Chemistry for Sustainable Development **20** (2012) 251–263

UDC 542.943.7

Obtaining Ultra-Pure Hydrogen for Fuel Cells in the Reactors with Membrane Separation

B. N. LUKYANOV

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
Prospekt Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: lukjanov@catalysis.ru

(Received July 5, 2011; revised October 25, 2011)

Abstract

Main catalytic processes and fuel types are described inherent in the production of hydrogen for low-temperature fuel cells. Different types of solid membranes for extracting hydrogen from gas mixtures are considered. Descriptions of new membrane reactors are presented and the prospects for their use in hydrogen energy engineering are assessed.

Key words: hydrogen, steam conversion, methane, carbon monoxide, fuel processor, membrane reactor, fuel cell, catalyst, adsorbent, reviews

Contents

INTRODUCTION

The transition of transport and industry to the use of hydrogen energy engineering becomes a reality nowadays [1]. The use of hydrogen as an energy carrier exhibits unparalleled environmental benefits as compared to traditional energy sources. Problems are almost solved by are now associated with hydrogen production, storage, making the systems of safe operation, transition to an electric circuit diagram with the help of fuel cells. The main methods for the obtaining hydrogen are completely determined: 1) as a by-product in the production of chlorine and recovering H_2 from flue gases in refineries (the cheapest method), 2) with the use of catalytic hydrocarbon conversion technologies, 3) in the form of synthesis gas *via* a partial oxidation of hydrocarbon feedstock (more expensive method as compared to the two previous methods), 4) *via* electrolysis (the most expensive and energy-consuming method, but the resulting hydrogen could be used with no fine purification). In spite of the enormous hydrogen reserves in the Earth's bowels [2] the geotechnology of its extraction (underground coal gasification) has found no application yet. Hydrogen amounts to about 10 % of the mass of living systems on our planet, but the main source for its producing is presented by hydrocarbon feedstock, in particular naturally occurring gas, wherefrom they extract more than 90 % of hydrogen all over the world.

The catalytic production of hydrogen is the most attractive in the case of the further conversion of hydrogen into electricity using fuel cells [3–5]. It should be noted that the hydrogen used in fuel cells with a proton exchange membrane (PEMFC) should have a high purity level ($C_{CO} \leq 10$ ppm). This is caused by poisoning the platinum electrocatalysts for hydrogen anode oxidation for the PEMFC operating temperature values ranging within 25–90 °C. One of the promising solutions of this problem consists in the use of membrane technology, which allows one to extract hydrogen gas from the reaction mixture and simultaneously to enhance the conversion level of the starting reagent as well as to reduce the temperature of the process [6–8]. Using membranes in catalysis is discussed in detail in a number of reviews [9, 10]; this topic also includes the development of catalytically active membranes and membrane reactors [11]. The hydrogen permeable membranes integrated into reactors can cause a significantly decrease in the size, cost and complexity of hydrogen generators.

In this paper we are considering the state-of-the-art of the catalytic hydrogen production with simultaneous extracting it from the reaction medium by means of selectively permeable asymmetric metallic membranes. The ultra-pure hydrogen (99.999 vol. %) obtained is intended for direct using as PEMFC, which causes promoting the development of hydrogen energy engineering.

CATALYTIC PROCESSES FOR OBTAINING HYDROGEN FROM DIFFERENT FUELS

For the production of hydrogen one can use various kinds of fuel. Typically, the fuel represents a mixture of either hydrocarbons, or derivatives thereof, or properly oil fuel species with the general formula $C_nH_mO_z$. The general pattern of the conversion of such fuels into hydrogen consists in a combination of five basic reactions such as steam reforming (steam conversion), catalytic partial oxidation, carbon monoxide steam reforming, selective CO oxidation and methanation reaction. Methanation is an adverse reaction since it consumes the hydrogen resulting from other reactions. However, this reaction is required for decreasing the CO concentration to a level acceptable in the PEMFC, and for removing CO_2 from the atmosphere of a spacecraft cab. The mentioned reactions could be performed simultaneously, if heavy hydrocarbons are completely reformed in the lower alkanes and CO. The remaining lower alkanes including CH_4, could be further converted into synthesis gas, or simply oxidized for obtaining energy.

Carbon monoxide can be converted into CO_2 *via* the reaction of water gas steam reforming, which provides obtaining additional hydrogen. The gross reaction (fuel → H_2) can be presented in the following form:

$$C_nH_mO_z + y(O_2 + 3.76N_2) + 2(n - y - z/2)H_2O \\ \rightarrow nCO_2 + 2(n - y - z/2 + m/4)H_2 + 3.76yN_2 \quad (1)$$

wherein n, m, z are the number of carbon, hydrogen and oxygen atoms in $C_nH_m0_z$, respectively; y is oxygen/fuel ratio.

It should be noted that the maximum efficiency of hydrogen production is almost independent on the fuel conversion mode (steam reforming, partial oxidation, autothermal mode) to be reached in a thermally neutral point [12]. Each type of fuel has unique physical and chemical properties. Table 1 [13] demonstrates that for the complete conversion of fuel into hydrogen and CO_2 different fuels require for different amount of oxygen, whereas the maxima of their energy efficiency values are different, although they were obtained in an ideal autothermal process (thermal effect $\Delta H = 0$). Traditionally, for the production of hydrogen fuel one uses oxygen-containing fuel species such as alcohols, aldehydes, ketones, *etc*. Among alcohols, methanol is the most attractive as fuel not only because of rather moderate conditions of conversion and a maximal energetic efficiency, but also due to the possibility of obtaining this substance from renewable sources [14–18]. The catalytic production of hydrogen from methanol for mobile, stationary and portable energy generators based on fuel cell is considered in detail in our review [19]. Another alcohol such as ethanol is usually used as a main additive to gasoline due to a high octane number and low toxicity thereof [20–23]. Recently, researchers' interest appeared in the production of hydrogen from phenol [24].

