Chemical Engineering Journal 154 (2009) 258–266

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Catalytic reactors with hydrogen membrane separation

B.N. Lukyanov*, D.V. Andreev, V.N. Parmon

Boreskov Institute of Catalysis, Pr. Akad. Lavrentieva 5, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 2 December 2008
Received in revised form 12 March 2009
Accepted 8 April 2009

Keywords:
Hydrogen
Processes of hydrogen generation
Fuel processor
Membrane reactor
Methods of membrane precipitation

ABSTRACT

The main catalytic hydrogen-generation processes efficiently utilizing hydrogen-permeable membranes are described. Different membranes for hydrogen separation from gas mixtures and preparation methods are considered. The catalytic reactors with an integrated membrane module and their advantages over traditional fixed-bed reactors are demonstrated. The prospects of membrane catalytic reactors in hydrogen energy are analyzed.

1. Introduction

Hydrogen – the main energy carrier of the future – will find wide application only when the problem of its low-cost separation from hydrogen-containing sources, such as water, natural gas, oil, coal, biomasses, timber, and industrial waste, will be solved [1]. In nature, hydrogen exists only in a bound state. At room temperature and atmospheric pressure, the specific hydrogen density is low, 0.089 kg m^{-3}. At the same time, the value of hydrogen energy per mass unit (120.7 MJ kg^{-1}) is higher than those of the known organic fuels. Utilization of hydrogen permits one to avoid the problem of direct electrification which is accompanied by large losses during electric power transmission. Hydrogen combustion is not accompanied by harmful exhausts as methane or carbonic acid. Note that the hydrogen used in fuel cells with proton-exchange membranes should possess high purity (CO content not higher than 10 ppm). This can be achieved by dividing hydrogen-rich gases into pure hydrogen and by-product gases using hydrogen-permeable membranes. Unfortunately, there are no systematical reviews concerning the application of membranes in hydrogen generation processes, though several attempts are known in the literature [2–4]. Efforts are focused on developing catalytic reformers using membrane hydrogen separation, which will be integrated into stationary, mobile and portable power plants and fuel-cell based apparatuses. The aim of the present work is to review the state of the art of designing such systems and to analyze the prospects of membrane reformers in hydrogen energy.

2. Hydrogen generation processes

The main source of hydrogen is natural gas (≥90%), however, an opportunity of commercial hydrogen generations from water via thermochemical decomposition upon nuclear reactor heat is in sight. The other fuels for hydrogen generation are alcohols (methanol, ethanol, glycerin), ethers (dimethyl ether), fossil and renewable fuels. The prospects of their utilization were considered elsewhere [5]. Table 1 illustrates the processes of hydrogen generation from natural gas and methanol in which it is appropriate to use membranes. The processes of hydrogen generation from hydrocarbon fuels are crucial in designing reactors and catalysts of conversion. The processes of methanol decomposition and steam reforming of methane and methanol are endothermal processes, the CO steam conversion and partial oxidations of methanol and methane are exothermal reactions and the autothermal methanol conversion proceeds at zero enthalpy. Methane steam reforming (MSR) is one of the most extensively studied and developed processes. It is a highly endothermal process which is limited by equilibrium. Thus, the theoretical calculations of the thermodynamic equilibrium show that in order to obtain high methane conversion (>90%), the process should be performed at high temperatures (≥850 °C), the total pressure and H_2O/CH_4 being as high as 1.0 MPa and 3, respectively.

Elevated pressures are usually used to increase energy efficiency of the whole process, however, this significantly increases the price of MSR equipment. High methane reforming can be obtained at relatively low temperatures with increasing hydrogen separation portion (Fig. 1) [6]. Thus, if one separates 90% of hydrogen from the reaction zone, the methane conversion degree becomes higher than 94% at 500 °C. At a thermodynamic equilibrium (without

---

* Corresponding author. Tel.: +7 383 3308 210.
E-mail address: lukjanov@catalysis.nsk.su (B.N. Lukyanov).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.04.023

Table 1
The main processes of hydrogen generation from natural gas and methanol.

Process name	Reactions and heat effects, kJ mole^{-1}	Power consumptions for
Steam reforming	$CH_4 + H_2O \Leftrightarrow CO + 3H_2, \quad \Delta H^\circ_{298} = +206$	Technology
	$CO + H_2O \Leftrightarrow CO_2 + H_2, \quad \Delta H^\circ_{298} = -41$	Reaction performance
	$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2, \quad \Delta H^\circ_{298} = +165$	Steam formation
	$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2, \quad \Delta H^\circ_{298} = +49.4$	
Steam-oxygen conversion	$CH_4 + 0.5H_2O + 0.25O_2 \Leftrightarrow CO + 2.5H_2, \quad \Delta H^\circ_{298} = +90$	Technology
	$CO + H_2O \Leftrightarrow CO_2 + H_2, \quad \Delta H^\circ_{298} = -41$	Reaction performance
	$4CH_3OH + 3H_2O + 0.5O_2 \leftrightarrow 4CO_2 + 11H_2, \quad \Delta H^\circ_{298} = 0.0$	Steam formation Oxygen recovery from air
Partial oxidation	$CH_4 + 0.5O_2 \Leftrightarrow CO + 2H_2, \quad \Delta H^\circ_{298} = -36$	Technology
	$CO + H_2O \Leftrightarrow CO_2 + H_2, \quad \Delta H^\circ_{298} = -41$	Steam formation
Methanol decomposition	$CH_3OH + 0.5O_2 \leftrightarrow CO_2 + 2H_2, \quad \Delta H^\circ_{298} = -192.2$	
	$CH_3OH \leftrightarrow CO + 2H_2, \quad \Delta H^\circ_{298} = +92.0$	

hydrogen separation), the same value of CH_4 conversion can be achieved at 850 °C, i.e. at a temperature exceeding the above value by 350 °C. The recently developed reactors with selective hydrogen-permeable inorganic membranes [7–11] can separate hydrogen from the reaction zone during its generation, the temperature should not exceed 500–600 °C. Both high separation selectivity and permeability – penetration rate that should be comparable with the reaction rate – are the governing characteristics of a membrane meant for a membrane reactor. The other important features of a membrane are: operation stability and life time [4,12].

3. Types of the membranes and their production

Abbot J.A. Nollet was the first to use word “membrane” (it means pellicle, capsule, diaphragm, thin parchment in Latin) in 1748. He was studying separations of different liquids such as alcohols and water with membranes [13]. Adolf Fick (1855) deduced the diffusion law from the analogy of mass and heat fluxes upon heat conductivity. He showed that mass flows are proportional to the concentration and reciprocally proportional to the membrane thickness. Thomas Graham (1854) discovered and studied the penetration of hydrogen through palladium, gas diffusions through ceramic membranes and determined the rates of diffusion of carbonic acid, hydrogen, oxygen, methane, air, and carbon oxide through rubber membranes [14]. The experimental works of Graham permitted Knudsen (1909) to develop a permeability model for mesopores, whereas the molecular diffusion laws hold in the macropores region [15]. In 1910, Sieverts published the law of hydrogen transfer through permeable palladium membranes [16]. Gryaznov was the first to use palladium-based membranes as catalysts for hydrogenation and dehydrogenation (1969) [17], which permitted a design of new catalytic membrane reactors [12,18].

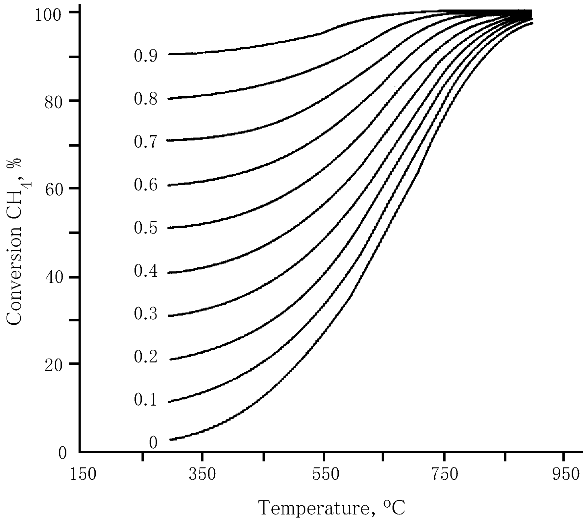

Fig. 1. Effect of the process temperature and separation hydrogen portion on the methane conversion (process pressure 1.0 MPa, $H_2O/CH_4 = 3$). Numbers on the curves indicate the degree of hydrogen separation [6].

