Advances on high temperature Pd-based membranes and membrane reactors for hydrogen purification and production

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Advances on High Temperature Pd-Based Membranes and Membrane Reactors for Hydrogen Purification and Production

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Abstract

Membrane technology applied in the chemical and energy industry has the potential to overcome many drawbacks of conventional technologies such as the need of large volume plants and large CO₂ emissions. Recently, it has been reported that this technology might become more competitive when operated at high temperatures. This is mostly associated with the required of heat integration at large scale. However, good membrane stability combined with high permeation rates and high perm-selectivities, has only been achieved at intermediate/low temperatures (< 500 °C). When operated at these lower temperatures in a fully integrated plant, there is often the need of electricity import, which strongly decreases the process efficiency and renders the membrane-based technology less competitive compared to conventional technologies. To improve the competitiveness of membrane technology further developments are required, demanding in particular an improvement in the preparation methods, the use of new materials and/or the development of novel reactor configurations. In this study, a comprehensive review on the latest advancements in membrane technology for H₂ separation at high temperature is presented. Special attention is given to the membranes prepared and presented in the literature in the last years for high-temperature applications, as well as the different membrane reactor configurations that have proposed, tested and evaluated for different reaction systems at elevated temperatures. Since concerns about the need of high temperatures in membrane technology are relatively new, this review is limited to the results reported in the literature during the last five years.

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Keywords

Membranes
Membrane reactors
Hydrogen production
Pd membranes

Highlights

• Review on high temperature membrane reactors for H₂ production
• Discussion on different preparation methods for Pd-based membranes
• Overview on recent works using Pd-based membranes above 500 °C
• Guidelines for further enhancement of membrane reactor technology

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Graphical abstract

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1. Introduction

Reduction in greenhouse gas emissions to the atmosphere is an important challenge that the scientific community is facing nowadays. The challenge agreed on worldwide during the latest Paris agreement consists of limiting the increase in the global temperature of earth to 2 °C by the end of this century, which is in its turn associated with a maximum CO2 concentration of 450 ppm in the atmosphere. Although different gases are responsible for climate change, it is well known that the gas with the largest (total) contribution to climate change is CO2, which concentration in the atmosphere has reached recently 400 ppm, as measured in the Mauna Loa observatory. In a recent report from the International Energy Agency (IEA) [1], various solutions are considered that in a short-term period are able to stabilize the continuous increase in the atmospheric CO2 concentration and can achieve the proposed objective and combat climate change. These strategies can be summarized in five different measures:

- An increase in the energy efficiency in industry, buildings and transport sectors should not yet be completely assured, which would imply considerable maintenance costs. On the other hand, membrane technology has not yet been developed for high temperature applications, since deterioration in performance has been observed when operating at temperatures above 500 °C. The use of high temperatures is in fact of especial interest for large-scale implementation of membrane technology in fuel conversion systems, as reported in the literature [4]. However, until now almost all efforts have been focused on the fabrication of membranes for low-temperature applications and only in the last few years there has been an advancement in the development of membranes for high-temperature applications. The enhancement on membrane stability for high temperatures has been achieved by improvements in the preparation methods, including the preparation of multi-layers, and by alloying Pd with other metals [14].

In this manuscript, a comprehensive review on the recent developments and applications of H2-based membrane technology for high-temperature applications is presented. First, different options for high temperature membranes are summarized. Subsequently, recent developments on high temperature membranes are presented. Finally, an overview on high temperature membrane reactors is given for different reactor configurations and different chemical systems.

2. Membranes for high temperature hydrogen separation

2.1. Introduction

On an industrial scale, hydrogen is currently mainly produced by reforming of natural gas, an endothermic reaction system carried out at high temperature (> 850 °C), followed by high and low temperature water-gas shift reactions and final hydrogen purification steps (see Fig. 1) [6]. The conventional system is only efficient at very large scales, where heat integration can be optimized and the excess heat can be exported in the form of steam/power. The main problems for this reaction system is related to thermodynamic constraints that limit both the steam methane reforming (endothermic) and water gas shift reactions (exothermic) (see Equations 1 and 2). To achieve high conversions and high hydrogen yields with high efficiency, complex heat integration is required [1]. Until today, this process is still responsible of considerable greenhouse gas emissions since carbon dioxide capture strategies have not (yet) been implemented at industrial scale. Furthermore, the system cannot be easily scaled down and becomes rather inefficient at smaller scales. The efficiency of the process can be increased by exploiting process integration and process intensification. In this respect, integrating hydrogen production reactions and hydrogen recovery through membranes results in shifting of the equilibria allowing obtaining higher efficiencies.
Steam methane reforming

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H = +206 \text{ kJ/mole}
\]  

(1)

Water gas shift

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -131 \text{ kJ/mole}
\]  

(2)

Microporous ceramic membranes are promising materials for high purity hydrogen production and separation. Based on their structure, microporous membranes for H₂ separation can be classified into crystalline (zeolites and MOF) and amorphous (such as silica, carbon, etc.) membranes. However, these membranes separate hydrogen by size exclusion (materials with a pore diameter smaller than 2 nm) and thus their perm-selectivity is still limited, compared to more expensive dense inorganic membranes. In addition, at high temperatures (>500 °C), and in the presence of steam, these materials are not stable for long-term operation (e.g. sintering). The limited perm-selectivity and thermal stability makes these membranes less suitable for integration in membrane reactors for high-purity hydrogen production.

Proton conducting membranes and in particular dense metal membranes (mainly palladium alloys) are currently the most suitable materials for high temperature applications (>500 °C) due to their high hydrogen perm-selectivity. The recent advances and challenges on these two types of membranes are presented and discussed next.

![Scheme of H₂ separation process using a dense proton conducting membrane. Reproduced with permission of Elsevier from (15,16).](image)

2.2. Proton conducting membranes

Dense proton conducting membranes are based on proton and electron conductivities that allow hydrogen to permeate. The hydrogen diffusion is driven by the chemical potential gradient across the membrane. These membranes are able to work in the range of 300 to 900 °C [15]. Although the perm-selectivity values obtained with proton conducting membranes are comparable to Pd or Pd alloy membranes, the hydrogen permeation rates through these single phase ceramic membranes are much lower. As reported by Rosensteel et al. [16], the hydrogen flux is nearly 600 times lower when comparing a 30 µm thick perovskite single phase ceramic membrane with a 2.9 µm thick Pd₉₀Al₁₀ membrane. This difference is decreased to a factor in the range of 30-250 when comparing some of the highest fluxes in two-phase composite membranes in the literature.

The hydrogen separation process of a dense proton conducting membrane consists of two steps (see Fig. 2): First, H₂ is absorbed on the surface of the membrane and dissociates into protons and electrons. Subsequently, the protons and electrons both diffuse through the membrane to the surface on the other side, where they recombine to form molecular H₂. In order to get H₂ separation, both surfaces of the membrane should have catalytic activity for H₂ dissociation and recombination. In these membranes, the hydrogen moves from the high partial pressure side (P₁H₂) to the low partial pressure side (P₂H₂) [15].

The hydrogen flux through these membranes is proportional to the ambipolar protonic-electronic conductivity and it is necessary to have high values for both to obtain a high hydrogen flux [6]. The hydrogen permeation process can be controlled by either the bulk membrane transport or by the surface process.

There are two types of ceramic-based H₂ membranes: single-phase and two-phase ceramic oxides. The single-phase ceramic membranes transport protons and electrons simultaneously and exhibit relatively low H₂ permeances due to their low electronic conductivity [16,18]. On the other hand, the two-phase composite membranes have been proposed as a good strategy to improve the hydrogen permeation rate. In these membranes a second phase, either metallic (cermets) or ceramic (cercers), is used as the electron-conducting phase and the ceramic oxide serves as the proton-conducting phase. In cermets the metal also enhances the hydrogen flux of the ceramic phase by increasing the electronic conductivity of the cermet [18]. Moreover, the addition of a secondary phase as an electronic conductor offers the advantage of providing a wide range of materials with different functional properties [19].