TABLE 1

Fuel types, calculated thermoneutral ratio values O_2/fuel (x_0) and the maxima of theoretical efficiency [22]

Fuel	$C_nH_mO_z$	n	m	z	ΔH, kcal/mol	$m/2n$	x_0	Efficiency, %
Methanol	CH_3OH	1	4	1	−57.1	2	0.230	96.3
Methane	CH_4	1	4	0	−17.9	2	0.443	93.9
Acetic acid	$C_2H_4O_2$	2	4	2	−116.4	1	0.475	94.1
Ethane	C_2H_6	2	6	0	−20.2	1.5	0.771	92.4
Ethylene	C_2H_4	2	6	2	−108.6	1.5	0. 418	95.2
Ethanol	C_2H_6O	2	6	1	−66.2	1.5	0. 608	93.7
Pentene	C_5H_{10}	5	10	0	−5.0	1	1.595	90.5
Pentane	C_5H_{12}	5	12	0	−35.0	1.2	1.814	91.5
Cyclohexane	C_6H_{12}	6	12	0	−37.3	1	2.143	90.7
Benzene	C_6H_6	6	6	0	−11.7	0.5	1.784	88.2
Toluene	C_7H_8	7	8	0	−2.9	0.57	2.161	88.6
Isooctane	C_8H_{18}	8	18	0	−62.0	1.13	2.947	91.2
Gasoline	$C_{7.3}H_{14.8}O_{0.1}$	7.3	14.8	0.1	−53.0	1.014	2.613	90.8

Natural gas [25] and liquefied petroleum gas [26], as well as their replacers (methane and propane) [27] are considered the most attractive fuels for hydrogen production because of enormous available reserves, high conversion efficiency as well as a well-developed gas distribution infrastructure. For the production of hydrogen, gasoline is also interesting, whereof an extensive infrastructure is present. However, since 2004 the USA terminated the research work concerning the topic of "Production of Hydrogen from Gasoline" [19]. Other fuel species those are not listed in Table 1 such as diesel, ethanol, biodiesel, alcohol from sugar were also considered as promising sources of hydrogen. Hydrogen (synthesis gas) is traditionally produced thereof by means a high-temperature gasification/pyrolysis of biomass and further catalytic reforming of gas-liquid products. Hydrogen production from coal by means of gasification thereof into CH_4 followed by using absorption catalytic conversion technology developed in the USA by the authors of ZEC (Zero Emission Carbon) project [28]. Approximately half the hydrogen produced is used in this case for the gasification stage, whereas the remainder is sent to the fuel cell in order to generate electric energy. The efficiency of coal conversion into electricity was equal to about 70 % [29]. Research work in this field is currently ongoing in the UK [30] and Japan [31].

MEMBRANE REACTORS

Types of membranes

In order to extract hydrogen from gas mixtures and to purify thereof one uses membranes based on palladium alloys. This problem was discussed in detail in our reviews [6, 7]. The effect of various substances on the hydrogen permeability of palladium alloys was studied by the authors of [32]. As one could see from Table 2, the maximum permeability of palladium with respect to hydrogen is exhibited by palladium membranes with 10 mass % of yt-

TABLE 2

Hydrogen Permeability with respect to hydrogen inherent in different palladium alloys at 350 °C [32]

Metal alloys	Maximum permeability, mass %	Normalized permeability (P_{alloy} / P_{Pd})
Y	10	3.8
Ag	23	1.7
Ce	7.7	1.6
Cu	40	1.1
Au	5	1.1
Ru, In	0.5, 6	2.8
Ag, Ru	30, 2	2.2
Ag, Rh	19, 1	2.6
Pure Pd	–	1.0

trium, the further are palladium alloys with ruthenium and indium. The widest practical use was found by membranes based on silver-palladium alloys (23 mass % of Ag).

The membranes could represent organic, inorganic or hybrid (organic/inorganic) systems. Organic polymeric membranes can be divided into polymeric and biological, inorganic membranes are presented by metallic and ceramic (porous and nonporous). Monolithic or microporous dense inorganic hydrogen permeable membranes are made basing on oxides and metals, whereas porous (composite, asymmetrical) are manufactured on a the substrate made of ceramics, carbon, polymer, glass, stainless steel, and a thin selectively permeable layer made of palladium or zeolite.

The membranes can be divided into microporous membranes (pore size less than 2 nm), mesoporous membranes (2–50 nm) and macroporous ones (>50 nm). Mesoporous and macroporous ceramic membranes are characterized by a low selectivity level with respect to hydrogen. Microporous ceramic membranes exhibit low hydrogen permeability. Palladium-based membranes have high hydrogen permeability and an infinite selectivity level with respect to hydrogen, whereby they are optimal for using in catalytic membrane reactors (CMR) in the case of steam reforming and other reactions associated with hydrogen production [33].

The design of the membranes could be divided into two types such as tubular (cylindrical) membranes and lamellar (disk, foil) ones. The former represent the bundles of thin-walled seamless or seam pipes loaded with internal or external gas mixture overpressure. The application of capillary tubes is especially useful for high-pressure CMR. Lamellar diffusion elements are of a great variety of constructive and technological design and, as a rule, they are made of foil bearing on a porous or ribbed substrate. In this case the foil is corrugated in order to reduce the impact of stress caused by the difference in the coefficients of linear expansion inherent in a foil material and a substrate. However, such elements retain their shape up to relatively low pressure values (1.0–2.0 MPa). The diffusion lamellar elements are 2–3 times cheaper than tubular ones.

The most efficient way to improve selective permeability inherent in Pd membranes and to achieve a high conversion level of hydrocarbons, which level is directly proportional with respect to the percentage of recovered H_2, is the creation of ultrathin membranes (about 10 μm or less). At the Institute of Catalysis of the SB RAS, the author of the present work *et al.* used a chemical vapour deposition (CVD) technique for manufacturing the membranes on composite stainless steel and γ-alumina porous substrates [7, 8]. The average pore size of stainless steel porous disks was equal to 5 μm, the porosity level amounting to 57 %, the disk diameter and thickness amounting to 20 mm and 0.5 mm, respectively. The substrates pre-treated in aqua regia, with further annealing in a flow of hydrogen at 450 °C in order to remove impurities and oxide films. Then, using the substrate as a filter, it was saturated with an aqueous suspension of γ-Al_2O_3, dried, calcined at 400 °C and pressed in order to reduce the total pore volume and more complete filling the pores with alumina.

The palladium membrane was produced in two stages. First of all, they activated the surface of a porous carrier of γ-Al_2O_3 alternately by 0.001 M $SnCl_2$ and $PdCl_2$ solutions to create active centers those serve as nuclei for the growth of metallic palladium film. This procedure was repeated for 10 times, each time washing the substrate with the carrier by distilled water. Then the resulting composite was dried and subjected to metallisation. For this purpose it was placed in a solution containing 4 g/L of $PdCl_2$, 180 g/L of NH_4OH (25 %), 35 g/L of Trilon B, and 1 g/L of hydrazine hydrate. The metallization process was carried out under permanent stirring for 3–4 h at 50–60 °C. The membrane was washed with distilled water during 1 h, dried and annealed in hydrogen at 450 °C. From data presented in Fig. 1, *a* one can see that before the reductive annealing the palladium particles represent beads with a diameter of 1–3 μm, having poor adhesion with respect to each other. Thereby the membrane is permeable also with respect to other gases alongside with hydrogen. After annealing in hydrogen the palladium particles caked together to form a dense film with a thickness