Membranes can be divided into organic, inorganic and hybrid membranes formed as organic/inorganic systems. Organic membranes are sub-divided into polymeric and biological membranes, whereas inorganic membranes are divided into metallic (solid phase) and ceramic (porous and nonporous) membranes. Monolith or microporous dense inorganic hydrogen-permeable membranes are prepared from oxides and metals. A porous (composite, asymmetric) membrane involves a support made of ceramics, carbon, polymers, glass, stainless steel and a thin selectively permeable layer of palladium or zeolite.

There are microporous (pore sizes less than 2 nm), mesoporous (2–50 nm) and macroporous (>50 nm) membranes. Compared to the conventional hydrogen-permeable membranes, mesoporous ceramic membranes (low selective), microporous ceramic membranes (low permeable), dense ceramic membranes (low permeable) and palladium-based membranes (highly hydrogen-permeable and infinitely selective towards hydrogen) are the best candidates for catalytic membrane reactors of reforming and other reactions associated with the hydrogen generation [19–29].

In the last few years, the most important works devoted to steam reforming, including the CO steam conversion, have been performed using Pd-membrane reactors [7–11,30–38]. For the first time, a reactor with a palladium membrane formed as a 100 μm thick disc was presented in Ref. [7]. In spite of high process temperature (700 or 800 °C), hydrogen permeability was low because of a sizable membrane. In [28,29], the authors used chemical metallization (electrolysis plating) to prepare a number of thin Pd membranes (10–26 μm thick) supported on the glass porous carrier. In the membrane reactor, a conversion of 88% was achieved at lower temperature, 500 °C. Unfortunately, the following problems were not solved: mechanical strength, thermal stability, high-temperature welding and construction of a membrane cell depending on the ceramic support. Shu and co-workers [9] used a porous steel disc or a tube as a support to prepare Pd and Pd–Ag-composite membranes. The methane conversion was 63% at 500 °C, the membrane life time was 47 h. Lin et al. [30] manufactured a membrane reactor using thin (20–25 μm) Pd membranes supported on the porous steel tube to obtain 45% conversion of methane at 500 °C, which exceeded the value obtained for a traditional MSR reactor by 15%. This relatively low methane conversion compared to Kikuchi [11] was associated with lower permeability of the support. In addition, Kikuchi used a new chemical vapor deposition (CVD) method to form Pd membranes [11]. This method has found wide use in Japan because it permits preparation of hydrogen-permeable membranes not only from palladium [39–41]. CVD was used to prepare two versions of the membranes on the porous supports. According to the first version, substrate is supplied to one side of the porous support and the other side is under vacuum to prevent appearance of any cracks or pinholes on the membrane formation. In the second version (counter diffusion CVD) substrate is supplied to the support from both sides. The authors used α-alumina (pore size 100 nm) as a support which was covered by γ-alumina in order to decrease pore sizes to 4 nm. The support covered by γ-alumina was placed into the furnace, impregnated by tetramethyl orthosilicate (concentration 0.98 mole m^{-3}) at 45 °C then oxygen or ozone were introduced at a flow rate of 200 ml min^{-1} at 600 °C. The as-prepared silicon oxide membranes exhibited the H_2/N_2 separation factor ~1000 and stable operation at 0.076 MPa of water steam and 500 °C, the life time was 21 h.

Bimodal catalytic membranes, containing an upper layer of silicon oxide with a selective hydrogen permeability and a bimodal-structured support, were prepared by introducing γ-alumina into an α-alumina micro-filtration membrane and its subsequent dipping into a nickel nitrate solution [42]. The hydrogen permeability of the nickel doped silicon oxide membrane was 1×10^{-5} m^3 m^{-2} s^{-1} kPa^{-1}, the H_2/N_2 separation factor was 680. The conversion of methane increased to 70% (compared to the value of 44% obtained in the equilibrium) at the steam/methane ratio 3:1, the temperature on the membrane 500 °C and the pressures in the reaction and penetration/permeability zones equal to 0.1 and 0.02 MPa, respectively.

A sol–gel method was also used to prepare mesoporous membranes by introducing metal salts ($RuCl_3$, $Pd(NH_3)_4Cl_2$, $RhCl_3$ and H_2PtCl_6) into a porous alumina support in the boehmite ashes [43]. These metal-dispersed alumina membranes were used in the low-temperature MSR (300–500 °C) and provided the methane conversion >85% at 500 °C, the separation factor ($\alpha = (H_2/N_2)_{\text{perm.zone}}/(H_2/N_2)_{\text{reforming zone}}$) was about 6. Microporous ceramic membranes (silicon oxide nanocomposites) are also under development now and exhibit excellent high-temperature hydrogen permeability [44,45].

It is common knowledge that repetitive saturations of palladium membranes by hydrogen and its subsequent separation cause decomposition of the membranes due to dilation. Note that Ag, Au, Pt, Rh, Ru, and Pb additives improve hydrogen permeability of the membrane and Sn and Cu hinder hydrogen transfer through membranes [4]. Copper additives decrease hydrogen permeability, however, one can observe a jump in the membrane permeability at the copper concentration 39–43 mass.% and 600 °C. Permeability of hydrogen through the Pd–Ag membrane depends on the silver concentration in the alloy. The coefficient of hydrogen permeability is maximum as the silver concentration is 23 mass.%. The maximum is associated with the fact that an increase in the silver concentration in the alloy is accompanied by an increase in the hydrogen solubility in the membrane, but the rate of hydrogen diffusion in the volume decays. Of prime importance is that an addition of silver provides a transition from hydrogen-rich phase β-PdH (unstable at temperatures above 300 °C) to α-PdH which is stable at higher temperatures. Systems Pd–In and Pd–In–Ru exhibit increased hydrogen permeability. An optimum combination of strength, plasticity, hydrogen permeability and corrosion resistance is exhibited by alloy Pd–In–Ru (6 mass.% In, 0.5 mass.% Ru). The reactors supplied with the Pd–In–Ru membranes were tested on the caprolactam production and hydrogenated desulfurization of the products and provided good hydrogen isolation from reforming gases. Pd alloys with La, Nd, Y and Sm additives (to 2 mass.%) were also analyzed. As follows from [46], an addition of a rare earth element increases hydrogen permeability by 1.5–2.0 times in the temperature range 177–427 °C.

To use membrane hydrogen separators in the on-board fuel processor, the authors [47] developed hyperfine palladium composite membranes with a metal porous support and a palladium film based on the double palladium alloys B-1 and B-2 (film thickness is not higher than 5 μm) which exhibited high thermal stability [47]. Alloy B-1 contains silver, gold, platinum, ruthenium, and aluminum and efficiently operates at the working temperatures 500–600 °C. Alloy B-2 does not contain precious metals and surpasses B-1 in permeability by 15–30%. Alloy B-2 can operate at temperatures to 600 °C and exhibits high efficiency in the temperature range 300–500 °C. Both alloys are resistant to hydrogen and exhibit high permeability. A several-thousand hours testing of B-1 based tubes did not reveal any changes in impermeability and efficiency upon operation in hydrogen mixtures containing CO_2 (to 50 vol.%), CO (to 10 vol.%), CH_4 (to 10 vol.%) and H_2O (to 23 vol.%) at the operation temperature 600 °C. At present, the problem of finding optimal membrane compositions for hydrogen energy is far from being solved, because there are no highly efficient palladium alloys. For this reason, the studies of solid palladium solutions containing different Periodic system elements are urgent and actively performed today.

