even more pronounced. However, the  $H_2$  permeated/ $CH_4$  feed ratio values for CRM conditions were slightly higher than those of DRM. This means that the operating conditions of CRM not only yield a considerable increase in conversion but also result in an increased production of hydrogen.

The commercial membranes exhibited high stability and robustness between 500 and 550 °C. Data previously reported [45] showed that the membrane reactor was



**Fig. 6** Methane conversion enhancement as a function of  $H_2$  recovery for different catalysts and membrane combinations applied in the membrane reactor. Rh/La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Pd/NaA/PSS membrane, permeation area =  $7.3 \times 10^{-4} \text{ m}^2$  [50] (○), Rh/La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-PdAg REB, permeation area =  $3 \times 10^{-4} \text{ m}^2$  [45] (hexagon), Rh/La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Pd-Ag REB, permeation area =  $5 \times 10^{-4} \text{ m}^2$  (◄), Rh/La<sub>2</sub>O<sub>3</sub>-Pd-Ag REB, permeation area =  $3.8 \times 10^{-4} \text{ m}^2$  [45] (square), Ru/La<sub>2</sub>O<sub>3</sub>-Pd-Ag REB, permeation area =  $5 \times 10^{-4} \text{ m}^2$  [43] (star), Ru/La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Pd-Ag REB, permeation area =  $6 \times 10^{-4} \text{ m}^2$  [46] (filled square). Reaction temperature = 550 °C. Reproduced with permission from [49]. Copyright (2011), with permission from Elsevier

**Fig. 7** Hollow fibre membranes. Reproduced with permission from [53]. Copyright (2012), with permission from Elsevier



operated for at least 1000 h on stream maintaining the same permeance and infinite  $H_2$  selectivity. Furthermore, for all the used catalysts reported, no carbon deposition was observed through TGA measurements [43–46].

In order to compare the data for the dry reforming reaction, we previously adopted the methodology proposed by Oyama and Lim [48] for methane and ethanol steam reforming. They defined an operability level coefficient (OLC) as the ratio of the actual permeation rate and the actual formation rate of a critical product in a membrane reactor, where the critical product is the one for which the membrane is permselective. This coefficient is equivalent to the hydrogen recovery parameter ( $H_2$  permeated/ $H_2$  produced). Figure 6 shows the methane conversion enhancement with hydrogen recovery for different catalysts and membranes with various permeation areas. The  $H_2$  recovery was increased by increasing the sweep gas flow rate. The experimental data are also compared with modeling results for DRM [49] and MSR [48] and they show the same tendency.

In addition, it can be observed that with high sweep gas flow rate, conversion enhancements of approximately 90% are reached for hydrogen recoveries close to 85%.

As said above, the next step in this line is to carry out both the methane reforming reactions and WGS in the same reactor to obtain one stream of pure  $H_2$  and another of wet  $CO_2$ .

## 5 Hollow Fiber Membranes and Membrane Reactors

The interest in the unification of membrane reactor and micro-reactor technologies has increased in the last few years. The novel membrane micro-reactors could present high catalytic efficiency without thermodynamic limitation. Nevertheless, this system requires the development of new materials allowing an efficient process.

The attractive physical and chemical properties of ceramic hollow fibers make them an interesting alternative for this application. The asymmetric ceramic hollow fibers (Fig. 7) are formed by a porous sponge-like structure around the circumference of the fiber and finger-like

micro-channels forming the inner layer [51–53]. This structure and the high surface/volume ratio with tubular geometry (diameter < 2 mm) could enable a relatively easy scale-up and allow their use as substrates for inorganic dense membranes and for the development of different catalysts.

Ceramic hollow fiber membranes constructed with alumina [51], Y-stabilized zirconia [54] or titania [55] have been synthesized employing phase inversion methods such as dry spinning, wet spinning and dry-jet-wet spinning. To improve the mechanical properties, metal materials were considered as candidates for producing hollow fiber membranes. However, there are not many reports concerning the preparation of stainless steel (SS) hollow fiber membranes [56]. Recently, Rui et al. [57] prepared SS porous hollow fiber membranes by combined dry-wet spinning and sintering techniques.