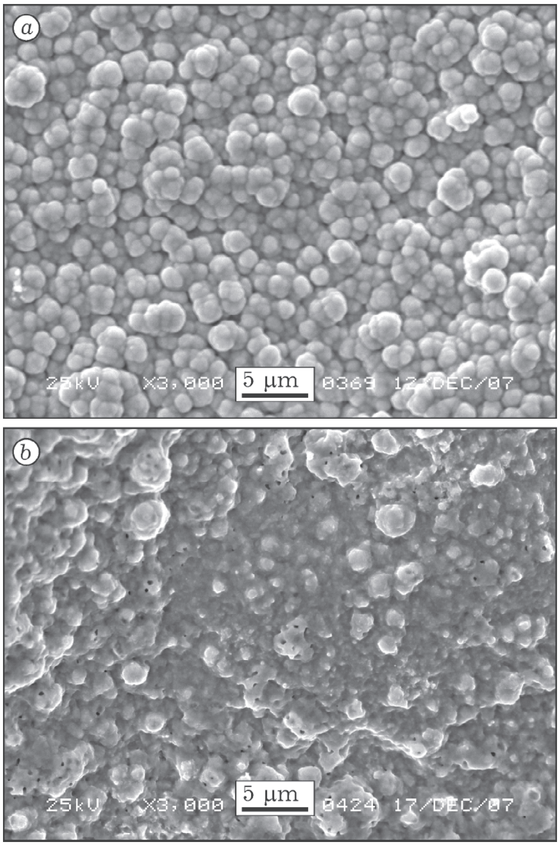

Fig. 1. Pd particles on a porous substrate of stainless steel at 450 °C before (*a*) and after (*b*) the procedure of reduction in flowing hydrogen.

of about 10 μm (see Fig. 1, *b*). This method allows applying thin (1–10 μm) palladium layers onto complex contoured membranes those are used in catalytic reactors.

At the Russian Federal Nuclear Center – the All-Russian Scientific Research Institute of Experimental Physics (RFNC-ARSRIEF) – a technology has been developed for manufacturing disk (foil) membranes by means of cold rolling the foil of palladium alloy B-1 20 μm thick with the following composition (mass %): Pd 81.51, Ag 14.9, Au 2.0, Pt 0.69, Ru 0.7, Al 0.2 [34]. The diffusion cell represents a disk frame made of stainless steel sheet with a thickness of 0.2 mm, which is welded to the membrane. The element consists of two of such discs, whose frames are interconnected to each other by means of arc welding. Membranes bear on porous plates or grids, whereas the space between the membranes is filled with a coarse grid. The gas mixture is supplied under pressure from outside of the module, whereas the hydrogen after diffusion is withdrawn from the internal cavity of the module through the exhaust pipe welded to the frame. The disc-shaped elements are connected to form the membrane module consisting of seven elements (Fig. 2).

The technology of manufacturing especially thin palladium membranes, the investigation of their technical characteristics, elucidating the mechanism of filtering hydrogen are presented in detail by the authors of [35]. For the production of the hydrogen filtering foil the authors borrowed several stages from gold leaf industrial manufacturing technology. After choosing the composition of Pd foil with 15 mass % of Ag and its chemical treatment the billet was rolled using a Quarto 125 rolling mill to obtain a thickness of 30 μm; the membranes obtained had no microcracks. As a substrate they used a metal grid made of stainless steel with a thickness of 130 μm with a mesh size of 2.0 μm in the light. The foil of the membrane was placed between two such grids, which provided the mechanical strength of the element. Measuring the filtration rate of hydrogen demonstrated that hydrogen transportation is determined to a significant extent by the rate of H_2 adsorption on the membrane rather than the H_2 diffusion through the bulk of the membrane.

Maximum filtration rate (permeability level) was achieved for a membrane with the thickness equal to 21.3 μm at 400 °C to amount to 0.1 mol $H_2/(m^2 \cdot s)$, *i. e.* 8.1 m^3 $H_2/(m^2 \cdot h)$ at a constant flow rate of purge gas (nitrogen) in the permeability zone equal to 90 cm^3/min, and

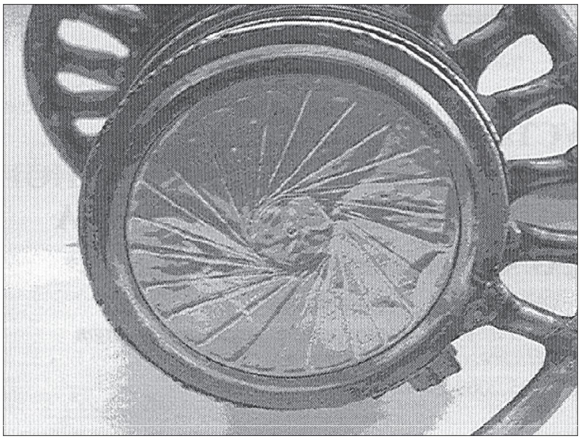

Fig. 2. Photo of the membrane module [34].

at the transmembrane H_2 partial pressure drop equal to 176.5 kPa. The authors are planning to significantly improve the extraction of hydrogen *via* reducing the thickness of the membrane foil (from 30 to 10 μm or less) and the content of precious metals therein. For example, going to ultrathin membranes with a 6-fold decrease in thickness (from 30 to 5 μm) provides a 42-fold increasing the hydrogen permeability, *i. e.* from 0.1 to 4.2 mol/($m^2 \cdot s$) [36].

The manufacturing of highly hydrogen permeable membranes of different composition with a high chemical and thermal stability, the choice of their geometric shape for the use in a catalytic reactor for producing hydrogen, great mechanical lifetime and reducing the cost of the membranes remains major problems in modern membrane technology for extracting the hydrogen from a reaction mixture.

DESIGN OF MEMBRANE REACTORS

According to the definition by IUPAC, a membrane reactor represents an apparatus wherein there processes using gas separation with the help of a membrane and chemical reactions are combined in one unit. We consider catalytic membrane reactors, wherein the catalytic function of the membrane is eliminated. This means that the fraction of reactions at the membrane is negligible as compared to the reactions in the bulk of the catalyst layer on the membrane. The target product is presented by hydrogen is withdrawn *in situ* from the reaction zone through a membrane permeability zone, and is used, for example, in a fuel cell. Other types of membrane reactors, with removing or introducing the reactants into the reaction zone are discussed in a review [37].

In catalytic membrane reactors, the membranes could be used either directly in the reactor or outside the latter. The location of the membrane is determined by the technological conditions of hydrogen production process, *i. e.*, by the type of reaction (exothermic or endothermic),by the temperature (less than 550 °C), by attaining a maximum thermal efficiency [34], by simplifying the scheme of the fuel processor [6]. In the methanol fuel processor, the membrane modules are placed directly within the reactor; both lamellar [38] and the cylindrical membranes are used [39–44]. Tubular Pd membranes with a thickness of 20 μm (2041 pcs, 2 m long, and 1 mm in diameter) were used directly within the reactor for steam methane oxidative reforming [42]. In the reforming zone there is a catalyst fluidized bed circulating at a temperature of 560 °C, H_2O/CH_4 ratio being equal to 4, the reactor pressure amounting to 2.2 MPa, with the hydrogen yield equal to 3.204 mol H_2/mol CH_4.

