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Membrane catalysis in the dehydrogenation and hydrogen production processes

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Contents

I. Introduction 352
II. Membrane catalysts for various dehydrogenation reactions 353
III. The possibility of application of membrane catalysis in the basic industrial processes for hydrogen production 359
IV. Conclusion 365

Abstract. Data on the applications of membrane catalysis in the dehydrogenation of organic compounds and hydrogen production are analyzed and generalized. It is shown that the integration of membrane reactors into existing plants is necessary for production of hydrogen of high purity. The steam reforming and oxidative reforming of methane and steam reforming of light alcohols seem to be the most promising processes for hydrogen production in membrane reactors. The bibliography includes 165 references.

I. Introduction

Some hydrogen properties such as extremely low atomic mass, high energy capacity and environmental safety of its oxidation by oxygen (giving only water) make it a promising energy carrier. Lately, this gas has been often assigned to so-called renewable energy sources.[1] However, there is no hydrogen in the pure form in nature. The main raw materials for hydrogen production are various hydrogen-containing compounds: hydrocarbons (natural gas, crude oil and so on), some synthetic products (alcohols, hydrides and so on) and water.

Metals or hydrides of metals and non-metals, which yield pure hydrogen when heated or brought in contact with water, can be considered as convenient hydrogen sources in laboratory and in movable units. Such systems typically have low efficiency but their use can neutralize one of the major drawbacks of hydrogen, namely, its low density. It is of principal importance, for example, for the use of hydrogen as a fuel for vehicles and aircrafts. The hydrogen density in some hydrides is substantially higher than in liquid H_2. Magnesium hydride,[2–4] carbon structures (fullerenes, nanotubes, *etc.*)[5–7] and some alloys[8–12] should be noted among the hydrogen carriers. These alloys are applied to manufacture cylinders that absorb large amounts of hydrogen under pressure and release it spontaneously or under weak heating; this ensures relative safety of storage and use of hydrogen.

Among the metals that react with water to give hydrogen, aluminium is particularly noteworthy. However, the reaction is hampered due to the oxide film on the aluminium surface. To activate the aluminium surface, gallium, indium, tin and several other metals are used.[13,14] They prevent the formation of the compact oxide film and weaken intergrain contacts, thus causing embrittlement of the metal and its disintegration into small crystallites.

The disadvantages of the production of hydrogen by water thermolysis at high temperatures are high energy consumption and difficulty of prevention of recombination on cooling.

There are several industrial methods for production of hydrogen each having some shortcomings. The reforming of methane and other hydrocarbons and coal gasification to give synthesis gas (the mixture of hydrogen and carbon oxides) are the most accessible and cheap methods. The reaction of methane with water is most attractive but carbon dioxide formation is accompanied by absorption of large amount of energy, while the formation of CO is slightly exothermic (Table 1). Therefore, partial oxidation of methane, which proceeds spontaneously with substantial energy release is more attractive.

The major disadvantage of the methods mentioned above is simultaneous formation of carbon oxides, which give rise to some environmental problems. In addition, if there is even a minor amount of impurities, for instance, of CO in hydrogen, problems due to irreversible catalyst poisoning occur during operation of fuel cells.[15] Depending on the method of synthesis, the volume ratio of hydrogen

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Table 1. Standard enthalpies of reactions with hydrogen evolution.

Method of synthesis	Reaction	ΔH /kJ mol^{-1}
Electrolysis, thermolysis of water	$H_2O \longrightarrow H_2 + 0.5\,O_2$	242
Methane reforming	$CH_4 + 2\,H_2O \longrightarrow 4\,H_2 + CO_2$	106
	$CH_4 + H_2O \longrightarrow 3\,H_2 + CO$	−25
Partial oxidation of methane	$CH_4 + O_2 \longrightarrow 2\,H_2 + CO_2$	−378
	$CH_4 + 0.5\,O_2 \longrightarrow 2\,H_2 + CO$	−267
Thermolysis of methane	$CH_4 \longrightarrow 2\,H_2 + C$	16

and carbon oxides can theoretically reach 2 – 4. However, 100% selectivity is not achievable, as a rule. For example, the volume ratio of H_2 and the $CO + CO_2$ mixture was found[16] to be 1.7 – 1.9 because of partial oxidation of hydrogen. Similar problems occur upon production of hydrogen from biomass, which has been lately intensively processed by fermentation (in this case, almost all carbon is released in the form of CO_2).

Despite the disadvantages mentioned above, at present, most of hydrogen is produced by steam reforming and partial oxidation of hydrocarbon raw materials, ~85% of which fall on natural gas, 7% on crude oil and 4% on coal.[17 – 19]

The carbon monoxide concentration in the obtained hydrogen can be reduced by carrying out the water-gas shift reaction followed by methanation. However, this method does not make it possible to reduce the CO concentration to the level of a few parts per million (ppm), which is required for the use of hydrogen in fuel cells. The use of membranes having high selectivity with respect to hydrogen is more effective and provides hydrogen of 99.999% purity. Even more interesting[1] is the integration of membranes into reactors, producing hydrogen, *i.e.*, the use of catalytic membrane reactors.

The present review is devoted to catalytic membrane processes with participation of hydrogen and their potential use for production of ultrapure hydrogen for various applications. These processes attract primary attention of researchers because hydrogen is expected to become a major energy source in the 21st century.

A series of reviews (for instance, see Refs 20 – 23) and a monograph[24] devoted to hydrogen production in membrane reactors were published in recent years. Nevertheless, only few papers and patents on hydrogen production in catalytic membrane reactors were published by Russian researchers.[25 – 27]

II. Membrane catalysts for various dehydrogenation reactions

1. The history of the membrane catalysis

The membrane catalysis is a relatively young and rapidly developing field of chemistry. A substantial contribution to its formation was made by Russian researchers. Less than 50 years have passed since the formulation of its basic tenets. After a period of accumulation of theoretical and experimental knowledge during the first two decades, rapid development of the membrane catalysis started at the end of the 20th century. International editions publish ever increasing numbers of books, articles and patents devoted to membrane reactors and processes involved (see, for example, reviews[28 – 40]); international conferences and symposia which pay special attention to the membrane catalysis and membrane reactors are held annually. The international conference 'Catalytic processes in membrane reactors' has been carried out every three years since 1994 under the auspices of the European Membrane Society, the tenth conference was held in St Petersburg in June, 2011.[41] Many studies reported at the Conference were about to be implemented in industry. In 2011, collective monograph[42] devoted to advances in the development and optimization of the manufacture of membranes for membrane reactors of various types and purposes was published.

The first membrane reactors were based on the unique ability of palladium and its alloys to absorb large amounts of hydrogen, which was discovered by T Graham in 1861.[43] Nearly 100 years later, Soviet physical chemists used a tubular palladium membrane in the study of the mechanism of ethylene hydrogenation.[44] However, the concept of membrane catalysis was formulated only in the 1960s.

Academician V M Gryaznov (1922 – 2001) was the first to demonstrate the benefits of combining catalytic and separation properties in a single material;[45] for his studies, he was recognized in the international scientific community as one of the founders of the science of catalysis in membrane reactors.†

In 1964, Gryaznov and co-workers discovered an effect of coupling of dehydrogenation and hydrogenation reactions on a palladium membrane. It was shown experimentally that if a compound able to give off hydrogen, for instance, cyclohexane, is fed into a palladium tube, while a compound able to absorb hydrogen, for example, *o*-xylene, is blown around the tube, then benzene may form inside the tube and toluene resulting from *o*-xylene hydrodealkylation can form outside the tube without supply of hydrogen gas.[46] The yields in both reactions were higher than the yields in these reactions carried out separately other conditions being the same. Somewhat later, a method for ethane to ethylene dehydrogenation on palladium membranes with oxidation of hydrogen withdrawn through the membranes by air oxygen was patented[47] in the USA. The yield of ethylene in this process considerably exceeded the equilibrium yield.

The discovery of such coupling marked the beginning of extensive studies of reactions with absorption and elimination of hydrogen on palladium membrane catalysts, and later oxidation reactions on silver membranes. Evolution of the membrane catalysis in Russia and abroad is shown in Table 2. A substantial part of the processes studied originally on membrane catalysts were reactions accompanied by elimination of hydrogen. This is not surprising since it is in these processes that the membrane form of catalysts is especially efficient: the degree of conversion in the target reaction often exceeds the equilibrium value and often the selectivity of formation of the target product also increases. In addition, this provides the extremely important opportunity to utilize ultrapure hydrogen that has passed through the membrane. This fact began to attract the attention of researchers because of the increasing demand of hydrogen power engineering in ultrapure hydrogen.

† This review is published in the year of the 90th anniversary of the birthday of V M Gryaznov and is dedicated to the memory of this outstanding scientist.

Table 2. Development of membrane catalysis in the 20th century.

