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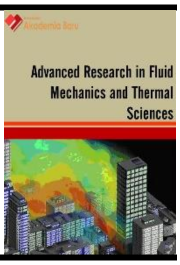

A Review on Hydrogen Separation through Inorganic Membranes

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ABSTRACT

The process of membrane separation is indicated as attractive choices than mature technologies for example cryogenic distillation as well as pressure swing adsorption. Hydrogen (H_2) of high purity can be acquired via membranes of dense metallic and mainly palladium as well as its alloys with highly selective properties to H_2. Composite membranes improvement via deposition of thin metallic layer on inorganic or porous polymeric supports is deemed as an effective technique in improving gas permeation of dense metallic membranes. Membranes of inorganic materials demonstrated excellent separation performance in purifying H_2. In addition, these membranes are appropriate for high temperature separation application, which is preferable through high-temperature WGS reaction as well as pre-combustion CO_2 capture. This paper presented mini review on hydrogen separation via inorganic membranes, taken into account both porous and nonporous type membrane to make known of recent investigation and for further optimization.

Keywords:
Inorganic membrane; hydrogen separation; palladium deposition; gas permeation

1. Introduction

Inorganic membrane has high potential in purification and separation of hydrogen (H_2) which also indicates rising significance in membrane reactors for processes related to H_2 manufacturing. Recent studies focused more on nonpolymeric materials for example metal, zeolites, ceramics and molecular sieving carbon. Compared to over thin-film palladium membranes, inorganic microporous membranes have various advantages [1]. Meanwhile, metallic membranes (for example palladium composites) as Figure 1 or other separation processes are needed, however it is understandable that

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there are still rooms for further advancement of H_2 gas separation membranes that can be implemented.

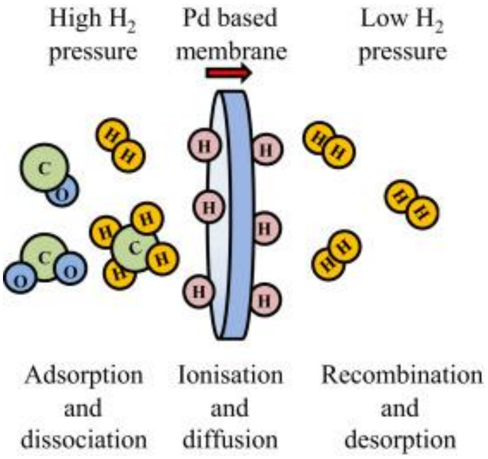


Fig. 1. Palladium-based membrane for H_2 purification [2]

Generally, there are two classifications of inorganic membranes for H_2 production as well as purification which are metal alloys and ceramics (perovskites), dense phase metal, and porous ceramic membranes. Preparation of porous ceramic membranes are usually done through hydrothermal or sol–gel techniques with high durability and stability in harsh impurity, hydrothermal and high temperature surroundings. In overall, inorganic ceramic membranes have low selectivity of H_2 with high flux. Particularly, microporous membranes have significant potential for usage in high temperature water gas shift reaction. Purification and separation are the crucial technologies in thermochemical practices in order to produce H_2 from fossil fuels. Membrane reactors demonstrate great potential in equilibrium shifting involving water–gas shift reaction for H_2 conversion from carbon monoxide. Membranes are also crucial in succeeding purification of H_2. Economical production of H_2 can be done via reaction among hydrocarbons and steam with supported nickel as catalysts known as steam reforming. High temperature for example of about 800°C is required for endothermic reaction due to CH_4 which is a stable hydrocarbon.