A hybrid adsorbent-membrane reactor (HAMR), comprising a hybrid fixed-bed catalyst with a membrane, coupled with methane steam reforming zone through a porous ceramic membrane with a CO_2 adsorbing system was investigated within the temperature and pressure range suitable for different transportation and stationary applications [5, 45]. According to the scheme of the HAMR (Fig. 3), the catalyst and adsorbent are located on the outside of the membrane, whereas additional adsorbent is located inside the membrane volume. There are different configurations of HAMR known: a) the catalyst is loaded on the reaction side, whereas the adsorbent is located in the permeability zone, and b) both the catalyst and the adsorbent are loaded on the reaction side, with no catalyst and adsorbent in the permeability zone. In the first case, the membrane separates the catalyst from the adsorbent,

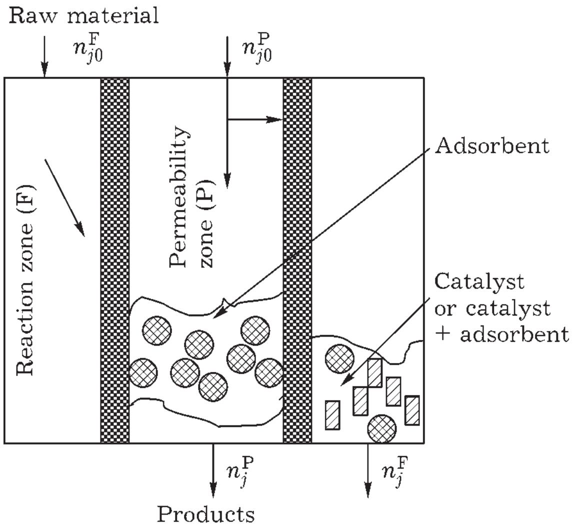

Fig. 3. Schematic diagram of an adsorbent-membrane reactor [45]: F – feed zone or reaction zone, P – permeability zone, n is the molar flow of the j-th reagent, 0 is the initial state of a reagent.

which allows permanently regenerating the adsorbent directly in the course of the process. This configuration of HAMR is advantageous as to compare with adsorptive reactors, where the continuity of the process requires the presence of many layers.

The authors of [46] proposed a membrane reactor with a fluidized bed and the two membranes such as Pd membrane for H_2 separation and a perovskite membrane for O_2 input placed in two sections due to temperature difference. In the upper section there is methane steam reforming (MSR) occurs with a water gas shift reaction (Pd membrane), whereas in the lower section there is the process of partial methane oxidation (PMO) (perovskite membrane). Testing the reactor was carried out for a low temperature MSR at a stoichiometric H_2O/CH_4 ratio. The PMO process for methanol was carried out in a membrane reformer with Pd membrane, the initial temperature being equal to 300 °C [47]. A membrane fluidized-bed catalytic reformer, wherein the MSR process was performed with heating the reactor through the wall, or the PMO process was carried out by means of entering air into the catalyst bed were tested by the authors of [48]. Hot catalyst grains were circulating from the oxidative reforming zone into the steam reforming zone in a pilot reactor with 0.13 m in diameter and 2.3 m high. The yield of the hydrogen extracted (with 99.999 % purity) was equal to 0.96 mol H_2/mol CH_4. Testing the industrial CMR with MSR was performed in order to determine an effect of different normalized flows in the reaction and permeability zones [49]. CMR advantages were demonstrated as compared to traditional MSR reactors; they are a simple process scheme, low temperature and fuel consumption at a higher level of methane conversion level.

The steam reforming of methane in a traditional reactor with a fixed-bed Ni catalyst with a simultaneous extraction of hydrogen through Pd membrane was studied by the authors of [50, 51]. The authors of [50] used a cylindrical membrane with the thickness of 2–3 μm and the area of 6.8 cm^2 on the substrate of the alumina fibre. The hydrogen permeability coefficient was equal to 9.5 $m^3/(m^2 \cdot h)$ at 528 °C. It was demonstrated that for a complete extraction of all the hydrogen formed (about 0.00048 m^3/h) at a space velocity of methane equal to $1.4 \cdot 10^6\ h^{-1}$ on the catalyst with the mass ranging from 6.5 to 404 mg, a membrane is required with the area greater than 20 cm^2. Coking the catalyst at the temperature of ~750 °C proceeded much more rapidly as compared to that at the temperature higher than at 800 °C even at $H_2O/CH_4 \approx 3.3$: the catalyst was deactivated during 5 h. Increasing the H_2O/CH_4 ratio from 2.0 to 5.0 resulted in 4-fold reducing the conversion level of methane and increasing the process selectivity level with respect to CO_2, whereas the selectivity level with respect to CO exhibited a two-fold decrease.

A tubular cylindrical Pd–Ag membrane (Ag 23 mass %) supported on a porous stainless steel was used in the MSR [51], whereby the industrial Ni–ZrO reforming catalyst was housed within a tube (outer diameter 1.6 mm, inner

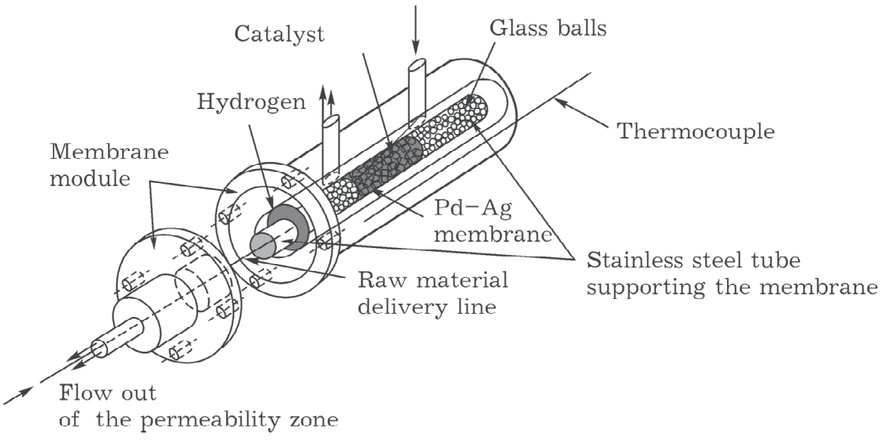

Fig. 4. Scheme Pd–Ag membrane reactor tube [51].

diameter 0.64 mm) (Fig. 4). The calculations of the membrane reactor involved the following parameters:

purge coefficient SF (sweep factor):

$$SF = N_{2g/f}/CH_{4in} \quad (1)$$

the conversion level of CH_4:

$$x_{CH_4} = [CH_{4in} - CH_{4out}/CH_{4in}] \cdot 100\ \% \quad (2)$$

where $N_{2g/f}$ is the nitrogen molar flow to hydrogen permeability zone; CH_{4in}, CH_{4out} are the molar flow rate values for methane at the inlet and outlet of the MR, respectively. The hydrogen extraction level

$$H_{2ext} = H_{2per}/H_{2r} \quad (3)$$

where H_{2per}, H_{2r} are hydrogen flows, the permeated through the membrane and produced in the SMR reaction, respectively.