Year	Event	Country	Ref.
1861	T Graham discovered the selective permeability of palladium to hydrogen and established that hydrogen dissolved in palladium is active in hydrogenation reactions	UK	44
1957–1958	Application of palladium membrane in the study of ethylene hydrogenation by M I Temkin and L O Appelbaum	USSR	45
1964	V M Gryaznov and co-workers discovered the phenomenon of reaction coupling on membrane catalysts	"	48
the 1970s	Studies of various hydrogenation and dehydrogenation reactions on palladium alloys by V M Gryaznov's school	"	28
1974	Launch of the pilot plant for hydrodemethylation of toluene in the membrane reactor containing 196 tubes of the Pd–Ni alloy	"	49
1979	Development of the first composite membrane catalyst for hydrogenation as a palladium alloy film supported on polydimethylsiloxane by V M Gryaznov and co-workers	"	49
1981	Launch of the pilot system for hydrogenation of dehydrolinalool in the membrane reactor with flat spirals of the Pd–Ru alloy	"	50
1985	K Otsuka and co-workers dimerized methane on silver/zirconium oxide stabilized by yttrium oxide	Japan	51
1986	H Suzuki carried out a series of dehydrogenation and hydrogenation reactions on zeolite membrane catalyst	"	52
1988	J Schmitz and H Gerke experimentally demonstrated that methane conversion in the steam reforming of methane can be increased by removal of hydrogen through membranes of palladium alloys	Germany	53
1991	A J Burgraff and J Ross carried out methanol reforming on catalytically active ceramic membrane of alumina prepared using sol–gel process	the Netherlands	54
1994	Launch of the first pilot system for steam reforming of methane using ceramic composite membrane reactor	Japan	55
1997	Launch of the pilot system for production of syngas using the techniques of ion conducting membranes	USA	56
1998	Launch of the pilot system with the membrane catalyst for hydrogenation of sunflower oil to hard fats	Russian Federation	57

At the end of the 20th century, the interest in the membrane catalysis dramatically increased, the number of publications related to this field started to grow exponentially (Fig. 1). The reason was more extensive practical application of membrane reactors related to the development of new materials, *viz*., composite asymmetric (anisotropic) polymeric and ceramic membranes, which considerably improved the efficiency of membrane catalysts. The use of thermally stable ceramic membranes extends the temperature range of their operation and makes it possible to increase the temperature of the process.

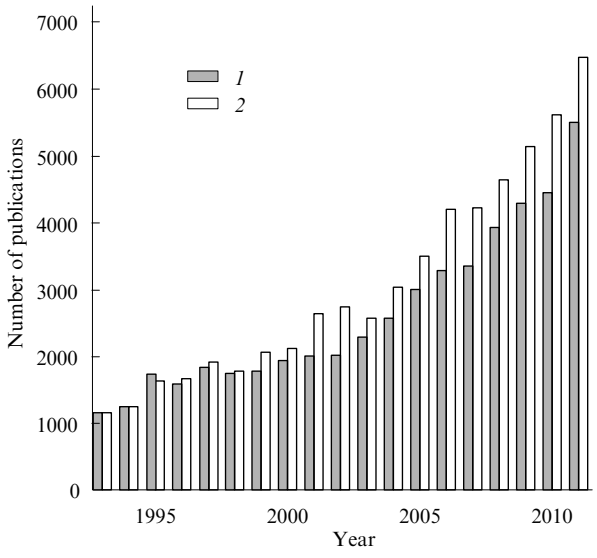


Figure 1. Change in the number of publications on the membrane catalysis from 1993 to 2011 according to internet publishing Science Direct.
(*1*) Membrane reactors, (*2*) membrane catalysts.

2. The main advantages of hydrogen-permeable membrane catalysts in reactions with the release of hydrogen

The reaction rates and selectivities in membrane catalytic systems can be increased owing to the directional transfer of reactants and energy (see below).

If the following reaction proceeds on a membrane catalyst (Fig. 2)

$$A \longrightarrow B + C$$

then selective removal of one of the products, *e.g*., product B, through the membrane catalyst will increase the conversion of A, which is restricted by thermodynamic equilibrium (Table 3). This provides a powerful tool to improve not only the rate but also the selectivity of the reaction.[48] A particular case and the most frequent example of such a process is the transfer of hydrogen from the area of its formation (B = H), which increases not only the equilibrium yield but also selectivity of the dehydrogenation.

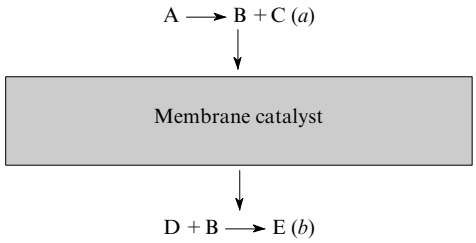


Figure 2. Diagram of the membrane catalyst selectively permeable to compound B and coupling of reactions (*a*) and (*b*) on the membrane catalyst.

Table 3. Equilibrium degrees of dehydrogenation of some hydrocarbons upon removal of formed hydrogen (the total pressure is 1 atm).

Reaction	T/K	The proportion of removed H_2		
		0	0.90	0.98
$C_2H_6 \longrightarrow C_2H_4 + H_2$	900	0.22	0.51	0.76
$C_3H_8 \longrightarrow C_3H_6 + H_2$	900	0.59	0.87	0.95
trans-But-2-ene $\longrightarrow$ $\longrightarrow$ butadiene + H_2	800	0.15	0.38	0.73
Isopentene $\longrightarrow$ isoprene + H_2	800	0.17	0.42	0.69
Ethylbenzene $\longrightarrow$ styrene + H_2	800	0.21	0.50	0.75

In turn, if reactant B for the reaction

$$D + B \longrightarrow E$$

is supplied into the reaction zone by diffusion through the membrane, this enables independent control of the surface concentrations of two reactants, B and D, and suppression of their competitive adsorption, which is unavoidable when conventional catalysts are used and which decelerates the target reaction.

An additional advantage of using membrane catalysts is the possibility to maintain the desired concentration of one reactant, such as hydrogen, along the entire length of the catalyst. As a rule, a low surface concentration of hydrogen is favourable to obtain products of incomplete hydrogenation without transformation of the starting compound into less valuable saturated products. One of the methods of controlling the surface concentration along the length of the reactor may be the change in the directions of compound flows on the opposite sides of the membrane. The hydrogen concentration increases along the membrane during dehydrogenation on the membrane catalyst, and conversely, decreases during hydrogenation. Since the driving force of hydrogen transfer through the membrane is the gradient of its concentration across the membrane, hydrogen transfer velocity for the same or opposite flow directions of the compound to be dehydrogenated and the hydrogen-removing gas on the other side of the membrane changes, and different hydrogen concentration profiles are formed along the membrane surface. This, in turn, affects the rates of dehydrogenation and hydrogenation reactions. Particularly, it was shown in some experimental studies [58, 59] that the counter-current supply of hydrogen and the compound to be hydrogenated on different sides of the membrane can increase the yields of intermediate hydrogenation products because the hydrogen concentration is maximum at the inlet of the hydrogenation zone where the starting compound is accumulated and undesired hydrogenation of the target product is unlikely. At the outlet of the hydrogenation zone, the hydrogen concentration is minimum and, hence, it can be insufficient for exhaustive hydrogenation to give the undesired saturated product. In the processes with hydrogen release such as water-gas shift where hydrogen is removed by an inert gas,[60] larger amounts of hydrogen can be recovered from the reaction zone in the counter-current mode than in the co-current mode.

If a compound penetrating through the membrane is formed on one of its surfaces and consumed at the other surface, the reaction coupling takes place. In this case, using the membrane catalyst, two processes can be simultaneously carried out in the same reactor with high efficiency without mixing of reactants or products.[48] Other advantages of the reaction coupling in membrane reactors are discussed below.

3. Dehydrogenation on compact palladium-based membranes

A great number of reactions with participation of hydrogen were studied during almost a half-century history of research in the field of membrane catalysis. The advantages of membrane catalysis are most evident for reactions whose rate is restricted by thermodynamic equilibrium, particularly, for the hydrocarbon dehydrogenation reactions.

Initially, such reactions were carried out on so-called compact (non-porous) membranes, which are palladium foils or tubes with 50 to 100 μm thick walls. The conditions of some processes promising for industrial applications that were implemented on such membranes are summarized in Table 4.

Dehydrogenation of cyclohexane to benzene was the subject of numerous studies.[61, 64] The use of this reaction as a model is due to relative low temperatures at which it occurs on metal catalysts and, therefore, to the lack of undesired side processes resulting in catalyst carbonization and deactivation. Even at 473 K, the removal of hydrogen through membranes made of palladium alloys made it possible to increase the conversion of cyclohexane from 18.7% (under equilibrium conditions) to 99.5%.[61]

In the isopentane dehydrogenation on a membrane made of Pd alloy with 10% Ni (Pd–10Ni) in the form of a tube with isopentane fed inside and an inert gas supplied outside, the yields of isoprene and isopentenes at 860 K were 18.6% and 10.5%, respectively.[62]

The major advantages of compact membrane catalysts for dehydrogenation based on palladium alloys are nearly 100% selectivity of hydrogen transfer and high catalytic activity in reactions involving hydrogen. In addition, such membranes are commercially available (foils and tubes of many palladium alloys are manufactured both in Russia and abroad). Designs of membrane reactors suitable for diffusion purification of hydrogen and for membrane catalysis (see review[25] for details) have been developed and tested.

The obvious disadvantages of the compact membrane catalysts are high cost of palladium and the necessity to use relatively high temperature to ensure the required efficiency of hydrogen removal from the dehydrogenation zone. In addition, since the hydrogen flux through the membrane is

Table 4. Temperatures of dehydrogenation reactions carried out on membrane catalysts of palladium alloys.