Tao et al. [15] recently stated in a review on proton conducting membranes that “despite great progress made in the recent years in terms of hydrogen separation using dense proton–electron conducting ceramic materials/membranes, there are several challenges to be overcome in order to bring this technology to the market: (1) low proton and electron conductivities for high H₂ flux generation, (2) low H₂ dissociation/recombination reaction rates at the membrane/gas interfaces, (3) low chemical stability in an acidic gas atmosphere at high temperature, (4) low mechanical strength and stability for long-term operation, (5) insufficient optimization of design and fabrication for the materials and membranes and their associated systems, (6) insufficient fundamental understanding of material/membrane performance and degradation and (7) relatively high cost with respect to commercialization”.

Since high permeation rates and high perm-selectivities are required for large-scale industrial implementation of membrane technology, this review is only focused on Pd-alloy membranes (reactors) and not on proton ceramic conductors.

2.3. Pd-based membranes

Dense metal membranes are commonly used for high purity hydrogen production. The mechanism of hydrogen permeation through dense metal membranes has been extensively studied. It is well known that it generally follows a solution-diffusion mechanism. The steps involved in hydrogen transport from a high to a low pressure gas region are the following [20] (Fig. 3): (a) diffusion of molecular hydrogen to the surface of the metal membrane, (b) reversible dissociative adsorption on the metal surface, (c) dissolution of atomic hydrogen into the bulk metal, (d) diffusion of atomic hydrogen through the bulk metal, (e) association of hydrogen atoms on the metal surface, (f) desorption of molecular hydrogen from the surface, (g) diffusion of molecular hydrogen away from the surface. For thicker membranes, or in general when the diffusion through the bulk of the membrane is limiting, the flux through the membrane follows the Sievert's law, meaning that the flux increases with the difference of the square root of the hydrogen partial pressures. However, the exponent n can vary between 0.5 and 1 as well described in [21].

Pd-alloys (mainly Pd-Ag, Pd-Cu and Pd-X-Au) are used to decrease the embrittlement problem and to decrease the poisoning of the membrane when in contact with H₂S and other pollutants (such as CO). “Non-Pd” based membranes make use of materials that present even higher hydrogen permeabilities compared to pure Pd, such as, niobium, vanadium or tantalum.
Furthermore, these metals are significantly cheaper compared to palladium. Therefore, the interest in these metals and their alloys has increased over the last years [22]. Nevertheless, these materials need a catalytic layer (usually Pd is used) on both sides in order to avoid their oxidation and facilitate the dissociation and recombination of hydrogen atoms. This type of membranes are not suitable for high operating temperatures, since at temperatures above 400 °C migration of metal elements between the core metal and the catalytic layer may prevail causing oxidation of the core metal with a corresponding decline in hydrogen permeation [23].

![Diagram](http://example.com/diagram.png)

**Fig. 3.** Solution-diffusion mechanism of hydrogen permeation through a dense metal membrane. Reproduced with permission of Elsevier from [6].

Pd-based membranes may be classified into unsupported and supported ones. Unsupported membranes are generally thick self-standing films (> 50 μm thick) in order to have a minimum mechanical stability. The main drawback of these membranes is their low hydrogen permeance associated to their large bulk diffusion resistance. Moreover, as palladium is very expensive (~20 €/g on 23rd September 2016 [24]), and since the permeation flux decreases with increasing the membrane thickness (i.e., more membrane area is required for the same hydrogen flux for thicker membranes) the costs of the membrane separation sharply increase by increasing the membrane thickness. Thus, there is an optimum in membrane thickness related to the required membrane stability and permeance and costs of the membrane separation. For this reason it is foreseen that the first industrially available membranes will be supported membranes. Supported membranes consist of a thin selective film deposited onto a porous support that provides mechanical stability. Note that in the total membrane cost, the cost of the support also becomes important, especially for very thin film membranes [25].

The selection of the support is of critical importance in the preparation of thin (< 5 μm) and defect-free palladium membranes. High surface roughness and the presence of large pores inhibit the deposition of thin palladium films. Asymmetric porous ceramic supports, having a gradual decrease in pore size from the bulk to the top layer, have a good surface quality to support very thin Pd-based films. However, they lack mechanical strength. Currently, the ceramic supports that are commercially available are asymmetric tubes and capillaries/hollow fibres. For example, Inopor produces ceramic tubular supports of different ceramic materials and pore sizes (http://www.inopor.com/). Metallic supports are more robust than ceramic ones, but the commercially available metallic supports, mainly tubular, have large and non-uniform pores and the surface has a rather low quality hindering their direct use as support for very thin Pd films. GKN (http://www.gkn-filters.de/), Pall (http://www.pall.com) and Mott (http://www.mottcorp.com/) are the main metallic support suppliers. In the case of membranes in which both the selective layer and the support are metallic and are operated above the Tamman temperature (half the melting point in absolute temperatures), interdiffusion of both metals occur, reducing the permeation performance of the membrane [26]. To solve this problem and to improve the quality of the surface, an inter-metallic diffusion barrier layer between the metallic support and the metallic selective layer is deposited.

In the last years, it has been observed that thin Pd-based supported membranes suffer from loss in hydrogen perm-selectivity during long-term operation at temperatures above 500 °C, even if porous metallic or porous ceramic supports are used. The main causes for the deterioration in the permeation properties of Pd membranes at high temperatures and some strategies for improvement of their stability are described hereafter.

For metallic supported membranes the main issue is the formation of undesired alloys when operating at high temperatures, which reduce the surface area and are responsible for the formation of pinholes. Medrano et al. [27,28] tested a metallic supported 4-5 microns thick Pd-Ag metallic supported membrane increasing the temperature from 500 to 600 °C.

![Graph](http://example.com/graph.png)

**Fig. 4.** a) H₂ permeance (open circles) and H₂/N₂ ideal perm-selectivity (closed circles) of a metallic supported thin Pd-Ag membrane as a function of time on stream at 500-600 °C; b) cross section and c) surface SEM image of the metallic supported membrane after the long-term permeation test. Reproduced with permission of Elsevier from [27].
Ideal perm-selectivities above 200,000 were reported at temperatures up to 600 °C with hydrogen permeances in the order of about 1.3·10^-6 mol m^-2 s^-1 Pa^-1. At these conditions, after 800 h of tests an increase in N_2 leakages were observed, leading to a decrease in selectivity to 2650 (Fig. 4a), which is still relatively high compared to literature data reported for metallic supported membranes. After the permeation tests, the selective Pd layer showed some defects in places where the thin ceramic interdiffusion barrier layer did not completely cover the metallic support (Fig. 4b), and holes were observed on the membrane surface (Fig. 4c). The EDX analysis confirmed the intermetallic diffusion between the metallic porous support elements and the Pd-Ag membrane that would be the cause for the defect formation.

Fernandez et al. [29] performed a long-term single gas test with a ceramic supported ~4 µm thick Pd-Ag membrane at 600 °C. After 6 days of low N_2 permeation, a sudden increase of N_2 leakage was observed and the SEM-EDX analysis results showed the presence of defects on the membrane (see Fig. 8). However, the origin of the pinhole formation was not elucidated. On the other hand, a 76 µm thick Pd-Ag unsupported membrane supplied by REB [30] was tested in the same study at the same conditions and it did not show any impurities in the H_2 permeate stream. Even though this membrane showed long-term stability at high temperature, its implementation at larger scale for the targeted application becomes rather expensive due to the large amount of Pd required and the low H_2 permeance of this membrane.

According to Guazzzone et al. [31] the mechanism for pinhole formation of supported thin Pd-based membranes is the self-diffusion of Pd. This phenomenon was observed at temperatures above 400-450 °C and it was attributed to the incoherent sintering of the small Pd clusters and/or Pd crystallites. Other research groups also reported similar causes for pinhole formation [32-33]. As an example, Fig. 6 shows the morphology of a 10 µm thick Pd film deposited onto oxidized porous metallic (code: M-32b) after a heat treatment at 550 °C for 48 h in a H_2 atmosphere [31]. The fresh Pd membrane presented Pd clusters including very small Pd crystallites (~50 nm). Upon the heat treatment, crystallites grew within the clusters reaching sizes in the order of 1-2 µm. Also, upon heating to high temperatures, pinholes were formed, and these were mainly found to be located at the boundaries of Pd clusters and Pd crystallites (as pointed out by the arrows in Fig. 6), with the diameter of the largest pinhole being around 1 µm. Smaller pinholes can also be observed in the same figure. Therefore, a thicker Pd membrane suffers from a lower leakage rate improving the thermal stability over time at a given temperature.