The selectivity level (X) is determined as

$$X = [X_{out}/(H_{2out} + CO_{out} + CO_{2out})] \quad (4)$$

where X_{out} is the reforming product at the outlet of MR (X_{out} = H_2, CO и CO_2, respectively).

The work was devoted to the investigation of MSR at a pressure ranging within 0.3–0.9 MPa for Ni–ZrO catalyst that is characterized by a high thermal stability and a high resistance with respect to coking as compared with a conventional catalyst Ni–Al_2O_3. It was demonstrated that the higher the total pressure drop in the reactor across the membrane the more significant is the increase in the outflow of hydrogen from the permeability zone. When the partial pressure of hydrogen in the reaction zone is equal to that within the permeability zone the outflow of hydrogen exhibits ceasing. An effect of shifting the equilibrium of the MSR reaction was confirmed: in the course of extraction through the membrane one observes increasing the level of methane conversion as compared to thermodynamically determined value. The best results are obtained when the purging ratio is equal to 1.6, at the temperature equal to 450 °C and the total pressure drop between the reaction zone and the zone of permeability amounting to 0.4 MPa: the level of methane conversion under these conditions was equal to 65 % at about 80 % hydrogen extraction level. The steam reforming of methane with the use of a membrane technique to produce H_2 and a sorbent for binding and extracting CO_2 considered in detail in review [52].

The analysis of data available from the literature demonstrates that for the extraction of hydrogen from the reaction mixture the membranes are most often used in the reactors with most known steam CO reforming reaction [53–64]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -\ 41.2\ \text{kJ/mol} \quad (5)$$

As far as a membrane reactor for CO steam conversion (water gas shift membrane reactor, WGSMR) is concerned, the conversion level values for CO and H_2O therein are substantially higher than the thermodynamic equilibrium conversion level for these reagents. The preparation of ultra-pure hydrogen in the continuous mode for a fuel cell fails can be performed in a membrane reactor for the steam conversion of CO at a high pressure (5 MPa). The effluent gas from the reaction zone contains mainly CO_2 and H_2O, and *via* condensing the steam one could readily bind carbon dioxide. The membrane reactor for steam CO reforming is most efficient in an integrated process of the combined cycle of coal gasification and the gasification coal/biomass mixture (integrated gasification combined cycle, IGCC) to allow simultaneously producing hydrogen, electricity, synthesis gas, liquid fuels and chemicals. The dynamic simulation of a membrane reactor for CO steam conversion for IGCC was performed in [63], where operating conditions for achieving the level of CO conversion higher than 95 % were investigated for Pd/Cu and Pd/Au membranes under laboratory conditions. It was demonstrated that a membrane reactor is achieved by of CO steam reforming allows attaining the conversion level of CO equal to 97.6 % with H_2 extraction level equal to 63.4 %, thereby the effluent gas from the reaction zone exhibited the following composition (vol. %): CO_2 66.4, H_2 32.4, CO 1.2 thus it could be used as fuel for gas turbines.

The effect of flow configuration in the membrane reactor for the steam conversion of CO without a purge gas was investigated by the authors of [64]. It was demonstrated that a co-current flow membrane reactor for the steam conversion of CO (Fig. 5) is more efficient than a countercurrent reactor with respect to the heat characteristics, since the co-current flowing causes the temperature rise in the catalyst bed to be minimized. This favourable effect is caused by heat exchanging with a flow in the permeability zone, which flow acts as a cooling medium along the reactor length. The coun-

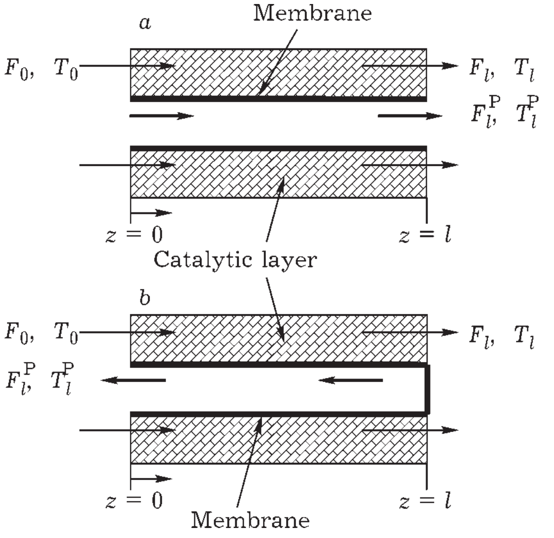

Fig. 5. Schematic diagram of a direct-flow (*a*) and counterflow (*b*) membrane reactors for the conversion of CO [64]. *F* is the molar flow rate, mol/s; *T* is the temperature, °C; *z* is the longitudinal coordinate of the reactor; *l* is the reactor length; *P* is the permeability zone parameter.

tercurrent facilitates the ignition CO conversion reaction, but this flow scheme provides increasing the temperature along the length of the reactor and there are multiple steady states occurring.

Circular membrane modules those are integrated into the reaction zone of the membrane reactor of CO steam reforming operate in the average at lower hydrogen partial pressures due to its continuous removal as compared to hydrogen pressure at the outlet from a methane steam reforming reactor [34].

Since the membrane productivity is determined by hydrogen pressure drop across the membrane, the surface area and thickness of the membrane, in this configuration the efficiency of the membranes is reduced. However, no need to supply heat to the reaction zone of the membrane reactor of CO steam conversion, compactness, comfortable temperature range for membranes and simple design cause the mentioned configuration to be the most attractive one. The hydrogen-containing gas from the reaction zone of a membrane CO steam reforming reactor together with the gas emission from the anode of the fuel cell is a fuel gas for a methane steam reforming reactor, the first reactor of the fuel processor. For this reason the optimization of a membrane CO steam reforming reactor consists in the fact that the remaining amount of hydrogen in the effluent gas could provide thermal conditions in the reactor of methane steam reforming rather than in the maximum extraction of hydrogen from the reaction zone of the CO conversion reactor.