High mechanical strength could be achieved for the hollow fiber membranes sintered in H<sub>2</sub> atmosphere, being effective in removing organic additives without metal oxidation. From these substrates, new types of supported Pd membranes were developed for H<sub>2</sub> separation. Ultrathin dense Pd membranes have been deposited by electroless plating (ELP) on alumina hollow fiber substrates [58]. The resulting composite membranes not only provided high separation area/volume ratios, but also reduced the cost and improved the permeability with a high hydrogen separation factor (> 1000) and good durability.

High-quality metal organic framework (ZIF-8) membranes supported on hollow YSZ ceramic fibers were also successfully prepared using a hydrothermal seeded-growth method. Good separations (H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ideal selectivity > 1000) between hydrogen and other hydrocarbons were achieved, and the permeance of hydrogen improved by almost an order of magnitude compared with previous reports [59].

Li and coworkers [53] reported key advances in the development of asymmetric ceramic hollow fibers for new reactor designs for heterogeneous gas phase catalytic

reactions. Three different hollow fiber reactor configurations were compared; a hollow fiber membrane reactor (HFMR), a catalytic hollow fiber micro-reactor (CHFMR) and a catalytic hollow fiber membrane micro-reactor (CHFMMR) (Fig. 8).

A Pd-based membrane (thickness of approximately 5 μm) was deposited on the outer surface of the asymmetric ceramic hollow fibers using an electroless plating technique. The Pd-based membranes showed high H<sub>2</sub> permeability and infinite H<sub>2</sub> selectivity under the different reaction conditions studied. To deposit the catalyst inside the micro-channels, wet impregnation, infiltration and sol–gel were employed. The catalyst deposition by wet impregnation methods was dependent on the pore size distribution of both the micro-channel entrances and the sponge-like region. However, infiltration and Pechini sol–gel methods [60] can overcome this limitation. The performance of the reactors in different reactions such as methanol steam reforming (Cu/ZnO<sub>x</sub> based catalyst), dry reforming of methane (4%Ru/ZrO<sub>2</sub>–La<sub>2</sub>O<sub>3</sub> catalyst) and water gas shift (10%CuO/CeO<sub>2</sub> catalyst) was compared with that of a traditional fixed-bed reactor configuration.

In the case of WGSR, the CHFMMR showed a performance 2.5 times higher than that in a traditional fixed-bed reactor (Fig. 9), and it was proposed as a key step in the intensification of heterogeneous catalytic gas phase processes by integration of membrane-reactor and micro-reactor technologies.

Li and coworkers [30, 61, 62] also published new contributions related to hollow fiber catalytic membrane reactors. The performance of the CHFMR based in a Pd–Ag membrane was also studied during the methanol steam reforming reaction [61]. A Cu/Zn/GaO<sub>x</sub> based catalyst was successfully deposited inside the finger-like region of the Al<sub>2</sub>O<sub>3</sub> hollow fibers by the co-precipitation technique. The CHFMR showed high catalytic activity along with a maximum selectivity. At 300 °C the CH<sub>3</sub>OH conversion was larger than that