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

CO_2 and H_2 are formed due to further reaction of carbon monoxide steam via exothermic reaction, usually indicated as the reaction of water–gas shift:

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

H_2 separation from CO or CO_2 is essential in obtaining H_2 with high purity from whichever syngas or water–gas shift reaction products [3]. Existing H_2 separation processes from similar streams comprise pressure swing adsorption (PSA), amine absorption (CO_2 separation) as well as membrane separation. Mature technology for example amine absorption processes will not be further elaborated. According to past H_2 separation experience in refineries, PSA is less economical than membrane systems in terms of unit recovery costs and relative capital investment [4]. If selective removal of H_2 from the reaction system is implemented, thermodynamic equilibria shifts of that responds will be on the products side, with greater CH_4 conversions to H_2 and CO_2 achieved even at low temperature. In fact, heightened steam reforming separation with real system of membrane catalytic was initially documented [5]; which is in par with computer simulation studies. Pd membranes which can be obtained commercially are very thick for efficient usage at such adequate temperatures [6]. High selectivity of separation as well as high permeability are the crucial membranes features for successful membrane reactors. High permeability indicates permeation rate which should be comparable to catalytic reaction rate. In addition, durability and stability of the membrane are also essential [7].

The different mechanical properties of molecular sieving carbon steels will be resulted as different microstructures formed during cooling. Furthermore, the diffusion less transformations obtain the martensite formation which is the highest hardness in iron-carbon system and the lowest hardness is obtained due to a diffusion transformation, which cause the ferrite and/or pearlite formation by a eutectoid reaction. Martensite is obtained during rapid cooling while ferrite and pearlite obtained from austenite during slow cooling near the equilibrium. Therefore, both steel microstructure and mechanical properties are related to steel thermal history. Pressure also has an influence on stability of phase of equilibrium. However, this parameter is not usually taken in account, mainly in solid state reaction. It is because the influence of pressure is limited. From the engineering material theory, the required properties of material can be changed by manufacturing process and heat treatment process method [8–10]. Therefore, present work planned to investigate the relationship between thickness, microstructure, mechanical properties, and heat treatment for intelligent selection of manufacturing process, properties, and application for particular purpose. This study being undertaken to compare microstructure effects of different thickness on metal in rapid cooling process. New approaches of manufacturing process have been introduced. For example, the application of hot stamping technique is used to form many types of car component. This process involves thermo mechanical effects where the sheet metal parts are quenched after forming process to improve the mechanical properties. It is important to investigate the thickness effects on microstructure development.

2. Dense (Non-porous) Membrane

Dense membranes have been widely investigated since decades ago to present days [11–16]. There are two classifications for dense membrane; metallic and proton conducting [17]. In H_2 purification, the most common membranes are the dense metallic membranes while Groups III–V metals are all permeable to H_2 [18]. Particularly, Palladium (Pd) based membranes have been thoroughly studied as a result of high permeability to H_2. Past reviews mostly focused on purification of through the introduction of dense metallic membranes [19]. In addition, a few exceptional reviews on Pd as well as Pd-alloy membranes were published [20,21]**.** Overall introduction on dense metallic membranes is discussed in this work. Permeation of H_2 across the dense metallic membranes follows the three steps of the exclusive solution-diffusion mechanism: (i) Production of atomic H_2 via chemical dissolution of molecular H_2 on the feed side of the membrane surface, (ii) Atomic H_2 diffusion across the bulk metal and (iii) Atomic H_2 association on the permeate side of the membrane for molecular H_2 reproduction. This mechanism of gas transportation is dissimilar to the commonly acknowledged solution-diffusion mechanism, as H_2 is the only one with the ability to cross the dense metallic membranes, thus, ideally the membranes ought to possess vast H_2 selectivity over other species of gases. Although dense metallic membranes have exceptionally high H_2 selectivity, the equivalent low gas permeance hinders their useful implementation.

