

Modern Technologies of Hydrogen Production

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Keywords: hydrogen production, hydrogen storage, Steam Reforming, water electrolysis, Biomass, biohydrogen, membrane catalysis

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Transitioning to energy-saving and renewable energy sources is impossible without accelerated development of hydrogen energy and hydrogen technologies. This review summarizes the state-of-the-art and recent advances of various hydrogen production processes, including but not limited to thermochemical and electrolytic processes. Their opportunities and limitations, operating conditions, and catalysts are discussed. Nowadays, most hydrogen is still produced by steam reforming of methane, its partial oxidation, or coal gasification. Considerable attention is also paid to natural gas pyrolysis. However, hydrogen produced using these technologies has a lot of impurities and needs additional purification. A series of technologies for hydrogen purification, including its filtration through palladium alloy membranes, and membrane catalysis, allowing hydrogen production and purification in one stage, are discussed. The main way to produce carbon-free hydrogen is water electrolysis using low-cost energy from nuclear or renewable sources. Both conventional and novel methods of hydrogen storage and transportation, which are an important part of the hydrogen economy, are reviewed. Biohydrogen production technologies are also discussed. Finally, prospects for further work in this field are provided. This review will be useful to researchers and manufacturers working in this field.

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Review

Modern Technologies of Hydrogen Production

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Keywords: hydrogen production; hydrogen storage; steam reforming; water electrolysis; biomass; biohydrogen; membrane catalysis



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1. Introduction

Economic and technological developments are impossible without energy consumption, which is constantly growing. At the same time, energy production leads to substantial environmental pollution. The main reasons for this are the emissions of carbon oxides, sulfur oxides, nitrogen oxides, and products of incomplete combustion of fossil fuels into the atmosphere. Particular attention is paid to carbon dioxide, which, according to a number of researchers, is the primary greenhouse gas. Therefore, the Paris Agreement focuses special attention on the energy sector. Significant efforts are being made to move towards energy conservation and new technologies associated with the use of environmentally friendly and renewable energy sources, such as solar panels, wind turbines, and tide stations [1,2]. However, to ensure an uninterrupted power supply, these sources should be used together with energy storage devices [3–8]. To level seasonal fluctuations in energy production, it is most appropriate to accumulate energy in the form of hydrogen.

Fuel cells can be used as autonomous or backup power sources [9–11]. To operate, they need hydrogen, which does not exist in a free state on the Earth. Moreover, hydrogen is currently required for a number of technologies, primarily for the production of ammonia, methanol, oil refining, metallurgy, and electronics. Hydrogen has long been considered as an alternative energy source due to its extremely high specific energy per unit mass—it is about three times higher than that of oil [12]. The total consumption of hydrogen in the world is about 115 million tons per year [13]. According to the International Energy Agency forecasts [14], hydrogen production should increase by 2.5 times in the next 30 years. Half of it will be spent on energy production, and another 30% will be spent for land transport,

while now only about 3% of hydrogen is spent for these purposes. However, according to [15], the production of hydrogen should grow faster and approach 700 million tons per year by 2050.

It is clear that hydrogen of different purities is required for different purposes. In metallurgy, in a number of chemical industries, or as a fuel, hydrogen can be used in a mixture with other gases [16,17], while high-purity hydrogen is required for microelectronics and the currently prevalent low-temperature fuel cells [11,18]. An important aspect is the impact of byproducts of hydrogen production on the environment, which largely determines the further development of various technologies for hydrogen production. Moreover, cost optimization for implementation should also be taken into account [19].

Nowadays, three quarters of hydrogen is produced by steam reforming of natural gas, and just under a quarter is by coal gasification [20]. According to other reports, oil refining also makes a significant contribution [21,22]. Nevertheless, it is obvious that technologies leading to pure hydrogen production based on electrolysis or photolysis of water are still less-demanded. A comparison of costs of hydrogen produced by different technologies and their energy efficiencies and carbon footprints is shown in Figure 1. Although coal gasification is the cheapest source of hydrogen, its high emissions (Figure 1) and level of hydrogen impurities make this approach less promising. Now, hydrogen production from coal is developing primarily in China [23]. Coal gasification can be performed directly under the ground. The product of this process is synthesis gas (syngas, a mixture of hydrogen and carbon monoxide), which contains methane, carbon dioxide, nitrogen, and small amounts of hydrogen sulfide [24,25].

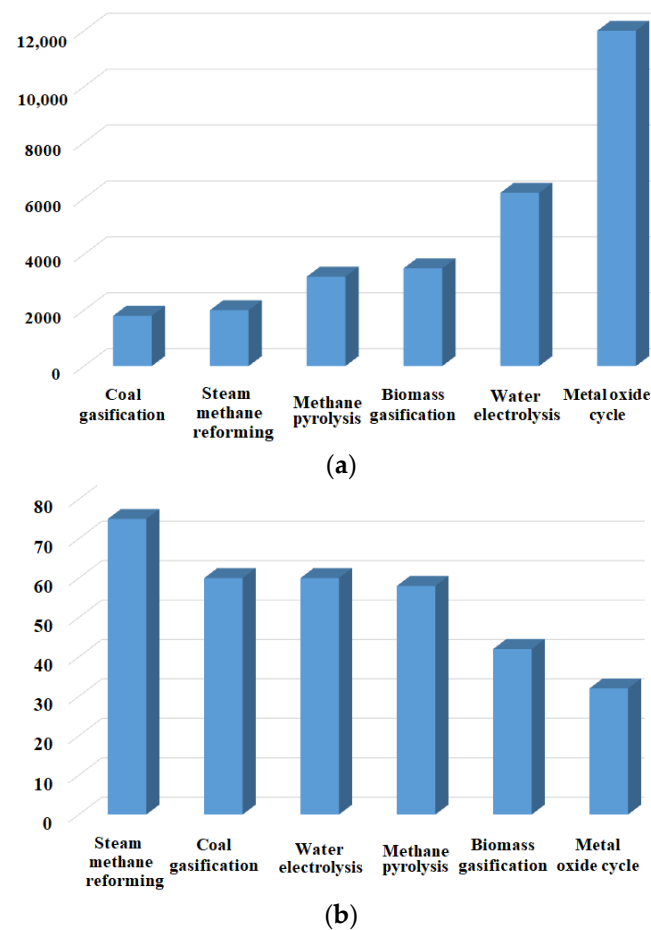


Figure 1. Cont.

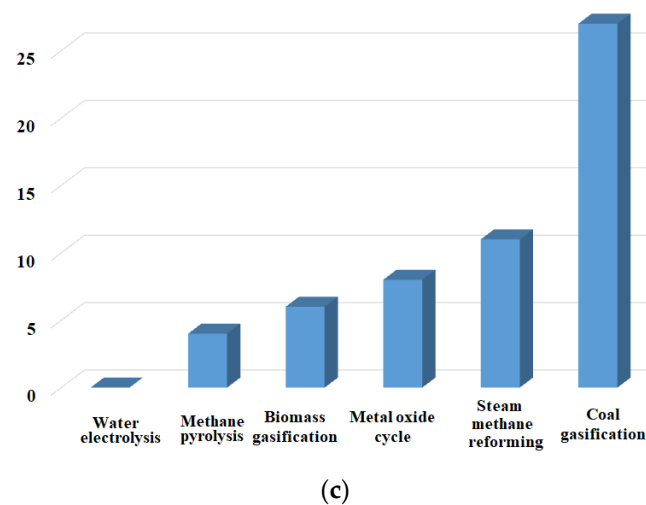


Figure 1. (a) Costs of hydrogen (EUR/t) produced by different technologies; (b) their energy efficiencies (%); and (c) carbon footprints (tCO₂/tH₂) [26–32].

In this review, the main methods of hydrogen production and the prospects for their development are discussed.