Okazaki et al. studied the changes in H_2 permeance and selectivity with time of thin Pd-based membranes (less than 5 µm thick) supported on porous α-Al_2O_3 substrates at temperatures of 300–850 °C. At 550 °C the membranes showed excellent hydrogen permeation and selectivity during more than 50 h of permeation testing [34]. At 600 °C an appreciable decrease in the hydrogen permeation flux was observed and at 850 °C, the permeation decreases dramatically until almost no hydrogen permeation was observed [35], as shown in Fig. 7. A similar loss in hydrogen flux was observed by Paglieri et al. under operation at 700–750 °C [36]. XPS analysis of the alumina supported Pd membranes after hydrogen permeation at 650 °C or higher, indicated that a considerable amount of aluminium is present in the Pd layer. At high temperatures and in the presence of Pd as catalyst, Al_2O_3 reacts with hydrogen and is reduced to aluminium. The Al subsequently interacts with the Pd forming an Al-Pd alloy, which has little or no hydrogen permeation. In contrast to the palladium alumina membrane, the hydrogen flux of the palladium–YSZ membrane was constant for 336 h after a slight decrease in the initial 50 h. Zhang et al. [37] also reported that the use of YSZ as intermediate material provides stability to a Pd-based membrane for temperatures above 600 °C.

Zeng et al. [38] tested ceramic supported 2.6-6.4 µm thick Pd-Ag membranes at high temperature and in N_2 and H_2 atmospheres. They found that Ag depleted crystallites are formed on the surface of Pd-Ag membranes at temperatures above 500 °C under H_2 atmosphere, that might be explained by a possible Ag sublimation phenomenon. In Fig. 8a it can be seen that the N_2 leakage rate increases when the membrane is annealed under H_2 at 650 °C, but the leakage rate decreases under N_2 atmosphere, suggesting that Ag sublimation prevails under H_2 atmosphere and not under N_2. In addition to Ag crystallite formation, defects were observed on the membrane (Fig. 8b).

Yakabe et al. [39] reported that the formation of pinholes during long-term operation can be related to impurities included during membrane preparation. The first versions of Pd membranes showed micropores after 3000 h operation due to the presence of such impurities as Al and Si according to EDX results (Fig). Afterward, a cold crucible method was used to manufacture very pure Pd-based membranes [40] and these membranes showed high H_2 purity (>99.99%) after 13000 h of operation at 550 °C. After the long-term test the membrane presented only two small leakage points.

In order to increase the thermal stability of Pd-based membranes an approach that many researchers followed is alloying of Pd with other elements such as Ag, Cu, Pt, In, Ru, Y and Rh [41]. Recently, Abu El Hawa et al. [32] demonstrated that doping of Pd with higher melting point elements, such as Pt (1768 °C) or Ru (2334 °C), enhances the thermal stability of Pd-based alloy membranes. It was found that the addition of 27% of Pt or 0.3% of Ru to Pd decreased the N_2 leakage growth over time at 500–600 °C. As an example, the leakage growth rates at 550 °C for the studied membranes are (from the highest to the lowest value): 8·10^-12 (4.9 µm thick Pd), 3·10^-12 (6.0 µm thick Pd-0.3%Ru), 2·10^-12 (6.3 µm thick Pd-17%Pt) and 1·10^-12 (4.4 µm thick Pd-27%Pt) mol m^-2 s^-1 Pa^-1. (see [32], for more results at different operating conditions).

The same group [41] reported that annealing treatments of Pd membranes at higher temperatures (e.g. 700 °C) than the operating temperature can...
improve the thermal stability since a denser microstructure is obtained. After performing a thermal treatment at 700 °C for 82 h in H\textsubscript{2} to a 4.9 µm thick Pd membrane, it presented a leakage growth rate in the order of 10\textsuperscript{-13} or 10\textsuperscript{-14} mol m\textsuperscript{-2}s\textsuperscript{-1}Pa\textsuperscript{-1}h\textsuperscript{-1}, which is at least one order of magnitude lower than for any of the Pd or Pd-alloys with similar thickness without the thermal treatment (Error! Reference source not found.). However, in all the cases the H\textsubscript{2}/N\textsubscript{2} ideal perm-selectivity after the long-term tests was lower than 2000.

Another issue that was reported by Miyamoto et al. [42] is the possible adherence of reactor components usually made of stainless steel (for example, the reactor itself or a metallic mesh used to separate the packed bed catalyst pellets from the membrane) on the Pd-alloy membranes. It was demonstrated that metallic impurities such as Ni, Cr and Fe, the main component elements of stainless steel, caused crack formation on the membrane (Fig. 10). The crack formation was strongly related to the interdiffusion of metals between the Pd membrane and metal particles, and it was found that the Kirkendall effect [43] was one of the dominant mechanisms for this crack formation. This issue becomes important for long-term high-temperature operation of Pd-based membrane reactors.

![Figure 7](image_url)  
Fig. 7. Hydrogen permeation flux versus operating time of Pd membranes supported on YSZ at 650 °C and Pd membrane supported on alumina at 650 and 850 °C. Reproduced with permission of RSC from [35].

![Figure 8](image_url)  
(a) (b)
Fig. 8. a) H\textsubscript{2} and N\textsubscript{2} fluxes at ΔP\textsubscript{H\textsubscript{2}} = 100 kPa during annealing of a 2.9 thick Pd-Ag membrane (M2) at 650 °C in H\textsubscript{2} and N\textsubscript{2}; b) SEM surface image of ceramic supported 2.6 µm thick Pd-Ag membrane (M1) after annealing in H\textsubscript{2} at 600 °C, presenting Ag crystallites and pinholes. Reproduced with permission of RSC from [38].

![Figure 9](image_url)  
Fig. 9. Comparison of long-term durability between the initial module and the improved module. Circles show the hydrogen flux and triangles the leakage rate periodically measured at the module. Reproduced with permission of Woodhead Publishing Series from [39].

![Figure 10](image_url)  
Fig. 10. SEM image of a stainless steel particle (SUS-304) adhered to the Pd-Ag membrane at 600 °C for 100 h. The formed crack is pointed out with a white circle. Reproduced with permission of Elsevier from [42].
Sealing issues with ceramic supported membranes for high temperature applications have been recently investigated in the literature. Different methods such as soldering or the use of inorganic adhesives have been studied, although they were not able to provide the required leak-free conditions. Another solution which is up to now the most promising approach, is based on the use of graphite gaskets. Chen et al. [44] described a method using graphite ferrules instead of using standard metal ferrules. The authors have shown that these graphite ferrules could successfully seal the membrane with Swagelok® connectors. Even at very high pressures up to 50 bar, the nitrogen leakage rate over the connectors was only about 0.35 ml/min. NGK uses a similar sealing method based on VCR stainless steel connectors [45] (Fig. 11a). Ligouri et al. [46] used graphite o-rings for sealing ceramic supported Pd membranes (Fig. 11b). Van Berkel et al. [47] reported the use of two different sealing techniques for Pd-based membranes. The permeation test results showed that a Pd-based membrane using graphite compression seals developed by ECN present a H₂/N₂ ideal perm-selectivity of 25000-35000 at 400 °C and 1 bar of pressure difference, while a similar membrane using a ceramic-metal connector developed by IMR (Fig. 11c) presented a lower H₂/N₂ ideal perm-selectivity (3000-6000) at the same operating conditions. Recently, Fernandez et al. [29] reported a sealing procedure based on high-temperature Swagelok fittings and graphite ferrules with which a leak-tight sealing was demonstrated for a week operation at 600 °C. The bottom part of the connector has been specially designed for membranes that will be immersed vertically in a fluidized bed to avoid gas holdup below the membrane (see Fig. 11d). In case of integration in packed bed reactors, simple Swagelok caps could be used. A summary of the performance of the Pd-based membranes at high temperatures (> 500 °C) for long periods of time (≥ 100 h) reported in the literature is shown Error! Reference source not found..