To achieve high separations, a few conventional methods have been used industrially such as pressure swing adsorption, cryogenic distillation and amine absorption. Unfortunately, these methods facing challenges to minimize the negative impacts on the environment, mostly expensive and required high energy loadings to run. For these reasons, utilizing membranes could counter the disadvantages of the traditional methods. Membranes act to provide a physical barrier between different component either in liquid phases, gas phases or between liquid and gas phase. The tailor-made semipermeable structures could control the permeation of molecules at different rates depending on the size of the pores and driving force involved in the operation Figure 2 shows H_2 separation through palladium membranes [22,23]. Reduction of materials cost as well as H_2 flux increment are among the many benefits of thin membranes. Purification of H_2 has been done using composite metal membranes or metal alloys. Nevertheless, metallic membranes are responsive to certain gases for example H_2 sulphide and carbon monoxide (CO). Therefore, ceramic membranes are desirable due to its inert property to poisonous gases. Essentially, the flux is directly proportional to the pressure in microporous membranes while the flux is proportional to the square root of the pressure in palladium membranes.

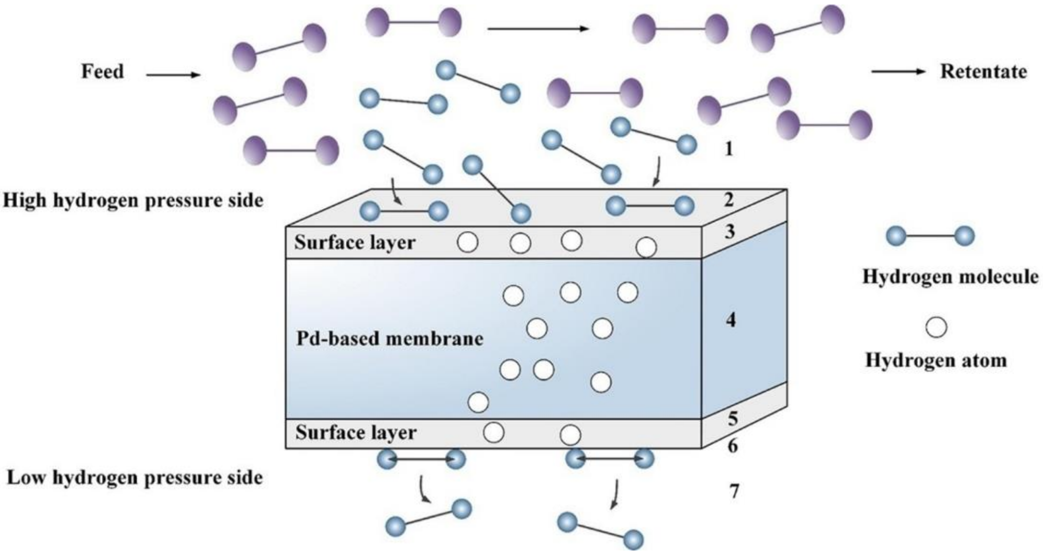


Fig. 2. H_2 Separation through Palladium Membranes [22]

Presently, there are numerous deposition technologies for diverse dense metallic layer exist for example chemical and physical vapor depositions, electroless plating as well as electroplating [24]. Electroless plating is the most widely utilized technique compared to others due to its efficiency in terms of cost as well as capability in covering supports with sophisticated geometries. H_2 selectivity of membranes of metallic composite is usually quantifiable compared to dense metallic homogeneous membranes [25]. This is attributed to the difficulty of thin supported metallic layer to be severely dense resulting to permeation of a minor quantity of other gas molecules across the membranes. However, selectivity of metallic composite membranes on H_2/gas stays at high level that is usually greater than other membranes styles. Severe constraints exist in the implementation of membrane of pure Pd [23]. Initially, Pd membrane went through phase transformation during operation at a temperature of lesser than 571 K under a pressure that is less than 20 bar which is also known as the H_2-induced embrittlement phenomenon. Next, surface poisoning caused by impurities particularly the sulphur species could lead to apparent reduction in the permeation of H_2. Lastly, Pd is deemed as a valuable metal, therefore membranes that are made of Pd usually possess restricted lifetime of about 2 to 3 years. These result to unfavourable investment as well as operating costs for commercial implementation. In order to solve these limitations, it was proposed for Pd to be alloyed with a sequence of other metallic components for example Cu, Ag, Ni, Au and Pt [26]. The dense metallic membranes can yield H_2 with up to 6N purity. Furthermore, it provides exceptionally high H_2