2. Steam Methane Reforming

The most attractive and common approach for hydrogen production is steam reforming of methane (SRM) (Figure 2) [33], which can be described by the following reaction:

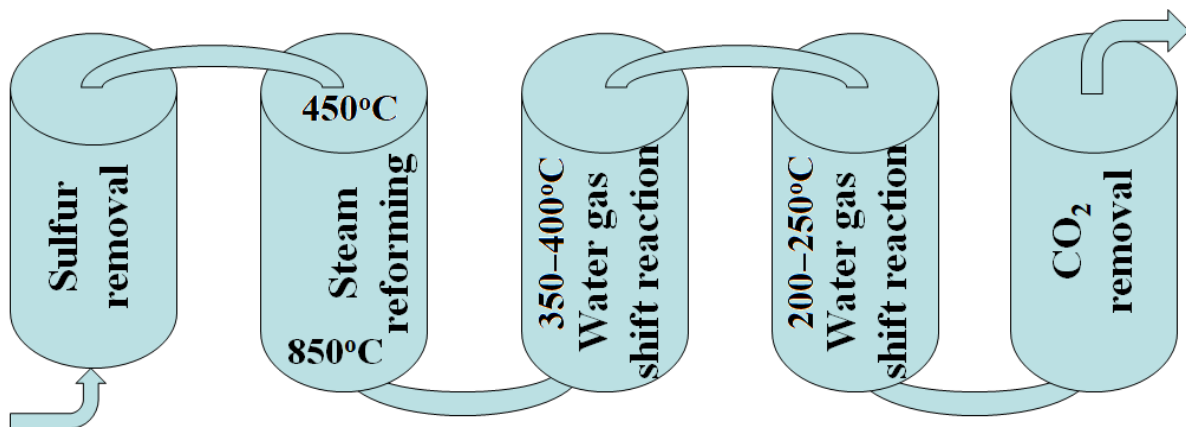
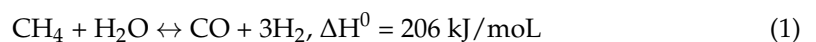
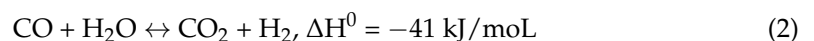


Figure 2. Scheme of steam–methane reforming for H₂ production.

This approach enables reaching a maximum yield of hydrogen (up to 3 moles of hydrogen and 1 mole of CO per 1 mole of methane). Moreover, carbon monoxide can interact with water steam at temperatures of 200–400 °C to form carbon dioxide and generate additional hydrogen (water–gas shift reaction) (Figure 2):



However, since the main process (Equation (1)) is endothermic, it requires high temperatures, at which the CO₂ yield is limited [34]. The need for high temperatures is also determined by the fact that activation of a highly symmetrical molecule of methane with strong C–H bonds requires a lot of energy. Moreover, as temperature decreases, the carbon

deposition on catalyst proceeds more intensively. It is also noted that the conversion of methane increases with increasing the steam-to-methane ratio up to five [35]. Both of the above processes (Equations (1) and (2)) are catalytic and can be accelerated by both noble and transition metals. In the series of noble metals, the catalytic activity decreases in the series $Ru > Rh > Ir > Pt$ [36,37]. High reforming activities and low rates of carbon formation are among advantages of these catalysts [38–40], but due to high cost, their use is limited. In this regard, the attention of researchers was attracted to the iron family metals [41]. However, iron is prone to oxidation, while cobalt is relatively expensive and toxic; therefore, catalysts based on nickel, whose activity is comparable to that of platinum and iridium, are more in demand [42,43]. The use of bimetallic catalysts is also effective and increases their activity, selectivity, and durability in comparison with monometallic catalysts, as well as limits carbon formation, oxidation, and sintering [44–48]. It is worth noting the use of catalysis to lower the reaction temperature [49].

The most serious problems are sulfur poisoning and activity loss due to rapid sintering and carbon formation (Figure 3). The use of supports, predominantly oxides, such as alumina and silica, increases the conversion degree and reduces the poisoning effect [50–52]. Even more effective are spinels ($MgAl_2O_4$, $ZnAl_2O_4$), which reduce carbon deposition and increase resistance to sintering [53,54], doped zirconia and ceria, etc. [55–57]. Their advantages include improved conversion and decreased carbon deposition [35,56]. The activation energy and reaction rate are significantly affected by the support's nature, dispersity, and structure [34,54,58–61].

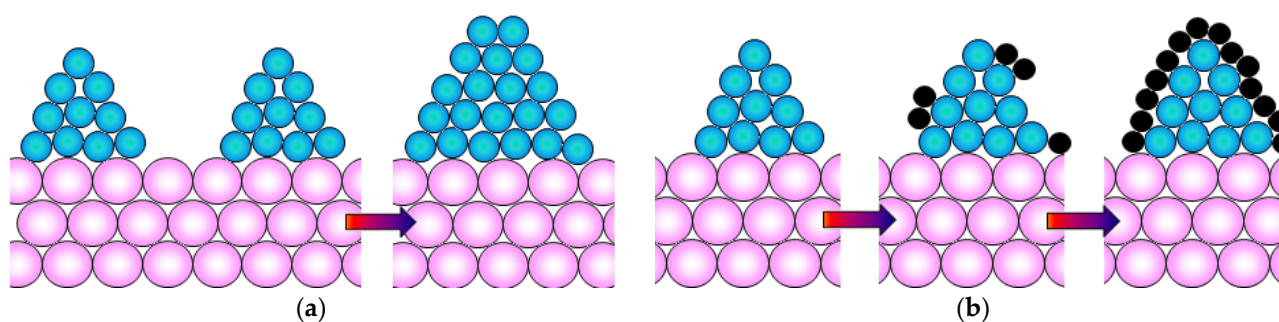
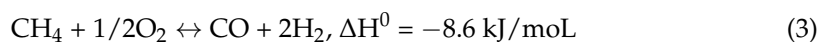


Figure 3. Schematic illustrations of the sintering (a) and coking (b) processes for SRM catalyst. Pink, blue and black balls denote support, metal catalyst and carbon, respectively.

A promising approach is the selective extraction of one of the products (hydrogen or carbon dioxide), leading to a shift in the thermodynamic equilibrium and thus increasing the hydrogen yield. Extraction of hydrogen is usually performed via a process of membrane catalysis, which we write about below. CO_2 extraction is also very promising [62–64]. Amines [37,65], calcium compounds [66,67], alkali metal zirconates, and silicates [68–71] have been used to absorb carbon dioxide. Direct extraction of CO_2 is possible using anion exchange membranes [72]. Using this approach, the hydrogen yield can be significantly increased [71,73]. Thus, according to [74], it can be more than 90%.

3. Partial Oxidation of Methane

Partial oxidation of methane (POM) is another common approach to hydrogen production [75–78]. In contrast to steam methane reforming, this process produces less hydrogen (Equation (3)) and is more difficult to control, since the released hydrogen is easily oxidized by oxygen. However, its undoubted advantage is that it is exothermic, although the released heat is small.



The product of Reaction (3), proceeding at 600–950 °C, is a POM syngas [79–82], which is often used for the synthesis of chemicals (methanol, dimethyl ether, etc.). High temperatures and low selectivity of the process (Equation (3)) lead to the formation of carbon as a byproduct, which deactivates catalysts [83–85]. At the same time, it is possible to further oxidize CO by steam (Equation (2)) by cooling the product flow to increase the hydrogen yield [86–88]. To compensate for the heat released, partial oxidation can be combined with steam reforming of methane. This is the so-called autothermal reforming of methane (Figure 4) [89].

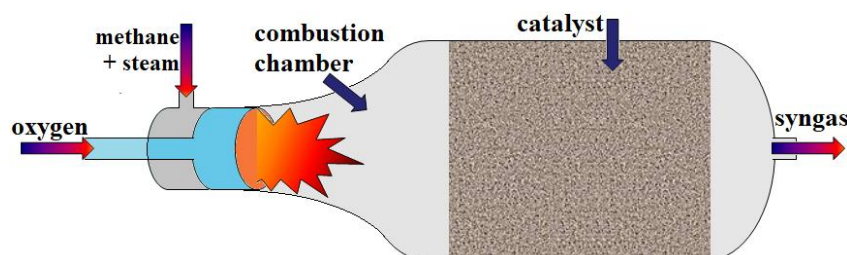


Figure 4. Scheme of the reactor for autothermal reforming.

Since partial oxidation of methane requires activation of the same bonds as for its steam reforming and many other processes, which are described in more detail below, the catalysts used for both processes turn out to be very similar. First of all, we are talking about platinum-group metals [83–85,90–93], among which rhodium should be noted [77,94,95]. Rhodium alloys with various transition metals are used to improve methane conversion and productivity [76,96–99]. At the same time, considerable attention is paid to transition metals, predominantly nickel [100]. The use of lanthanum–nickel alloys leads to an increase in the CO₂ fraction in the reaction products [90].