Design of hyperfine membranes (about 10 μm) was the most efficient way to increase selective permeability of Pd-membranes and to obtain high conversion of methane at 500–600 °C, which is in direct proportion to a portion of the isolated hydrogen [6,48–51]. A thin, defect-free palladium membrane (6 μm thick) supported on the macroporous stainless steel tube (MPSS) was manufactured via the multidimensional plating mechanism [6]. The hydrogen flux was 0.260 mole m^{-2} s^{-1}, the pressure difference across the membrane was 0.1 MPa and the temperature was 500 °C. The methane conversion was 96.6% at the following reaction conditions: 550 °C, 0.5 MPa, feed space velocity 800 cm^3 (g cat.)$^{-1}$ h^{-1}, steam/methane = 3, sweep gas flux 500 cm^3 min^{-1}, the hydrogen separation was 90.4%. A 13 μm thick membrane Pd/CeO_2/MPSS, prepared by the updated chemical precipitation method, provided a hydrogen flux of 0.275 mole m^{-2} s^{-1} at 550 °C and 0.2 MPa, the methane conversion was >97% on the stable operation of the composite membrane during 300 h [48]. A combined method of electroless plating and chemical vapor deposition was used to prepare a thin Pd–Ag asymmetric composite membrane (4 μm) on the commercial porous steel tube [49]. The membrane installed in a MSR provided a conversion degree of 80.72% at 500 °C and 0.5 MPa. The membrane exhibited high operation stability during 11 thermal cycles and 20 variable cycles with respect to gas. For composite membrane Pd–Pd/γ-Al_2O_3-/α-Al_2O_3 (layer thickness: Pd 2–3 μm, Pd/γ-Al_2O_3 3–4 μm, α-Al_2O_3 200 μm) at 400 °C, the values of hydrogen permeability of the dense palladium layer and support α-Al_2O_3 were 8.8 m^3 m^{-2} h^{-1} $atm^{-0.5}$ and 170–200 m^{-2} h^{-1} atm^{-1}, respectively, i.e. the support resistance was about 5% of the total resistance [51]. At 430 °C, hydrogen permeability of the membrane did not practically change during 660 h.

Deposition of a thin continuous metal layer on the porous catalysts presents difficulties. To avoid the problem it was suggested [18] to deposit thin metal films on the continuous film layer of polymer. Traditionally, metal-polymeric composites are made of highly permeable polymers as polyethylene, polypropylene, etc., which exhibit low selectivity towards hydrogen. An anisotropic metallized polydiphenylenephthalide membrane, made of several layers with different porosities and covered by a palladium layer (≈1 μm), showed the hydrogen output as high as 13.8 m^3 m^{-2} h^{-1} at 200 °C and the pressure difference 1.0 MPa. Since the process of methane steam reforming requires temperatures above 400 °C, the authors [18] developed and prepared palladium–indium–yttrium

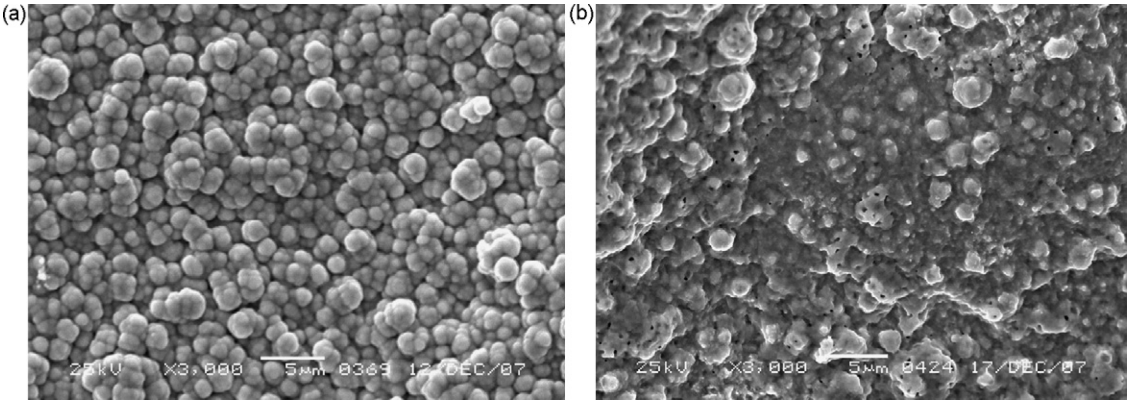

Fig. 2. Palladium particles on the porous stainless steel support before reduction in hydrogen at 450 °C (a) and after reduction (b).

(or ruthenium) composite membranes based on the metal oxides. For a 2 μm palladium thick layer, the membrane output of hydrogen was 10.0 $m^3\ m^{-2}\ h^{-1}$ at 400 °C and the pressure drop 0.2 MPa. The membrane held high selectivity during 450 thermal cycles.

The main problem in preparing thin defect-free membranes (15 μm thick) is roughness and large surface pores of the support. Beside the above mentioned methods of palladium deposition on the porous supports, use has been made of the magnetron [52] and aerosol sputtering methods [53], however, CVD has significant advantages over them. Thus, CVD permits deposition of palladium on the differently shaped supports prepared from conducting and non-conducting materials, which is very important for manufacturing of catalytic reactors.

The authors of this work used CVD to prepare membranes on the composite porous stainless steel and γ-alumina supports. As a support we used porous stainless steel discs with an average pore size of 5 μm, the porosity was 57%. The diameter and thickness of the discs were 20 and 0.5 mm, respectively. The supports were pretreated in the chloroazotic acid and calcined at 450 °C in a hydrogen flow to remove impurities and an oxide film. Using the support as a filter, it was saturated with an aqueous γ-Al_2O_3 suspension, dried, calcined at 400 °C and finally pressed to reduce the total pore volume and to provide complete filling of the pores with alumina. Palladium membranes were prepared in two stages. At first, the surface of porous support γ-Al_2O_3 was activated in turn by 0.001 M solutions of $SnCl_2$ and $PdCl_2$ to form active centers acting as nucleuses of growth of a metal palladium film. The procedure was repeated for 10 times, each time the support and the carrier were washed with distilled water. The resulting composite was dried and subjected to metal coating. For this purpose, the composite was placed into the solution with the following content: $PdCl_2$ 4 $g\ l^{-1}$, NH_4OH (25%) 180 $g\ l^{-1}$, Trilon B 35 $g\ l^{-1}$ and hydrate hydrazine 1 $g\ l^{-1}$. Metal coating was accompanied by constant mixing for 3–4 h at 50–60 °C. Then the membrane was washed in distilled water for 1 h, dried and calcined at 450 °C in hydrogen. As follows from Fig. 2(a), before the recovery annealing the palladium particles formed as balls 1–3 μm in diameter were insufficiently interconnected. Note that the membrane was not vacuum tight. After annealing in hydrogen, the palladium particles conglomerated between themselves to form a dense film 10 μm thick (Fig. 2(b)). The method allows deposition of thin (1–10 μm) palladium layers on the complex profile membranes utilized in the catalytic reactors.

Experimental data on the thin composite membranes suggest that it is difficult to simultaneously improve hydrogen permeability, ideal separation factor or permselectivity, chemical and/or thermal stability of membranes. At sufficiently high hydrogen permeability of the membrane, one can obtain almost complete conversion of methane at temperatures not higher than 500 °C (Table 2).

4. Catalytic membrane reformers

According to the IUPAC definition, a membrane reactor is a system that provides the performance of separation by a membrane and chemical reaction in one unit. A catalytic membrane reformer

Table 2
Hydrogen separation efficiency of Pd membranes[a].

Membrane	Preparation method	Thickness, μm	Temperature, °C	Driving force, MPa	H_2 flux, mole $m^{-2}\ s^{-1}$	Separation factor, H_2/N_2	CH_4 conversion, %	Ref.
Pd/MPSS	ELP/O	10	480	0.1	0.089	1000	n/d	[54]
Pd/MPSS	ELP	19–20	500	0.101	0.015–0.030	$\leq$5000	n/d	[55]
Pd/MPSS	ELP	5	400	0.1	0.155	100–200	n/d	[56]
Pd/PG	ELP	13	500	0.202	0.189	∞	88	[28]
Pd/Al_2O_3	ELP	7–15	400	0.1	0.086–0.134	100–1000	n/d	[56]
Pd/HF	ELP	3–4	430	0.1	0.136	1000	n/d	[50]
Pd/Al_2O_3	CVD	0.5–1.0	350–450	0.1	0.050–0.100	100–1000	n/d	[57]
Pd–Ag/PG	ELP	21.6	400	0.202	0.067	∞	88	[28]
Pd–Ag/MPSS	ELP	15	500	0.202	0.103	∞ (H_2/Ar)	n/d	[58]
Pd–Cu/Al_2O_3	ELP/O	3.5	350	0.1	0.056	$\geq$7000	n/d	[59]
Pd–Cu/Al_2O_3	ELP/O	1.5	350	0.1	0.499	93	n/d	[59]
Pd–Ag	Cold rolling	50	500	0.1	0.01	∞	70	[32]
Pd/MPSS	MD/ELP	6	500	0.1	0.260	∞ (H_2/Ar, He)	96.9	[47]
Pd/MPSS	MD/ELP	6	550	0.1	0.300	∞ (H_2/Ar, He)	96.9	[47]
Pd–Ag/MPSS	IM/ELP	4	500	0.1	0.280	∞	80.2	[49]
Pd–CeO_2/MPSS	CMS/ELP	13	500	0.2	0.275	∞	97	[48]

[a] Here: Legend: MPSS—macroporous stainless steel; PG—porous glass; HF—alumina hollow fiber; ELP—electroless plating; O—osmotic pressure method; CVD—chemical vapor deposition; MD/ELP—multidimensional plating mechanism; IM/ELP—improved method of electroless plating; CMS/ELP—combined method of physical sputtering and electroless plating; n/d—not determined.