3. Membrane reactors for high temperature systems: current status

3.1. The membrane reactor concept

Around 80% of the total hydrogen produced worldwide comes from the reforming of fuel sources, normally natural gas [49]. The benchmark technology is based on the fired tubular reformer (FTR) in fixed bed configuration. A detailed description of this process has been provided by Martinez et al. [50]. Natural gas is used as feedstock and after desulfurization it is first pre-reformed with the required amount of steam at around 500 °C over a Ni-based catalyst to remove the higher hydrocarbons and prevent carbon deposition. The pre-reformed gas is reformed at 890 °C and 32.7 bar into syngas over a Ni-based catalyst. The syngas is later fed to an adiabatic WGS reactor operated between 330-430 °C. After, the shifted syngas is cooled to ambient temperature and the H₂-rich syngas is fed to a PSA (Pressure Swing Adsorption) unit, where H₂ is produced with a purity higher than 99.999%. The PSA-off gas is combusted in the reformer burner together with part of the natural gas to supply the heat demanded by the endothermic reforming reactions. A scheme of the full plant integration is presented in Fig. 12.

According to recent investigations, this process can achieve an equivalent reforming efficiency of 81% with the associated costs of hydrogen of 0.21 €/Nm³ [4]. Although high efficiencies are achieved, all CO₂ produced is emitted to the atmosphere, thus enormously contributing to the greenhouse gas effect. Applying CCS technologies in this process considering a MDEA absorption unit for CO₂ separation, the equivalent reforming efficiency of the process decreases to 67%, leading to an increase in the costs of hydrogen to 0.28 €/Nm³. Therefore, it is important to develop novel systems which allow high reforming efficiencies while accomplishing CO₂ capture in order to limit the impact on the economics of traditional processes. In this respect, the use of membrane reactors has been proposed as an efficient technology that can produce high-purity hydrogen with high efficiencies and can largely reduce CO₂ emissions to the atmosphere.

![Fig. 11. Different sealing methods for Pd-based membranes based on: a) VCR connectors, b) graphite o-rings, c) ceramic-metal connection, d) Swagelok-graphite based connectors. All images reproduced with permission from Elsevier and MDPI from [29,45–47].](https://example.com/fig11.jpg)

![Fig. 12. Schematic representation of the steam methane reforming process for hydrogen production at industrial scale. Reproduced with permission of Elsevier from [4].](https://example.com/fig12.jpg)
Table 1
Permeation and leakage rate data for Pd-based membranes tested at high temperature (> 500 °C) for long periods (≥ 100 h).

<table>
<thead>
<tr>
<th>Institution</th>
<th>Pd-alloy/support</th>
<th>Thickness (µm)</th>
<th>Additional thermal treatment (apart from annealing)</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>N₂ leak growth rate (mol m⁻² s⁻¹ Pa⁻¹ h⁻¹)</th>
<th>Final N₂ permeance (mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Final H₂/N₂ ideal permselectivity</th>
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<td>TECNALIA-TUE [27]</td>
<td>Pd-Ag/YSZ-Al₂O₃/Hastelloy X</td>
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<td>500.575</td>
<td>600</td>
<td>&lt;5.8·10⁻¹⁰</td>
<td>&gt;200,000</td>
<td></td>
</tr>
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<td></td>
<td></td>
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<td>600</td>
<td>200</td>
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<tr>
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<td>1.9·10⁻⁹</td>
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<td>REB [29,48]</td>
<td>Pd-Ag</td>
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<td>600</td>
<td>260</td>
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*Helium leakage rate.

Thermodynamic and techno-economical assessments on membrane reactors for H₂ production processes have been presented in the literature [4,51]. In the best scenario, membrane reactors can achieve equivalent reforming efficiencies close to the ones measured for the benchmark technology and much higher in comparison to other technologies with carbon capture, when operated at temperatures around 600 °C, where the costs of hydrogen production are minimized. The use of lower temperatures leads to a less optimal heat management in the full reforming plant and energy (heat) should be imported externally with an adverse effect on the process economics.

The main application of membrane reactors is hydrogen production, especially related to the good characteristics for hydrogen permeation of metal based membranes like Pd. Different processes such as reforming of methane, alcohols, partial oxidations or dehydrogenations have been investigated in this configuration and improved efficiencies have been achieved compared to traditional packed bed reactors. For most of the cases hydrogen is extracted through the membranes, although hydrogen addition for Fischer-Tropsch reaction has also been recently investigated in the literature [52].

The use of membrane reactors for fuel reforming processes has been presented in the literature in a very wide range of temperatures (300 to 700 °C). When considering the performance of the membrane, it is difficult to find a good compromise between high permeation (and permselectivities) and long-term stability, which is the main requirement for the exploitation of membrane technology in large-scale processes. Therefore, many efforts are now ongoing in this research field to find this compromise required by industry.

This section is focused on the different membrane reactor configurations proposed and used in the literature for high-temperature applications in the last few years. In general the packed bed membrane reactor (PBMR)
configuration represents the most explored concept, mostly related to the simplified housing for the membranes. Further on and in order to achieve improved heat and mass transfer integration systems, novel reactor concepts have also been explored, such as the fluidized bed membrane reactor configuration (FBMR). In the next sections, recent advancements on membrane reactor configurations are discussed, mostly focused on tubular membrane configurations, since it shows many advantages compared to planar membrane configurations (viz. improved mechanical stability, possibility of thinner membrane layers, etc).

3.1.1. The packed bed membrane reactor configuration

The PBMR concept has been the most studied membrane reactor configuration in the literature, as it has some advantages compared to other reactor systems, especially related to membrane integration and simplicity in operation. In general, the PBMR configuration refers to a system, where a catalyst is placed inside a reactor in a fixed bed configuration and in contact with the membrane. For this concept, the catalyst can be placed either inside the membrane or in the shell part of the reactor, while selective gas permeation can take place either from the reaction side through the permeate side (gas separation) or from the membrane side to the catalytic bed for selective feeding of reactants resulting in the membrane reactor configuration for distributive feeding. A more detailed representation of the packed bed membrane reactor configuration can be found in Fig.

![Fig. 13. Schematic representation of a fixed bed membrane reactor configuration with the catalyst confined in the shell part. Reproduced with permission of Elsevier from [6].](image)

The concept allows the use of sweep gas in the permeate side to maximize the driving force for gas separation. The use of sweep gas from inside the membrane increases the partial pressure difference resulting in almost zero partial pressure in the permeate side, which is associated to an increase in hydrogen production. Furthermore, the use of sweep gas leads to a decrease in the surface area required for gas separation and, in general, its use is interesting when the resulting gas mixture can be further used for a different process. For instance, to produce gas mixtures with H₂/N₂ (3/1) for ammonia plants, or when gas separation downstream is not complex, like with steam that can be easily separated by condensation. When sweep gas is used, the membrane reactor can be operated either in co-current or in counter-current mode, both yielding different partial pressure profiles in the reaction section and inside the membrane.

When concerning the use of membrane reactors for high-temperature applications, steam methane reforming (SMR) and autothermal reforming of methane (ATR) are the two most studied processes as the reactions are favored at high temperatures as compared to other reactions carried out at much lower temperatures like water gas shift (WGS) or reforming of alcohols.

In 2012, Saric et al. [53] studied the SMR reaction in a bench-scale membrane reactor using a ceramic-supported Pd-based membrane operated at 580 °C and 28 bar. The membrane thickness was 3.8 μm and the SMR reaction was carried out over a commercial Ni-based catalyst supplied by Sulchemie. Results of this work showed that sustained methane conversions between 80-95% with high hydrogen recovery factors (60-80%) could be obtained for almost 1100 h operation. However, at the end of the experiments the membrane showed gas leakage and the concentration of CO₂ in the permeate side was around 12%, whereas the CO content was around 56-154 ppm. In 2013 Dittmar et al. [54] also carried out the SMR reaction using Pd-membranes (12 μm thickness) prepared by PVD/EP and PVD/ELP onto a tubular metallic ITM support. These membranes were 190 mm in length and 6 mm in diameter. To avoid metallic interdiffusion, ceramic YSZ layers were deposited between the support and the Pd layer. The experimental evaluation was performed in a fixed bed reactor of 820 mm in length and 27.7 mm inner diameter filled with commercial Ni-based catalyst pellets. The SMR reaction was carried at 600 °C with a S/C ratio of 3. The pressure in the retentate side was kept at 16 bar, whereas the permeate side was operated at 1.3 bar and the reaction was sustained for several hundred hours without degradation of the membrane at temperatures up to 650 °C with a purity in the permeate of around 99.5%. In the best scenario, a methane conversion of 60% was achieved with a hydrogen recovery above 70%.