Reaction	Catalyst	T/K	Ref.
Dehydrogenation of cyclohexane to cyclohexene	Pd–23Ag	398	61
Dehydrogenation of isopentane and isopentenes to isoprene [a]	Pd–10Ni, Pd–10Rh, Pd–10Ru	743–870	62
Dehydrogenation of n-butane to but-1-ene and isobutane to isobutene	Pd–25Ag	603	63
Dehydrogenation of cyclohexane to benzene	Pd–(4.5–7)Ru	623	64
Steam reforming of methanol	Pd–23Ag, tube	500–600	65
Dehydrogenation of cyclohexane-1,2-diol to catechol	Pd–(7; 15)Rh; Pd–(37; 39; 42)Cu, foil	503–773	66
Aromatization of propane	Pd	823	67
Photolysis of water	Pd, TiO_2-coated	800	68
Dehydrogenation of cyclohexanol to cyclohexanone	Pd–Ru	623–723	69
Dehydrogenation of cyclohexane	amorphous Pd–(15; 17.5; 20)Si	423–498	70
Dehydrogenation of isopropyl alcohol	Pd–10 Ru, foil	495	71

[a] In pilot systems.

inversely proportional to its thickness for the same driving force, in accordance with the Fick law, it is desirable to use the membranes as thin as possible, but the thickness of the compact membranes acceptable in terms of mechanical strength is no less than 25–30 μm.

Practical applications of catalytic membrane processes required development of membranes in which a thin continuous layer of a palladium alloy is deposited by a strong support that is highly permeable to hydrogen. Such membrane catalysts were developed and called composite ones.

4. Composite membrane catalysts for dehydrogenation

The composite membranes consist of two or more layers differing by their structure or chemical composition. One of the layers acts as a mechanically strong, but gas-permeable substrate. It can be a porous plate or tube of a metal or thermally stable and corrosion-resistant oxide. This macroporous material is coated by a thin film of a catalyst, most often a palladium alloy. As a rule, it is this layer that ensures selective permeability to hydrogen and the catalytic activity. In some instances, the substrate can be non-porous, but highly permeable to some compound, most often, for hydrogen in the reactions under consideration. It is also possible to use substrates of organic polymers; however, these materials have usually low thermal stability, therefore, their use is limited to low-temperature reactions, which is unacceptable for dehydrogenation processes requiring relatively high temperatures.

To obtain a defect-free film of the active metal and suppress the mutual diffusion of the substrate and the catalyst, a very thin intermediate layer of heat-resistant material is often inserted between the substrate and the active layer. Since the compactness and small thickness of the active layer are the key factors of high selectivity and efficiency of the composite membranes, the methods for its deposition are the subjects of numerous studies and are being constantly improved (see, for instance, monograph [42]). It was suggested to use vacuum deposition, electrical and chemical deposition, chemical vapour deposition (CVD), magnetron and plasma sputtering for the application of the active layer.

In the best composite membranes, the thickness of the compact layer of the palladium alloy can be no more than 200 nm. These membranes exhibit all the advantages of the compact membrane catalyst, including selective permeability and catalytic activity, but the hydrogen flux through unit surface is much greater and the amount of the expensive metal per unit volume of the composite is much lower than those in compact membrane catalysts in the form of foil or tubes.

The composite membranes can also comprise two or more layers of various compact metals. A thick layer of relatively inexpensive metals, highly permeamble for hydrogen, such as vanadium, niobium, tantalum or titanium, is coated by barrier layers to prevent mutual diffusion of the metals of different layers, and then by thin layers of chemically stable metal or a hydrogen-permeable alloy. The maximum hydrogen flux is obtained for vanadium membranes ($Pd/SiO_2/V$) coated by layers of silicon dioxide (the barrier layer) and palladium.[72, 73] The palladium layer in these membranes has a number of functions, including catalytic action and the increase in selectivity of hydrogen transport. The surface of the transition metals serving as a substrate in these membranes is easily oxidized, the oxidation resulting in fast loss of permeability. The compact palladium coating protects the transition metals against oxidation.

An interesting version of the composite membrane with a porous ceramic tube as a support for palladium–silver alloy was reported.[74] The porous ceramic tube was placed into a thin-walled tube (50–70 μm) made of the Pd–Ag alloy, the minimum clearance between the tubes being 20–40 μm. Such a clearance is required for easy insertion and removal of the ceramic tube and also to prevent any stresses occurring upon direct contact of the tubes. This composite exhibited the selectivity to hydrogen relative to nitrogen (α_{H_2/N_2}) of more than 5000 and also high chemical and mechanical stability during long-term continuous operation. Composite metal–ceramic membranes produced by chemical deposition or sputtering turned out to be much less durable.

The shortcomings of the composite membrane catalysts include the complexity of their preparation and their shorter operation life compared to compact membranes. This is due to both differences in thermomechanical and chemical properties of the constituents and higher propensity of a thin palladium layer to mechanical damage. Nonetheless, catalytic properties of these membranes are under vigorous research. Some examples of studied processes are collected in Table 5.

Table 5. Operating temperatures of composite membrane catalysts containing metals in some reactions.

Reaction	Catalyst	T/K	Ref.
Dehydrogenation and hydrogenation of cyclohexene	a Pd – Ni tube, coated by a thin layer of gold	473 – 573	75
Dehydrogenation of cyclohexane	a tube of porous glass impregnated with platinum	480	76
Oxidation of CO to CO_2	anodic Al_2O_3 with the platinum layer	465	77
Dehydrogenation of ethane	the same	473	77
Water gas shift	a tube of porous glass coated by the palladium layer and Fe – Cr oxide catalyst	673	78
Dehydrogenation of cyclohexane	a tube of Vycor porous glass impregnated with palladium	288 – 345	79
Dehydrogenation of methanol to formaldehyde	porous Al_2O_3 coated by palladium and containing phosphorus and copper in the pores	550	80

The design of laboratory and pilot membrane reactors with composite membranes practically does not differ from the design of reactors with compact membranes. For instance, catalytic membrane units for removal of oxygen dissolved in water by hydrogenation on palladium-containing polypropylene fibres[81] are similar to multitubular membrane reactors containing compact tubes of palladium alloys.[38]

5. The catalyst – membrane systems

One and the same material rarely features both selective permeability and catalytic activity. The simplest way to carry out a catalytic reaction with introduction or removal of the reaction participants consists in separation of membrane and catalyst functions by placing, for instance, a conventional bulk catalyst into a reactor with a catalytically inert membrane (possessing no catalytic properties or poor catalytic properties for the particular reaction). This almost infinitely expands the choice of suitable membranes and active catalysts, which moreover possess larger specific surface areas as compared with compact membranes. However, some advantages of compact membrane catalysts are lost in this case, particularly, durability of the system, which becomes determined by the properties of the bulk catalyst. The kinetics of the process changes because the number of its elementary steps increases. For instance, hydrogen formed upon dehydrogenation on the surface of the bulk catalyst approaches the membrane surface from the gas phase in molecular rather than in atomic form, and the additional steps of adsorption and dissociation are required for its diffusion. At the same time, the thermodynamic and energetic advantages of the membrane catalysis are preserved. Some dehydrogenation processes studied in the catalyst – palladium-containing membrane systems are listed in Table 6.

The catalyst – palladium-containing membrane systems are most attractive for researchers because there are ample opportunities to vary membranes and catalysts. The reactors of this type are called fixed bed membrane reactors. The catalyst bed can be brought into a fluidized state, which affords a number of advantages to the process (see review [94]).

In recent years, carbon materials have acquired ever greater importance for membrane catalysis and gas separation. They are characterized by high selectivity, permeability, hydrophobicity, corrosion resistance and significant thermal stability. Many types of carbon membranes are produced by carbonization of various classes of polymeric materials in the form of hollow fibres or thin films on a porous material.[95] Separating properties of these membranes depend on their microstructure and are controlled by the conditions of thermal treatment and chemical modification of the precursors; it is possible to manufacture both mesoporous and carbon molecular sieve membranes,[96] whose separating properties are determined by the effective diameter of molecules in the mixture. Carbon is widely used as the substrate for heterogeneous catalysts, therefore, such application of carbon membrane materials is not surprising.[97 – 99]

Table 6. Operating temperatures of the catalyst – metal-containing membrane systems in some reactions.

Reaction	Membrane	Catalyst	T/K	Ref.
Steam reforming of methane	Pd – 23Ag, tubes	Ni	723	82
Dehydrogenation of borneol to camphor	Pd – 5.9Ni, Pd – 10Ru, Pd – 10Rh, foils	Cu, wire	520	83
Dehydrogenation of butane to butadiene	Pd – 9.8Ru	$Cr_2O_3 – Al_2O_3$	723 – 823	84
Dehydrogenation of cyclohexane to benzene	Pd, tube	Pt/Al_2O_3	473	85
Dehydrocyclization of alkanes	Pd – Ag, foil	zeolite ZSM	723 – 823	86
Steam reforming of methane [a]	Pd, foil or tubes	Ni (spherical)	1123	87, 88
Methane reforming	Pd, tube	Pt/Sn, Rh or Ni	400	89
Steam reforming of methane	a palladium layer on the Vycor glass tube	Ni	350 – 500	90
Dehydrogenation of methylcyclohexane to toluene	Pd – 23Ag, tube	sulfided platimun	573 – 673	91
Dehydrogenation of ethane to ethene	Pd – 23Ag, tube	Pd/Al_2O_3	660	92
Dehydrogenation of methanol to methyl formate	a tube of Pd – Ru	Cu	433 – 513	93

[a] In pilot units.