One of the main problems of nickel and some other catalysts are oxide and carbon deposits. To suppress their formation, supports based on oxides of zirconium, titanium, cerium, and lanthanum are used [95,101–103]. Support optimization is also used to increase the degree of methane conversion and the CO₂ fraction in the POM products [104].

To date, an approach is also being developed where the oxygen sources (oxygen carriers) for the partial oxidation of methane are oxides of nickel, copper, iron, and other metals, which are reduced to a metal and then oxidized again (Figure 5) [63,105,106]. As a development of this approach, it is possible to combine oxidation with the capture of released CO₂ by calcium oxide [107]. However, according to [31], the cost of hydrogen produced using this approach exceeds the cost of hydrogen produced using any others.

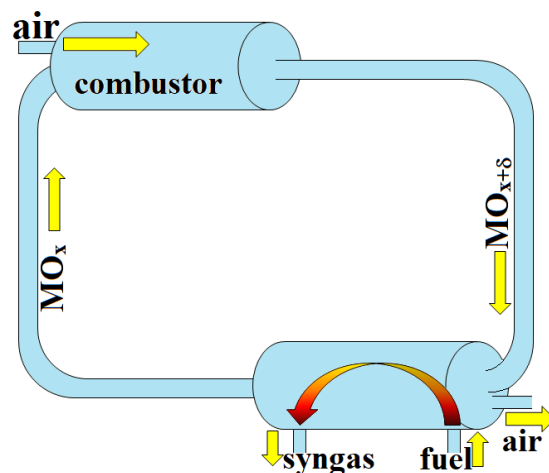
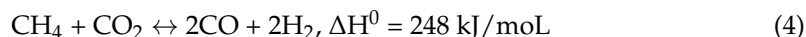


Figure 5. Scheme of hydrogen production with the use of chemical looping combustion.

4. Carbon Dioxide Reforming

Another common approach is the carbon dioxide reforming of methane, which is often called 'dry reforming of methane (DRM)', since CO₂ is a substitute for water in steam methane reforming [108,109]:



This process is endothermic, and its heat is comparable to that of steam reforming of methane. Accordingly, this process proceeds at high temperatures (700–1000 °C). A CO-rich synthesis gas is produced using this technology, and therefore, DRM can hardly be considered as a method for hydrogen production. Even in the case of DRM syngas use for the synthesis of organic compounds, it is better to combine this process with steam methane reforming (Equation (1)) to increase the H₂/CO₂ ratio up to two [110,111]. Interest in dry reforming of methane is primarily stimulated by the problem of CO₂ management [65,112].

A lot of attention is drawn to the choice of catalysts. The DRM process proceeds via sorption of methane and carbon dioxide molecules, which lowers their dissociation energy [113]. Wei et al. showed that catalysts with optimum binding of oxygen and carbon atoms to the catalyst surface exhibit maximum catalytic activity [114]. As a rule, despite high binding energy, the activation of CO₂ molecules turns out to be lower. Bitter et al. suggested that methane is activated on metal sites, while CO₂ is activated on acid sites of the support [115].

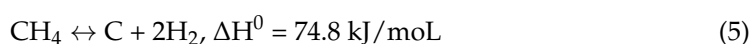
Platinum-group metals, primarily ruthenium and platinum, exhibit high catalytic activity in the dry reforming of methane (Table 1), which allows the process to proceed at relatively low temperatures [115]. However, nickel catalysts are more often used for this process due to their lower cost [110,112,116,117]. Moreover, the activity of catalysts in DRM depends on catalyst support (primarily its basicity and redox ability) and metal–support interactions (Table 1). The basicity of the support determines its activity in sorption and activation of gas molecules, while redox properties can promote the catalytic process as a whole and determine the main directions of the process and its byproducts. Thus, supports are primarily used to ensure high activity of a catalyst material and to minimize carbon deposits [118–120].

Table 1. Comparison of the catalyst activity in DRM (feed-gas ratio CH₄:CO₂ = 1:1).

Catalyst		T (°C)	Conversion (%)		Time on Stream (min)	Reference
Metal	Support		CH ₄	CO ₂		
Ni	La ₂ O ₃	650	62	67	3000	[121]
Ni	SiO ₂ /TiO ₂	650	65	54	1440	[122]
Ni	Activated carbon	900	80	98	500	[123]
Ni	MgO/Ce _{0.8} Zr _{0.2} O ₂	800	95	96	12,000	[124]
Ni	Al ₂ O ₃	800	63	82	1200	[125]
Ni	CeO ₂ -Al ₂ O ₃	850	100	100	600	[126]
Ni	SBA-15	800	88	89	300	[127]
Ni-Co	SBA-15	25	29	19	600	[128]
Ni-La	SBA-15	750	88	96	660	[129]
Co	Sr/La ₂ O ₃	800	94	99	1800	[130]

5. Methane Pyrolysis

Unfortunately, all the processes described above lead to the production of carbon oxides as byproducts and, with the exception of CO₂ reforming, do not solve the carbon footprint problem [131]. In this regard, in recent years, interest in the well-known process of natural gas pyrolysis (Equation (5)) has increased significantly.



Based on the stoichiometry of reaction (5), solid carbon is the only byproduct, and there are no greenhouse emissions, which contribute to atmospheric pollution with carbon oxides [131–134]. Therefore, it is often believed that it is possible to produce hydrogen with zero carbon footprint, which should help solve the carbon management problem [131,135–137]. The carbon byproduct generated by methane pyrolysis is predominantly a carbon black that can be used in metallurgical (steel) industry as carbon additive or production of carbon fibers for variety applications, including car tires. There is an opinion about the possibility of using carbon in direct-carbon fuel cells [138]. However, assuming that pyrolysis will provide a significant portion of hydrogen production, the amount of carbon will significantly exceed the needs for its use.

Unlike previous technologies, in methane pyrolysis there are no reagents with a chemical affinity for its components, and therefore maximum activation energy is required. In this regard, its implementation is possible only at temperatures above 1100 °C. The reaction proceeds through the formation of methyl radicals and hydrogen atoms and further similar transformations of sequentially formed hydrocarbons. The temperature of pyrolysis can be reduced by using catalysts that promote these processes initiated by molecular [139,140] or dissociative adsorption of hydrocarbons [141–143]. Dissociation of hydrocarbons is facilitated by the transfer of electrons from the C–H bonds of methane to vacant d-orbitals of transition metals [144–148]. An increase in catalytic activity in the series Fe < Co < Ni has been reported [144,146,149]. Nickel catalysts exhibit maximum activity (Table 2), which rapidly decreases due to blockage by the formed carbon layer [146,148,150].

Iron-based catalysts exhibit significantly lower activity in methane pyrolysis (Table 2), but at the same time, they are cheaper and show better resistance towards carbon deposits. Fe catalysts can operate stably at temperatures up to 1000 °C [145,151–153] due to higher carbon diffusion, which is three orders of magnitude higher than that of nickel-based catalysts [131,145]. This helps to ‘clean’ the catalyst surface and maintain its activity for a longer time. The least-demanded are cobalt catalysts because of their toxicity and lower activity compared to nickel [154,155].

Considerable attention is also paid to oxide supports, which are designed to prevent both the agglomeration and the deactivation of catalyst particles [150,153,156,157]. In catalytic pyrolysis, nickel-based alloys with cobalt, palladium, copper, and some other metals are also actively used. The second metal is used as a so-called promoter, leading to additional acceleration of the process [145,146,158]. It should be noted that the role of the second metal in this case is not quite traditional. Often, it is introduced to increase the rate of carbon diffusion in the alloy, enabling it to work at higher temperatures and providing less deactivation of nickel by carbon deposits [159–161].

Table 2. Comparison of the catalyst activity in methane pyrolysis.