The reaction of CO steam reforming is carried out within a medium-temperature layer (350–520 °C) of the catalyst, wherewith the number of membrane modules could be different. When the number of modules in the section is equal to 5, the contribution of the fifth module in the production of hydrogen is less than 1 %. As far as the fuel processor with the thermal efficiency equal to ~80 % is concerned, the membrane reactor design optimum with respect to hydrogen productivity should be configured as a sequence of three sections each of those consists of one catalyst layer and four membrane modules. The temperature of the synthesis gas at the inlet of the membrane reactor should be equal to 350 °C with the ratio $H_2O/CH_4 = 2$ in the methane steam reforming reactor.

The authors of [34] stated that the disc membranes allow one to coordinate easily the rate of hydrogen formation within the catalyst bed and the rate of hydrogen evolution by the membrane, whereas the fact could not be achieved in the case of cylindrical membranes, where ~20 % of total catalyst volume is efficiently used. However, this statement could not be accepted, since the in the case of correct organizing the catalyst packing the catalyst is 100 %, whereas matching the hydrogen evolution rate with the layer permeability represents quite easy task. Owing to a high reaction rate

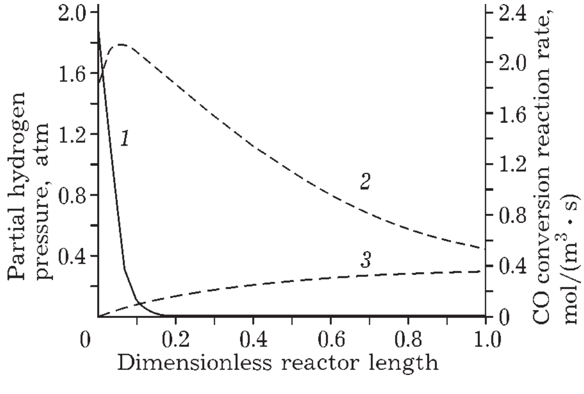

Fig. 6. Profiles of radially averaged reaction rate (*1*) and hydrogen partial pressure (*2*, *3*) along the length of a direct-flow membrane reactor for CO conversion in the reaction zone (*2*) and in the permeability zone (*3*) [32].

of CO steam conversion the main portion of hydrogen, as demonstrated by mathematical modelling [32], is evolved at the initial part (~20 %) of the total length of the reactor (Fig. 6). As far as the remaining part of the membrane reactor (~80 %) is concerned, the catalyst of the reaction zone could be replaced by an inert packing; in this case, with varying the area (length) of the membrane one could achieve an almost complete extraction of hydrogen from the reaction zone.

When using disc membranes it is important to choose the mode of emptying the permeability zone from hydrogen. In the case when there is no forced gas purging this zone, a non-optimal pressure drop across the membrane occurs in the course of hydrogen formation. With the equality of hydrogen partial pressure values within the reaction zone and the permeability zone the membrane ceases permeating the hydrogen and the membrane efficiency decreases. Another disadvantage of the used disc membranes of palladium foil consists in the thickness (20 μm): the level of hydrogen extraction in this case does not exceed 50 % (Fig. 7).

The most developed reactor design with flat membranes was demonstrated by Japanese scientists from the Mitsubishi Heavy Industries Ltd. and Tokyo Gas Co. basing on pioneering research work by the authors of [65–67]. The setup completed in Tokyo Gas Co. (2004) with hydrogen productivity equal to 40 nm^3/h [68] operated at 550 °C, at a pressure of 0.9 MPa with a ratio of H_2O (steam)/CH_4 = 3. Steam purging was used for the extraction of hydrogen from the zone of permeability up to the pressure value amounting to 0.04 MPa. The hydrogen purity was better than 99.99 %, whereas the energetic efficiency of the apparatus reached 72–76 %. The reformer had 224 membrane elements, made in the form of rectangular tubes 44 mm wide, 460 mm long and 10 mm thick. A pair of elements was combined in one reactor tube with the size of 86×226×615 mm (Fig. 8), seven of the reactor tubes were placed together into one block, whereas the whole setup consisted of 16 such blocks (Fig. 9).

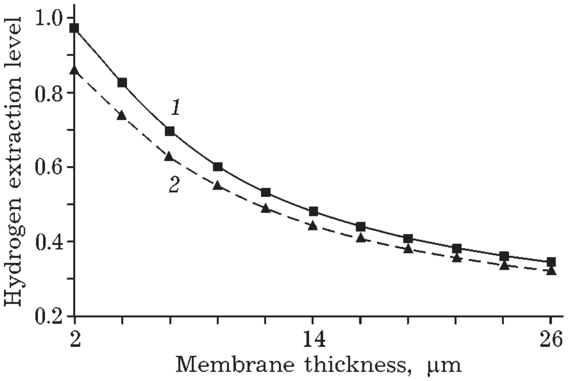

Fig. 7. Effect of the membrane thickness on hydrogen extraction level at different flow directions in the reaction zone and the permeability zone: *1* – counterflow, *2* – direct-flow [32].

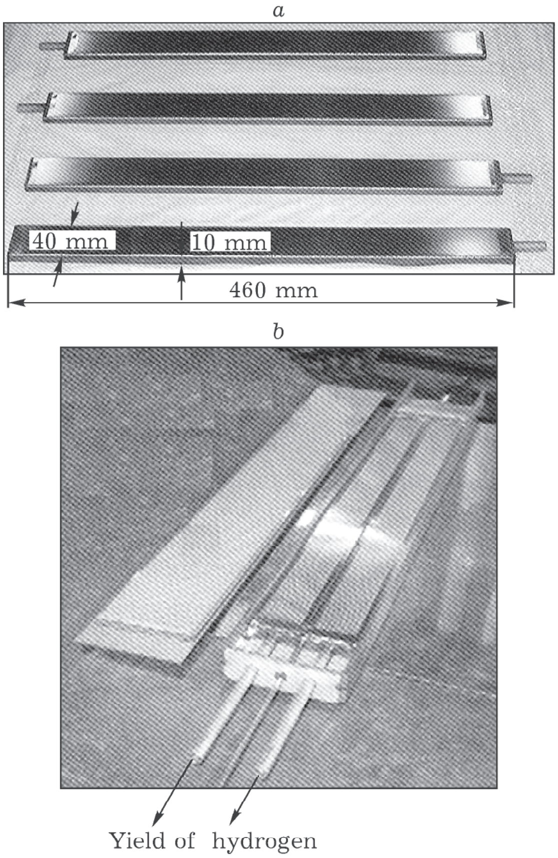

Fig. 8. Membrane elements in the shape of flattened tubes (*a*) and the block of the membrane elements (*b*) [68].