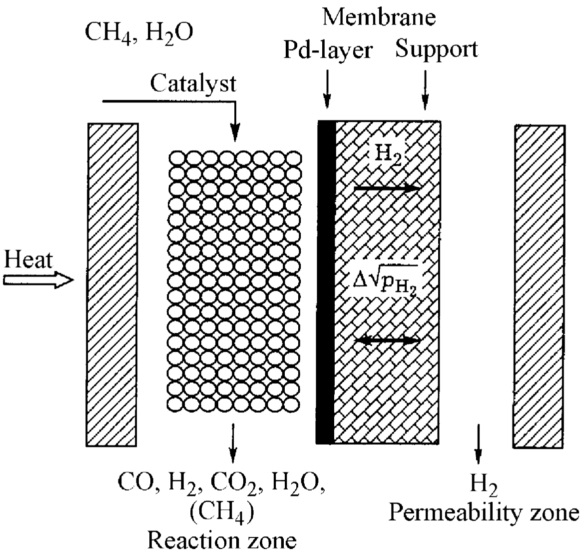

Fig. 3. Schematic of the catalytic membrane reformer. Hydrogen is uninterruptedly isolated from the reaction zone using a membrane. A hydrogen flow passing through the membrane is proportional to the difference of square roots of hydrogen partial pressures at the inlet and outlet membrane sides.

(CMR) is a reactor in which a membrane does not practically play the role of a catalyst, because a number of the reactions occurring on the membrane is negligibly small as compared to the reactions occurring in the catalyst layer over the membrane. Hydrogen – the desired product – is *in situ* removed through the membrane into a permeability zone (Fig. 3) and can be used, for example, in a fuel cell (FC). The other membrane reactors providing either removal or supply of reagents to the reaction zone were reviewed elsewhere [60].

The main role of a membrane in catalytic membrane reactors is separation, although the products of methane and water conversion considerably affect its permeability. This question was considered in detail by Gryaznov et al. [18]. It was established that at 700–900 °C, methane, carbon monoxide and dioxide do not decrease hydrogen transfer over a wide range of partial pressures and water steam slightly increases hydrogen permeability of the palladium membrane containing 6 mass.% of ruthenium. Carbon-black formation can worsen filtration activity of a membrane ($CO + H_2 \Leftrightarrow H_2O + C$) if the MSR procedure is not followed, as in the case of overheating of the reaction zone. Carbon does not deposit on the membrane as ratio H_2O/CH_4 is kept higher than 2.5. According to [47], the presence of methane and carbon dioxide does not practically affect hydrogen permeability of the palladium membranes over a wide temperature range.

Catalytic membrane reformers are used in the processes of MSR and methane partial oxidation (POX) [61,62] as well as the reformers of CO steam conversion [63–68] and CO selective oxidation [69]. In CMR POX the multilayered palladium membranes on the TiO_2 support were used. Note that the thickness of a Pd layer varied from 10 to 21 μm. In the CO selective oxidation reactor, the membranes were made of zirconium oxide stabilized by yttrium oxide. Ceramic membranes were used in the catalytic membrane reactor of CO steam conversion [63]. Unfortunately, they did not provide the concentration of CO <10 ppm, which is required for a fuel cell with a proton-exchange membrane (PEMFC). As a result, it is necessary to perform the final gas cleaning from CO using, for example, methanation or selective oxidation processes. The Eltron Pd membranes were specially designed for the CO high-temperature steam conversion. Compared to the traditional palladium membranes, hydrogen permeability of the Eltron membrane is 20 times higher and the cost is 10 times lower [65]. The silicon composite membranes provide: the CO conversion higher than 95%, selectivity towards H_2/CO, H_2/CO_2 and H_2/N_2 ranging within 15–40 and separation factor (H_2/CO) 20–45 at 220–290 °C and 0.2–0.6 MPa [66]. The ultra thin palladium membranes (1.6 μm Pd/23 mass.% Ag) provided a very good cleaning of gases from CO [67].

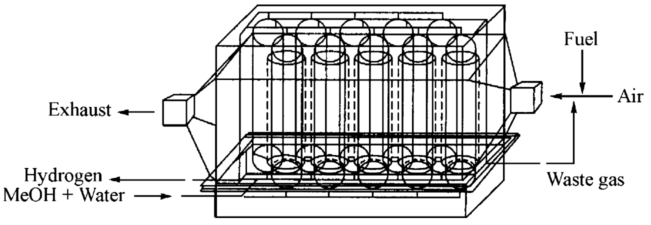

Fig. 4. Schematic of the 30 kW power methanol fuel processor with 10 modules (3 kW power each) [71].

At present, the catalytic membrane reformers for hydrogen generation from different hydrocarbons fuels such as methane, methanol, ethanol, gasoline, etc., using steam or autothermal (steam-oxygen conversion) reforming belong to the best developed reactors. Much attention in literature was focused on the use of palladium membrane reactors in generating super-purity hydrogen, including patents [70–82]. A catalytic membrane reformer or a membrane fuel processor takes the place of a traditional multicomponent fuel processor as one module providing a simultaneous performance of a reaction and separation. Compact sizes of CMR attract much interest of the designers of hydrogen-fueled electrical vehicles. For commercial and research activities, the catalytic membrane reformers with a wide output range ($1\,cm^3 H_2\,h^{-1}$ to $10^4\,cm^3 H_2\,h^{-1}$ and higher) are used.

Catalytic membrane reformers are divided into tubular and plate-type diffusion reactors. The first are designed as a bundle of thin-wall seamless drawn or sutural tubes pressurized either by external or internal gas mixture overpressure. Capillary tubes are used in high-pressure catalytic membrane reformers. Plate diffusion elements feature a great variety of design and technologic implementations, and are usually made of foil based on the porous or ribbed supports. The foil is corrugated to reduce the effect of tension caused by different linear expansion coefficients of foil and support materials. However, such elements hold their shape up to relatively low pressures, 1.0–2.0 MPa. The plate diffusion elements are 2–3 times lower in cost than the tubes.

Let us consider several catalytic membrane reactors. In [71], a $30\,kW_e$ electric power CMR was designed for a vehicle (Fig. 4). The volume of the module was 3.9 l, the weight (without flanges) 5.7 kg, the hydrogen output $2.3\,nm^3\,h^{-1}$ (see schematic in Fig. 5). A membrane hydrogen separator was integrated into the CMR. The membrane was made of alloy Pd–Cu 25 μm thick, though Pd–Ag and Pd–V–Ni–Cr alloys were also tested. Specific flow rate of the hydrogen flow increased with an increase of both tem-

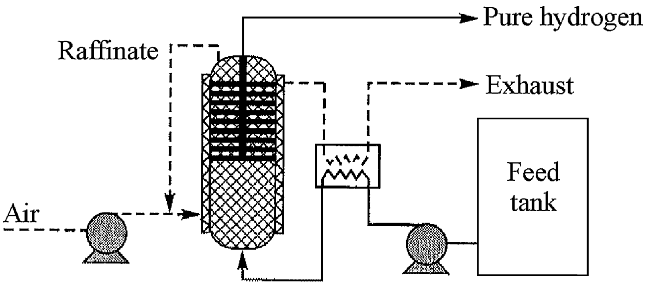

Fig. 5. Schematic of the 3 kW power methanol reforming module providing pure hydrogen [71]. The reformer bottom is filled with platinum catalyst supported on the metal grid. Membrane Pd–Cu tubes are at the top.