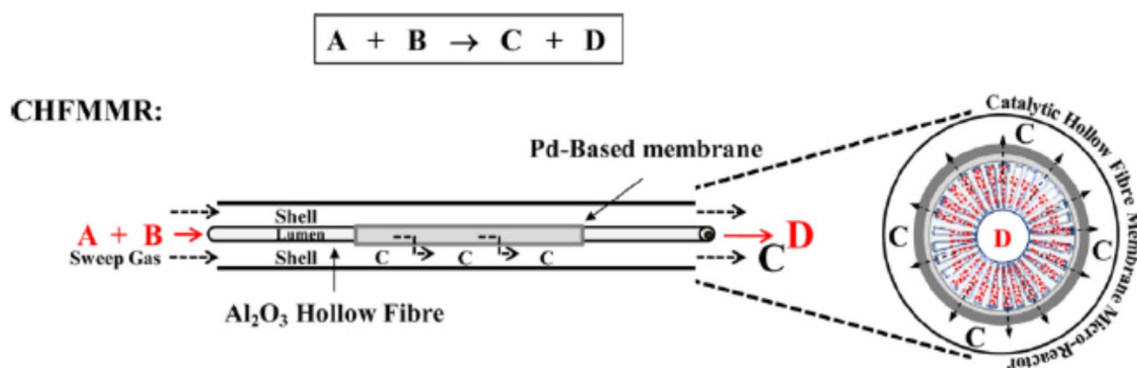
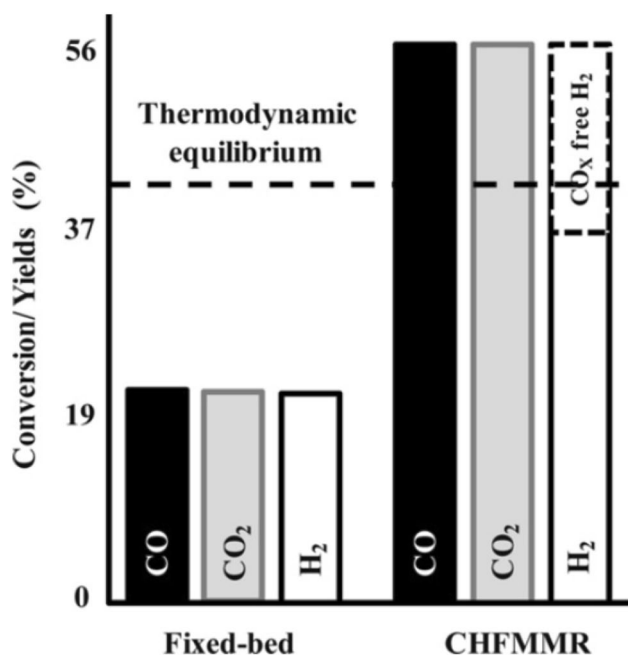


Fig. 8 A schematic representation of a CHFMMR. Reproduced with permission from [53]. Copyright (2012), with permission from Elsevier



**Fig. 9** CO conversion, CO<sub>2</sub> and H<sub>2</sub> yields at 450 °C during WGS reaction in a fixed-bed reactor and in the CHFMMR. The catalytic activity tests were carried out under atmospheric pressure, with a feed mixture Ar/CO<sub>2</sub>/H<sub>2</sub>O ratio equal to 9/1/1 and a space velocity of 80 L g<sup>-1</sup> h<sup>-1</sup>. The 10%CuO/CeO<sub>2</sub> catalyst was prepared by the sol-gel Pechini method and tested after calcination for 1 h at 400 °C. Reproduced with permission from [53]. Copyright (2012), with permission from Elsevier

obtained in the conventional fixed-bed reactor and the CO concentration also decreased.

Rahman et al. [62] deposited a Pd–Ag layer on the shell side of YSZ hollow fiber by ELP and impregnated a NiO(10 wt%)/MgO–CeO<sub>2</sub> catalyst in the finger like side. Both were integrated into a membrane micro-reactor for ethanol reforming. A decrease in hydrogen recovery was observed (71–55%) increasing the temperature until 550 °C. The authors concluded that the membrane area per volume of catalyst was restrictive at high temperatures.