Kune et al. [55] also proposed a catalyst module for the integration of a Pd-based membrane operated under reforming conditions at 550 °C and 8 bar. This module was named membrane on catalyst (MOC), where they investigated the total amount of catalyst (Ni based) required in the concept to maximize its performance. The module mounted a thin Pd membrane (6-10 μm thickness) prepared on a porous ceramic barrier (NiO-8YSZ) to avoid inter-diffusion of the metals of the support material (Ni based). They proposed a NiO catalyst with 60 wt% for the designed feedstock flow rates, with which natural gas conversions above 60% were achieved.

A comparison of experimental data obtained with a fixed bed membrane reactor with calculations using a 1D reactor model was carried out by Di Marcoberardino et al. [56] for methane steam reforming. The reactor had 10 commercial membranes supplied by REB research, which are 3.18 mm in diameter and 200 mm in length, while the catalyst was a commercial CPO Ni-Al₂O₃ catalyst. The membranes (Pd-Ag) were supported on inconel tubes and were 3 μm thick. Although the purpose was to validate the modelling approach, the methane conversions achieved in the membrane reactor were not very high, with conversions up to 47.4% and recovery factors of 28.1% at 600 °C and 5 bar pressure. Similarly, Patracsi et al. [57] also studied SMR hydrogen production in a fixed bed membrane reactor and compared their experimental data with model predictions. The experiments were carried out in a fixed bed reactor filled with PtNiCeO₂ catalyst in contact with a Pd membrane prepared by ECN, which has a 4-5 μm thick Pd layer deposited onto a porous alumina support and provides a permeation area of 175 cm². Experimental results showed that at 525 °C over 90% methane conversion could be achieved with a high hydrogen recovery over 80% for a feed flow rate of 0.24 NL/min of methane. Moreover, they also found experimentally that an increase in pressure above 10 bar did not improve the performance of the concept, as higher hydrogen fluxes were not observed, contrary to the expectations. Possible causes were not confirmed, but the observed absence of an increase in the hydrogen flux at higher operating pressures might be associated with poisoning of the membrane by CO and/or concentration polarization effects.

A Pd-Ru alloy membrane was tested by Abu El Hawa et al. [58] in 2015 to check the stability of the membrane under SMR conditions at high temperature using a Ni-based catalyst. A 5 μm membrane deposited on a porous YSZ over a stainless steel substrate was prepared by ELP. The use of a Pd-Ru alloy membrane was proposed due to the higher permeabilities of this alloy compared to pure Pd and the increased mechanical strength. The hydrogen permeation at reaction conditions was very stable for more than 1000 h at 580 °C, 29 bar and a S/C of 3 showing purities above 95%, as can be observed in Fig. The measured gas leakages were most likely coming from the thermal cycles done during the membrane annealing, which might have caused membrane deterioration due to the differences in thermal expansion of the membrane components. Furthermore, almost full conversion was achieved, well above the calculated thermodynamic equilibrium without membranes. Moreover, the amount of hydrogen recovered was above 80%, thus showing a high performance of the membranes at these conditions. However, the purity of the recovered hydrogen was not sufficiently high for further energy applications such as fuel cells.

![Fig. 14. Methane conversion, H₂ recovery and H₂ purity as a function of time on stream for SMR at 29 bar and 550 °C using a 5 μm Pd-Ru based membrane.](image)
Reproduced with permission of Elsevier from [58].

The membrane reactor concept has also been extended with an enhanced system using selective CO2 absorption, thus showing a dual process intensification system as presented by Wu et al. [59]. First, the authors calculated based on a thermodynamic analysis that the methane conversion can be largely increased at temperatures of around 500 °C when 95% of the CO2 is absorbed, in contrast to the relatively low equilibrium conversion of only 52% without any sorption enhancement. The experimental validation of the concept was carried out with a 7.2 μm thickness Pd based membrane prepared by ELP on a porous ceramic support with an average pore diameter of 0.2 μm. The packed bed membrane reactor was filled with 5 g of a catalyst with CaO 35.9 wt% sorbent for CO2 sorption (sorption capacity of 1.6 mol/kg) and a Ni based catalyst supported on alumina for the reforming reaction. The experiments carried out at 500 °C showed a fuel conversion of 62.6%, while the improvement compared to the thermodynamic equilibrium when the reaction was carried out at 600 °C was 27.2% higher. However, in this case the selectivity for H2 separation was rather low (9 for a mixture H2/N2) after the first cycle and it completely deteriorated after ten consecutive cycles without periodic regeneration of CaO sorbent.

Very recently Kyriakides et al. [60] optimized the experimental conditions of a fixed bed membrane reactor for a low-temperature steam methane reformer. The membrane used in this work is a 4.5-μm Pd-Ru membrane coated on a ceramic porous alumina support, all supplied by NORMAT. The catalyst used was a Ni-Pt supported on a CeZnLa foam to increase the surface area for reaction. In total 23.2 g of this foam supported catalyst was used in the experiments. The reaction was carried out at an average temperature range of 450-550 °C and at 10 bar pressure. To fully optimize the reformer reactor, also the use of sweep gas (N2 or steam) on the overall performance was investigated. For the set of experiments it was shown that the inlet flow rate of the reactants was the main parameter to fine tune the optimal operating conditions. When the inlet flow rate is decreased, there is enough time to separate all the hydrogen produced. Similarly, the addition of sweep gas into the permeate side helps in achieving a better performance, especially because the flow regime inside the membrane is changed from laminar to turbulent, thus reducing concentration polarization effects. In the best scenario, fuel conversions above 96% were achieved at 550 °C, where N2 leakages were not observed at any time during the experimental evaluation as revealed by chromatography analyses.

Dry reforming of methane is another process widely studied in the literature for H2 production that has been extended to membrane technology. In dry reforming, steam is not fed to the reactor, which leads to important energy savings related to the absence of steam formation at high temperatures. However, the process is exposed to higher carbon formation rates and a reduced amount of H2 production, since the H2 originating from steam is not playing a role in the process as it does in steam methane reforming. In 2012, Silva et al. [61] obtained hydrogen through CO2 reforming of methane on a packed bed membrane reactor using a commercial Pd-Al membrane (Antherm Research). To study the performance of the process was evaluated by comparison with a conventional packed bed reactor. In both cases a Pt/CeZrO2/Al2O3 catalyst was used. In total 1.5 g of the catalyst (including the support material) was required and was diluted with quartz particles (2 g) to achieve a required bed height of 5 cm. The reaction was carried out at 550 °C with a gas mixture of CH4:CO2 = 1:1 and a feed flow rate of 100 mL/min. The driving force for gas separation was created by feeding Ar as sweep gas to the inside of the membrane, where the total pressure of both sides was kept the same (atmospheric). Results showed that high hydrogen recovery factors could be achieved (over 75%) for high methane conversions (60%), above those that can be obtained in a conventional reactor at equilibrium conditions. For all the experiments, an infinite selectivity to H2 was measured through the membrane without any deterioration in its performance.

Garcia-Garcia et al. [62] also carried out dry reforming of methane in a packed bed membrane reactor using a novel Pd based membrane (5 μm thickness) supported on an Al2O3 hollow fibre support, which gives a total surface area of 4.4 cm2. The authors also compared the performance of the process with a conventional fixed bed reactor and the membrane reactor configuration using a more conventional Pd based membrane on a stainless steel support with a thickness of 17 μm and a total surface area of 22 cm2. All the experiments were carried out over a 4% Ru/Co3O4-La2O3 catalyst and the activity was tested at different temperatures up to 550 °C with a feed ratio of He/CH4/CO2 of 8/1/1 and atmospheric pressure at both sides and sweep gas (Ar) from inside the membrane. Both membrane reactors achieved similar methane conversions, which were 72 % higher than the conversions obtained in the conventional reactor and 34% above the thermodynamic equilibrium. However, the hollow fibre membrane reactor used much less Pd (about 15 times) as compared to the commercial Pd membrane and had a much lower surface area, where for both membranes the ideal perm-selectivity measured remained above 5000 after operation at high temperatures as measured by gas chromatography.