perature and pressure through a membrane. At 300 °C and the hydrogen partial pressure 0.414 MPa, the specific flow rate of hydrogen was 30 $cm^3\ min^{-1}\ cm^{-2}$. The presence of CO in the reformer reduced the hydrogen flow rate by ≈25 vol.%, because the CO irreversible adsorption locked the centers of adsorption (dissociation) of hydrogen. The samples of $CuO/ZnO/Al_2O_3$, $CuO/ZnO/TiO_2$ and $CuO/Cr_2O_3/TiO_2$ were tested as reforming catalysts. A residue gas flow containing nonseparated hydrogen (≈25 vol.%) was directed to the catalytic combustion zone located around the modules (Fig. 4). The heat released by combustion was utilized in the methanol steam reforming. To heat up the system which is usually cold, a liquid methanol portion was injected through an injector into the combustion zone and set on fire. As temperature increased to ≈45 °C, the catalytic combustion began. A steel grid with supported Pt/Al_2O_3 was used as a combustion catalyst. Five minutes after the cold start, the flow temperature at the jacket outlet was about 350 °C. In a minute, the hydrogen generation started in the module which was heated to 100 °C. After 12 min of heating, the temperature of the heating flow was 500 °C. By the twentieth minute, the reformate temperature at the module outlet was 300–320 °C. Note that each module provided the maximal hydrogen output 2.3 $nm^3\ h^{-1}$, the hydrogen purity was 99.9999% and the CO concentration was lower than 1 ppm. Specific characteristics of the fuel processor were: power density of the processor 1 $kW\ l^{-1}$ (0.84 $kW\ kg^{-1}$), total volume 40 l and total weight 50 kg. The methanol conversion was 95%, the hydrogen separation by a steel membrane was 75% and the total thermal effectiveness of the system was 89%. The period of transition (response time) from full loading to restart (after a short stop of the processor) was about 2 min.

A comparison of 50 kW power catalytic membrane reactors for steam and autothermal methanol reforming (ATR) showed that the volume of the latter was smaller by 13 l [72]. The autothermal catalytic membrane reactor is schematically shown in Fig. 6. To provide heating of the CMR-ATR, they used the heat resulting from the catalytic fuel combustion and the hydrogen from the FC anode exhaust, the overall efficiency of the CMR-FC system was about 84%.

The US patent [73] suggests a compact multi-fuel converter for vehicles with an integrated hydrogen separator (Fig. 7). The fuel processor is designed as an U-shaped tube. A heated gas flow is directed from burner 1 (top part) to the reactor through flange 2 to heat the catalytic zone of cylindrical reactor 3 and cylindrical membrane reactor 4. The evaporated fuel mixture is supplied through flange 5 into the right cylinder filled with the catalyst. A gas mixture resulting from the reforming is directed through the U-shaped outlet at the top into membrane unit 4. The reformate containing small amounts of hydrogen is released through flange 6. Hydrogen is isolated from the reformate using the membrane and released from collector 7. The compact membrane fuel processor is schematically shown in Fig. 8. The processor has three concentric zones: zone 1 is meant for fuel gas pass, zone 2 acts as a hydrogen collector and zone 3 (inner) is meant for the gases which heat the processor. Membrane filter 4 permits the isolation of hydrogen from the reformer and its supply to the fuel cell through flange 5. The overall sizes of the membrane processor are: diameter 5 cm, length 50 cm, area about 0.4 m^2. Patent [74] describes a catalytic heat-conjugated membrane reactor for methanol steam reforming (quick heating of the reformer owing to the catalytic oxidation of alcohols or hydrocarbons and residue reformate).

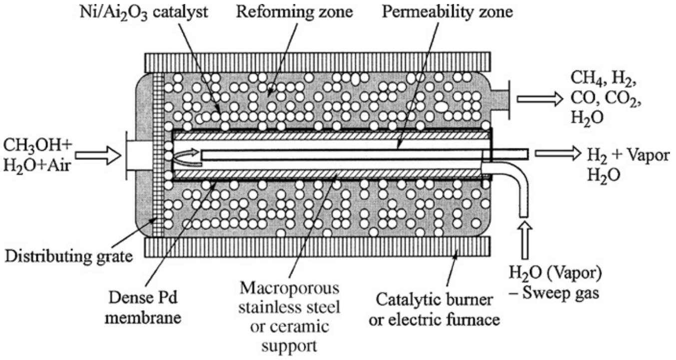

Fig. 6. Schematic of the membrane reformer for autothermal methanol conversion supplied with countercurrent sweep gas [72].

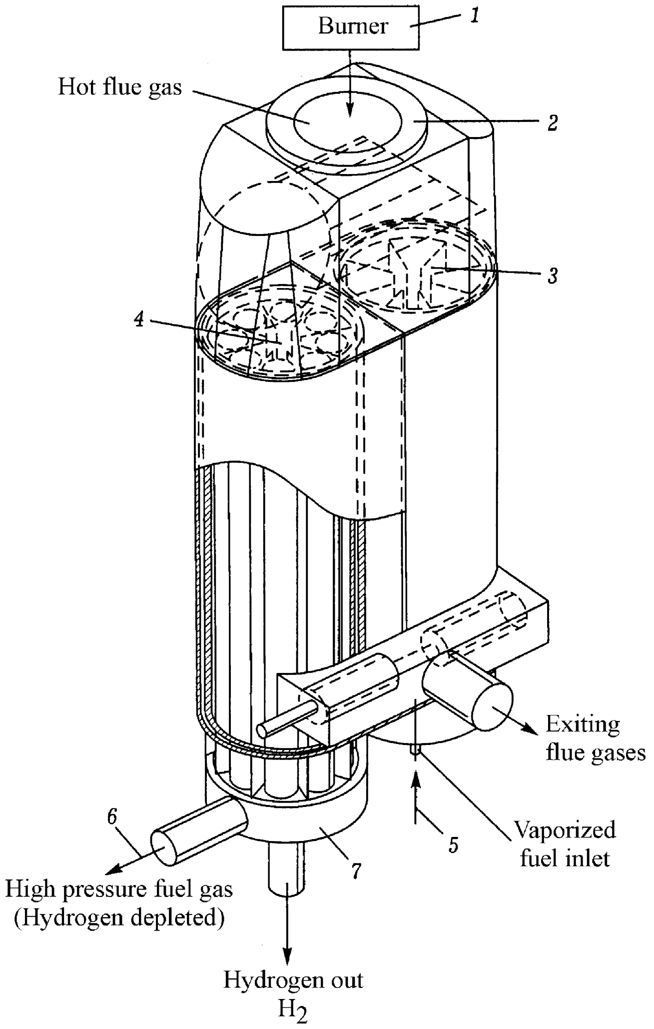

Fig. 7. Compact methanol fuel processor based on the steam reforming and membrane hydrogen separation [73].

A novel membrane reformer providing both steam and oxidation methane reforming is suggested in [75]. In the reforming zone, the fluidized catalyst bed is quickly circulating. Hydrogen is released

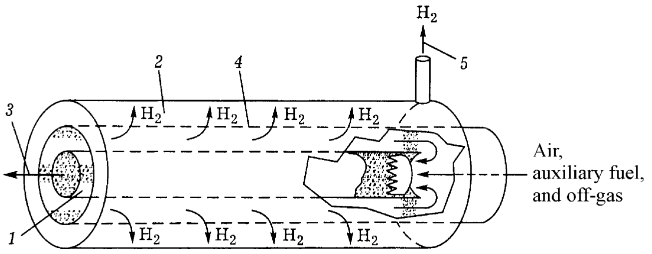

Fig. 8. Compact membrane reformer-processor [73].

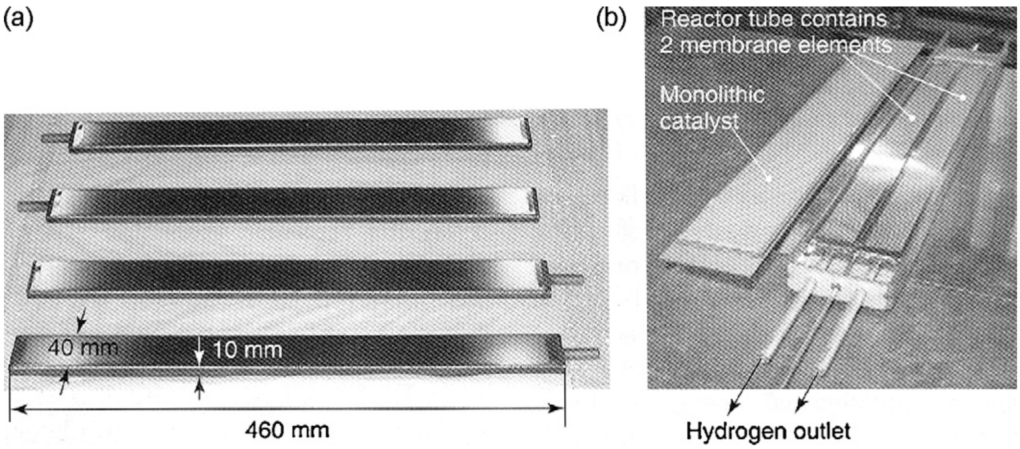

Fig. 9. Left: Design of composite palladium membrane elements used by Tokyo Gas for their methane steam membrane reformer. Right: Arrangement of two elements in one reactor tube [83].

from the reaction zone through filtration tubes (2941 pieces) 2 m in length, ≈1 mm in diameter which are supplied with Pd membranes 20 μm thick. The air oxygen is supplied through a number of dense perovskite oxygen-permeable tubes (15224 pieces) 2 m in length, ≈4.9 mm in diameter, the membrane thickness is ≈55 μm. Some reformer characteristics: process temperature 560 °C, H_2O/CH_4 4, reactor volume 0.015 m^3, pressure in the reactor 2.2 MPa, hydrogen output (mole H_2/mole CH_4) 3.204. The efficiency of the unit volume of the membrane reactor is 8.2 times higher than that of the traditional commercial tubular reactor with a fixed catalyst bed with similar characteristics.