Catalyst	T (°C)	Feed Gas Composition	Conversion of CH ₄ (%)	Reference
Ni/SiO ₂	650	CH ₄	85	[162]
55% Ni – 15% Cu/MgO·Al ₂ O ₃	675	CH ₄	80	[163]
12.5% Ni – 12.4% Co/La ₂ O ₃	700	N ₂ :CH ₄ = 1:9	82	[164]
50% Ni – 10% Fe/Al ₂ O ₃	675	N ₂ :CH ₄ = 7:3	68	[144]
50% Ni – 10% Pd/Al ₂ O ₃	675	N ₂ :CH ₄ = 7:3	75	[165]
20% Fe/WO ₃ + ZrO ₂	800	N ₂ :CH ₄ = 1:2	90	[166]
Fe – 5.1% Mo/Al ₂ O ₃	750	CH ₄	69	[167]
65% Fe/Al ₂ O ₃	750	CH ₄	70	[168]
Fe sponge	1000	CH ₄	85	[169]

Even less-active are carbon catalysts (activated carbon, carbon black, acetylene black, etc.), which operate only at temperatures from 800 to 1000 °C [131,170–172]. At the same time, they are widely used in this process due to their low cost and high stability, since in this case the process becomes autocatalytic and only a small amount of catalyst is needed to initiate it. Moreover, carbon catalysts are also stable to sulfur and other impurities contained in natural gas [131,173]. Active catalytic centers of carbon catalysts are believed to have multiple defects on their surface, which is confirmed by the dependence between the number of defects in graphene layers, initial temperatures, and reaction rates [174].

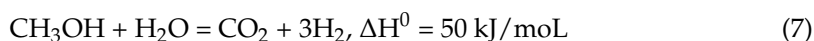
Recently, considerable attention has been paid to methane pyrolysis over molten metals or salts. This results in the long-term activity of catalysts due to prevention of rapid carbon deposition [133,175–180]. An additional advantage is the high heat capacity of the melt, which ensures the stability of the catalytic process.

Despite the great attention to hydrogen production by methane pyrolysis and optimism regarding its environmental friendliness, this method has many disadvantages. Among them, first of all, it is worth mentioning the high energy consumption. Moreover, formation of carbon as a co-product is a huge problem, as through this process we lose half of the potential methane energy. Moreover, as was mentioned above, the amount of carbon formed in the production of potentially demanded hydrogen is an order of magnitude higher than the need for carbon [131–133]. Since methane pyrolysis proceeds at high temperatures and is not quite selective, the hydrogen produced still contains a lot of impurities and also requires deep purification.

6. Reforming of Biomass and Bio-Alcohols

Biomass is an excellent renewable feedstock and can cover a major part of humanity's needs for precursors for organic synthesis and energy carriers. There are various approaches to its processing. For example, biomass can be used as a source of methane (biomethane) and, using approaches similar to those described above, be converted into hydrogen-rich synthesis gas [181–183]. Steam reforming of lignin [184,185], products of fermentation of biomass containing an aqueous solution of ethanol [186–189] or methanol produced by dry distillation of lignin seems to be even more attractive. Many authors note the attractiveness of the direction associated with the reforming of aqueous solutions of various organic compounds, including biomass processing products, wastewater, etc. in milder conditions (230–270 °C and autogenous pressure)—so-called 'aqueous phase reforming' [184,190,191]. It should be noted that at present, biomass is also considered a promising and renewable carbon source for the production of chemicals.

The advantage of alcohol steam reforming is milder reaction conditions, e.g., lower temperatures, compared to SMR. For ethanol and methanol, the overall reactions of alcohol steam reforming can be expressed by Equations (5) and (6), respectively:



Although the main products of these processes are hydrogen and CO₂, other byproducts, e.g., CO, which negatively affect the operation of low-temperature fuel cells, are also presented. However, their concentrations are lower than in SRM, while the hydrogen yield is higher. Therdthianwong et al. reported the implementation of this process without any catalyst at a pressure of 25 MPa in supercritical water in the temperature range of 500–600 °C [192]. In the catalyst's presence, these processes proceed even more easily. Thus, the steam reforming of ethanol usually proceeds at temperatures of 400–500 °C, while in the case of methanol, the reaction temperature is in the range of 300–400 °C [193].

Despite a significant difference in temperatures with methane and ethanol steam reforming, the same catalysts (noble metals, copper, or nickel) are often used for these processes [194–197]. The reason for this is that its initiation also requires activation of C-H and O-H bonds [198]. The activity of catalysts based on noble metals is usually higher, but

copper and nickel are used more often due to their low costs. As in the processes described above, alloys of these metals are often used to increase the catalytic activity [198–200].

Perhaps in steam reforming of alcohols even more attention is paid to choosing catalyst supports [201,202]. In accordance with the predominant opinion, the role of metal in this process is the activation of alcohols, while sorption of water vapor occurs on the support (Figure 6). In this case, the main catalytic transformation processes described by Reactions (6) and (7) occur at the interface between the catalyst and its support [187]. Finely dispersed oxides of metals with a charge of 2–4 (zinc, aluminum, silicon, etc.) are commonly used as a support [203–209]. Obviously, the support surface area should be considered. For example, it was shown that the activity of zirconia-supported catalysts increases by increasing the dispersion of ZrO_2 particles [210]. In this regard, mesoporous oxides are also used as supports [195,211]. The catalyst activity can be additionally increased by doping supports based on zirconia or titania with trivalent elements or cerium ($M_xZr(Ti)_{1-x}O_{2-\delta}$) [212,213], which increase the mobility of oxygen ions in these oxides [214].

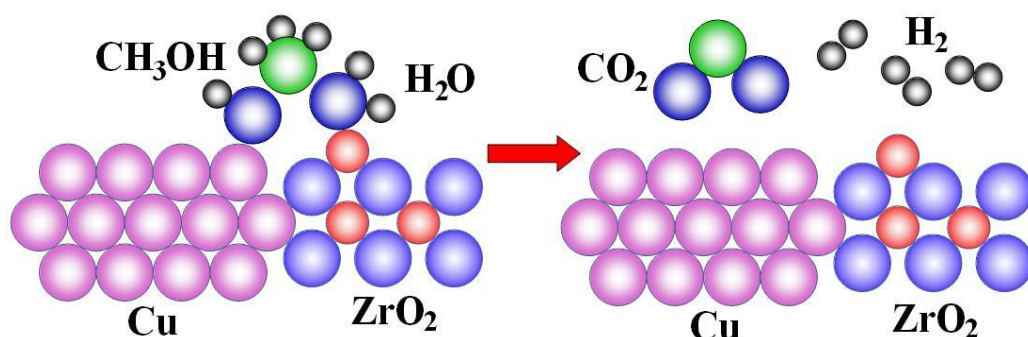


Figure 6. Scheme of methanol steam reforming with the use of Cu/ZrO₂ catalyst.

The use of highly dispersed carbon supports, including carbon blacks and nanodiamonds, in steam reforming of alcohols has been reported [215]. At first glance, their activity seems not quite clear, since carbon is not an active water sorbent. It has been shown that its activity is determined by the high content of oxygen-containing groups (OH, CO, and COOH) on the carbon particle surface and that it increases upon special surface treatment [193,216]. A successful combination of catalyst and support reduces the CO concentration in the reaction products.

In recent years, biological methods of hydrogen production from biomass have been actively developed. They are based on the ability of microorganisms (primarily bacteria) to consume biomass and release hydrogen (the so-called microbial conversion of biomass). Dark (as no light is required) fermentation is the simplest approach, which uses anaerobic bacteria to produce enzymes (it is a part of their anaerobic digestion) capable of converting biomass into hydrogen, organic acids (mostly acetic and butyric acids), and carbon dioxide [217–219]. However, the hydrogen yield is significantly limited by the metabolism of the bacteria (once the hydrogen partial pressure exceeds a critical value, a different metabolic pathway can be switched on) and depends on many factors such as substrate, temperature, pH, toxic substances, competitive bacteria, etc. At the same time, there is information on increased hydrogen yield obtained, for example, by the addition of metal ions and oxide nanoparticles [218] or the use of genetically modified bacteria [220]. A significant advantage of this method is the ability to produce hydrogen around-the-clock. Increased hydrogen yield is provided by photofermentation under anaerobic conditions, which allows processing of biomass into hydrogen using light energy for photosynthesis [219,221].

The problem with all the methods of microbial biomass conversion (including the microbial electrolysis described in the last section) is the low hydrogen yield, and therefore, these promising methods are still at an early stage of development. Another problem

with many of them is the incomplete conversion of biomass and the formation of waste containing a large amount of fatty acids that need further processing [222]. However, according to [223], by 2050, biomass will provide more than 25% of energy demand. The reason for this is that the absorption of CO₂ during the formation of biomass compensates for its emissions during energy production, which leads to a carbon neutral scenario [224].