6. The coupling of reactions in the membrane reactors

As noted above, coupling of reactions enables one to carry out two different processes in a single reactor divided by a membrane catalyst without separation of the reaction products or isolation of the products of each reaction (see Fig. 2). In addition, the reactant diffusing through the membrane approaches the catalyst surface in the most reactive (atomic) form, resulting in the increase in the rate of hydrogenation. If the reactions are coupled, both kinetic and thermodynamic effects of the use of membrane catalysts are manifested; in addition, high thermal conductivity of metallic membranes opens up the possibility of energy coupling, *i.e.*, the heat of the exothermic reaction can be used for the endothermic reaction.

Almost all known examples of coupled reactions in membrane reactors are related to catalyst – membrane systems (Table 7). For instance, coupling of butane dehydrogenation on commercially available chrome – alumina catalyst and hydrogen oxidation on membranes of palladium binary alloys increased the butane conversion and selectivity of dehydrogenation to butadiene.[84] In the simultaneous synthesis of styrene and cyclohexane in the integrated membrane reactor, styrene yield increased to 87%, which exceeds the equilibrium value.[106]

The coupled reactions in the membrane reactors can be additionally controlled by changing the directions of reactant supply into different reactor compartments (see Section 2). For example, the counter-current mode was much more efficient than the co-current mode in the case of coupling of borneol dehydrogenation to camphor on the copper catalyst with hydrogenation of cyclopentadiene on the membrane catalyst of palladium – ruthenium foil.[58] The selectivity of formation of cyclopentene, resulting from partial hydrogenation, especially increased. Similar results were also obtained for the coupling of dehydrogenation of cyclohexane with hydrogenation of penta-1,3-diene.[105]

Even more impressive effect was found for the coupling of dehydrogenation of ethylbenzene and hydrogenation of benzene when co-current and counter-current modes were compared.[107] The maximum yield of styrene was achieved with the use of the counter-current mode, the flow velocity in the hydrogenation chamber was more than two orders of magnitude lower than the velocity that would have to be created without coupling of reactions to achieve the same degree of hydrogen recovery from the dehydrogenation zone.

7. Membrane microreactors

In the last decade, a new type of chemical reactors has gained acceptance, those are microchannel chemical reactors. This type of reactor, figuratively called 'lab on a chip', has already been successfully used to solve some problems in biochemistry, biomedicine, analytical chemistry and catalysis. The term 'microreactor' means in this case a reactor fabricated by the methods used in the electronic technology for manufacturing silicon microdevices rather than a conventional tubular reactor for testing catalysts. The reactants are introduced into the reactor *via* microchannels in silicon plates that are similar to microchips in electronics. The inner surface of these channels is coated by a catalytically active material, while the heat exchangers are embedded into the microreactor by photolithography, electrochemical deposition and casting (for more details about the structure of the microreactors, see Ref. 108). Such reactors have a size of the order of tens of millimetres and a very high ratio of the active surface to the volume. Their small size minimizes the risk of damage during storage and handling. High rates of heat and mass transfer ensure proceeding of reactions under more homogeneous conditions and with higher yields than in conventional reactors. Appreciably less amounts of catalyst and reactants are needed to carry out any process in microreactors than in a conventional system. They can withstand more severe reaction conditions without the risk of a sharp rise in temperature or explosions.

These advantages of the microreactors attract much attention of researchers. A great number of studies devoted to catalytic reactions in such vessels have been published. The most important of them are discussed in reviews.[109 – 112] We will only dwell on the studies in which membrane microreactors were used for reactions with elimination of hydrogen.

The membrane microreactor usually consists of three parts, those are the reaction chamber, separation membrane and the reactor cap (body), which are tightly connected to each other to create the microreactor. The general design of microreactors can vary depending on the reaction catalyst type.

In the microreactor for dehydrogenation of cyclohexane to benzene, 12 reactor chips were arranged on a single silicon wafer.[113] The reactor was 20 mm long, 14 mm wide and 3 mm high. 80 microchannels were etched in the reaction chamber, each was 50 μm wide, 400 μm deep and 8 mm long. The catalyst was a platinum bed of 20 nm

Table 7. Operating temperatures of membrane catalysts in reaction coupling.

Reaction coupling	Catalyst	T/K	Ref.
Dehydrogenation of cyclohexane and hydrodemethylation of *o*-xylene	Pd, tube	703	46
Dehydrogenation of *trans*-but-2-ene and hydrodemethylation of toluene	Pd, Pd – 20Ag, tubes	653 – 713	45
Dehydrogenation of isopentenes and hydrodemethylation of toluene or air oxidation of hydrogen	Pd – 5.9Ni, tube	723	100
Dehydrogenation of isopropanol and hydrogenation of cyclopentadiene	Pd – 10Ru, foil	493	101
Dehydrogenation of borneol and hydrogenation of cyclopentadiene	Pd – 5.9Ni; Pd – 10Ru; Pd – 15Rh, foil	473 – 543	102
Dehydrogenation of butane and air oxidation of hydrogen	Pd – 9.8Ru; Pd – 5.5Sn; Pd – 23Ag, foil	753 – 823	103
Dehydrogenation of cyclohexanol to cyclohexanone and hydrogenation of phenol	Pd – 9.8Ru, foil	500 – 550	104
Dehydrogenation of cyclohexane and hydrogenation of penta-1,3-diene	Pd – 6Ru, foil	490	105
Dehydrocyclization of undecane and hydrodemethylation of dimethylnaphthalene	Pd – 5.9Ni, tube	860	106

thickness deposited on the titanium oxide substrate. The 4 μm thick palladium foil of 8 mm length and 6 mm width served as the membrane. The real area of the membrane was 80 times larger due to the foil corrugation. The reactor cap with inlet and outlet tubes was fabricated of polydimethylsiloxane. The three parts of the reactor were hermetically combined using polyimide. The experiments with use of this reactor showed that the cyclohexane conversion to benzene was 18.9% at 573 K,[113] which is close to the equilibrium value.

A membrane microreactor for conversion of water gas with the removal of forming hydrogen was reported.[114] Its membrane had four layers, *viz*., copper, aluminium, spin-on-glass and palladium layers. To create a structured substrate for the palladium film, channels of a special pattern were etched in the copper and aluminium layers and in the spin-on-glass layer. Copper was used as the catalyst of oxidation of CO formed in a preceding microreactor upon methanol reforming. Hydrogen was removed through the membrane. This microreactor was a hybrid system combining the reactor for water-gas shift reaction and hydrogen separator.

Another membrane microreactor used for oxidation of carbon monoxide to dioxide,[115] represented a combination of etched silicon and a palladium layer of thickness of 700 nm as a membrane catalyst.

A promising version of a membrane microreactor was suggested by Kiwi-Minsker *et al.*[116] The reaction zone was structured by a bundle of thin (7 μm in diameter) parallel fibres of stainless steel coated by a catalyst and placed into conventional tubular reactor (Fig. 3). A laminar flow of reactants was formed in the microchannels among fibres. A palladium – silver membrane divided the reactor into two concentric zones, a bundle of fibres was introduced into each of them. Dehydrogenation of propane with the removal of hydrogen through the membrane occurred in one zone. Simultaneously in the second zone, the diffusing hydrogen was oxidized by air oxygen with generation of heat necessary to maintain the endothermic reaction in the first zone. The propane and air flows were redirected at some intervals from one zone to another to regenerate deactivated catalyst by burning carbon deposits on its surface in the hydrogen oxidation zone, thus ensuring continuous production of propene. The propane conversion in this type of reaction coupling was ~10% at 823 K, whereas the selectivity with respect to propene was 97%.

To obtain syngas from methanol, a microreactor consisting of 21 units was devised.[117] Each of these units represented stainless steel frame containing a carbon molecular sieve membrane with embedded fine-dispersed nickel catalyst. The space between two units was 100 to 1400 μm and was sealed by thermally stable square stainless steel gaskets (3 × 3 cm) of 500 μm thickness. Flat monolithic stainless steel plates between which the assembly was squeezed had branch pipes for introduction of reactants and removal of products. The overall volume of the reactor was only 0.45 cm^3. The vapour-phase decomposition of methanol was carried out at temperatures from 453 to 653 K. The conversion of methanol at 553 K in the reactor with 21 units was 91%, the yield of hydrogen was 1.48 moles per mole of CH_3OH. The conversion increased with the increasing number of units used in the microreactor and with the decrease of the size of microchannels at a constant volume ratio of H_2 and CO equal to 2.