The membrane area of each element was equal to ~460 cm^2, whereas the total membrane area was approximately equal to 10.3 m^2. The membrane represented Pd alloy in the form of a foil with a thickness of less than 20 μm obtained by means of cold rolling with hot pressing in a structured substrate [66] having a corresponding protective coating or a porous layer protecting from intermetallic diffusion. The reformer with the width of 1.2 m, the thickness

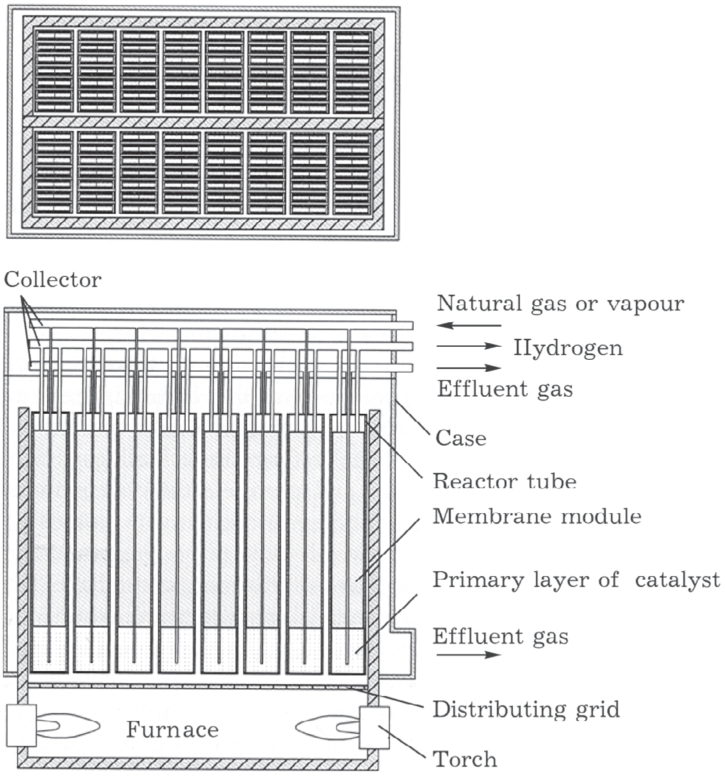

Fig. 9. Schematic diagram of the setup for obtaining hydrogen completed in Tokyo Gas Co. [68].

of 0.75 m and the height of 1.35 m (including insulation) was very compact. The installation was placed in a container with the size of 3.56×2.56×2.3 m. The container volume was by 70 % lower as compared to the traditional set for obtaining hydrogen with pressure swing adsorption. Installation worked more than 3000 h at the hydrogen filing station in Tokyo.

CONCLUSION

The types of fuels for the production of hydrogen, membrane types and the designs of membrane reactors considered demonstrate that it is promising to use them in hydrogen energy engineering. A membrane reactor generates ultrapure hydrogen; the hydrogen in a fuel cell generates electricity, whereas the fuel cell alongside with the electricity generates water, whose vapour serves as a gas for purging hydrogen from the reactor. Thus, the use of catalytic membrane reactors allows one to minimize the volume of a fuel processor with maximizing its energetic efficiency.

The price of a reactor in common increases in proportion with respect to its volume. A membrane reactor exhibits a high energetic efficiency (>80 %), a high compactness, good dynamic performance, a low fuel conversion temperature, a one-stage generation of ultra-pure hydrogen. As to compare with traditional tubular reactors with a fixed catalyst bed the reactors with integrated membrane modules have a considerably smaller volume. Since the permeability of the membrane with respect to hydrogen determines the size of a membrane reactor, whereas the fraction of hydrogen recovered is proportional to the surface of the membrane, then the transition to a super-thin (<10 μm) defect-free membrane is the main way to increase the efficiency of membrane reactors.

Significant disadvantages of the membranes are presented by relatively low operation resource (less than several thousand hours) because their mechanical strength is not high enough, as well as since the cost of the main component such as palladium is quite high. Nevertheless, recent progress in the development of ultrathin composite membranes on different media indicates the prospects of implementing the membrane technology in hydrogen energy engineering.