7. Reversible Hydrogen Carriers

One of the serious problems of hydrogen energy is storage and transportation of hydrogen, as it is difficult to liquefy it. In the case of compressed hydrogen, the high weight of gas cylinders/tanks is the main limitation to its transportation (tank weight is more than an order of magnitude higher than that of hydrogen). Transportation of liquid hydrogen is no less problematic [11,225]. In this regard, chemical methods of hydrogen storage have become very popular in recent years (Figure 7). The highest weight-storage density of hydrogen is achieved in metal borohydrides (Figure 8) [226]. However, there are significant problems with their hydrolysis products, which are boric acid or its salts. They are toxic and not easily rehydrogenated to borohydrides. In this regard, the ammonia cycle (Equation (8)) has significant advantages.

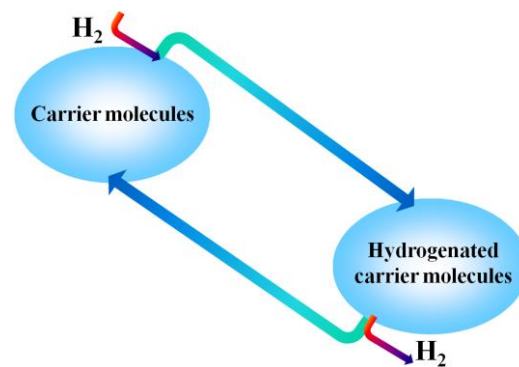
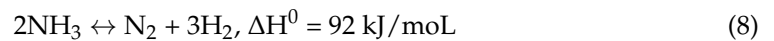


Figure 7. Hydrogen carrier reaction pathways.

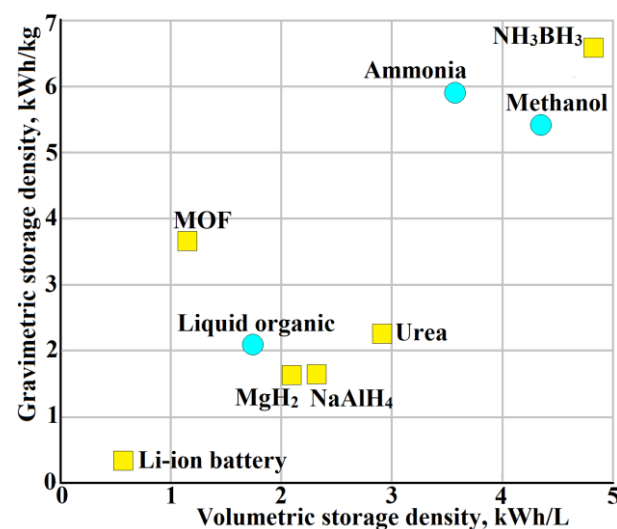


Figure 8. Gravimetric and volumetric energy storage densities for some solid (yellow squares) and liquid (blue circles) carriers.

One of the ammonia decomposition products is nitrogen (Equation (8)), which can be discharged into the atmosphere and is relatively easily recovered from it through liquefaction and distillation. This method is second only to the borohydride method in terms of gravimetric hydrogen density [227]. Ammonia production is the well-known Haber–Bosch process. Both for it and for the reverse process (dehydrogenation of ammonia), an important task is the selection of a catalyst, primarily for the efficient adsorption of nitrogen and hydrogen. For this purpose, catalysts based on iron and ruthenium are most often used [228]. Mayenite ($\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}$), with cavities capable of efficiently absorbing hydrogen, should be mentioned among oxide systems [229,230]. The ammonia cycle is being actively developed in a number of countries, but its use is associated with a number of problems that should be mentioned, among which are the toxicity of concentrated ammonia and incomplete conversion limited by the thermodynamic equilibrium. The ability of ammonia to cause fuel cell degradation even at a low content in the fuel (on the order of ppm) should be also noted [231]. Some disadvantages can be effectively mitigated by using membrane catalysis [33,232].

Liquid organic hydrogen carriers provide the most comfortable transportation by transport or in pipelines. Cyclic compounds, which transform into aromatic compounds upon dehydrogenation (benzene, toluene, cyclohexane, methylcyclohexane, decalin, etc.), predominate among them [233–235]. Typical examples are the benzene cycle based on hydrogenation of benzene and dehydrogenation of cyclohexane:



One of the most common cycles is the toluene cycle due to its high selectivity, reversibility, and the absence of carcinogenic products [236]. The hydrogen storage capacity of toluene is 6.1%, while the maximum theoretical storage capacity of liquid organic carriers reaches values just above 8%.

Heterocyclic compounds are considered promising hydrogen carriers due to their reduced dehydrogenation temperature. Among them, the most widely represented systems include nitrogen–heterocyclic compounds [237–243]. There are also works on cyclic hydrocarbons with sulfur atoms [244] and boron [245].

Most often, catalysts based on platinum-group metals on oxide supports are used for hydrogenation and dehydrogenation of organic carriers. Their high catalytic activity allows, in some cases, achieving full dehydrogenation at temperatures of about 300 °C [233,243,245–254]. In recent years, much attention has been paid to cheaper catalysts that do not contain platinum-group metals, e.g., iron and manganese-based catalysts [255–257].

The advantages and disadvantages of various storage methods are summarized in Table 3.

Table 3. Comparison of various hydrogen storage methods.

Storage Method	Advantages	Disadvantages
Compressed H ₂	- Commercialized	<ul style="list-style-type: none"> - Low volumetric storage capacity - High pressure - Limited storage time - Special transportation configuration - Safety issues

Table 3. Cont.

Storage Method	Advantages	Disadvantages
Liquid H ₂	<ul style="list-style-type: none"> - Increased storage capacity (1.6–1.7 times more than that of compressed H₂) - Commercialized 	<ul style="list-style-type: none"> - High liquefaction energy (requires cryogenic temperature (−253 °C)) - Boil-off effect - Hydrogen leakage - Special transportation configuration - Safety issues
Cryo-compressed H ₂	<ul style="list-style-type: none"> - Increased storage capacity (2–3 times more than that of compressed H₂) 	<ul style="list-style-type: none"> - High energies of compression and liquefaction - Low availability of infrastructure - High cost of infrastructure
Solid carrier	<ul style="list-style-type: none"> - Lightweight; high storage density; superior reversibility and cycle stability; high charging–discharging rate (forms materials with physisorption) - Reversibility; high volumetric density (for materials with chemisorption) - Unlimited storage time 	<ul style="list-style-type: none"> - Requires low temperatures or high pressures to store and elevated-to release H₂ (for materials with physisorption) - Poor sorption kinetics; irreversible reactions (materials with chemisorption) - Requires a new infrastructure (immature technology)
Ammonia	<ul style="list-style-type: none"> - High hydrogen storage capacity - High auto-ignition temperature (650 °C) 	<ul style="list-style-type: none"> - Toxicity/safety issues - High energy input
Liquid organic hydrogen carrier	<ul style="list-style-type: none"> - Excellent safety - High gravimetric and volumetric hydrogen storage capacity - Unlimited storage time 	<ul style="list-style-type: none"> - Requires elevated temperatures for both hydrogenation and dehydrogenation - Limited experience

8. Hydrogen Purification and Membrane Catalysis

Nowadays, the most common type of devices for power generation using electrochemical oxidation of hydrogen or hydrogen-containing fuel are proton-exchange membrane fuel cells operating at temperatures up to 100 °C [11]. High-purity hydrogen is required for them. They should not contain even trace CO impurities, which irreversibly poison platinum catalysts at these temperatures [258–260]. Unfortunately, hydrogen produced using all the processes described above is not suitable for direct use in such devices and must be deeply purified. Hydrogen can be purified using polymeric, molecular sieving carbon, and other membranes with nanosized pores [261–263]. However, all of them can only reduce the impurity content. This can also be achieved using membranes with mixed oxygen and electron conductivity [264]. Membranes are also often used in membrane reactors for the safe conversion of natural gas in the presence of oxidizers [34,265,266].