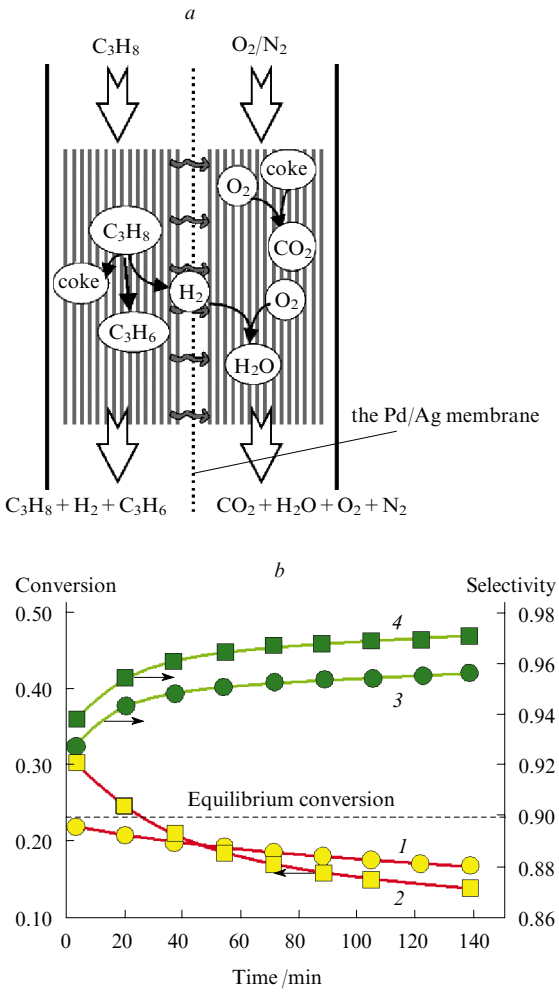


Figure 3. Diagram of two-zone microstructured membrane reactor (*a*) and dependences of propane to propene conversion (*1*, *2*) and selectivity to propene (*3*, *4*) in microstructured reactor without a membrane (*1*, *3*) and with a membrane (*2*, *4*) at 823 K and 0.14 MPa (*b*).[116]

Thus, the available data of the laboratory studies show that the use of membrane catalytic systems for production of hydrogen can not only solve the problem of purification of hydrogen from undesirable impurities but also improve the performance and simplify the processes due to avoidance of some steps of product separation.

III. The possibility of application of membrane catalysis in the basic industrial processes for hydrogen production

1. Dehydrogenation of alkanes and alkenes

During the last decade, experimental and theoretical studies were carried out to elucidate the possibility of integrating membranes into catalytic hydrogen production processes; a series of pilot membrane catalytic units for the production of ultrapure hydrogen were designed. We will consider some of the areas of these works.

Catalytic dehydrogenation of low-molecular alkanes like ethane, propane, isobutane to the corresponding alkenes is used more and more often in petrochemical industry along with traditional cracking processes. The

reactions are catalyzed by alumina-supported chromium oxide or platinum with various promoters increasing the selectivity of the processes and protecting the catalysts against deactivation caused by carbon deposition. The maximum conversion of the starting reactant in the catalytic dehydrogenation of alkanes, as in other dehydrogenation processes, is limited by the thermodynamic equilibrium; also there are additional problems related to high endothermicity of reactions (permanent heat input is required), side reactions of cracking, isomerization and further dehydrogenation to dienes and also carbonization (coking) of catalysts at high temperatures (it is necessary to stop dehydrogenation in fixed-bed reactors every 20–30 min and carry out oxidative regeneration).

Many of the listed problems can be solved by using membranes selectively permeable to hydrogen in the catalytic dehydrogenation reactors: by removing hydrogen from the reaction zone, it is possible to increase the conversion of the starting paraffin at a given temperature or lower the temperature of reaching the required degree of conversion. Lowering the temperature results not only in energy saving but also in the decrease in the reactant loss in side reactions and coking; therefore, deactivation of the catalysts is decelerated and the interval between regenerations increases. In addition to the target alkenes, the process yields pure hydrogen.

The composite membranes based on porous ceramics with a thin layer (of the order of micrometres) of a palladium alloy seem most attractive for application in hydrocarbon dehydrogenation processes in terms of selectivity and purity of hydrogen produced. Their major shortcoming is the above-mentioned (see Section II.4) low mechanical strength of the thin metal layer, due to which flow-through defects are often formed and the selectivity of the membranes to the hydrogen transfer gets lost. In addition, due to the adsorption of dehydrogenation products (alkenes, dienes) and their further transformations on the surface of the palladium alloy, irreversibly adsorbed products are formed, resulting in a decrease (or even the loss) of membrane permeability to hydrogen.

The asymmetric ceramic membranes are more stable and chemically inert but less selective ($\alpha_{H_2/N_2} = 100-500$) under the dehydrogenation conditions; they are produced by depositing thin layers of silicon or titanium oxides on a macroporous oxide substrate. In the reactor with a membrane with a moderate selectivity to hydrogen ($\alpha_{H_2/C_3P_8} = 70-100$), which was obtained by CVD of a selective silica layer, the propane conversion at 773 K was almost two times higher than in a conventional reactor.[118]

When a composite membrane with a 9 μm-thick Pd–Ag alloy layer deposited on an α-Al_2O_3 tube was inserted into the reactor for isobutene dehydrogenation on the chrome–alumina catalyst,[98] the alkane conversion substantially increased not only in comparison with the conversion in a conventional reactor, but also with its equilibrium value (Fig. 4).

It seems obvious at first glance that the effectiveness of the membrane catalytic systems for alkane dehydrogenation is determined (all other things being equal) by the selectivity and efficiency of the membrane, which removes hydrogen. However it was shown [119] that in spite of 40% withdrawal of hydrogen formed at 830–873 K in the fixed bed membrane reactor containing the chrome–alumina catalyst and an asymmetric membrane selectively permeable to hydrogen

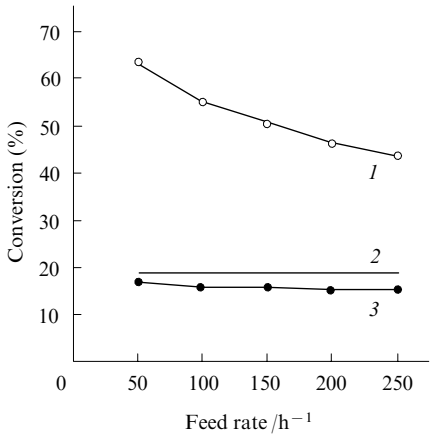


Figure 4. Isobutane conversion *vs.* isobutane feed rate (per mass unit of the catalyst) to the reactor with the composite Pd–Ag/α-Al_2O_3 membrane (*1*), according to equilibrium data (*2*) and in the conventional reactor (*3*) at 723 K.[98]

made of silica-coated alumina, ethane conversion in the ethane dehydrogenation process increased insignificantly. Assuming that the beneficial effect of the removal of hydrogen from the dehydrogenation zone was not manifested due to the low reaction rate on the catalyst surface, it was concluded that for introducing this membrane process in industry, it is necessary to revise the general approach to the improvement of membranes based on the increase in the hydrogen flux through them. It was even suggested that the use of membranes selectively permeable to ethylene rather than to hydrogen would be more useful for dehydrogenation of ethane to ethylene. However, a progress in this direction can hardly be expected in the nearest future because the membrane separation of ethylene from ethane represents a much more difficult problem.

In an earlier study,[120] dehydrogenation of propane in a conventional fixed bed reactor with the Cr_2O_3/Al_2O_3 or $Pt-Sn/Al_2O_3$ catalysts was compared with the same process in the membrane reactor with silica membrane selectively permeable to hydrogen. The increase in the yield of propene at 808 K in the membrane reactor was no more than 5%. Both catalysts became deactivated in the membrane reactor faster than in conventional one. It was concluded that the bulk catalysts should be specially selected for membrane reactors based on their resistance to coking. The ratio of the rates of the target reaction on the bulk catalyst and the removal of hydrogen trough a membrane is also important as too fast removal of hydrogen from the catalyst surface results in intensification of formation of high density products. This effect had been studied quite a long time ago taking reactions of dehydrogenation of butenes on the Pd–Ag membrane catalyst [121] and isopentenes on the compact Pd–Ni membrane catalyst [122] as examples. It was found that there is an optimal concentration of hydrogen in the dehydrogenation zone below which the yield of dehydrogenation products sharply decreases.

To obtain the optimal concentration of hydrogen in membrane fixed bed reactors, available tools are the variation of the velocity of the sweep gas in the permeate zone and the choice of either counter-current or co-current mode in the reactor.

2. Dehydrogenation of cyclohexane and methylcyclohexane

Dehydrogenation of cyclohexane is a convenient model catalytic process which occurs at realtivelly low temperatures and practically without formation of side products. Cyclohexane and methylcyclohexane are characterized by high hydrogen content (7.19 mass % and 6.16 mass %, respectively). As in other hydrocarbon dehydrogenation processes, their conversion to the corresponding aromatic hydrocarbons is limited by the thermodynamic equilibrium, and to achieve the most complete elimination of hydrogen from these naphthenes, the equilibrium has to be shifted by using, for instance, membranes selectively permeable to hydrogen. The membrane catalysts in the form of tubes or foil of palladium (or its alloys) exhibit high efficiency in the cyclohexane dehydrogenation process,[61,64] and a 100% conversion was reached[123] under conditions where the equilibrium conversion was only ~18%. It was also demonstrated that the degree of removal of hydrogen from the dehydrogenation zone can be raised by increasing the sweep gas flow rate or by coupling dehydrogenation and hydrogenation reactions.[105] In the latter case, some heat of hydrogenation was successfully used for dehydrogenation of cyclohexane.