Also Sumurunronnasak et al. [63] studied hydrogen production by dry reforming of methane (CH4:CO2 = 1:1) in a catalytic membrane reactor mounting a Pd/Ag,Cu alloy membrane deposited onto a porous stainless steel disk of circular shape with a Ni-based catalyst in a packed bed configuration. In total 60 mg of this catalyst was tested with an inlet flow rate of 20 mL/min at 550 °C and 2 bar pressure. As depicted in Fig. 15, CH4 and CO2 conversions were largely increased when the reaction was carried out in the membrane reactor configuration. While in a conventional packed bed reactor the achieved methane conversion was just 33%, the use of the membrane reactor leads to an increase in methane conversion to 65% with a hydrogen recovery of 35% via the membrane. For both configurations, a sustained reaction of 3 h was obtained. However, much longer experimental results are needed for assessing the viability of membrane reactors for dry reforming of methane.

Autothermal reforming of methane is another process for H2 production where a small amount of oxygen is fed to the reactor in order to have partial oxidation of the fuel supplying the heat demanded by the highly endothermic reforming reaction. However, due to the possible formation of hot-spots related to the highly exothermic reaction, its use in packed bed configurations is more limited as compared to fluidized bed configurations as described in the next section. Recently autothermal reforming of methane in a membrane reactor for hydrogen production has been investigated by Yan et al. [64]. The membrane was prepared by ELP onto a ceramic tube support of Al and Zr. This membrane was 5-6 μm thick with a length of 200 mm and a diameter of 13 mm and catalytic tests were carried out with a feed with a molar ratio of CH4:aIr/H2O equal to 1:1:2 over a Ni-based catalyst (10% Ni loading). At 650 °C and atmospheric pressure a methane conversion of 99.1% was achieved, which is much higher in comparison to the conversion measured in the conventional reactor (around 50%), with a high hydrogen yield (73.6%). For these experiments the driving force for hydrogen separation was provided by feeding N2 as sweep gas.

Reforming of alcohols in packed bed membrane reactors operated at high temperatures has also been reported in the literature. For instance, Lopez et al. [65] used four Pd-Ag Inconel membranes for hydrogen production suitable for a PEM-fuel cell. These membranes have a total surface area of 30.4 cm2 and a Pd-Ag thickness of 30 μm. Ethanol reforming was performed over a Pd- Rh catalyst and it was found that optimal conditions are at 650 °C and a pressure of 9-11 bar in the reactor side with an amount of steam somewhat above the stoichiometric ratio. Hydrogen yields of 3.1 mol per mol of ethanol fed into the reactor were obtained and a maximum hydrogen recovery of around 70% was achieved. Espinal et al. [66] also carried out steam reforming of ethanol, although in their study with a cobalt hydrotalcite catalyst doped with potassium. These authors used a 30 μm thick Pd-Ag membrane supported on porous stainless steel providing a total area of 7.1 cm2. Two different configurations were investigated: in the first configuration the hydrogen permeable membrane acted as a gas purification system and in the second configuration the membrane was immersed in the catalytic bed, thus the configuration of a packed bed membrane reactor. Tests were carried out at
temperatures up to 600 °C and pressures up to 18 bar in the reactor side without sweeping gas inside the membrane, thus obtaining hydrogen with a high purity suitable for further applications. For instance, at 12 bar pressure, S/C equal to 3 and 600 °C, 3.7 \text{ mol} \text{STP} per \text{ mol} of fuel and gram of catalyst were achieved, which results in about 80% hydrogen recovery. At the end of the experiments (in total more than 650 h) the performance of the catalyst and the membrane reactor remained constant as verified by repetition of some experiments at different moments in time. Furthermore, the measured selectivities (considered as infinite) and H₂ recovery values were practically identical to the obtained values before all the tests.

Very recently, Hedayat et al. [67] carried out an experimental and exergy analysis of ethanol steam reforming over a Pd-Re/Co₃O₄ catalyst. They evaluated the performance of a packed bed membrane reactor for conditions at 600-650 °C and pressures of 4-12 bar. The membrane used in this study was similar to the one described in Espinal et al. [66]. An increase in the H₂ selectivity was measured when increasing the S/C ratio in the feed, and a hydrogen yield of 55% with a hydrogen recovery factor (HRF) of 90% was obtained at 650 °C and 12 bar pressure and an intensive permselectivity for H₂ separation through the membrane for all the investigated conditions. As far as the exergy analysis is concerned, an efficiency of 50% was measured under these conditions. This value is relatively low due to the heat losses in the reactor and the permeate side. However, the exergy efficiency could be largely increased by recovery of the retentate gas in an insulated reactor.

Also other less common fuels have been used as primary feedstock in packed bed membrane reactors for high temperature applications. Lin et al. [68] studied the autothermal steam reforming of glycerol in a packed bed membrane reactor. The membrane was produced by using a two-layer membrane made of a transition metal oxide of very high cost compared to other fuels. For the experiments a Pd/Ag alloy membrane (31 μm thickness) was used supported on a stainless steel tube (Pall Corp.), while the catalyst was prepared by sequential impregnation of CeO₂ and Ni over an alumina support. Experiments were carried out in the range of 450-700 °C using a feed ratio of \text{CH}_3\text{OH} to \text{H}_2\text{O} ranging from 0.5 to 3. Experimental results showed that very high glycerol conversions could be achieved at 600 °C with a water to gas ratio of 3 with a hydrogen recovery obtained at these temperatures not high and only when working at 500 °C recoveries above 85% were measured.

Another reaction reported in the literature refers to the dehydrogenation of isobutene over a Cr based catalyst for the production of isobutene as hydrogen is a product of the equilibrium limited reaction [69]. The membrane reactor tests were carried in a packed bed membrane reactor at 550 °C mounting a commercial REB metallic supported membrane, with which the advantages of in-situ removal of hydrogen were demonstrated leading to higher isobutene yields. Actually, much higher conversions were achieved compared to those calculated using thermodynamic equilibrium. However, remarkably, at higher temperatures (600 °C) the membrane showed catalytic activity for the decomposition of isobutene and isobutene, thus leading to a high coke formation rate, as well as other undesired products such as methane or propane, with a corresponding decrease in selectivity.

Counterintuitively, thinner membranes do not always show an increased performance of the membrane reactor in the packed bed configuration. Actually, it has been verified both experimentally and numerically that in many cases the rate of gas permeation through the membrane is higher than the transport of the gas from the bulk of the reactor to the wall of the membrane. This is one of the main disadvantages associated with this configuration and it is referred to as “concentration polarization”, which is a bed-to-wall mass transfer limitation [70,71]. Other disadvantages of packed bed configurations include a large pressure drop associated to the catalytic bed (which can be solved by the use of bigger particles with the corresponding increase in internal mass transfer limitations) and difficulties in the heat management for highly endothermic or exothermic systems due to the lack of freedom in membrane/heat arrangement.

All these drawbacks may limit the further development of the technology of membrane reactors, especially concerning scale-up of the systems. To reduce all these limitations novel membrane reactor configurations have been reported in the literature, especially the use of the fluidized bed membrane reactor (FBMR) configuration. The advantages of this concept are discussed in the next section together with an overview of recent research reported in the literature for high-temperature applications.

### 3.1.2. The fluidized bed membrane reactor configuration

The FBMR configuration has gained interest over the last years as a consequence of the limitations encountered in packed bed membrane reactor configurations. In this system, permselective membranes for \text{H}_2 separation are immersed in a catalytic bed fluidized in the bubbling regime. Many different advantages characterize this concept, such as the continuous refreshment of the membrane wall leading to a reduction in the bed-to-wall mass transfer limitations and a virtual isothermal conditions in the bed. This last advantage is especially important when carrying out highly exothermic reactions like auto-thermal reforming, were the formation of hot spots in packed bed configurations makes this processes very difficult to be handled. Furthermore, the fact that solids are in continuous motion in the bed also allows more freedom in membrane and heat exchange arrangements with a corresponding improvement in fluidization behaviour of the bed [72,73].