A compact methanol steam reforming reactor with an integrated hydrogen separator is presented in [76]. For the steam methanol reforming, it was suggested to use a palladium membrane reactor with two jackets, in which the processes of steam methanol reforming and CO conversion are performed at a time [77]. Hydrogen is separated from the reformate using palladium tubes. The reactor worked at 1.2 MPa and 350 °C, the methanol conversion was 97%, the hydrogen separation by a membrane unit was 74%.

A new hybrid adsorption-membrane reactor with a hybrid fixed catalyst bed, in which the reaction of methane steam reforming is conjugated with the CO_2-adsorption system, was studied at the temperature range 400–480 °C and pressures to 3 MPa, which are required for different transport and stationary applications [78]. The authors in [79] suggested a membrane assisted fluidized bed reactor with a Pd membrane for hydrogen separation and a perovskite membrane for oxygen supply. The membranes are placed into two sections because of different temperatures. Thus, the steam methanol reforming and CO steam conversion proceed in the upper section (Pd membrane) whereas the partial oxidation (perovskite membrane) proceeds on the lower section. The reactor was tested on the low-temperature methanol steam reforming, ratio H_2O/CH_4 was stoichiometric. The process of partial methanol reforming was performed in a reformer with a palladium membrane, the starting temperature was 300 °C [80]. In [81], the membrane assisted fluidized bed reformer was tested during MSR (the reactor was heated through a wall) and POX (air was introduced through a catalyst layer). In the pilot reactor (diameter 0.13 m, height 2.3 m), the heated catalyst particles were circulated from the oxidation reforming zone to the steam reforming zone. The yield of hydrogen (purity grade 99.999%) was 0.96 mole H_2 $mole^{-1}$ CH_4. In Ref. [82], the commercial catalytic membrane reactor of methane steam reforming was tested to reveal effects of different fluxes in the reaction and permeability zones. Compared to the traditional reactor, the advantages of CMR-MSR are: less complicated process flow diagram, low process temperature and low fuel consumptions at higher methane conversion.

The most advanced technical demonstration of packed-bed membrane reformer for methane steam reforming has been reported from Japan, where this technology has been developed since 1991 by a consortium involving Mitsubishi Heavy Industries and Tokyo Gas based on pioneering studies by Kikuchi, Uemiya and coworkers [8,11,29]. The unit commissioned in Tokyo Gas in 2004 has a hydrogen capacity of 40 nm^3 h^{-1} [83], and operates at 550 °C and 0.9 MP, a with S/C ratio of 3. Steam sweep is used to remove the hydrogen, and the permeate is evacuated to a pressure of 0.04 MPa. The purity of the hydrogen is above 99.99%, and energy efficiency of the unit reaches 72–76%. The reformer has a scalable design with 224 membrane elements that are flat rectangular tubes,

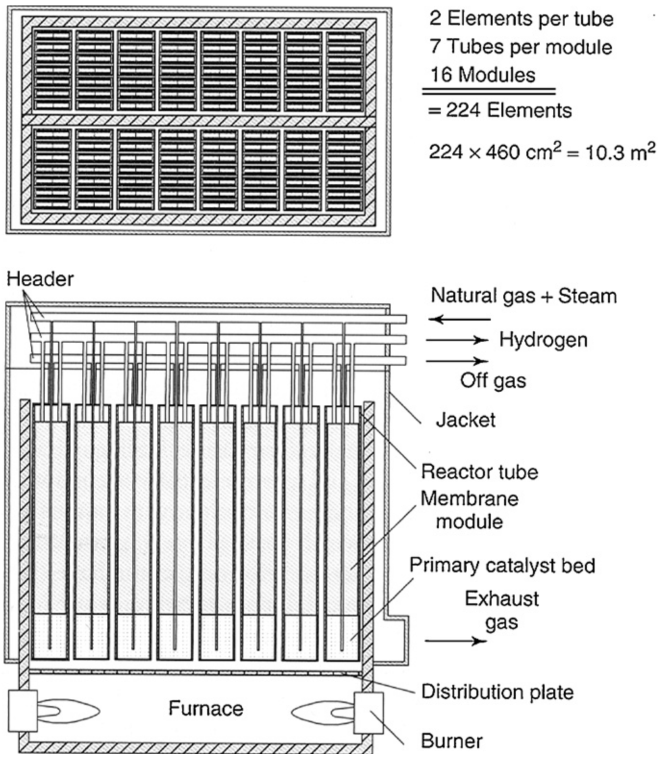

Fig. 10. Scalable design of the methane steam membrane reformer developed by Tokyo Gas [83].

each 40 mm wide, 460 mm long, and 10 mm thick (Figs. 9 and 10). Two of these elements each are combined to one reactor tube with dimensions 86 mm × 22 mm × 615 mm, and seven reactor tubes are arranged to from one unit, of which 16 comprise the whole module. Each element has a membrane area of ca. 460 cm^2, which leads to a total membrane area of ≈10.3 m^2. The membrane is a total palladium-alloy foil which is cold-rolled to a thickness of <20 μm and hot-pressed to structural support [11], using a suitable coating or a porous blanket for protection against intermetallic diffusion. With a width of 1.2 m, a depth of 0.75 m, and height of 1.35 m (including insulation), the reformer is very compact. The whole unit is installed in a container which is 3.56 m long, 2.56 m wide, and 2.3 m high; this represents a 70% reduction in volume as compared to a conventional system with purification by pressure swing adsorption. The system has been operated continuously for more than 3000 h at a hydrogen filling station in Tokyo.

5. Conclusions

1. Catalytic membrane reformers feature high energy efficiency (≥80%), compact dimensions, good dynamic characteristics, low temperature of the carbon reforming; provide a one-step generation of super-pure hydrogen and the conversion of feed which considerably exceeds the equilibrium value. The resulting hydrogen does not contain CO and can be utilized in low-temperature fuel cells. Compared to the traditional tubular reactors, the reformers with the integrated membrane modules for hydrogen separation from the reaction zone and oxygen supply to the reaction zone increase the hydrogen output by eight times.
2. Different constructions of catalytic membrane reformers were developed for vehicles and power plants using membrane isolation of hydrogen from reformats. For vehicles, the catalytic membrane reactors with autothermal reforming are preferred because of the less complicated heat supply of the reforming zone. The catalytic membrane reactors with steam methane reforming are preferred for power plants, because they provide higher separation of hydrogen from fuels.
3. A significant drawback of the known catalytic membranes is short operation life. Thus, the reforming catalysts used in the catalytic membrane reactors can operate for more than 1000 h whereas the best membrane samples exhibit stable operation during several hundreds of hours. A short operation life of the known membranes, insufficient mechanical strength and, what is more important, high cost of their main component (palladium) hinder wide application of catalytic membrane reactors. However, the advances in the development of hyperfine composite membranes on different supports suggest good prospects for introducing membrane technologies into future hydrogen energy. A cartridge-type change of the membrane modules in the catalytic membrane reactors is a way to increase their operation life.