REFERENCES

1 Grishin V. M., Glukhin I. N., Nikitin V. A., Sokolov B. A., Starostin A. N., Cherno S. V., Shcherbakov A. N., Fofanov G. A., *Altern. Energ. i Ekol.*, 3, 59 (2008) 133.
2 Marakushev A. A., Marakushev S. A., *Altern. Energ. i Ekol.*, 1 (2008) 152.
3 Mordkovich V. Z., *Khim. i Zhizn'*, 5 (2006) 8.
4 *Khim. i Biznes*, 3, 61 (2004) 63.
5 Lukyanov B. N., Lysikov A. I., Okunev A. G., *Chem. Sustain. Dev.*, 18, 2 (2010) 115.
URL: http//www.sibran.ru/English/csde.htm
6 Lukyanov B. N., *Chem. Sustain. Dev.*, 15, 6 (2007) 625.
URL: http//www.sibran.ru/English/csde.htm
7 Lukyanov B. N., Andreev D. V., Parmon V. N., *Chem. Eng. J.*, 154, 1–3 (2009) 258.
8 Lukyanov B. N., Andreev D. V., *Khim. Prom. Segodnya*, 9 (2009) 27.
9 Dalmon J.-A. in: Handbook of Heterogeneous Catalysis, in Ertl G., Knoezinger H., Weitkamp J. (Eds.), Wiley-VCH, Weinheim, 1977, Ch. 9.3, p. 1387.
10 Dixon A. G., *Catalysis*, 14 (1999) 40.
11 Khassin A. A., Sipatrov A. G., Parmon V. N., *Membrany. Ser. Kritich. Tekhnol.*, 4, 28 (2005) 6.
12 Ahmed S., Krumpelt M., *Int. J. Hydrogen Energy*, 26 (2001) 291.
13 US Pat. No. 6713040B2, 2004.
14 Asprey S. P., Wojciechowski B. W., Peppley B. A., *Appl. Catal. A: Gen.*, 179 (1999) 51.
15 Amphlett J. C., Mann R. F., Peppley B. A., *Int. J. Hydrogen Energy*, 21, 8 (1996) 673.
16 Peppley B. A., Amphlett J. C., Keams L. M., Mann R. F., *Appl. Catal. A: Gen.*, 179 (1999) 21.
17 Peppley B. A., Amphlett J. C., Keams L. M., Mann R. F., *Appl. Catal. A: Gen.*, 179 (1999) 31.
18 Idem R. O., Bakhshi N. N., *Chem. Eng. Sci.*, 51, 14 (1996) 3697.
19 Lukyanov B. N., *Usp. Khim.*, 77, 11 (2008) 1065.
20 Fatsikostas A. N., Verykios X. E., *J. Catal.*, 225 (2004) 439.
21 Galvita V. V., Semin G. L., Belyaev V. D. Yurieva T. M., Sobyanin V. A., *Appl. Catal. A: Gen.*, 220 (2001) 123.
22 Liguras D. K., Goundani K., Verykios X. E., *J. Power Sources*, 130 (2004) 30.
23 Comas J., Laborde M., Amadeo N., *J. Power Sources*, 138 (2004) 61.
24 Polychronopoulou K., Fierro J. L. G., Efstathhiou A. M., *J. Catal.*, 228 (2004) 417.
25 Fukada S., Nakamura N., Monden J., *Int. J. Hydrogen Energy*, 29 (2004) 619.
26 Rample T., Heinzel A., Vogel B., *J. Power Sources,* 86 (2000) 536.
27 Fathi M., Holmen A., Schubert K., *Chem. Eng. J.*, 101 (2004) 93.
28 Ziok H. J., 2nd Int. Workshop on In-Situ CO_2 Removal (ISCR) (Proceedings), Stuttgart, Germany, 2005.
29 Nawaz M., Ruby J., 26th Conf. on Coal Utilization and Fuel Systems: Coal Technology Association (Proceedings), Clearwater, FL, 2001.
30 Paterson N. A., 2nd Int. Workshop on In-Situ CO_2 Removal (ISCR) (Proceedings), Stuttgart, Germany, 2005.
31 Lin S. Y., Suzuki Y., Hatano H., Harada M., *Energy Conv. Manag.*, 43 (2002) 1283.
32 Gummalla M., Vanderspurt T. H., Emerson S. She Y., Dardas Z., Olsommer B., in: Inordanic Membranes for Energy and Environmental Applications, in Bose A. C. (Ed.), Springer, New York, 2008, p. 255.
33 Tereshchenko G. F., Orekhova N. V., Ermilova M. M., *Membrany. Ser. Kritich. Tekhnol.*, 1, 33 (2007) 4.
34 Kirillov V. A., Meshcheryakov V. D., Brizitskiy O. F., Terentiev V. Ya., *Teor. Osnovy Khim. Tekhnol.*, 44, 3 (2010) 243.
35 Didenko L. P., Voronetskiy M. S., Sementsova L. A., Barelko V. V., Bykov L. A., Ivanyuk A. G., Chepelenko V. N., Brizitskiy O. F., Terentiev V. Ya., *Altern. Energ. i Ekol.*, 10 (2010) 154.
36 Hien D. T., Gielens F. C., Gardeniers J. G. E., *J. Microelectromech. Syst.*, 14, 1 (2005) 113.
37 Dittmeyer R., Caro J., in: Handbook of Heterogeneous Catalysis, in Ertl G., Knoezinger H., Weitkamp J. (Eds.), 2nd ed., Wiley-VCH, Weinheim, 2008, vol. 4, ch. 10.7, pp. 2198–2248.
38 Han J., Kim Il-soo, Choi K.-S., *J. Power Sources*, 86 (2000) 223.
39 Lattner J. R., Harold M. P., *Appl. Catal. B: Environ.*, 56 (2005) 149.
40 US Pat. No. 5938800, 1999.
41 JP Pat. No. 303842, 2004.
42 Chen Z., Yan Y., Elnashaie S. S. E., *Chem. Eng. Sci.*, 58 (2003) 4335.
43 US Pat. No. 215374, 2003.
44 US Pat. No. 6447736 B1, 2002.
45 Fayyaz B., Harale A., Park B. G., Liu P. K. T., Sahimi M., Tsotsis T. T., *Ind. Eng. Chem. Res.*, 44 (2005) 9398.
46 Patil C. S., Annaland M. van Sint, Kuipers J. A. M., *Chem. Eng. Res. Des.*, 84 (2006) 399.
47 Qi C. X., Amphlett J. C., Peppley B. A., *Appl. Catal. A: Gen.*, 302 (2006) 237.
48 Boyd T., Lim C. Y., Grace J., John A., Alaa-Eldin M., *Int. Chem. Reactor Eng.*, 3, A26 (2005) 1.
49 Gallucci F., Comite A., Capannelli G., Basile A., *Ind. Eng. Chem. Res.*, 45 (2006) 2994.
50 Kleinert A., Grubert G., Pan X., Hamel C., Seidel-Morgenstern A., Caro J., *Catal. Today*, 104 (2005) 267.
51 Basile A., Campanari S., Manzolini G., Lulianelli A., Longo T., Liguori S., De Falco M., Piemonte V., *Int. J. Hydrogen Energy*, 36 (2011) 1531.
52 Barelli L., Bidini G., Gallorini F., Servili S., *Energy*, 33 (2008) 554.
53 Basile A., Criscuoli A., Santella F., Driolli E., *Gas Separat. Purif.*, 10 (1996) 243.
54 Barbieri G., Brunette A., Granato T., Bernardo P., Drioli E., *Ind. Eng. Chem. Res.*, 44 (2005) 7676.
55 Basile A., Chiappetta G., Tosti S., Violante V., *Separat. Purif. Technol.*, 25 (2001) 549.
56 Barbieri G., Drioli E., Santell F., Violante V., Capannelli G., Vitulli G., *Gas Separat. Purif.*, 10 (1996) 53.
57 Brunette A., Barbieri G., Drioli E., *Energy Fuels*, 23 (2009) 5073.
58 Criscuoli A., Basile A., Driolli E., *Catal. Today*, 56 (2000) 53.
59 Tosti S., Basile A., Chiappetta G., Rizzello C., Violante V., *Chem. Eng. J.*, 93 (2003) 23.
60 Uemiya S., Sato N., Ando H., Kukuchi E., *Ind. Eng. Chem. Res.*, 30 (2002) 585.

61 Dolan M. D., Donelson R., Dave N. C., *Int. J. Hydrogen Energy*, 35 (2010) 10994.
62 Amelio M., Morrone P., Gallucci F., Basile A., *Energy Conversion Manage*, 48 (2007) 2680.
63 Koc R., Kazantzis N. K., Ma Y. H., *Int. J. Hydrogen Energy*, 36 (2011) 4934.
64 Adrovera M. E., Anzolaa A., Schiba S., Pederneaa M., Borio D., *Catal. Today*, 156, 3?4 (2010) 223.
65 Uemiya S., Sato N., Ando H., Matsuda T., Kukuchi E., *Appl. Catal.*, 67 (1991) 223.
66 Kukuchi E., *Catal. Today*, 56 (2000) 97.
67 Uemiya S., Sato N., Ando H., Kude Y., Asugino K., Matsuda T., Kukuchi E., *J. Membr. Sci.*, 56 (1991) 303.
68 Yasuda I., Tsuneki T., Shirasaki Y., 7th Int. Conf. on Catalysis in Membrane Reactors (ICCMR-7) (Book of Abstracts), Centraro, Italy, 2005, p.138.