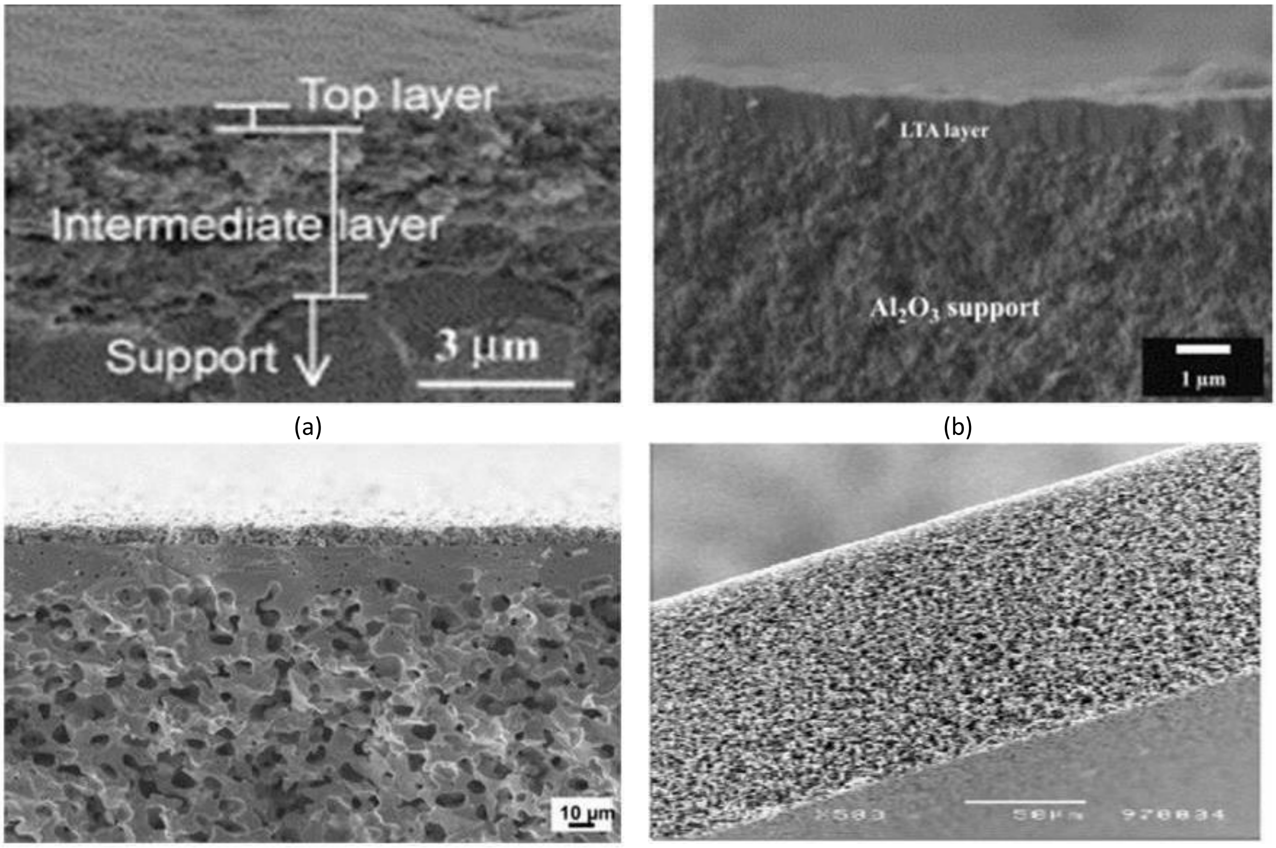
recovery proportion of ≥95% under specific conditions [27]. It frequently displays sensible H_2 permeation across a wide scope of temperature between 300-700 °C. Effects of alloy proportion, thickness of membrane, possible impurities (H_2O and CO) as well as test conditions on Pd-alloy membranes performances were broadly and rigorously explored through experimental work [5]. The density functional theory (DFT) methods are utilized in predicting permeation of H_2 as well as the membrane's resistance to poisoning according to varied alloys, providing a guideline in designing membranes made of Pd-alloy. In overall, exploration of dense metallic membranes in the purification of H_2 has been conducted since more than half a century ago [8]. Vicinanza *et al.,* [28] investigated hydrogen transport properties on Pd-alloys membrane. From their findings, hydrogen solubility increased when $Pd_{77}Ag_{23}$ membrane thickness was changed from 11.2 to 2.2 µm. The highest hydrogen permeability of $1.1x10^{-8}$mol $m.m^{-2}s^{-1}Pa^{0.5}$ was obtained at thickness 2.2 µm and 400°C. Different with [28], Wang *et al.,* [29] studied the separation of hydrogen at extreme temperature using hollow fiber membrane made up of nickel. Summary on recent dense membranes studied for hydrogen separation by previous researcher is illustrated in Table 1 below.