Extremely high-purity hydrogen can only be obtained using dense metallic membranes based on palladium and its alloys, through which only hydrogen can permeate [267]. It should be noted that vanadium is more permeable to hydrogen, but V-based membranes are prone to extreme hydrogen embrittlement. Alloys of palladium with copper, silver [268–272], or ruthenium [273,274] are characterized by the highest hydrogen permeability. The widespread use of palladium membranes is limited by their high cost and relatively low productivity, which can be increased by reducing the Pd-membrane thickness. However, the possibility of this approach is limited by the need to maintain sufficient membrane strength to withstand a significant pressure drop. Another approach is the creation of composite membranes, e.g., films based on highly porous oxide supports, in particular, anodic alumina, coated with palladium alloys [275,276]. Oxide supports provide mechanical strength, while the high selectivity of hydrogen extraction is determined by the Pd-coating, the small thickness of which, along with the porosity of the oxide layer, pro-

vides high hydrogen permeability. Vanadium-based membranes with palladium coating combine both high hydrogen permeability and resistance to embrittlement [277].

Membrane reactors are also used to produce high-purity hydrogen from methane, alcohols, and other reagents in one stage using membrane catalysis (Figure 9) [33,278–280]. Among other advantages of this approach, it is worth noting the possibility of reducing the process temperature and increasing the hydrogen yield by removing it from the reaction zone and thereby shifting the thermodynamic equilibrium [198,216,281–283].

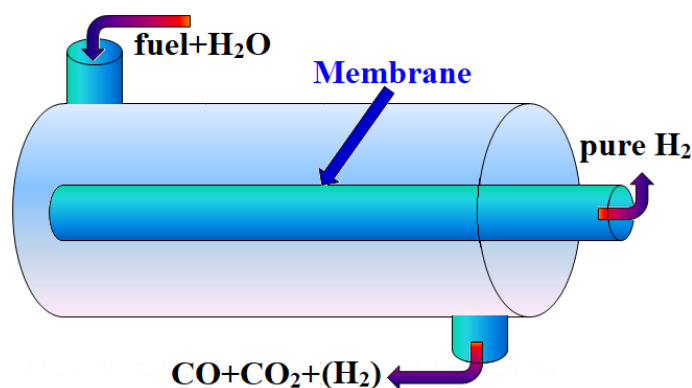


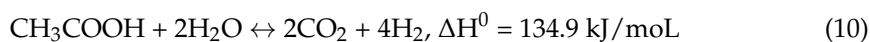
Figure 9. Scheme of hydrogen production with the use of membrane catalysis.

The most obvious example is the water–gas shift reaction described by Equation (2). The removal of hydrogen from the reaction zone leads to an increase in the CO conversion and increases the hydrogen purity [284,285]. A recent publication [116] describes various approaches to hydrogen production using ceramic membranes. However, membranes based on palladium alloys, which produce high-purity hydrogen, are more commonly used in these processes [33]. It should be noted that the water–gas shift reaction is most suitable for increasing both the hydrogen yield and its purity in the SRM and POM processes. However, these processes proceed at high temperatures, which are unfavorable for the water–gas shift reaction. In this regard, it is preferable to divide the process into two or three stages: in the first stage, methane conversion occurs at high temperatures, and then the water–gas shift reaction occurs through the reaction of CO and excess water vapor at temperatures of 200–450 °C (Figure 2) [286,287]. For example, Tokyo Gas Company produces high-purity hydrogen from methane with the additional oxidation of CO at temperatures of 400–500 °C [288].

Alcohols can be obtained from biomass and can be considered a renewable feedstock. The steam reforming of alcohols proceeds at lower temperatures, which are actually optimal for both the main process (reforming) and the water–gas shift reaction. Therefore, in this case, the process is carried out in one stage, significantly increasing the conversion of alcohols above the thermodynamic equilibrium [289]. Thus, the application of membrane reactors with membranes made of palladium–silver or palladium–ruthenium alloys with Cu- or Ru-based catalysts at temperatures of 200–350 °C achieves methanol conversion of 85–100% with high-purity hydrogen yield of 40–97% [198,290]. Similar results have been obtained for composite membranes based on anodic alumina with a selective palladium layer [281].

In the case of ethanol steam reforming in membrane reactors, the ethanol conversion varied from 40 to 99–100%, while the high-purity hydrogen yield can be low and varied from 10 to 93% [291]. The main reason for this is a higher process temperature (400–600 °C), which determines the lower selectivity of the process and worsens the thermodynamics of the water–gas shift reaction. Membranes made of both palladium–copper or palladium–silver alloys [291–294] and a wide range of composite membranes have been used [291,295–298]. Catalysts based on noble metals (Pt, Ru, or Ir) as well as catalysts based on nickel, cobalt, and copper have been used.

Acetic acid is one more product of biomass fermentation. It can also be converted into hydrogen according to Equation (10):



In Reaction (10), the maximum yield of pure hydrogen in the permeate zone reached 70% using reactors with palladium–silver membranes and Ni catalysts at a temperature of 400–450 °C [299].

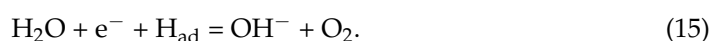
9. Water Electrolysis

Electrolysis of water using renewable energy sources is the main completely environmentally friendly method of hydrogen production today. However, its disadvantages are obvious [300]. The maximum efficiency of electrolyzers and fuel cells under the most favorable conditions (at low currents) is about 70%. Therefore, at best, only half of the energy spent to produce such hydrogen can be generated back from it. Moreover, electrolyzers are quite expensive. In this regard, at present, hydrogen produced by electrolysis is usually 2–4 times more expensive than hydrogen produced from natural gas [301,302].

The thermodynamic potential of the water electrolysis reaction is 1.23 V. However, electrolysis is actually carried out at even higher potentials. To understand the reason for this phenomenon, consider the electrolysis mechanism. According to the current concept, the hydrogen evolution reaction (HER) proceeds by the following pathways (Equations (11)–(13)):



where H_{ad} represents an adsorbed hydrogen atom on the catalyst surface. It can act as a reaction center for the reduction of another H^+ ion (Equation (12)) or can react with the second adsorbed hydrogen atom to form a hydrogen molecule (Equation (13)) [303]. In alkaline electrolyzers with anion-exchange membranes, processes (11) and (12) proceed by the following equations [304]:



In any case, an adsorbed (unbonded) hydrogen atom is formed in the first step. Obviously, a much higher potential than 1.23 V is generally needed for the H–O bond to break in the acid medium. The same problems are typical for the oxygen evolution reaction (OER). Thus, both these processes require additional energy, which is expressed in terms of overvoltage in electrochemistry (analogous to the activation energy in kinetics). It is the high overvoltage of HER and OER reactions that is one of the main problems that limit the water electrolysis application [305]. This overvoltage can be reduced by adsorption of radicals formed at the first stages of electrolysis to reduce energy losses during their formation. However, as the sorption energy increases, the desorption of products from the surface becomes more difficult. Therefore, the dependence of the current density on the metal–H binding energy has a volcano-like pattern (Figure 10), as for many other processes of hydrogen production, and platinum-group metals (Pt, Rh, and Ir) with mild hydrogen adsorption energies are the most favorable for the electroreduction of hydrogen [306,307]. An additional contribution to the overvoltage is made by the concentration effects and the resistance of electrodes and the electrolyte [308]. Moreover, the contribution of ohmic losses is higher with increasing electrolysis intensity, since

$$U_{\text{Ohm}} = IR, \quad (16)$$

where R is the total resistance of the electrolysis cell, and I is the current.

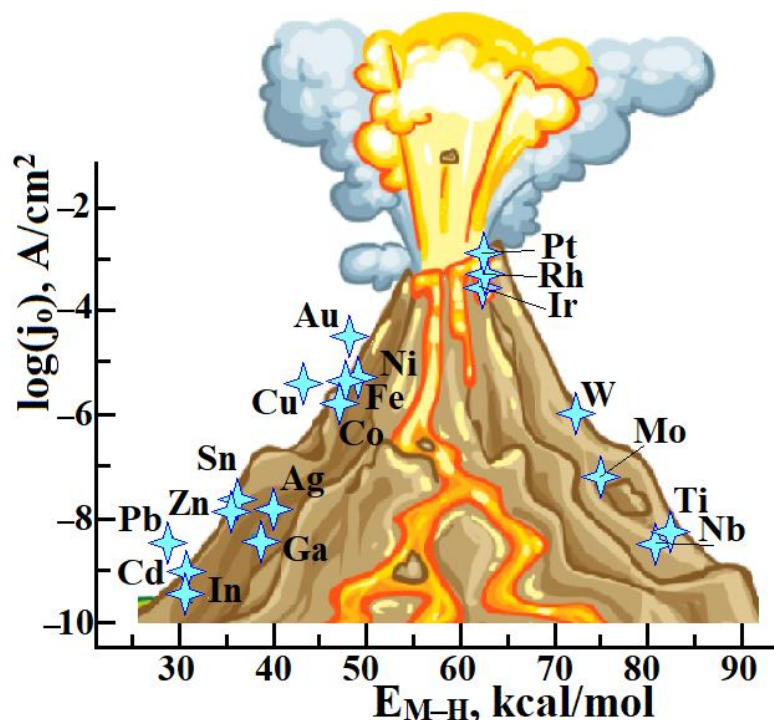


Figure 10. Dependence of exchange current density vs. the M–H bond energy in acidic media (according to [306]).