The conversion of cyclohexane in the dehydrogenation process carried out at 468 K in a 'tube-in-tube' flow-type membrane (Pt/Al_2O_3) reactor enclosing a bundle of hollow carbon fibres through which the formed hydrogen was selectively removed[97] was 36%; this value appreciably exceeds the equilibrium conversion of cyclohexane under these conditions (Fig. 5). Cyclohexane was considered[124] as a promising material for hydrogen storage; its disadvantage, however, is a relatively high melting point (280.5 K) limiting its application in the regions with cold climate. To reduce this temperature, it was proposed to add methylcyclohexane freezing at 146.4 K to cyclohexane. Addition of only 25 mol.% of methylcyclohexane results in lowering of the mixture melting point to 223 K. It was shown for dehydrogenation of mixtures of cyclohexane and methylcyclohexane in a flow reactor with the 0.5% Pt/Al_2O_3 catalyst and a tubular palladium membrane that the conversion of each of the components is independent of the presence of the other component and the hydrogen flux through the membrane is the same for pure cyclohexane and for mixtures containing 20% and 50% of methylcyclohexane.

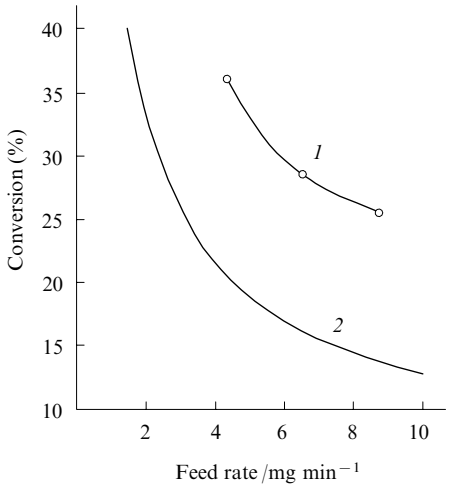


Figure 5. Cyclohexane conversion *vs.* feed rate to the membrane reactor with carbon membranes (*1*) and at equilibrium (*2*).[97]

Thus, despite a few examples demonstrating substantial increase in the conversion of hydrocarbons if dehydrogenation is carried out in the membrane reactors, the use of these reactors in industrial processes is possible only after solving such issues as cheapening of the most successful palladium membranes, the choice of the suitable flow pattern on opposite sides of the membrane and optimal arrangement of the catalyst in the reactor.

The transition to oxidative dehydrogenation in membrane reactors may be efficient to enhance the conversion of alkanes and to increase the heat supply to the endothermic dehydrogenation process. This method of producing hydrogen has remained undemanded for a long time, but in recent years it has been under active study at the Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences.[16] The features of partial oxidation of methane by oxygen in a laboratory tubular lantanum ferrite–strontium reactor were investigated. Long-term tests showed stable performance of the system for more than 7000 hours at the level of methane conversion of at least 98.8% and a selectivity of at least 90%.

3. Steam reforming of alcohols

Methanol and ethanol are most acceptable as hydrogen sources as they are liquid over a wide range of temperatures, which facilitates storage and transportation of these alcohols. In addition, they can be produced from various precursors, particularly, from coal, natural gas, biomass, *etc*. Steam reforming of methanol and ethanol occurs under milder conditions than steam reforming of, *e.g.*, methane. The disadvantage of the use of the alcohols as precursors of hydrogen consists in the presence of CO among the products in amounts inadmissible for further utilization of thus obtained hydrogen in the fuel cells with platinum catalysts.

Alcohol reformers must be equipped with systems serving for removal of CO. Therefore, integration of membranes selective to hydrogen directly into catalytic reactors for steam reforming of alcohols is of great interest and, in recent years, has attracted attention of researchers. There is a large number of papers and patents on the steam reforming of methanol and ethanol in membrane reactors. A series of reviews[22,23,125–127] is devoted to this subject.

a. Steam reforming of methanol

The steam reforming of methanol includes the following reactions:

$$CH_3OH + H_2O \longrightarrow CO_2 + 3\,H_2, \quad \Delta H^\circ_{298K} = 49.7\ \text{kJ mol}^{-1} \qquad (1)$$

$$CO + H_2O \longrightarrow CO_2 + H_2, \quad \Delta H^\circ_{298K} = -41.0\ \text{kJ mol}^{-1} \qquad (2)$$

$$CH_3OH \longrightarrow 2\,H_2 + CO, \quad \Delta H^\circ_{298K} = 92.0\ \text{kJ mol}^{-1} \qquad (3)$$

Endothermic reactions (1) and (3) are reversible and are accompanied by volume increase, while exothermic reaction (2) is known as water-gas shift reaction. As a result of these reactions, a mixture of hydrogen and carbon oxides is formed, the ratios of the products depending on the conditions and the catalyst used. The $Cu–Zn/Al_2O_3$ catalyst with various additives, which increase the catalyst stability and the yield of hydrogen, are the catalysts of choice.

Movable units for production of hydrogen in remote areas were described in an early publication[65] devoted to applications of membranes permeable to hydrogen in meth-

anol steam reformers. Later on, with the growth of needs in portable installations for the production of pure hydrogen for laboratory purposes, methanol reformers working at temperatures of 530–600 K and pressures of 1–25 atm with the membranes based on Pd, Pd/V/Pd, Pd_3Ag, $Pd_{60}Cu_{40}$ were designed.[128] The REB Research and Consulting company (USA) has developed the design and arranged the production of a series of portable reformers differing by their sizes and performance.

The effects of the sweep gas flow rate and the relative directions of this gas flow and the reactant flow in the reactors with compact and composite membranes were investigated in a series of studies [129–133] dealing with methanol steam reforming. The complete transformation of methanol was observed at 573 K and the $H_2O:CH_3OH$ ratio > 5 on the $Cu–Zn–MgO/Al_2O_3$ catalyst with the 50 μm thick membrane of Pd–Ag alloy.

To avoid formation of CO, it was proposed to add small amounts of oxygen into the reaction mixture for methanol steam reforming. In this case, the process occurring in the reformer can be described by reactions (1) and (4).

$$CH_3OH + 0.5\,O_2 \longrightarrow CO_2 + 2\,H_2, \quad (4)$$

$$\Delta H^{\circ}_{298\,K} = -192.2\ \text{kJ mol}^{-1}$$

In the membrane reformer with a compact tubular membrane of the Pd–Ag alloy, the best results were obtained [132] at 533 K with the ratio of oxygen to methanol equal to 0.09. In this process, oxygen was consumed completely, the yield of hydrogen that passed through the membrane was 28.6%. Oxidative steam reforming of methanol was also carried out in the flow membrane reactor with a 50 μm-thick flat membrane of the Pd–Ag foil.[133] It was shown that the addition of oxygen at 530 K not only decreased the CO concentration but also increased the methanol conversion and performance of the membrane reformer with respect to hydrogen.

By now, compact reactors for the methanol steam reforming have been designed. Particularly, the methanol microreformers of small productivity with respect to hydrogen were designed at the Boreskov Institute of Catalysis of Siberian Branch of RAS in collaboration with the National Innovation Company 'New Energy Projects'.[134] Such a reformer has dimensions of $65 \times 90 \times 85$ mm and contains microchannel plates of the area of 12 cm^2, ensuring hydrogen flux of 320 l h^{-1} .

b. Steam reforming of ethanol

The major reaction of hydrogen production by the steam reforming of ethanol yields six molecules of hydrogen from one molecule of the alcohol:

$$C_2H_5OH + 3\,H_2O \rightleftharpoons 2\,CO_2 + 6\,H_2 \quad (5)$$

In addition, a series of side reactions, which decrease the selectivity with respect to hydrogen, proceed simultaneously.

$$C_2H_5OH \rightleftharpoons CH_4 + CO + H_2 \quad (6)$$

$$C_2H_5OH \rightleftharpoons CH_3CHO + H_2 \quad (7)$$

$$C_2H_5OH + H_2O \rightleftharpoons 2\,CO + 4\,H_2 \quad (8)$$

$$CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2 \quad (9)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (10)$$

The advantages of the use of ethanol for production of hydrogen include environmental safety of this compound and its renewability due to production from biomass. Bioethanol, which is a multicomponent aqueous solution containing 8% to 12% of ethanol, apart from other components, may be used directly in the steam reforming.

Despite the seeming similarity between reforming of methanol and ethanol, these processes are carried out under different conditions and lead to different products. In the ethanol steam reforming [see reactions (5)–(10)], acetaldehyde and methane can be formed in addition to hydrogen and carbon oxides; the usual catalysts of this process are noble metals and also Ni, Co and Cu supported on oxides like Al_2O_3, MgO, SiO_2 or La_2O_3. The temperatures of steam reforming of methanol and ethanol are also different: 500–600 K and 650–1000 K, respectively.

The distribution of products of reforming depend on the catalyst used.[135, 136] In the conventional reactor at 920 K with Rh, Pd, Ni, Co supported on MgO as catalysts [136] and the water : alcohol molar ratio of 8.5 : 1, the products were a mixture of hydrogen, carbon oxides, methane, acetaldehyde and ethylene. The highest activity and stability were demonstrated by the Rh/MgO catalyst; however, its selectivity with respect to hydrogen was low. On the contrary, the selectivity of the Ni/MgO catalyst with respect to hydrogen exceeded 95%, but strong carbonization of the catalyst was observed during the steam reforming.

The activity of platinum metals supported on alumina in the ethanol steam reforming varies in the following series: $Rh \gg Pt > Pd > Ru$.

The complete transformation of ethanol at 800 K occurs on the Rh/Al_2O_3 membrane containing 1% rhodium and on the Ru/Al_2O_3 membrane containing $\geqslant 5\%$ ruthenium.