Table 1
Recent dense membranes for H_2 separation by various researchers

Membrane	Experimental conditions	H_2 permeability flux (mol $m^{-2}s^{-1}$)	Ref
$Pd_{78}Cu_{11}Ag_{10}$	• 773 K	0.45	[30]
$Pd_{84}Cu_{11}Ag_5$	• 773 K	0.30	
$Pd_{81}Cu_{19}$	• 773 K	0.15	
Ni	• Hollow fibre membrane • Membrane thickness 256 µm • 1000°C	7.66	[29]
Cermet membrane, Pd with Y_2O_3-stabilized ZrO_2	• Porous substrate • 18 µm thickness	-	[31]
Perovskite $BaCe_{0.85}Tb_{0.05}Co_{0.10}O_{3-\delta}$	• Hollow fibre membrane • No coating • 900°C • 150 µm thickness	0.063 mL $min^{-1}cm^{-2}$	[32]
	• Hollow fibre membrane • Ni-coated • 900°C • 150 µm thickness	0.109 mL $min^{-1}cm^{-2}$	
	• Hollow fibre membrane • Pd-coated • 900°C • 150 µm thickness	0.205 mL $min^{-1}cm^{-2}$	

3. Porous Membrane

Porous membranes based on inorganic materials basically consist of porous metallic supports or ceramic support under porous layer that possess different morphology and structural characteristics [33]. SEM images in Figure 3 illustrated the difference between porous and dense membrane, and symmetrical and asymmetric structure of inorganic membranes. Similarities between porous membrane and dense membrane discussed previously are that it comprised of solid layer from either metals or electrolytes. According to Fard *et al.,* [33], presence of electrolyte layer permits the diffusion of hydrogen to pass through the pores. In gas separation application, two types of porous membrane known are microporous (diameter <2nm) and mesoporous (diameter 2 to 50 nm). Another pore size which is macroporous is mostly studied for ultrafiltration and microfiltration. For microporous membrane, the gas transport properties followed molecular sieving mechanism, in which certain molecules cannot pass through the membrane. Thus, hydrogen molecules which known to be very small molecules can easily pass through the membrane layer. To add, microporous-type membrane usually resulted in high separation factors. Three materials for synthesis of porous membrane are silicas, zeolites and metal-organic framework (MOF).



(a) (b)

(c) (d)

Fig. 3. (a) Porous membrane [34] (b) Dense membrane [35] (c) Asymmetric membrane [36] (d) Symmetric membrane [37]