There are four main electrolysis methods, depending on the type of membrane used: (1) proton-exchange membrane water electrolysis, (2) alkaline electrolysis, (3) high-temperature electrolysis with solid oxide membranes, and (4) microbial electrolysis (Figure 11, Table 4). Proton-exchange membrane electrolyzers use Nafion-type perfluorinated membranes and noble metal-based electrocatalysts that are stable during the operation of such cells [309–311]. The latter are the most widespread due to their compactness, fast response, and high efficiency. Their disadvantage is the high cost of materials and a whole cell. Base-metal electrocatalysts and non-perfluorinated membranes can be used in alkaline electrolysis, which reduces the cost [312]. Initially, cheap porous membranes from asbestos impregnated with an alkali solution were used in alkaline electrolysis cells [313]. In recent years, a new approach associated with the use of polymeric anion-exchange membranes has been actively developed. However, the hydrogen electroreduction rate in alkaline media is usually 2–3 orders of magnitude lower than that in acidic media [313,314]. High-temperature solid oxide electrolysis requires a lot of energy due to high operating temperatures and pressures [315]. At the same time, a number of researchers note that the use of steam at elevated temperatures increases the electrolysis efficiency [316,317]. Electrolysis using renewable energy sources is the most promising. However, the stochasticity of these sources results in the variability of their operation and requires heating to high temperatures at each start-up cycle. Moreover, significant energy losses due to heat exchange are possible, which depend on the cell design and size. It is also worth noting the developing direction based on the use of microbial electrolysis cells [318]. Another interesting approach includes a two-step electrochemical–chemical cycle for water splitting [319]. In this process, the hydrogen and oxygen evolution reactions are carried out in different chambers. Low-temperature (25 °C) hydrogen reduction is accompanied by the release of hydroxide ions, which oxidize nickel (II) hydroxide at the anode:



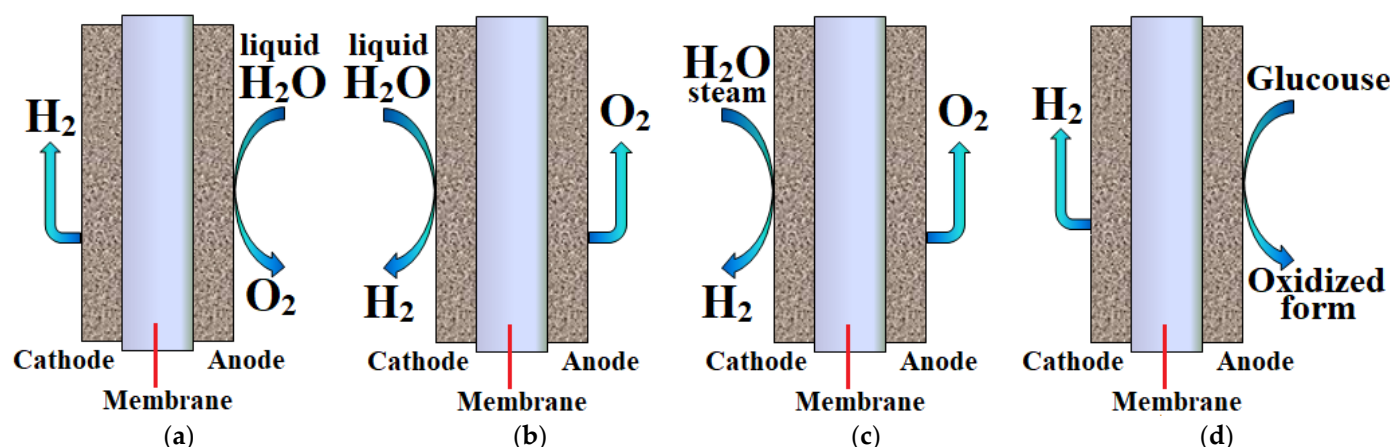


Figure 11. The main types of electrolysis methods: (a) proton-exchange membrane water electrolysis; (b) alkaline electrolysis; (c) high-temperature electrolysis with solid oxide membranes; and (d) microbial electrolysis.

Table 4. Comparison of different water electrolysis methods.

Electrolysis Method	Advantages	Disadvantages
Alkaline electrolysis (Commercialized)	<ul style="list-style-type: none"> - Low cost - High durability - Non-metal electrocatalytic 	<ul style="list-style-type: none"> - Energy efficiency is 70% - Low-purity H₂ - Low operating pressure - Limited current density - Corrosive environment - Gas crossover
Proton-exchange membrane water electrolysis (Good prospects for commercialization)	<ul style="list-style-type: none"> - Energy efficiency is 80–90% - Ultra-pure H₂ (99.99%) - High operating pressure - High current density - Quick response 	<ul style="list-style-type: none"> - High cost - Acidic environment - Low durability
High-temperature electrolysis with solid oxide membranes (Laboratory scale)	<ul style="list-style-type: none"> - Energy efficiency is 90–100% - High operating pressure - High current density - Non-metal catalysis 	<ul style="list-style-type: none"> - Large size - Long start-up - Low durability

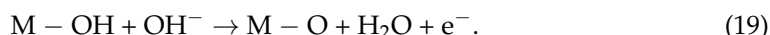
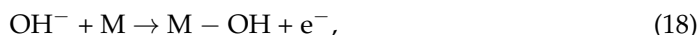
At the second stage, NiOOH decomposes at an elevated (90 °C) temperature with nickel (II) hydroxide regeneration.

Noble metals (Pt, Pd, Ru, Ir, and Rh) demonstrate excellent catalytic activity in the reaction of hydrogen electroreduction and stability when operating in an electrolyzer [320–322]. To optimize diffusion processes and reduce the noble metal amount, they are usually deposited on supports from nanodispersed carbon materials [323]. Supports based on carbon nanomaterials doped with heteroatoms are also widely used due to their increased conductivity [324,325]. An effective strategy for increasing the activity of catalysts based on noble metals is the formation of alloys or composites with other, more often base, metals or their compounds [326–330]. In this way, the overvoltage of this process can be reduced to 10–50 mV [331].

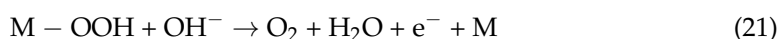
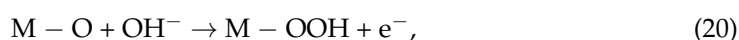
Transition metal compounds can be used for hydrogen electroreduction instead of platinum-group metals. Thus, the authors of [332,333] concluded that the electronic structure of some transition metal carbides is similar to platinum in many aspects and can exhibit similar catalytic properties. These assumptions were confirmed by Vrabel et al. [334], but the overvoltage of the hydrogen electroreduction reaction turned out to be quite high.

The properties of molybdenum carbide nanostructures turned out to be even more attractive [335]. Phosphides [336] and sulfides of a number of transition metals [337–339] exhibit high catalytic activity in this reaction.

The four-electron oxygen evolution reaction is much more complicated. The following mechanism is currently proposed [305]. In alkaline media, it involves the sorption of hydroxyl ions on catalytic metal centers (M) with electron release (Equation (18)) followed by the formation of oxide centers (M – O) as a result of deprotonation (Equation (19)):



Then, oxide centers transform through the formation of peroxide groups (Equations (20) and (21)):



or direct formation of an oxygen molecule from two oxide centers:



Another mechanism of OER that is also widely discussed in the literature involves the participation of lattice oxygens of catalysts [340–343]. An important step in this mechanism is the formation of oxygen vacancies [344]. Such a mechanism is often suggested for mixed oxides with an oxygen-deficient lattice of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ type. They generally exhibit high oxygen mobility and rapid oxygen exchange between the gas phase and the lattice. Oxygen vacancies and a mixed oxidation state of these structures also provide fast oxygen transfer in such materials.