The process of ethanol steam reforming on cerium oxide or copper – cerium catalytic systems with different copper contents was studied [137] using a water – ethanol mixture with the molar ratio of 3 : 1 at temperatures from 673 to 823 K. The formation of hydrogen, carbon monoxide and dioxide, methane, ethylene, acetaldehyde and acetone was observed over the whole temperature range. The optimum copper content was found to be 5 mass % – 10 mass %, which ensured about 85% conversion of ethanol and resulted in the 50%, 7.5% and 0.5% yields of hydrogen, methane and carbon monoxide, respectively. The maximum yields of methane, ethylene, acetaldehyde and acetone were observed when pure cerium oxide was used. The major advantage of the copper – cerium catalytic systems is low content of CO among the products. It is highly favourable for the use of the produced gas in the fuel cells.

However, the use of hydrogen-rich gas mixtures in low-temperature fuel cells with the platinum catalyst requires the absence of even trace amounts of CO. Thus, integration of hydrogen permeable membranes into ethanol reformers is as relevant as the integration into methanol reformers. To date, a large number of experimental and theoretical studies of membrane steam reforming reactors have been performed.

A comparative study of ethanol steam reforming in conventional tubular and membrane reactors was carried out [138] with temperature variation between 673 and 773 K and pressure variation from 2 to 3.6 bar and a water to alcohol molar ratio of 11 : 1. It was shown that the advantages of the use of membrane reactors are especially essential at higher temperatures and pressures.

A study of bioethanol transformation on the Co/Al_2O_3 catalyst in conventional and membrane reactors at temperatures of 523–673 K, pressure of 1.5 bar and water : ethanol molar ratio of 18.7 : 1 demonstrated[139,140] that the ethanol conversion is higher in the membrane reactor. When the Pd–Ag membrane is used, a conversion equal to that in the conventional reactor was reached at a lower temperature and, therefore, it was accompanied by lesser coking of the catalyst. The total pressure in the reaction zone is of primary importance. Its increase from 1.5 to 3 bar, while maintaining the pressure of 1 bar in the permeate zone, results in the increase in the degree of separation of pure hydrogen from 30% to 90% as the difference in the pressures is the driving force of hydrogen transfer, and enhanced hydrogen removal leads to increasing alcohol conversion.

c. Processing of methane in membrane reactors

The major component of natural gas is methane; its content is usually 90% or more depending on the gas field. Natural gas is a raw material for power industry whose contribution to the energy balance of most countries has increased rapidly in recent decades. This is related to the convenience of its transportation and the advantage of its use in power generation over coal and oil because its utilization requires simpler boiler equipment and reduces the environmental damage from power companies as a result of more complete combustion of gas and lower content of impurities in it. In addition, the explored natural gas reserves seem sufficient for production for at least the next 150 years. The global continental natural gas reserves are estimated at not less than 187.5 trillion cubic metres, whereas the world reserves in the continental shelf and the continental slope of the world ocean are 10^{16} cubic metres; Russia accounts for $\sim$24% of the continental natural gas reserves.

Another important source of methane is the associated gas of oil production. At present, the use of this source of methane is faced with some engineering problems and, hence, most of the associated gas is simply flared. The third important source of methane is related to its formation during decomposition and processing of biological products. This allows one to consider methane as a partially renewable resource.

However, methane cannot be liquefied at reasonable temperatures, which is inconvenient for, *e.g.*, its utilization as motor fuel, despite its good antiknock properties. Nevertheless, taking into account the relatively low cost and accessibility of natural gas, methane and other components thereof may serve as an alternative raw material for chemical substances thaditionally produced from refined petroleum products.

At present, only small part of produced natural gas (not more than 5%) is used for chemical processing. This is related to the fact that methane is the most chemically stable hydrocarbon. During processing of methane, new carbon–carbon bonds are formed with simultaneous elimination of hydrogen atoms. This requires substantial energy consumption; for instance, the energy of dissociation of the first carbon–hydrogen bond is 435.4 kJ mol^{-1} (Ref. 141). For this reason, besides direct syntheses of hydrocarbons with $\geqslant$2 carbon atoms from methane (so-called methane coupling), processes based on transformation of methane into other compounds with their further transformation into hydrocarbons of the desired composition are under active development. The chemical processing of methane is mainly production of hydrogen and organic compounds of different classes.

Among processes of direct synthesis of organic compounds from methane, most important are oxidative and non-oxidative coupling of methane, which can be based on both conventional thermal and specific methods of activation of CH_4 molecules, including photolytic dissociation, photocatalysis, plasmochemical methods and so on. There are also studies where membrane reactors were used to carry out such processes. However, since this review is devoted to the processes of dehydrogenation and production of hydrogen, consideration of the direct synthesis of organic compounds from methane by oxidative coupling is beyond this scope and will not be discussed below.

4. Chemical processing of methane

The two-step processes of chemical processing of methane essentially include production of syngas whose further treatment results in the production of hydrogen together with additional products of various composition.[142] The most important processes of this type are steam reforming of methane, methane reforming with carbon dioxide (carbon dioxide reforming or dry reforming), steam reforming of methane with carbon dioxide and partial oxidation. The application of most of these methods in combination with the use of membrane reactors provides significant advantages.

a. Steam reforming of methane

The steam reforming of methane to syngas is among the methane processing processes that are developed most actively. This process patented by BASF (Germany) in 1926 found its wide application in the second half of the 20th century. It replaced syngas production processes based on coal processing. The methane steam reforming is a widespread method because it yields mixtures containing up to 75% of hydrogen.

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO, \quad \Delta H = 165 \text{ kJ mol}^{-1} \qquad (11)$$

Hydrogen can be used in various processes, the major of which is the ammonia synthesis.[143]

The complete conversion of methane in conventional reactors occurs only at high temperatures from 800 to 900 °C. If the process is carried out in membrane reactors, its temperature can be appreciably reduced by removal hydrogen while maintaining the same conversion of the starting compound.[144–146] Thermodynamic calculations indicate[147] that removal of hydrogen from the reaction mixture through palladium membranes at 1000 K, 2 MPa and the $H_2O : CH_4$ ratio of 2 results in the increase of conversion of methane from 43.7% to 94.0%. It was established experimentally[53] that selective removal of hydrogen through the 100 μm-thick membrane made of the Pd–Ag (25%) alloy from the products of steam reforming of methane on a nickel catalyst at 973 K ensures 90% conversion of methane.

Even more impressive results were obtained for reactors with palladium-based membranes. Particularly, it was possible to achieve almost complete conversion even at 823 K;[144] in conventional reactors, the conversion does not exceed 27% at this temperature. Similar results were also obtained in other studies,[145,146] in which methane

conversion reached 85%–90% at 773 K. The use of palladium membranes at lower temperatures (423 and 573 K) leads to loss of advantages of membrane reactors with respect to conventional reactors and the methane conversion does not exceed 16.5%.[148]

The carrying out of steam reforming of methane in the membrane reactors ensures not only significant reduction of the process temperature but also production of ultrapure hydrogen suitable for the use in low-temperature fuel cells from one of the reactor outlets.[149] Therefore, the promising area of the use of reactors with the membranes based on palladium and its alloys is processing of methane in reformers containing granulated catalyst of methane steam reforming and a palladium membrane through which hydrogen is withdrawn (Fig. 6).

The design of a membrane module for production of hydrogen of the 99.9988% purity was reported;[150] the unit has operated for more than 1000 h. The catalytic membrane was made of a palladium – silver alloy deposited on a ceramic substrate (NiO + 8 mol.% Y_2O_3–ZrO_2).

However, the cost-performance of reactors with palladium-based membranes is limited due to high price of palladium. Therefore, a series of studies were devoted to application of reactors with membranes based on cheaper materials. Particularly, a silica membrane with $Ni/Ce_{0.15}Zr_{0.85}O_2$ as a catalytically active component was used.[151] The obtained system operated stably and ensured a 80% conversion of methane *versus* 40% corresponding to the equilibrium conversion.

b. Methane reforming with carbon dioxide

Syngas with equimolar contents of hydrogen and carbon monoxide can be obtained by carbon dioxide reforming of methane. Carbon dioxide, one of the greenhouse gases, whose emission is tightly restricted at present, is used in this process. This method of methane processing makes it possible to reduce coking of the catalyst.[152, 153] The process is described by the reaction:

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO, \quad \Delta H = 247 \text{ kJ mol}^{-1} \qquad (12)$$

As in the case of methane steam reforming, the temperature of the process can be decreased by using membrane reactors from 1073 K (if the conventional nickel catalyst is used) to 773–823 K (in the case of palladium membrane). The 37.5% conversion of methane was observed[152] at 823 K, this is twice the conversion in the conventional reactor at the same temperature. In the reactor with composite membrane of palladium on a porous ceramic substrate, methane conversion was 54% at 773 K.[154] Similar conversion was observed at 923 K on the composite membrane with Pd–Mn/Ni–Al as the active component, whereas conversion of >70% was achieved on La–Ce/Ni–Al at 973 K.[155]

In all the cases mentioned above, coking proceeded to a lesser degree than in steam reforming processes at the same temperatures. The steam reforming of methane with carbon dioxide combines the steam and carbon dioxide reforming processes; it affords syngas with almost any ratios of components, which is highly important for its special-purpose uses.[142]

c. Partial oxidation of methane

In partial oxidation of methane, synthesis gas is produced with a volume ratio of hydrogen to carbon monoxide of 2 : 1.

$$CH_4 + 0.5O_2 \longrightarrow 2H_2 + CO, \quad \Delta H = -35 \text{ kJ mol}^{-1} \qquad (13)$$

Partial oxidation of methane is actively studied since the 1980s. Studies with the use of reactors with catalytic membranes based on perovskites are examples of application of membrane reactors in this process. In this case, by varying permeability of the membrane to oxygen, it is possible to control the delivery of oxygen into the reaction zone, where its interaction with methane occurs in a necessary stoichiometric ratio. For instance, the 96% conversion of methane was reached on such a catalyst at 1123 K, the gas mixture at the reactor outlet contained 65% of hydrogen and 31% of carbon monoxide.[156] The membrane based on ferrite of the composition $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ was used in another study.[16] At 1223 K, almost complete conversion of methane was achieved with this catalytic system, the selectivity to carbon monoxide being 92%–95%.