More recently, Kawi and coworkers [63] have successfully developed a triple-layer hollow fiber catalytic membrane reactor consisting of: (1) Ni-based catalyst (outer) layer (LaNiO<sub>3</sub> perovskite), (2) porous inorganic support (middle) layer; and (3) ultrathin Pd-based membrane (inner) layer, for the catalytic decomposition of methane. However, a slight decrease in the CH<sub>4</sub> conversion occurred due to the formation of carbon on the catalyst surface. Due to high H<sub>2</sub> permeability of the ultrathin Pd–Ag membrane, a hydrogen recovery close to 84% could be obtained. Furthermore, with this complex reactor design, mechanical damages of the Pd–Ag membrane can be prevented as the membrane is not directly exposed.

## 6 MSR and WGS Reactions Occurring in a Single Vessel Trying to Produce Only H<sub>2</sub> and CO<sub>2</sub>

Few papers have been published so far using this new concept. Some of them were briefly described in the previous section [17, 23]. Therefore, we have opted to first analyze relevant articles concerning the use of each reaction in membrane reactors to produce H<sub>2</sub> and CO<sub>2</sub> and then extend the coverage to the use of bi-functional catalysts.

To combine the steam methane reforming and water gas shift reaction in a single vessel, Gil et al. [23] employed a catalytic hollow fiber membrane reactor (CHFMR). This reactor type was built by incorporating a Ni/SBA-15 catalyst into micro-channels, followed by coating of a 3.3 μm Pd membrane on the outer surface of the hollow fiber using an electroless plating method. The incorporation of Ni/SBA-15 catalyst was carried out by synthesizing the catalyst in-situ via a two-step process: (i) incorporation of SBA-15 via a sol-gel method and (ii) incipient wet impregnation of nickel.

They found that the removal of hydrogen from the reaction zone was the main reason for the deactivation of the Ni-based catalyst. Nevertheless, an effective methane conversion close to 53%, with a CO<sub>2</sub> selectivity of 94% and a H<sub>2</sub> recovery of 43% were achieved at lower temperatures (560 °C).

In order to reach a more significant equilibrium displacement, they recommended to develop an alternative methodology of fabricating the reactor and more coke resistant catalysts.

A recent work from the same group [17] employed Rh/CeO<sub>2</sub> as the more coke-resistant catalyst for MSR. Another difference from Ni catalysts is that Rh/CeO<sub>2</sub> was prepared prior to being incorporated inside the hollow fiber, which is more similar to the method employed at an industrial scale, such as washcoating onto ceramic monoliths. However, the catalyst incorporation inside CHFMRs was less efficient, due to the previous step of depositing a dense Pd based layer. Using an appropriate catalyst mass of 4 wt% Rh/CeO<sub>2</sub> catalyst, results in methane conversions surpassed the equilibrium values with no detectable catalyst deactivation. The authors concluded that the improved methodology of incorporating catalyst into the micro-channels of CHFMR is the key step for more efficient membrane reactor design. In addition, electroless plating of Pd membranes need to be modified or even replaced, allowing the catalyst deposition inside micro-channels of the hollow fibers without changes in their catalytic properties.

## 7 Conclusions and Perspectives

In the near future, it is expected to see more work focused on membrane reactors where specific catalysts for MSR and WGS are used together in a single vessel to obtain two streams of pure hydrogen ( $\text{CO} < 10$  ppm) and wet carbon dioxide.

The combination of efficient  $\text{CO}_2$  capture and membrane reactors will be further explored.

Tailored catalysts are still needed, able to operate at the lowest possible temperatures with high activity, selectivity and improved stability. Therefore, it is necessary to optimize the concentration of noble metal in proven formulations. Consequently, more work in this area is expected in the years to come.

The intensive use of hollow fiber and micro-channel membrane reactors will be intensified to better control mass and heat transfer phenomena that limit the industrial application of this technology.

Another hot area is the procurement of pilot plant data showing the accomplishment of desirable industrial goals such as minimal heat and mass transport limitations, catalyst selectivity and durability (no carbonaceous residues formation and sintering limitation).

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### Compliance with Ethical Standards

**Conflict of interest** The authors declares that they have no conflict of interest.

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