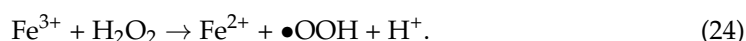
The lowest OER overvoltage potentials (about 100–200 mV) were achieved for catalysts based on iridium and ruthenium oxides, which are characterized by an intermediate energy of binding with oxygen-containing radicals [345–349]. The OER rate can be increased by doping these oxides with transition metals. These additives also reduce the catalyst cost [345,350–353]. Among active catalysts, it is also worth noting materials based on platinum [354] and transition metals [355,356] as well as their compounds, including oxides and hydroxides [357,358]. Similar to HER, the use of alloys of platinum and transition metals is effective [354]. Recently, metal–organic frameworks (MOFs) have also been used as catalysts in water electrolysis [359].

At present, the main challenge is to intensify the electrolysis process and make it more efficient [360]. In this way, in addition to improving catalysts properties, the possibility of achieving this through special external force fields is being widely studied. For example, the effect of a supergravity field [361] and ultrasonic action [362] on the performance of electrolytic cells has been studied. The magnetic field application can improve both the mass transfer in the electrolytic cell through increasing the electrolyte convection and the cell performance [363–365]. Jing et al. improved the electrolyzer characteristics through a repetitive, pulsed, high magnetic field [366]. The rate of hydrogen production increased by 15–20% at a magnetic field strength of 10,000 GS [367]. It is important to note that increasing the voltage on the electrolyzer enables the production of hydrogen under high pressure [308], which avoids the energy-consuming stage of hydrogen compression before cylinder filling.

The most widespread PEM electrolyzers contain expensive components such as catalysts based on platinum metals and perfluorinated sulfonic acid membranes. Therefore, the stability of their operation along with a long service life are extremely important issues. A serious problem in electrolysis plants is the degradation of both catalysts and membranes. During the electrolyzer operation, recrystallization of platinum catalyst particles occurs,

resulting in a gradual decrease in the surface area of the catalyst, along with its activity [368]. Moreover, partial dissolution of the catalyst or bipolar plates occurs due to their interaction with a corrosive medium of membranes, which is accompanied by the migration of metal ions incorporated into them by ion-exchange [369,370]. This leads to a significant decrease in the membrane proton conductivity due to a decrease in both the concentration of protons and their mobility. The latter is a result of the so-called “polyalkaline” effect: a decrease in the ion mobility of a compound when there are two types of ions with different mobilities in conduction channels [371]. In this case, the hydrogen crossover leads to a reduction of the metal ions formed due to the catalyst dissolution in the membrane matrix [372,373].

Moreover, an important process is the chemical degradation of membranes [374,375] as the result of the attack of free radicals formed from hydrogen peroxide [376]. In membranes, hydrogen peroxide interacts with dissolved transition metal ions, generating radicals. The same processes also occur when the membrane is treated with the Fenton reagent, which is usually used to study membrane degradation in an accelerated mode [377]:



Most articles report the degradation of perfluorinated sulfonic acid membranes. The radicals formed in these processes attack both side and main perfluorinated chains. The processes with the participation of $-\text{OCF}_2$ and C–S bonds, which are most easily attacked by radicals, are characterized by the highest rate. This is accompanied by a decrease in membrane conductivity due to the loss of functional groups [378]. The main chains degrade much more slowly by the gradual elimination of the terminal carboxyl groups. Moreover, membrane degradation is also catalyzed by noble metal nanoparticles deposited in the membrane [376]. In this regard, much attention is paid to the selection of operating conditions of electrolyzers, under which degradation of their components can be minimized [379,380].

In photoelectrolysis of water, water electrolysis occurs using the solar energy absorbed by a semiconductor (usually titania) while applying electric current [381,382].

By using reversible hydrogenases, green microalgae or cyanobacteria are able to direct hydrogen production under special conditions (oxygen-free) in direct biophotolysis while consuming CO_2 [219,383]. In indirect biophotolysis, carbohydrates formed from carbon dioxide at the first step are processed into hydrogen at the next stage [384]. However, the use of this interesting technology is limited by its low efficiency [21,385].

Microbial electrolysis is a relatively new approach to biohydrogen production from organic substances present in biomass, food waste, and/or wastewater [386]. It uses electrochemically active microorganisms (electrogenic bacteria) that oxidize organic matter, generating carbon dioxide, protons, and electrons at the anode. The electrons are then transferred to the cathode to reduce protons, producing hydrogen due to a relatively low (0.2–0.8 V) potential difference [387]. A significant reduction in voltage and total energy consumption compared to classical water electrolysis (in the absence of microorganisms) is achieved due to the fact that the oxidation of water oxygens at the anode is replaced by organic matter oxidation. However, the presence of microorganisms in the solution imposes significant restrictions, such as neutral pH and low salinity of the solution, which causes low electrical conductivity and reduces the hydrogen production efficiency, which hinders microbial electrolysis cell commercial use [387]. One of the trends is the use of membraneless single-chamber microbial electrolysis cells, which also provide high process efficiency [388]. It should be noted that, as well as for other microbial methods of hydrogen production, microbial electrolysis is characterized by low performance and today remains only a promising method for hydrogen production.

Thermochemical water splitting is another promising technology of hydrogen production [389]. Various photoelectrodes are often used to carry out this process more effectively [390], while solar power and nuclear reactors are considered the likely energy

(heat) sources. Today, the construction of such stations requires high costs. This technology is complex, and reports on its effectiveness vary widely.

10. Conclusions

The rapid development of renewable energy and the stochastic nature of its main sources dictate the need for energy storage. The hydrogen cycle is the most promising for mitigation of season fluctuations. According to forecasts, there will be an increase in hydrogen production and a significant redistribution of its application areas, with the electric power industry and transport being the major hydrogen consumers. Comparison of the main hydrogen production processes is given in Table 5.

Table 5. Comparison of the advantages and disadvantages of the main hydrogen production processes.

Process	Advantages	Disadvantages
Steam reforming	Existing infrastructure, low-cost technology	CO and CO ₂ emission, high temperatures required, catalyst regeneration required
Partial oxidation	Existing infrastructure, low desulfurization requirement	CO and CO ₂ emission, high temperatures required, formation of heavy oils and coke along with H ₂ , catalyst regeneration required
Auto thermal reforming	Existing infrastructure, developed technology	CO and CO ₂ emission, high-purity O ₂ required
Biomass gasification	Cheap feedstock, recycling of industrial waste, neutral CO ₂ emission, high biomass conversion efficiency	H ₂ yield variation due to different biomass compositions, high operating temperatures, seasonal availability
Pyrolysis	Low CO ₂ emission	High energy consumption, large carbon amounts, poor fuel efficiency, hydrogen requires deep purification
Electrolysis	CO ₂ zero emissions, O ₂ is a byproduct, existing infrastructure, high-purity H ₂	Expensive

Preference is given to methods that produce high-purity hydrogen without significant emission of carbon oxides. From this point of view, the most promising is water electrolysis using renewable sources. However, the high cost of such hydrogen dictates the need for both its improvement and intensification.

Another promising approach is biomass processing with subsequent hydrogen production from its fermentation products, in particular, bio-alcohols. In this approach, emissions of carbon dioxide during hydrogen production are leveled by its absorption during the biomass cultivation.

At the same time, considerable attention will be paid to the manufacturing of catalysts that can improve the efficiency of hydrogen production, both by advanced and traditional methods. It is noteworthy that many methods of hydrogen production use catalysts of similar composition based on platinum or transition metals and their alloys. This is especially due to the need to activate the C-H bonds in compounds from which hydrogen is produced. In this case, catalysts with an intermediate sorption energy of hydrogen sources exhibit the greatest activity. Increasing attention is also being paid to catalyst supports, which are designed not only to ensure their high dispersion and surface area but also to promote hydrogen production and reduce catalyst poisoning, primarily due to carbon deposition.

One of the promising methods for intensification of high-purity hydrogen production is membrane catalysis using membranes based on palladium alloys. Their unique selectivity produces high-purity hydrogen in a single technological cycle. In this case, the removal of hydrogen from the reaction zone both reduces the process temperature and increases the yield of reaction products in excess of the stoichiometric ones determined by thermodynamics.

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