The first description of the FBMR configuration was given by Adris et al. [74] and it was proposed for selective hydrogen separation using \text{Pd} based membranes. Over the last decade, this configuration has gained more and more attention, especially once it has been demonstrated that \text{Pd} based membranes can sustain perm-selectivities over long time even in vigorous fluidization regimes [75]. Despite the potential advantages of this configuration, this concept is much less investigated in the literature in comparison to packed bed configurations and it is often used for intermediate temperatures. High temperature fluidized bed membrane reactors have been used over the last five years for fuel reforming and dehydrogenation of alkenes. The gain in freedom for membrane arrangement has led to more sophisticated configurations aiming at virtual auto-thermal operation. For instance, Gallucci et al. [48] proposed the use of additional U-shaped \text{Pd} membrane immersed in the catalytic bed from which air is fed. Thus, the permeated hydrogen is combusted in a highly exothermic reaction supplying the heat required for the reforming processes. Another sophisticated reactor is the so-called Two-Zone Fluidized Bed Membrane Reactor (TZFBR) proposed by Medrano et al. [76]. This concept has been proposed and used for processes that suffer from fast catalyst deactivation due to carbon deposition like the dehydrogenation of alkenes. In this concept the fuel is fed at an intermediate position in the bed and the deactivated catalyst is regenerated by combustion of the carbonaceous deposits onto the catalyst particles with a small amount of oxygen fed from the bottom. This reaction produces a high amount of heat that is released in the catalytic bed to sustain auto-thermal operation. A schematic description of the two novel concepts is presented in Fig. 16.

![Fig. 16. Left: Fluidized bed membrane reactor configuration with U-shaped membrane to sustain autothermal operation [48]; right: Two-zone fluidized bed membrane reactor for continuous catalyst reactivation. Reproduced with permission of MDPI from [76].](image)

In 2013, Roses et al. [75] studied the stability of a fluidized bed membrane reactor for methane steam reforming. Experiments were carried out during two weeks at temperatures ranging from 500 to 630 °C and pressures from 2 to 5.3 bar in the reactor. The tests were carried out using 10 commercial dead-end membranes of 3.2 mm in diameter prepared by ELP and a Pd-Ag layer of 3.2 μm supplied by REB Research and Consulting immersed in a catalytic partial oxidation (CPO) catalyst. The long term tests evidenced the mechanical strength of these membranes under bubbling fluidization conditions, where the purity of the permeated hydrogen remained high during the whole period of experiments. The long-term tests with the measured CO impurities below 10 ppm. All the tests were carried out in two different configurations; first in a conventional fluidized bed reactor without membranes and subsequently in the FBMR configuration. For all the cases an increase in \text{H}_2 yields and in fuel conversion was observed. Remarkably, the performance of the membrane reactor was recovered after the complete set of experiments.
Overview of the main achievements obtained recently in membrane reactors operated at high temperatures in packed bed and in fluidized bed configurations.

### Table 2

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<th>T (°C)</th>
<th>P (bar)</th>
<th>X_{ad} (%)</th>
<th>HRF (%)</th>
<th>Ref.</th>
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<tr>
<td>Packed bed membrane reactor configuration</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Ceramic supported Pd membrane</td>
<td>3.8</td>
<td>SMR</td>
<td>Ni-based</td>
<td>580</td>
<td>28</td>
<td>80-95</td>
<td>60-80</td>
<td>[53]</td>
</tr>
<tr>
<td>Pd membrane onto a tubular metallic ITM support/YSZ ceramic barrier</td>
<td>12</td>
<td>SMR</td>
<td>Ni-based</td>
<td>600</td>
<td>16</td>
<td>60</td>
<td>&gt;70</td>
<td>[54]</td>
</tr>
<tr>
<td>Thin Pd membrane on a porous ceramic barrier (NiO-YSZ)</td>
<td>6-10</td>
<td>SMR</td>
<td>Ni-based</td>
<td>550</td>
<td>9</td>
<td>&gt;60</td>
<td>-</td>
<td>[55]</td>
</tr>
<tr>
<td>10 commercial metallic supported membranes</td>
<td>3 outside and 1.5 inside</td>
<td>SMR</td>
<td>CPO Ni-AlO$_2$</td>
<td>600</td>
<td>5</td>
<td>47</td>
<td>28</td>
<td>[56]</td>
</tr>
<tr>
<td>Ceramic supported Pd membrane</td>
<td>4-5</td>
<td>SMR</td>
<td>Pt(NiO$_2$Co)</td>
<td>525</td>
<td>10</td>
<td>90</td>
<td>&gt;80</td>
<td>[57]</td>
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<tr>
<td>Pd-Ru membrane on a porous YSZ barrier over stainless steel by ELP</td>
<td>5</td>
<td>SMR</td>
<td>Ni-based</td>
<td>580</td>
<td>29</td>
<td>65-80</td>
<td>&gt;80</td>
<td>[58]</td>
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<tr>
<td>PBMR+CO$_2$ absorption: Pd based membrane prepared by ELP on a porous ceramic support</td>
<td>n.a.</td>
<td>SMR</td>
<td>CaO/Al$_2$O$_3$</td>
<td>600</td>
<td>1.3</td>
<td>91.2</td>
<td>-</td>
<td>[59]</td>
</tr>
<tr>
<td>Pd-Ru membrane coated on a ceramic porous alumina support</td>
<td>4-5</td>
<td>SMR</td>
<td>Ni-Pt/CeZrO$_2$</td>
<td>550</td>
<td>10</td>
<td>96</td>
<td>-</td>
<td>[60]</td>
</tr>
<tr>
<td>Pd-Ag alloy provided by REB Research</td>
<td>50</td>
<td>Dry reforming</td>
<td>Pt/ZrO$_2$/Al$_2$O$_3$</td>
<td>550</td>
<td>1 (Ar sweep gas)</td>
<td>&gt;60</td>
<td>&gt;75</td>
<td>[61]</td>
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<tr>
<td>Pd based membrane supported on an Al$_2$O$_3$, hollow fibre support</td>
<td>5</td>
<td>Dry reforming</td>
<td>Ru/ZrO$_2$/LaO$_2$</td>
<td>525</td>
<td>1 (Ar sweep gas)</td>
<td>&gt;40</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td>Pd$_3$Ag$_2$Cu$_4$ alloy membrane on a porous stainless steel disk</td>
<td>15.5</td>
<td>Dry reforming</td>
<td>Ni-based</td>
<td>550</td>
<td>2</td>
<td>65</td>
<td>35</td>
<td>[63]</td>
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<tr>
<td>Pd membrane prepared by ELP on a ceramic tube support of Al and Zr</td>
<td>5-6</td>
<td>ATR</td>
<td>Ni/AlO$_2$</td>
<td>650</td>
<td>1 (N2 sweep gas)</td>
<td>99</td>
<td>-</td>
<td>[64]</td>
</tr>
<tr>
<td>Pd based metallic membrane from REB</td>
<td>30</td>
<td>Ethanol reforming</td>
<td>Pd-Rh/CoO$_2$</td>
<td>650</td>
<td>10</td>
<td>99</td>
<td>70</td>
<td>[65]</td>
</tr>
<tr>
<td>Pd-Ag membrane over porous stainless steel support</td>
<td>30</td>
<td>Ethanol reforming</td>
<td>Co/Mg/Al hydrotralcite</td>
<td>600</td>
<td>18</td>
<td>99</td>
<td>80</td>
<td>[66]</td>
</tr>
<tr>
<td>Pd-Ag membrane over porous stainless steel support</td>
<td>30</td>
<td>Ethanol reforming</td>
<td>Pd-Rh/CoO$_2$</td>
<td>650</td>
<td>12</td>
<td>99</td>
<td>90</td>
<td>[67]</td>
</tr>
<tr>
<td>Pd/Ag alloy membrane supported on stainless steel</td>
<td>31</td>
<td>Ethanol reforming</td>
<td>Ni/Co$_2$O$_3$/Al$_2$O$_3$</td>
<td>700</td>
<td>1-3</td>
<td>&gt;99</td>
<td>-</td>
<td>[68]</td>
</tr>
<tr>
<td>commercial REB metallic supported membrane</td>
<td>5 µm Pd on a Pd-Ag layer</td>
<td>Glycerol reforming</td>
<td>Isobutane dehydr.</td>
<td>C$_2$MCM-41</td>
<td>550</td>
<td>1 (vacuum)</td>
<td>&gt;50</td>
<td>-</td>
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<table>
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<tr>
<th>Fluidized bed membrane reactor configuration</th>
<th></th>
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<tr>
<td>10 Pd-Ag commercial membranes prepared by ELP</td>
<td>3.2</td>
<td>SMR</td>
<td>CPO catalyst</td>
<td>600</td>
<td>3.5</td>
<td>55</td>
<td>-</td>
<td>[75]</td>
</tr>
<tr>
<td>5 Pd-Ag membranes supported by ELP on ZrO$_2$</td>
<td>4</td>
<td>SMR</td>
<td>Ru/Cr$_2$O$_3$/ZrO$_2$</td>
<td>600</td>
<td>1.3 (vacuum)</td>
<td>89.3</td>
<td>23</td>
<td>[29]</td>
</tr>
<tr>
<td>5 Pd-Ag membranes supported by ELP on ZrO$_2$</td>
<td>4</td>
<td>ATR</td>
<td>Ru/Cr$_2$O$_3$/ZrO$_2$</td>
<td>600</td>
<td>1.3 (vacuum)</td>
<td>96.7</td>
<td>35</td>
<td>[29]</td>
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<td>5 commercial REB membranes</td>
<td>4</td>
<td>ATR</td>
<td>Ru/Cr$_2$O$_3$/ZrO$_2$</td>
<td>600</td>
<td>1.3 (vacuum)</td>
<td>92.9</td>
<td>20</td>
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<tr>
<td>Pd-Ag membrane prepared by ELP on metallic Hastellox X support</td>
<td>5</td>
<td>SMR</td>
<td>Ni/Co$_2$O$_3$/Al$_2$O$_3$</td>
<td>600</td>
<td>4</td>
<td>&gt;70</td>
<td>28</td>
<td>[27]</td>
</tr>
<tr>
<td>Pd-Ag membrane prepared by ELP on metallic Hastellox X support</td>
<td>5</td>
<td>ATR</td>
<td>Ni/Co$_2$O$_3$/Al$_2$O$_3$</td>
<td>600</td>
<td>4</td>
<td>&gt;80</td>
<td>35</td>
<td>[27]</td>
</tr>
<tr>
<td>Pd-Ag membrane prepared by ELP deposited on hollow fibre of alumina</td>
<td>n.a.</td>
<td>Propane dehydr.</td>
<td>Pt-Sn/MgAl$_2$O$_4$</td>
<td>600</td>
<td>1 (vacuum)</td>
<td>&gt;40</td>
<td>-</td>
<td>[77]</td>
</tr>
<tr>
<td>Commercial Pd-Ag REB membrane</td>
<td>50</td>
<td>Propane dehydr.</td>
<td>Pt-Sn/MgAl$_2$O$_4$</td>
<td>575</td>
<td>1 (vacuum)</td>
<td>&gt;30</td>
<td>-</td>
<td>[76]</td>
</tr>
</tbody>
</table>