References

[1] Methanol or Hydrogen? Outlook for Development of Fuel Cells in the World, Chemistry and Business 3 (61) (2004) 63 (in Russian).
[2] G.Q. Lu, J.C. Diniz da Costa, M. Duke, S. Giessler, R. Socolov, R.H. Williams, T. Kreutz, Inorganic membranes for hydrogen production and purification: a critical review and perspective, J. Colloid Interface Sci. 314 (2007) 589.
[3] B.N. Lukyanov, Catalytic membrane reformers with a membrane hydrogen separation, Chem. Sustain. Dev. 15 (2007) 625 (in Russian).
[4] G.S. Burkhanov, N.B. Gorina, N.B. Kolchugina, N.R. Roshan, Palladium alloy in hydrogen energetics, Rossiiskii Khim. Zh. 50 (4) (2006) 36.
[5] R. Peters, Fuel processors Handbook of Heterogeneous Catalysis, vol. 6, 2008, p. 3045.
[6] J. Tong, Y. Matsumura, H. Suda, K. Haraya, Experimental study of steam reforming of methane in a thin (6 μM) Pd-based membrane reactor, Ind. Eng. Chem. Res. 44 (2005) 1454.
[7] M. Oertel, J. Schmitz, W. Weirich, et al., Steam reforming of natural gas with integrated hydrogen separation for hydrogen production, Chem. Eng. Technol. 10 (1987) 248.
[8] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Steam reforming of methane in hydrogen-permeable membrane reactor, Appl. Catal. 67 (1991) 223.
[9] J. Shu, B.P.A. Gradjean, S. Kaliaguine, Methane steam reforming in asymmetric Pd and Pd–Ag/porous SS membrane reactors, Appl. Catal. A 119 (1994) 305.
[10] G. Barbieri, V. Violante, F.P. Di Maio, A. Criscuioli, E. Drioli, Methane steam reforming analysis in palladium-based catalytic membrane reactor, Ind. Eng. Chem. Res. 36 (1997) 3369.
[11] E. Kikuchi, Membrane reactor application to hydrogen production, Catal. Today 56 (2000) 97.
[12] G.F. Tereshchenko, N.V. Orekhova, M.M. Ermilova, Metal containing membrane reactors, Crit. Technol. Membr. 1 (33) (2007) 4.
[13] J.A. Nollet, Lecons de physique-experimental, Hippolyte-Louis Guerin, Paris, 1748.
[14] T. Graham, Phil. Mag. 32 (1861) 402.
[15] M. Knudsen, Ann. der Physik 28 (1909) 75.
[16] A. Sieverts, W. Krumbhaar, Ber. Deut. Chem. Ges. 43 (1910) 893.
[17] V.M. Grayznov, Catalysis by selectively permeable membranes, Dokl. Akad. Nauk SSSR 189 (1969) 794 (in Russian).
[18] V.M. Gryaznov, M.M. Ermilova, N.V. Orekhova, A.M. Klochkov, Metal and metal containing membranes for separation of hydrogen from industrial gases, Ross. Khim. Zh. 37 (2) (1993) 44 (in Russian).
[19] G.J. Hwang, K. Onuki, S. Shimuzu, Separation of hydrogen from a H_2–H_2O–HI gaseous mixture using a silica membrane, AIChE J. 46 (2000) 92.
[20] R.V. Siriwardane, J.A. Poston Jr., T.H. Lee, S.E. Dorris, U. Balachandran, Characterization of ceramic hydrogen separation membrane with varying nickel concentrations, Appl. Surf. Sci. 167 (2000) 34.
[21] L. Li, E. Iglesia, Modeling and analysis of hydrogen permeation in mixed proton-electronic conductors, Chem. Eng. Sci. 58 (2003) 1977.
[22] M. Shirai, M. Arai, Hydrogenation of furan with hydrogen atoms permeating through a palladium membrane, Langmuir 15 (1999) 1577.
[23] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, A one-step conversation of benzene to phenol with a palladium membrane, Science 295 (2002) 105.
[24] V.R. Choudhary, A.G. Gaikwad, S.D. Sansare, Non-hazardous direct oxidation of hydrogen to hydrogen peroxide using a novel membrane catalyst, Angew. Chem. Int. Ed. 40 (2001) 1776.
[25] T. Matsuda, I. Koike, N. Kubo, E. Kikuchi, Dehydrogenation of isobutene in a palladium membrane reactor, Appl. Catal. A: Gen. 96 (1993) 3.
[26] J.P. Collins, R.W. Schwartz, R. Sehgal, T.L. Ward, C.J. Brinker, G.P. Hagen, C.A. Udovich, Catalytic dehydrogenation of propane in hydrogen permselective membrane reactor, Ind. Eng. Chem. Res. 35 (1996) 4398.
[27] N. Itoh, W.C. Xu, S. Hara, K. Kakehida, Y. Kaneko, A. Igarashi, Effects of hydrogen removal on the catalytic reforming of n-hexane in a palladium membrane reactor, Ind. Eng. Chem. Res. 42 (2003) 6576.
[28] S. Uemiya, Y. Kude, K. Asugino, N. Sato, T. Matsuda, E. Kikuchi, A palladium/porous glass composite membrane for hydrogen separation, Chem. Lett. 17 (1988) 1687.
[29] S. Uemiya, N. Sato, H. Ando, Y. Kude, K. Asugino, T. Matsuda, E. Kikuchi, Separation of hydrogen through palladium thin film supported on porous glass tube, J. Membr. Sci. 56 (1991) 303.
[30] Y.-M. Lin, G.L. Lee, M.H. Rey, An integrated purification and production of hydrogen with a palladium membrane-catalytic reactor, Catal. Today 44 (1998) 343.
[31] Y.-M. Lin, S.-L. Liu, C.-H. Chuang, Y.-T. Chu, Effect of incipient removal of hydrogen through palladium membrane on the conversion of methane steam reforming. Experimental and modeling, Catal. Today 82 (2003) 127.
[32] F. Gallucci, L. Paturzo, A. Fama, A. Basile, Experimental study of the methane steam reforming reaction in a dense Pd/Ag membrane reactor, Ind. Eng. Chem. Res. 43 (2004) 928.
[33] F. Gallucci, L. Paturzo, A. Basile, A simulation study of the steam reforming of methane in a dense tubular membrane reactor, Int. J. Hydrogen Energy 29 (2004) 611.
[34] J.N. Armor, Applications of catalytic inorganic membrane reactors to refinery products, J. Membr. Sci. 147 (1998) 217.
[35] S.I. Prokopiev, Y.I. Aristov, V.N. Parmon, N. Giordano, Intensification of hydrogen production via methane reforming and the optimization of H_2:CO ratio in catalytic reactor with a hydrogen-permeable membrane wall, Int. J. Hydrogen Energy 17 (1992) 275.
[36] S.L. Jorgensen, P.E. Nielsen, P. Lehrmann, Steam reforming of methane in a membrane reactor, Catal. Today 25 (1995) 303.
[37] K.A. Petersen, P.E. Nielsen, S.L. Jorgensen, Membrane reforming for hydrogen, Catal. Today 46 (1998) 193.
[38] J.S. Oklany, K. Hou, R. Hughes, A simulative comparison of dense and microporous membrane reactors for the steam reforming of methane, Appl. Catal. A: Gen. 170 (1998) 13.
[39] M. Nomura, K. Ono, S. Gopalakrishnan, T. Sugawara, S.-I. Nakao, Preparation of a stable silica membrane by a counter diffusion chemical vapor deposition method, J. Membr. Sci. 251 (2005) 151.
[40] M. Nomura, M. Seshimo, H. Aida, K. Nakatani, S. Gopalakrishnan, T. Sugawara, T. Ishikawa, M. Kawamura, S.-I. Nakao, Preparation of a catalytic composite silica membrane reactor for steam reforming reaction by using a counterdiffusion CVD method, Ind. Eng. Chem. Res. 45 (11) (2006) 3950.
[41] M. Nomura, Development of crystalline and amorphous silica membranes and their permeation properties, Maku 30 (4) (2005) 198.

[42] T. Tsuru, H. Shintani, T. Yoshioka, M. Asaeda, A bimodal catalytic membrane having a hydrogen-permselective silica layer on a bimodal catalytic support: preparation and application to the steam reforming of methane, Appl. Catal. A: Gen. 302 (1) (2006) 78.

[43] M. Chai, M. Machida, K. Eguchi, H. Arai, Promotion of hydrogen permeation on metal-dispersed alumina membranes and its application to a membrane reactor for methane steam reforming, Appl. Catal. A: Gen. 110 (1994) 239.

[44] Y. Iwamoto, T. Nagano, N. Uno, Y.H. Ikuhara, H. Moti, S. Yamazaki, High-temperature separation of hydrogen by microporous ceramic membranes, Maku 30 (2005) 247.