From review by Pera [38], inorganic microporous stabilized silicas membrane is selective to H_2 molecules and provide high permeation at high temperature. Also, silica-based membrane are the most commonly applied materials for separation of hydrogen with more than 400 published articles in that area [38]. Advantage of this membrane is their thermal, mechanical and chemical conditions that are stable in various operating parameters. Group of researchers [39] presented their quantitative analysis on hydrogen separation via silica membrane, taking account various flow patterns to simulate the typical methanol steam reforming stream. They concluded that silica membrane has excellence performance in separating hydrogen from the mixture gas at single stage. They validated their findings with previous literature by [40] due to limited modeling studies paper. On the other hand, van Gestel *et al.,* [41] developed a novel silica-based sol-gel membrane to separate hydrogen from other gases. Interestingly, the performance of hydrogen separation showed a good hydrogen selectivity. Another notable study on silica membranes were done by Zhang *et al.,* [42] in which they successfully developed triphenylmethoxysilane-based silica membrane that have high selectivity over 12,000 at temperature 300°C. Continuation of their work, they tested the performance of triphenylmethoxysilane-derived silica to separate hydrogen from hydrogen-toluene gas mixtures [43]. Apart from silica, crystal zeolites are also well-known as materials for hydrogen separation. Similar to [39], Cardoso *et al.,* [44] investigated quantitative analysis for gas separation but via zeolite membranes. In their work, they derived Maxwell-Stefan thermodynamics factors for isotherms which can be further used to predict binary permeation through the membrane. Synthetic zeolites are preferable for commercial usage as it possess high purity and consistent performance [45]. Current researches focus more on utilization of "zeotypes" materials such as silicoaluminophosphate (SAPO), lanthanide silicate and aluminophosphate (AlPO) [17,46,47]. SAPO-34 membrane layered on α-Al_2O_3 tubular support investigated by [48] for hydrogen separation was found to exhibit high permeability for H_2 which was 6.96×10^{-6} mol m^{-2} s^{-1} Pa^{-1}. There are various recent literatures can be found on enhanced porous dense membrane specifically for application in hydrogen separation [49–52].

4. Comparison of H_2-selective Membrane

Hydrogen is a substance with elevated energy which can be utilized as CO_2 transformation reagent. There are two categories of CO_2 hydrogenation primary products which are chemicals and fuels. Fuels requirement increases with increase energy usage. Nevertheless, resources of fossil fuels are decreasing with robust fluctuations of fuel prices in the current years. Hence, development of alternative fuels from sources of non-fossil processes and fuels is highly required. CO_2 hydrogenation products for example hydrocarbons and methanol are exceptional fuels in internal combustion engines and can be transported and stored easily. In addition, methanol is a raw material that can be found as intermediates in the chemical industries. Nevertheless, potential issues regarding storage, production and transportation of hydrogen should be noticed. Generation of hydrogen for chemical recycling of CO_2 can be done via important sources utilization of the residual fossil fuels (primarily natural gas) or via splitting water (through electrolysis or other cleavage). Figure 4 shows the separation performance on descriptive H_2-selective membranes for the separation of H_2/CO_2 plotted on the upper bound of 2008 Robeson [9]. Nevertheless, each inorganic membrane has its peculiar weaknesses. Dense metallic membranes are extremely responsive to implementation settings such as impurities and temperature. Furthermore, high cost of fabrication is one severe drawback of dense metallic membranes, hence is the cause to their suitability for small-scale implementation in the production of H_2 of ultrahigh purity. Inorganic membranes of microporous characteristic such as carbon molecular sieve, silica and zeolite membranes illustrate proficient chemical stability and mechanical property [10]. Still, water vapor contained in the feed gas could cause substantial drop of membrane performance. Additionally, it is challenging to transform inorganic membranes into membranes with high surface area for the purpose of large-scale implementation.

H_2-selective polymeric membranes made of glassy polymers have the capability to tolerate adequately high temperature (above 100°C) due to the high temperature of glassy transition possessed by these polymers. Conversely, renowned trade-off phenomenon among H_2/CO_2 selectivity and H_2 permeability exists thus limits the production of polymeric membranes that is H_2-selective with high-performance quality. In addition, apparent reduction in H_2/CO_2 selectivity under high partial pressure of CO_2 could be caused by CO_2-induced plasticization. As for certain recently constructed membrane materials, thermally rearranged (TR) polymer and MOF membranes normally exhibit high gas permeability compared to conventional membranes with some exceptional membranes demonstrate promising results in H_2/CO_2 selectivity. However, these works only focused on laboratory-scale. Hence, orderly research under accurate settings is essential in evaluating their capability for real implementation. Commercial TR and MOFs polymers production is also crucial for the purpose of large-scale implementation. To the extent of our familiarity, H_2-selective membrane for large scale commercial usage is currently in non-existent, each membrane needs to solve its vital shortcoming when competing with commercially existing processes of pressure swing adsorption and absorption in H_2 purifications [10,53]. Table 2 shows summary of H_2 separation membrane characteristics.