Fernandez et al. [29] also studied the behaviour of ceramic supported membranes under fluidization conditions for steam methane reforming and autothermal reforming processes at elevated temperatures (500-600 °C). The thin Pd-Ag membranes (4 µm thick) supported on alumina tubes with an outside zirconia layer were prepared with an electrophoresis plating process. In total five membranes of 1 cm in diameter and 14.5 cm in length were used in the reactor. The performance of the membrane reactor was compared first with a conventional fluidized bed reactor and subsequently with the performance of another membrane reactor mounting commercial REB membranes (self supported 76 µm thick). All the experiments were carried out at conditions slightly above the minimum fluidization velocity for the particles used, which were a Ru/Ce$_2$O$_3$/ZrO$_2$$_2$O$_2$ catalysts (150-250 µm particle size) mixed with ZrO$_2$ particles as filler material. Results showed that the equilibrium fuel conversion can be overcome with the use of membrane reactors and that higher hydrogen recovery factors (HRF) are achieved with the ceramic supported membranes as compared to the commercial self supported membranes. However, after all the tests, the required purity in the permeate side was not achieved with the thin ceramic supported membranes as impurities were above 500 ppm. On the other hand, the metallic supported membranes were able to maintain very high permeeselectivities over the whole set of experiments and the impurities in the permeate side were below 1.5 ppm. Membrane characterization revealed the formation of pinholes on the surface of the ceramic supported membrane, although it was difficult to find a feasible explanation.

Medrano et al. [27] also studied both reactions in a fluidized bed membrane reactor using a thin Pd-Ag membrane (around 5 µm layer) prepared by ELP supported on a metallic Hastellox tube. This membrane was 13 cm in length and 9.5 mm in diameter and was immersed in a catalytic bed of Ni/CaAlO$_2$ particles (300 gram and 150-250 µm particle size). Experiments were carried out at different temperatures (500-600 °C), steam-to-carbon ratios (2-4), pressures (2.5 bar) and fluidization regimes, with vacuum in the permeate side. All the experiments were repeated for a conventional fluidized bed configuration and it was observed that the thermodynamic equilibrium was overcome for all the conditions tested in the fluidized bed membrane reactor. However, high purities were not measured in the permeate side. This was mainly attributed to the fact that the membrane was previously tested for more than 800 h continuous operation under hydrogen atmosphere at high temperatures to investigate the stability of the membrane. N$_2$ leakages were measured only after this long-term test which included more than 150 h operated at 600 °C. Therefore, the membrane used for SMR and ATR reactions started with a H$_2$ content in the permeate of 99.8 % vol. Characterization carried out after all the tests revealed the formation of pinholes on the surface as well as interdiffusion of metallic components to the selective Pd-Ag layer.

The catalytic dehydrogenation of propane has also been studied in a FBMR by Medrano et al. using hollow fibre membranes [77] and commercial metallic supported membranes [76] in the novel TZFBR-MR presented in 0. Hollow fibre membranes were prepared by deposition of Pd-Ag by ELP on asymmetric alumina fibres prepared via phase-inversion/sintering technique leading to membranes with 3 mm in diameter and 6 cm in length. Due to the
lack of mechanical strength, one of these membranes was housed in a porous alumina shell to avoid damage by the particles of the fluidized suspension. The catalyst used was a Pt-Sn based catalyst for dehydrogenation reactions supported on MgAl₂O₄ to reduce its acidity, thereby reducing carbon formation. On the other hand, the commercial metallic supported Pd-Ag membrane supplied by REB Research was directly immersed in the catalytic bed. Experiments were carried out in different configurations: first in a conventional fluidized bed reactor, subsequently on the novel TZFBR and finally in the TZFBR with the membrane inside. All experiments were carried out at atmospheric pressure in the reactor and vacuum from inside the membrane at temperatures ranging from 500 to 600 °C. It was first observed that the process suffers from a strong deactivation in the conventional bed due to carbon formation on the surface of the catalyst. However, this disadvantage can be circumvented in the TZFBR with continuous catalyst regeneration, thus leading to steady state operation. The equilibrium achieved was further overcome by the use of the membranes, leading to increased yields to propylene.

Concluding, the fluidized bed membrane reactor is a configuration much less explored for high temperature processes and only several studies have been reported in the literature in the last years. This is partly related to the complex hydrodynamics prevailing in a fluidized bed in the presence of internals and the difficulties in obtaining reliable models to predict the behavior of the fluidized bed membrane reactor. Nevertheless, it is anticipated that this concept will gain more and more interest in the coming years since many of the drawbacks associated with packed bed membrane reactor configurations can be alleviated which will become more and more important with the further advancements in the development of novel ultra-thin membranes.

All the results presented in packed bed and in fluidized bed membrane reactor configurations have been summarized in Table 2.

4. Conclusions

Membranes and membrane reactors for high-temperature applications are being studied in various national and international projects for a variety of reactions. While it has often been demonstrated that membrane reactors outperform conventional systems, both in terms of product yield and process efficiency, its industrial exploitation is still hampered by the lack of knowledge on the stability of the membranes and their sealing in the reactor at high temperatures.

This review has reported the ongoing developments in this field and particularly on the stability of the different membranes for hydrogen production at high temperatures. Although the review shows that membranes with extremely high perm-selectivities maintained over 600-1000 h have been produced, even still longer proof of concepts are required before commercialization of these devises can commence.

From a scientific point of view still several questions are left to be answered to be able to further improve these membranes and their high-temperature stability:

1. What is the mechanism of “membrane deterioration” at high temperature? Is it related only to Pd crystal growth?
2. Can the membrane be stabilized with other metals, and which is the best alloy to be used?
3. Can these membranes be used at high temperature in reactors, or is it the reactor operation that deteriorates the membrane stability?

5. Acknowledgements

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References


[76] J.A. Medrano, I. Julián, J. Herguido, M. Menéndez, Pd-Ag membrane coupled to a two-zone fluidized bed reactor (TZFBR) for propane dehydrogenation on a Pt-Sn/MgAl₂O₄ catalyst, Membranes (Basel). 3 (2013) 69–86.