[45] B.K.R. Nair, M.P. Harold, Pd encapsulated nanopore hollow fiber membranes: synthesis and permeating studies, J. Membr. Sci. 290 (1+2) (2007) 182.

[46] I.N. Avertseva, N.R. Roshan, A.P. Mishchenko, High-purity Hydrogen Production and Utilization, Ural Dpt. of the USSR Academy of Sciences, Sverdlovsk, 1989, pp. 47–49.

[47] V.A. Goltsov, Hydrogen in metals. Questions of atomic sciences and engineering. Ser.: Atomic-Hydrogen Energetics 1 (2) (1977) 65 (in Russian).

[48] J. Tong, Y. Matsumura, H. Suda, K. Haraya, Thin and dense Pd/CeO_2/MPSS composite membrane for hydrogen separation and steam reforming of methane, Sep. Purif. Technol. 46 (2005) 1.

[49] J. Tong, L. Su, Y. Kashima, R. Shirai, H. Suda, Y. Matsumura, Simultaneously depositing Pd–Ag thin membrane on asymmetric porous stainless steel tube and application to produce hydrogen from steam reforming of methane, Ind. Eng. Chem. Res. 45 (2006) 648.

[50] J. Tong, Y. Matsumura, Pure hydrogen production by methane steam reforming with hydrogen-permeable membrane reactor, Catal. Today 111 (2006) 147.

[51] X.L. Pan, G.X. Xiong, S.S. Sheng, N. Stroh, H. Brunner, Thin dense Pd membranes supported on α-Al_2O_3 hollow fibers, Chem. Commun. (2001) 2536.

[52] V. Jararaman, Y.S. Lin, M. Pakals, R.Y. Lin, Fabrication of ultrathin metallic membranes on ceramic supports by sputter deposition, J. Membr. Sci. 99 (1995) 80.

[53] Z. Li, H. Maeda, K. Kusakabe, S. Morooka, H. Anzai, S. Akiyama, Preparation of palladium–silver alloy membranes for hydrogen separation by spray pyrolysis method, J. Membr. Sci. 78 (1993) 247.

[54] A.W. Li, W.Q. Liang, R. Hughes, Characterization and permeation of palladium/stainless steel composite membrane, J. Membr. Sci. 149 (1998) 259.

[55] P.P. Mardilovich, Y. She, Y.H. Ma, M.H. Rei, Defect-free palladium membrane on porous stainless, AIChE J. 44 (1998) 310.

[56] R. Dittmeyer, V. Höllein, K. Daub, Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium, J. Mol. Catal. 173 (2001) 135.

[57] G. Xomeritakis, Y.S. Lin, Fabrication of thin palladium membrane supported in a porous ceramic substrate by chemical vapor deposition, J. Membr. Sci. 120 (1996) 261.

[58] M.C. Iliuta, B.P.A. Grandjean, F. Larachi, Methane nonoxidative aromatization over Ru-Mo/HZSM-5 at temperatures up to 973 K in a palladium–silver/stainless steel membrane reactor, Ind. Eng. Chem. Res. 42 (2003) 323.

[59] F. Roa, J.D. Way, Influence of alloy composition and membrane fabrication on the pressure dependence of the hydrogen flux of palladium–copper membranes, Ind. Eng. Chem. Res. 42 (2003) 5827.

[60] R. Dittmeyer, J. Caro, Catalytic membrane reactor Handbook of Heterogeneous Catalysis, vol. 4, 2008, p. 2198.

[61] A. Basile, L. Paturo, An experimental study of multilayered composite palladium membrane reactors for partial oxidation of methane to syngas, Catal. Today 67 (2001) 55.

[62] A. Basile, L. Paturo, F. Lagana, The partial oxidation of methane to syngas in a palladium membrane reactor: simulation and experimental studies, Catal. Today 67 (2001) 65.

[63] J. Huang, L. El-Azzami, W.S.W. Ho, Modeling of CO_2-selective water gas shift membrane reactor for fuel cell, J. Membr. Sci. 261 (2005) 67.

[64] A. Brunetti, G. Barbieri, E. Drioli, T. Granato, K.-H. Lee, A porous stainless steel supported silica membrane for WGS reaction in catalytic membrane reactor, Chem. Eng. Sci. 62 (18–20) (2007) 5621.

[65] X. Xie, C.R.I.V. Evenson, M.V. Mundschau, H.A. Wright, P.J. Grimmer, High-pressure operation of dense hydrogen transport membranes for pure hydrogen production and simultaneous CO_2 capture, in: Proceedings of the Annual International Pittsburgh Coal Conference, 2006 Pittsburgh, 23rd, 2006, pp. 17.4/1–17.4/10.

[66] A. Brunetti, G. Barbieri, E. Drioli, T. Granato, K.-H. Lee, B. Sea, D.-M. Lee, WGS reaction in membrane reactor using a porous stainless steel supported silica membrane, Chem. Eng. Process. 46 (2) (2007) 119.

[67] B. Arstad, H. Venvik, H. Klette, J.C. Walmsley, W.M. Tucho, R. Holmestad, A. Holmen, R. Bredesen, Studies of self-supported 1.6 vv Pd/23 wt.% Ag membranes during and after hydrogen production in catalytic membrane reactor, Catal. Today 118 (1–2) (2006) 63.

[68] S.E. Battersby, D. Miller, M. Zed, J. Patch, V. Rudolph, M.C. Duke, J.C.D. da Costa, Silica membrane reactors for hydrogen processing, Adv. Appl. Ceram. 106 (1–2) (2007) 29.

[69] K. Kusakabe, S. Fumio, T. Eda, M. Oda, K.-I. Sotowa, Hydrogen production in zirconia membrane reactors for use in PEM fuel cells, Int. J. Hydrogen Energy 30 (9) (2005) 989.

[70] M.P. Harold, B. Nair, G. Kolios, Hydrogen generation in a Pd membrane fuel processor: assessment of methanol-based reaction systems, Chem. Eng. Sci. 58 (2003) 2551.

[71] J. Han, Il-soo Kim, K.-S. Choi, Purifier-integrated methanol reformer for fuel cell vehicles, J. Power Sources 86 (2000) 223.

[72] J.R. Lattner, M.P. Harold, Comparison of methanol-based fuel processors for PEM fuel cell systems, Appl. Catal. B: Environ. 56 (2005) 149.

[73] C.L. Verrill, et al., Compact multi-fuel steam reformer, US Patent 1999/5938800.

[74] R. Min-Ho, Method for rapidly generating hydrogen and reactor module therefore, Jap. Patent, JP 2004-303842.

[75] Z. Chen, Y. Yan, S.S.E.H. Elnashaie, Novel circulating fast fluidized-bed membrane reformer for efficient production of hydrogen from steam reforming of methane, Chem. Eng. Sci. 58 (2003) 4335.

[76] J. Wheeldon, et al., Compact methanol steam reformer with integrated hydrogen separation, US Patent US2003215374.

[77] R. Autenrieth, System for the water vapor reforming of a hydrocarbon, US Patent US2002 6447736 B1.

[78] B. Fayyaz, A. Harale, B.G. Park, P.K.T. Liu, M. Sahimi, T.T. Tsotsis, Design aspects of hybrid adsorbent-membrane reactors for hydrogen production, Ind. Eng. Chem. Res. 44 (2005) 9398.

[79] C.S. Patil, M. van Sint Annaland, J.A.M. Kuipers, Experimental study of membrane assisted fluidized bed reactor for H_2 production by steam reforming of CH_4, Chem. Eng. Res. Des. 84 (2006) 399.

[80] C.X. Qi, J.C. Amphlett, B.A. Peppley, Product composition as a function of temperature over NiAl-layered double hydroxide derived catalysts in steam reforming of methanol, Appl. Catal. A: Gen. 302 (2006) 237.

[81] T. Boyd, J. Grace, C.Y. Lim, A.E.M. Adris, Hydrogen from an internally circulation fluidized bed membrane reactor, Int. J. Chem. Reactor Eng. 3 (2005) A55.

[82] F. Gallucci, A. Comite, G. Capannelli, A. Basile, Steam reforming of methane in membrane reactor: an industrial case study, Ind. Eng. Chem. Res. 45 (2006) 2994.

[83] I. Yasuda, T. Tsuneki, Y. Shirasaki, 7th International Conference on Catalysis in Membrane Reactors (ICCMR-7)—Book of Abstracts, Cetraro, Italy, September 11–14, 2005, p. 138.