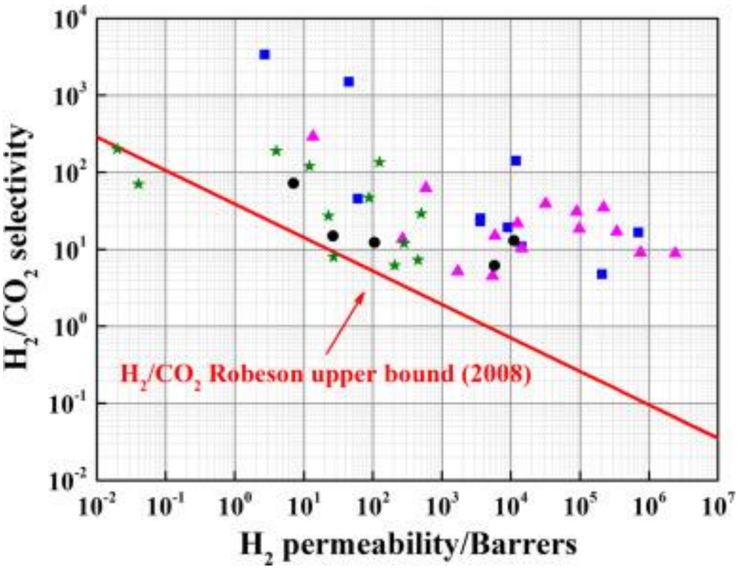


Fig. 4. Separation performances of representative H_2-selective membranes in separating H_2/CO_2 (triangle: MOF membranes, square: microporous inorganic membranes, circle: mixed matrix membranes, star: polymeric membranes) [9]

Table 2
Summary of H_2 separation membrane characteristics

Composite membrane	Thickness (mm)	Operation Temperature (°C)	Approx. Max. Separation Rate (mL min^{-1} cm^{-2})	Advantages	Disadvantages
Ceramic/ceramic	0.1 to 0.5	700 to 950	0.1	- inexpensive - Resistant to poisons	- low H_2 flux - brittle
High-temperature cermet	0.1 to 0.5	700 to 950	1.0	- better H_2 flux than pure ceramics - inexpensive - integrated catalyst - less brittle	- susceptible to poisons - lower H_2 flux than H_2-perm. metal
High-temperature cermet w/ H_2-perm metal	0.1 to 0.5	550 to 950	4	- high H_2 flux - integrated catalyst - less brittle	- expensive - susceptible to poisons
Intermed.-Temp. Composite Membrane	0.5 to 0.5	300 to 750	>10	- highest H_2 flux - compatible with desulfurization system	- susceptible to poisons - difficult to fabricate

4. Conclusions

This work has presented a mini review on inorganic membranes for hydrogen separation. Membrane offers the best alternative for gas separation whilst inorganic materials permits higher separation of hydrogen gas. Amongst the listed materials, Pd-based membranes are favoured for hydrogen separation due to simplicity of one-step operation and excellent selectivity of Pd to H_2. For greener future, enhancement of energy efficient systems as well as fuel-switching towards fewer carbon exhaustive energy sources for example renewable energy and hydrogen are required. Currently, commercialised inorganic membrane for this application is still limited. Therefore, in-depth research in optimum method for hydrogen separation are vital as alternative for current technology in separation and purification of H_2 (e.g. Cryogenic distillation and PSA).

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