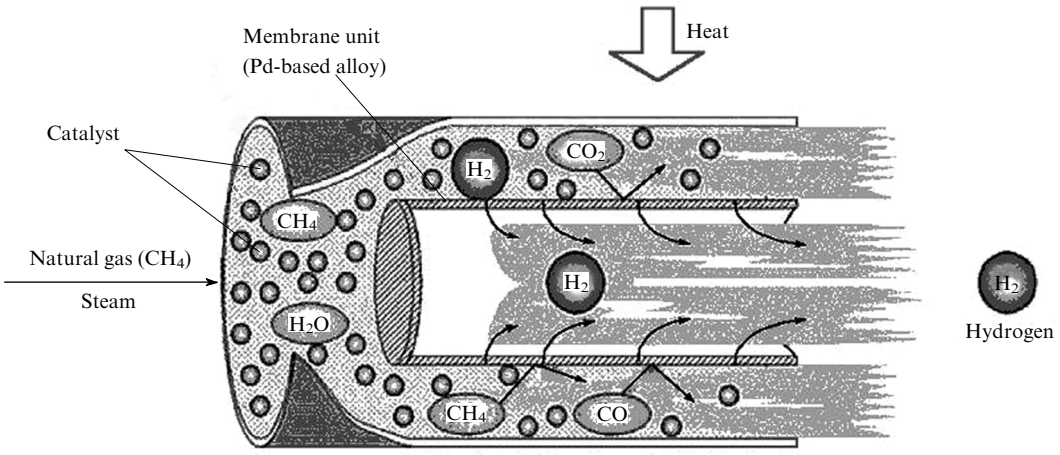


Figure 6. Scheme of a membrane-catalytic unit for hydrogen production.[150]

However, it was noted in the study cited above[156] that enhanced demands are placed on the design of the reactor because mechanical destruction of the membrane is possible during operation; therefore, this method for syngas production cannot compete with traditional methane reforming.

Partial oxidation of methane was successfully carried out under milder conditions (823–923 K) but with lower degree of conversion when membrane catalytic system with a ceramic membrane with deposited La–Ce/MgO particles was used.[157]

d. Reactions of non-oxidative coupling of methane

It was shown in studies dealing with non-oxidative coupling of methane in membrane reactors[158, 159] (Fig. 7) that removal of hydrogen through the membrane accelerates the process.

Nonetheless, non-oxidative coupling of methane cannot be considered as an alternative to other methods of chemical processing of methane when its traditional activation by heating is used. The reactions of non-oxidative methane coupling at high temperatures (1073–1173 K) are accompanied by deep dehydrogenation to give free carbon, and, therefore, lead to unproductive consumption of raw materials. These reactions can also be carried out at lower temperatures if the necessary energy is supplied in an unconventional way. The most widely used methods are based on photochemical transformations of molecules. In this case, the molecules participating in further transformations acquire the required energy by absorption of photons. Methane can be activated as a result of light absorption by proper methane molecules, which leads to abstraction of hydrogen atoms from the molecules and formation of methyl radicals capable to further transformations, or as a result of light absorption by the catalyst. In the latter case, the energized surface of the catalyst ensures coupling of methane molecules adsorbed on this surface. These methods for activation of molecules are defined as photodissociation and photocatalysis, respectively. In both cases, the energy which is required to carry out non-oxidative methane coupling corresponds to UV region of the electromagnetic spectrum.

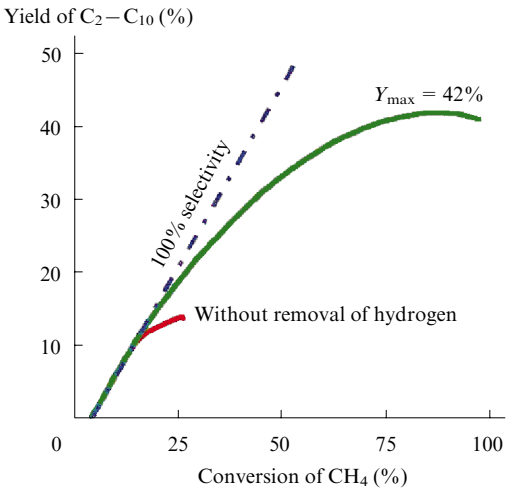


Figure 7. Effect of the hydrogen removal on methane conversion at 1038 K.[160]
Y_{max} is the product maximum yield.

The investigations in the area of photoactivation in the coupling reactions of methane were started quite recently. Particularly, silica and alumina were used as photocatalysts.[160] In the reactor filled with pure methane, the 5.9% conversion of CH_4 to C_2-C_6 hydrocarbons was reached after 18 h of irradiation with the light of a xenon lamp at room temperature; the predominant product was ethane (60%).

The possible applications of photocatalysis to other processes of chemical processing of methane were demonstrated in a number of studies. Particularly, the use of V_2O_5/SiO_2 (0.6 vol.%) as a photocatalyst made it possible to carry out partial oxidation of methane at relatively low temperature (493 K) and to obtain formaldehyde with the selectivity of up to 92%.[161] However, the methane conversion did not exceed 3%.

The possibility of photocatalytic reforming of methane was also demonstrated. The use of non-thermal activation of methane made it possible to observe its noticeable transformations even at room temperature.[162] The products of carbon dioxide reforming of methane were obtained at 473 K using photocatalyst based on Ga_2O_3 (see Ref. 163); the side products of this process included compounds formed in non-oxidative methane coupling, mainly ethane. It was also shown that at room temperature, only formation of methane coupling products is possible.

Studies of other methods for chemical processing of methane were also carried out.[163] However, conversion of methane did not exceed 5%–7% even after long-term (for more than 15 h) UV irradiation in all cases. There is only one example of non-oxidative methane coupling with the use of membrane catalysis.[164] In a reactor with the tube made of the Pd–Ru alloy, which served to remove hydrogen from the zone of the reaction initiated by UV irradiation of a mercury lamp at 543 K, the 13.5% conversion of methane to the C_2 hydrocarbons was reached. This value can be significantly increased by rising temperature and increasing the surface of the membrane through which hydrogen is separated.

The analysis of the available published data indicates that the use of membrane reactors for chemical processing of methane is highly promising. Especially important results were obtained in the production of pure hydrogen based on the use of membrane reactors with palladium alloy membranes. To date, pilot and industrial systems including such reactors have been designed.[165] Taking into account the growth of the production of natural gas the major component of which is methane, one can expect further development of methods for its chemical processing not only for the purposes of hydrogen power engineering but also for the production of liquid fuels and various products of organic synthesis. There is no doubt that membrane catalysis will play a significant role among these methods.

IV. Conclusion

In the past decade, the interest of researchers in the integration of membrane reactors into the systems for production of high-purity hydrogen has increased. For instance, almost a quarter of the reports at the recent 10th international conference 'Catalytic Processes in Membrane Reactors' was devoted to hydrogen production from

organic raw materials using membranes selectively permeable to hydrogen.[41]

Composite membranes based on palladium alloys suitable for production of high-purity hydrogen were used in most of the studies. Simultaneously, the search for new materials for membranes and development of hydrogen production processes based on them are under active progress. Among them, membranes made of silica fibres, which are highly selective to hydrogen, and membranes based on mixed oxides (mainly with perovskite structure), which are permeable to oxygen ions, deserve special mentioning.

The most promising processes for the production of hydrogen in membrane reactors are steam and oxidative reforming of methane and also steam reforming of light alcohols. The use of processes for preparation of aqueous methanol and ethanol solutions from biomass ensures virtually inexhaustible resources for the reforming. The implementation of these processes in membrane reactors, including high-performance reactors and microreactors, draws attention of researchers due to relatively mild conditions and possibility to vary the performance with respect to hydrogen over a wide range.

Taking into account the growth of the production of natural gas the major component of which is methane, it can be expected that the interest in the use of membrane methods in chemical processing of methane will be preserved in the future. This view is supported by the design of pilot catalytic membrane systems for the production of hydrogen by methane reforming. In addition, as the oil reserves are being exhausted, the problem of the use of natural gas for organic synthesis, including the production of liquid fuels, will arise. In this connection, the studies of dehydrogenation of hydrocarbons and oxidative and non-oxidative methane coupling become highly important. Many of such reactions are accompanied by energy consumption or little energy evolution, which accounts for rather low yields if the process is carried out by conventional means. On the contrary, the reaction of oxidative coupling can give off much heat, presenting a major hazard if conducted on an industrial scale. In both cases, it is preferable to carry out such processes in membrane reactors because their yields can be increased by removal of products or by controlled supply of reactants.

The above facts give grounds for confidence in further development and application of membrane catalysis in a wide range of chemical processes.

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